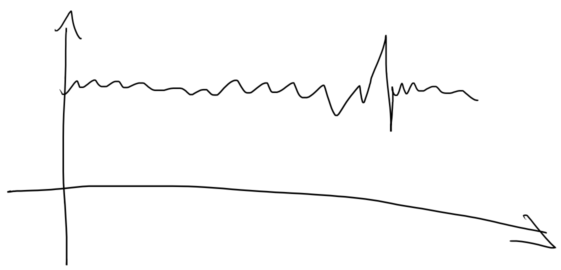
$$\int d\Omega_{3N} = \frac{2\pi^{3N/2}}{\Gamma\left(\frac{3N}{2}\right)}$$

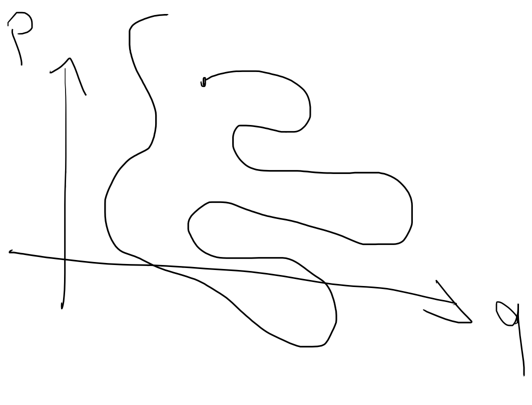
Ensembles



$$f_{meas} = \lim_{T\to\infty} \frac{1}{T} \int_{t_0}^{t_0+T} f(t)\,dt$$

phase space

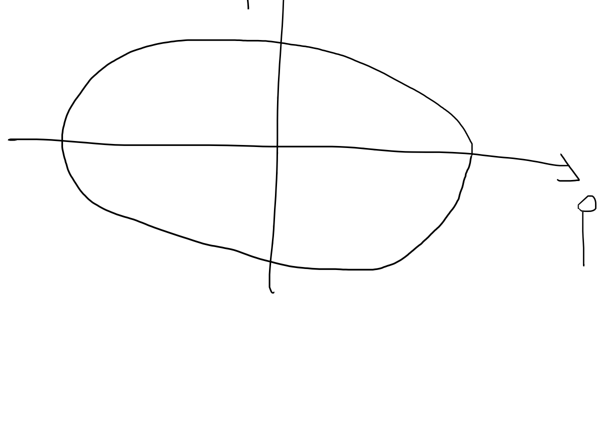
$$\left.\begin{matrix}(q^i, & p^i) \\ 3N & 3N\end{matrix}\right\} \text{6N dimensional space}$$

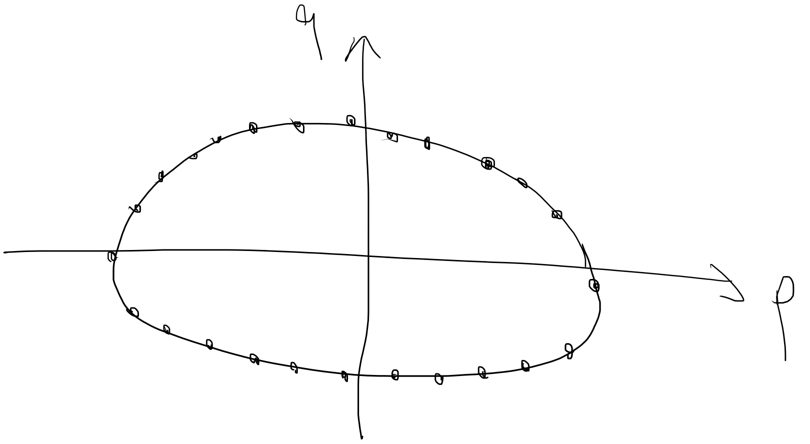


1D Harmonic oscillator

$$H = E$$

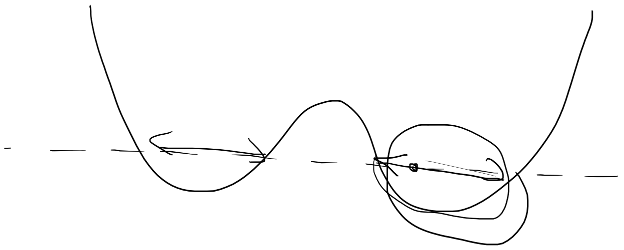
$$\frac{p^2}{2m} + \frac{1}{2} m w^2 x^2 = E$$





$$\langle f \rangle = f_{ens} = \sum f_i P_i = \frac{1}{T}\int_0^T f(t)\,dt = f_{meas}$$

ergodic hypothesis



$\rho(p,q)$: density of points in phase space corresponding to the ensemble

$dp\,dq$: some volume

$\rho(p,q)\,dp\,dq$: # of members of the ensemble within the volume $dp\,dq$

If ρ is normalized to

$$\int \rho(p,q)\, dp\, dq = 1$$

$\rho(p,q,t)\,dp\,dq$: probability that a randomly chosem member of the ensemble is in the volume $dp\,dq$

