Phys. 528 lecture 5

Micro-canonical Ensemble

Macrostate : N, V, E

$$E - \frac{\Delta}{2} \le H(q,p) \le E + \frac{\Delta}{2}$$

$$\rho(q,p) = \begin{cases} \text{const.}, & E - \frac{\Delta}{2} \le H(q,p) \le E + \frac{\Delta}{2} \\ 0, & \text{otherwise} \end{cases}$$

Equal a priori probabities

$$\omega = \int_{E - \frac{\Delta}{2} \le H(q,p) \le E + \frac{\Delta}{2}} d^{3N}q \, d^{3N}p$$

Ensemble average

$$\langle f \rangle = \frac{1}{\omega} \int d\omega \, f(q,p)$$

$\langle f \rangle \simeq \overline{f}$ (time ave.)

ergodic hypothesis

$\Omega(N, V, E; \Delta) \propto \omega$

How to determine const. of proportionality?

i) <u>Free particles</u>

First, consider the case $N=1$.

$$\varepsilon(n_x, n_y, n_z) = \frac{\hbar^2 \pi^2 (n_x^2 + n_y^2 + n_z^2)}{2m V^{2/3}}$$

$$\Sigma(1, V, E) \cong \frac{1}{8} \frac{4\pi}{3} n^3(E),$$

where $n^2(E) = \dfrac{2mEV^{2/3}}{\pi^2 \hbar^2} = \dfrac{p^2(E) V^{2/3}}{\pi^2 \hbar^2}$

$$\Sigma(1, V, E) = \frac{\pi}{6} \frac{p^3(E) V}{\pi^3 \hbar^3} = \frac{4\pi}{3} \frac{p^3(E) V}{h^3}$$

The total # of quantum states with energy $\leq E$ is equal to the volume of the corresponding phase space divided by h^3:

$$\Sigma(1, V, E) = \int \frac{d^3x\, d^3p}{h^3}\, \theta\left(E - \frac{p^2}{2m}\right)$$

For $N > 1$, $\quad E = \sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2m}$

$$\Sigma(N, V, E) = \alpha \int d^{3N}q\, d^{3N}p\, \theta\left(E - \sum_{r=1}^{3N} \frac{p_r^2}{2m}\right),$$

where α is the constant of proportionality to be determined.

$$\Sigma = \alpha V^N \int d^{3N}p\, \theta\left(2mE - \sum_{r=1}^{3N} p_r^2\right)$$

The integral is the volume of a $3N$ dimensional hypersphere of radius $\sqrt{2mE}$.

$$I = \frac{\pi^{\frac{3N}{2}}}{\frac{3N}{2}!} (2mE)^{\frac{3N}{2}}$$

Thus $$\Sigma(N,V,E) = \alpha V^N \frac{\pi^{\frac{3N}{2}}}{\left(\frac{3N}{2}\right)!} (2mE)^{\frac{3N}{2}}$$

Comparing to the previous result,

$$\Sigma(N,V,E) = \frac{V^N}{h^{3N}} \frac{(2\pi m E)^{3N/2}}{(3N/2)!},$$

we see that $\alpha = \dfrac{1}{h^{3N}}$

ii) <u>Harmonic oscillator</u>

$$H(q,p) = \frac{p^2}{2m} + \frac{m\omega^2 q^2}{2}$$

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

$$\Sigma(E) = \mathrm{Int}\left(\frac{E}{\hbar\omega} - \frac{1}{2}\right) \approx \frac{E}{\hbar\omega}$$

the corresponding volume in phase space is

$$\sigma = \int dq\, dp\ \Theta(2mE - p^2 - m^2\omega^2 q^2)$$

let $x = m\omega q$, $dq = \frac{dx}{m\omega}$

$$\sigma = \frac{1}{m\omega}\int dx\,dp\;\theta\left(2mE - (p^2 + x^2)\right)$$

$$\sigma = \frac{\pi}{m\omega}\,2mE = 2\