Stationary system: $\frac{\partial \rho}{\partial t} = 0$

$$\frac{d}{dt}\int_{\omega} \rho\, dp\, dq = \int_{\omega} \frac{\partial \rho}{\partial t}\, dp\, dq \Leftarrow$$

$$= -\int_{\partial \omega} (\rho \vec{v}) \cdot d\vec{S}$$

$$= -\int_{\omega} \vec{\nabla} \cdot (\rho \vec{v})\, dp\, dq \Leftarrow$$

$$\frac{\partial \rho}{\partial t} + \vec{\nabla} \cdot (\rho \vec{v}) = 0 \qquad \vec{v} = (\dot{p}^i, \dot{q}^i)$$

$$\vec{\nabla} = \left(\frac{\partial}{\partial p^i}, \frac{\partial}{\partial q^i}\right)$$

$$\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial p^i}\left(\rho \dot{p}^i\right) + \frac{\partial}{\partial q^i}\left(\rho \dot{q}^i\right) = 0$$

$$0 = \underbrace{\frac{\partial \rho}{\partial t} + \frac{\partial \rho}{\partial p^i}\dot{p}^i + \frac{\partial \rho}{\partial q^i}\dot{q}^i}_{\frac{d}{dt}\rho\left(p^i(t),\, q^i(t),\, t\right)} + \rho\underbrace{\left(\frac{\partial \dot{p}_i}{\partial p_i} + \frac{\partial \dot{q}^i}{\partial q^i}\right)}_{\overset{\shortparallel}{0}}$$

$$\left.\begin{aligned} \dot{p}_i &= -\frac{\partial H}{\partial q_i} \\ \dot{q}_i &= \frac{\partial H}{\partial p_i} \end{aligned}\right\} \qquad \frac{\partial \dot{p}_i}{\partial p_i} = -\frac{\partial^2 H}{\partial p_i \partial q_i} = -\frac{\partial^2 H}{\partial q_i \partial p_i}$$

$$\frac{\partial \dot{p}_i}{\partial p_i} = -\frac{\partial \dot{q}_i}{\partial q_i}$$

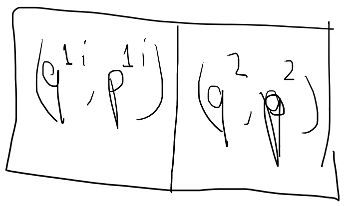
$$0 = \frac{d\rho}{dt} = \frac{\partial \rho}{\partial t} + \frac{\partial \rho}{\partial p_i}\dot{p}_i + \frac{\partial \rho}{\partial q_i}\dot{q}_i$$

$$= \frac{\partial \rho}{\partial t} + \frac{\partial \rho}{\partial p_i}\left(-\frac{\partial H}{\partial q_i}\right) + \frac{\partial \rho}{\partial q_i}\frac{\partial H}{\partial p_i}$$

$$0 = \frac{\partial \rho}{\partial t} + \{\rho, H\}$$ Louivelle's thm

stationary system: $\frac{\partial \rho}{\partial t} = 0$

$$\boxed{\{\rho, H\} = 0}$$



$$\rho_{12}(q^1, p^1; q^2, p^2)$$

$$= \rho_1(q^1, p^1)\,\rho_2(q^2, p^2)$$

$$\ln \rho_{12} = \ln \rho_1 + \ln \rho_2$$

$$\{\ln \rho, H\} = 0$$

$$\ln \rho = C - \beta E + \vec{\gamma} \cdot \vec{P} + \vec{\delta} \cdot \vec{M}$$

$$\ln \rho = C - \beta E$$

$$\boxed{\rho = e^{C - \beta E}}$$

If the system is isolated, $E = \text{const}$

$\Rightarrow \boxed{\rho = \text{const}}$

If w is the volume of phase space available to the system, $\rho = \frac{1}{w}$

$\rho = \text{const}$: microcanonical ensemble

$\rho = \frac{1}{Z} e^{-\beta E}$; canonical ensemble

Microcanonical ensemble

Ω ; # of microstates available to the system

$$\rho = \frac{1}{W}$$

$$W \propto \Omega$$

$$\boxed{\Omega = \frac{W}{W_0}} \qquad W_0 = ?$$

Example ideal gas

$$W = \int_W d^{3N}p \, d^{3N}q = V^N \int_{E^0 - \frac{\Delta}{2} < E < E^0 + \frac{\Delta}{2}} d^{3N}p = V \int d\Omega_{3N} \int dp \, p^{3N-1}$$

$$W = V \left(\int d\Omega_{3N} \right) \frac{p^{3N}}{3N} \Bigg|_{p = p_{min}}^{p = p_{max}}$$

$$E = \sum_{i=1}^{N} \frac{p_i^2}{2m} = \frac{p^2}{2m}$$

$$\omega = V \left(\int d\Omega_{3N} \right) \frac{(2mE)^{3N/2}}{3N} \Bigg|_{E=E^0-\frac{\Delta}{2}}^{E=E^0+\frac{\Delta}{2}}$$

$$\omega = V \frac{\cancel{2}\pi^{3N/2}}{\Gamma\left(\frac{3N}{2}\right)} \frac{1}{\cancel{3N}} (2m)^{3N/2} \cancel{\left(\frac{3N}{2}\right)} E^{\frac{3N}{2}-1} \Delta$$

$$\omega = V \frac{\pi^{3N/2}}{\Gamma\left(\frac{3N}{2}\right)} \frac{(2mE)^{\frac{3N}{2}}}{E} \Delta$$

$$\Omega = \frac{V^N \Delta}{E \omega_0} \frac{\pi^{3N/2}}{\Gamma\left(\frac{3N}{2}\right)} (2mE)^{\frac{3N}{2}} \Leftarrow$$

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

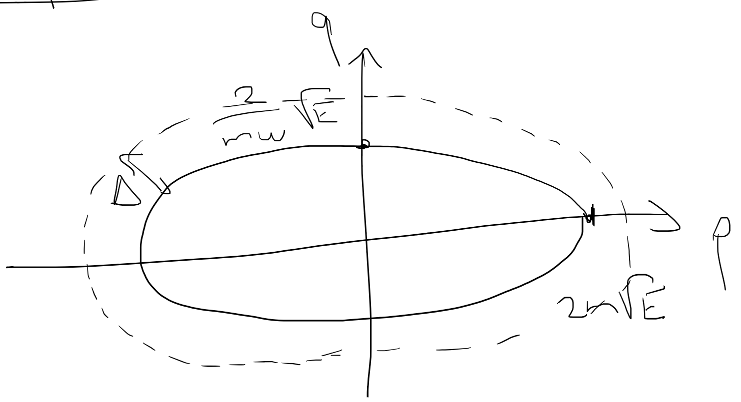
$$= \frac{\Delta V^N}{E} \frac{\pi^{3N/2}}{\Gamma\left(\frac{3N}{2}\right)} (2mE)^{\frac{3N}{2}} \left(\frac{1}{h^{3N} 2^{3N} \pi^{3N}} \right) \Leftarrow$$

$$\Rightarrow \frac{1}{\omega_0} = \frac{1}{(2\pi\hbar)^{3N}} = \frac{1}{h^{3N}} \Rightarrow \omega_0 = h^{3N}$$

Quantum uncertainty principle

$$\Delta p \, \Delta x \sim h \qquad \Delta p \, \Delta x \geq \frac{h}{4\pi}$$

Example



$$\text{area} = \pi \sqrt{\frac{2}{m\omega^2}} \sqrt{2m} E$$

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

area of the ring

$$= \varpi = \frac{2\pi}{\omega} \Delta$$

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

$$\left(\frac{p}{\sqrt{2m}\sqrt{E}}\right)^2 + \left(\frac{q}{\sqrt{\frac{2}{m\omega^2}}\sqrt{E}}\right)^2 = 1$$

$$\Omega = \frac{\varpi}{\omega_0} = \boxed{\frac{2\pi}{\omega} \frac{\Delta}{\varpi_0} = \Omega}$$

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

$$\Omega = \frac{\Delta}{\hbar\omega} = \frac{2\pi}{\omega}\frac{\Delta}{\varpi_0}$$

$$\varpi_0 = 2\pi\hbar = h$$

$$\frac{w}{w_0} = \boxed{\int_{\omega} \frac{d^{3N}p \, d^{3N}q}{(2\pi\hbar)^{3N}} = \Omega}$$

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

<u>QM treatment</u> isolated system with energy E.

$$\varepsilon = \hbar\omega\left(n_x + n_y + n_z + \frac{3}{2}\right)$$

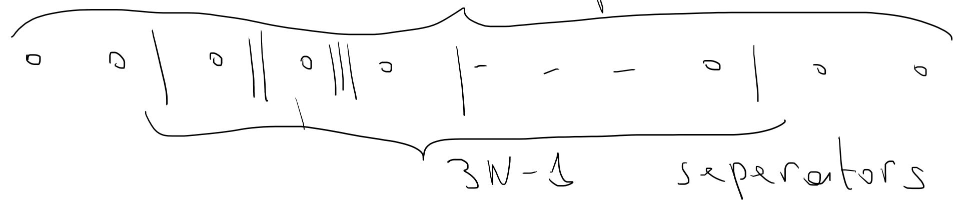
$$E = \sum_{i=1}^{N} \hbar\omega\left(n_x^i + n_y^i + n_z^i + \frac{3}{2}\right)$$

$$M = \frac{E}{\hbar\omega} - \frac{3N}{2}$$

$$M = \sum_{i=1}^{N} \left(n_x^i + n_y^i + n_z^i\right)$$

In how many ways can the integer M be written as the sum of 3N integers?

M spheres



3N-1 seperators

$$M = \underbrace{2+1+0+1+0+0+1\cdots+2}_{3N \text{ integers}}$$

$$\Omega(M) = \frac{(M+3N-1)!}{M!\,(3N-1)!}$$

$$S = k\ln\Omega = k\ln\frac{(M+3N-1)!}{M!\,(3N-1)!}$$

$$= k\left[\ln(M+3N)! - \ln M! - \ln 3N!\right]$$

$$\simeq k\left[(M+3N)\ln(M+3N) - \cancel{(M+3N)}\right.$$

$$- M\ln M + \cancel{M}$$

$$\left.- 3N\ln 3N + \cancel{3N}\right]$$

$$S \simeq k\left[M\ln\left(\frac{M+3N}{M}\right) + 3N\ln\left(\frac{M+3N}{3N}\right)\right]$$

$$= kM\left[\ln\left(1+\frac{3N}{M}\right) + 3\frac{N}{M}\ln\left(1+\frac{M}{3N}\right)\right]$$

$$S \simeq \frac{kE}{\hbar\omega}\left[\ln\left(1+\frac{3\hbar\omega N}{E}\right) + \frac{3N\hbar\omega}{E}\ln\left(1+\frac{E}{3\hbar\omega N}\right)\right]$$

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_N = \frac{k}{\hbar\omega}\left[\ln(\ \ ) + \cancel{\frac{3N\hbar\omega}{E}\ln(\ )}\right]$$

$$+ \frac{k\cancel{E}}{\hbar\omega}\left[\frac{-\frac{3\hbar\omega N}{E^2}}{1+\frac{3\hbar\omega N}{E}} - \cancel{\frac{3N\hbar\omega}{E^2}\ln(\ )}\right.$$

$$\left. + \frac{3N\hbar\omega}{\cancel{E}}\ \frac{\frac{1}{3\hbar\omega N}}{1+\frac{E}{3\hbar\omega N}}\right]$$

$$\frac{1}{T} = \frac{k}{\hbar\omega}\ln\left[1+\frac{3\hbar\omega N}{E}\right] + \frac{k}{\cancel{\hbar\omega}}\left[\frac{-3\cancel{\hbar\omega}}{E+3\hbar\omega N}\right.$$

$$\left. + 3N\cancel{\hbar\omega}\ \frac{1}{E+3\hbar\omega N}\right]$$

$$\boxed{\frac{1}{T} = \frac{k}{\hbar\omega}\underbrace{\ln\left[1+\frac{\hbar\omega 3N}{E}\right]}_{\approx 0} + \frac{k}{E+\underbrace{3\hbar\omega N}_{\text{ignore}}}(3N-3)}$$

$$\frac{E}{3N\hbar\omega} \gg 1$$

$$\frac{1}{T} = \frac{k}{E}3N \Rightarrow E = 3NkT$$

$$E = \underline{3N}\cdot 2\cdot\frac{kT}{2}$$

Equipartition Thm If H is the sum of quadratic terms

$$E = \left(\frac{kT}{2}\right)(\#\text{ of quadratic terms})$$

Classical Description

$$\omega = \int d^{3N}p \, d^{3N}q$$

$$E-\frac{\Delta}{2} \leq \sum_{i=1}^{N}\left(\frac{p_i^2}{2m} + \frac{q_i^2}{\frac{2}{m\omega^2}}\right) \leq E+\frac{\Delta}{2}$$

$$\tilde{p} \equiv \frac{p}{\sqrt{2m}} \qquad \tilde{q} = \frac{q}{\sqrt{\frac{2}{m\omega^2}}}$$

$$\omega = \int d^{3N}\tilde{p} \, d^{3N}\tilde{q} \, \left(\sqrt{2m}\right)^{3N}\left(\sqrt{\frac{2}{m\omega^2}}\right)^{3N}$$

$$E-\frac{\Delta}{2} \leq \sum_{i=1}^{N}\left(\tilde{p}_i^2 + \tilde{q}_i^2\right) \leq E+\frac{\Delta}{2} \quad \Leftarrow$$

$$\omega = \left(\frac{2}{\omega}\right)^{3N} \int d^{6N}x = \left(\frac{2}{\omega}\right)^{3N} \int_{\sqrt{E-\frac{\Delta}{2}}}^{\sqrt{E+\frac{\Delta}{2}}} r^{6N-1} \, dr \, \Omega_{6N}$$

$$\sqrt{E-\frac{\Delta}{2}} < R < \sqrt{E+\frac{\Delta}{2}}$$

$$\omega = \left(\frac{2}{w}\right)^{3N} \frac{(R^2)^{3N}}{6N}\Bigg|_{R^2=E-\frac{\Delta}{2}}^{R^2=E+\frac{\Delta}{2}} \Omega_{6N}$$

$$= \left(\frac{2}{w}\right)^{3N} \frac{\cancel{(3N)}\, E^{3N-1}\Delta}{2\,\cancel{6N}} \Omega_{6N}$$

$$= \left(\frac{2}{w}\right)^{3N} \frac{E^{3N}}{2}\left(\frac{\Delta}{E}\right)\Omega_{6N}$$

$$\int d\Omega_{3N} = \frac{2\pi^{3N/2}}{\Gamma\left(\frac{3N}{2}\right)} \Rightarrow \Omega_{6N} = \frac{2\pi^{3N}}{\Gamma(3N)}$$

$$\boxed{\omega = \left(\frac{2}{w}\right)^{3N} E^{3N}\left(\frac{\Delta}{E}\right)\frac{\pi^{3N}}{\Gamma(3N)}}$$

$$S = k \ln \frac{\omega}{\omega_0}$$

$$= k\ln\omega - k\ln\omega_0 \qquad \Gamma(3N) = (3N-1)!$$

$$= k\left[\cancel{\ln\left(\frac{\Delta}{E}\right)}_{\text{ignore}} + 3N\ln\left(\frac{2\pi E}{w}\right) - \ln\Gamma(3N) - \ln\omega_0\right]$$

$$S = k\left[3N \ln\left(\frac{2\pi E}{\omega}\right) - 3N \ln 3N + 3N - \ln w_0\right]$$

$$S^{cl} = k\left[3N \ln\left(\frac{2\pi E}{3N\omega}\right) + 3N - \ln w_0\right]$$

$$S^{QM} = \frac{kE}{\hbar\omega}\left[\ln\left(1+\frac{3\hbar\omega N}{E}\right) + \frac{3N\hbar\omega}{E}\ln\left(1+\frac{E}{3\hbar\omega N}\right)\right]$$

$$S^{QM} = k\left[\frac{E}{\hbar\omega}\ln\left(1+\frac{3\hbar\omega N}{E}\right) + 3N\ln\left(1+\frac{E}{3\hbar\omega N}\right)\right]$$

$$3\hbar\omega N \ll E$$

$$= k\left[\frac{\cancel{E}}{\cancel{\hbar\omega}}\,\frac{3\cancel{\hbar\omega}N}{\cancel{E}} + 3N\ln\left(\frac{3\hbar\omega N + E}{3\hbar\omega N}\right)\right]$$

$$= k\left[3N + 3N\ln\left(\frac{E}{3\hbar\omega N}\right) + 3N\ln\left(1+\frac{3\hbar\omega N}{E}\right)\right]$$

ignore

$$= k\left[3N + 3N\ln\left(\frac{E}{3\hbar\omega N}\right) + 3N\,\cancel{3N\frac{\hbar\omega}{E}}\right]$$

$$= k\left[3N\ln\left(\frac{2\pi E}{3N\omega}\right) + 3N - \ln w_0\right]$$

$$\frac{\cancel{E}}{\cancel{3}\hbar\cancel{\omega N}} = \frac{2\pi \cancel{E}}{\cancel{3N\omega}\,\omega_0^{\frac{1}{3N}}} \Rightarrow \omega_0^{\frac{1}{3N}} = 2\pi\hbar = h$$

$$\boxed{\omega_0 = h^{3N}}$$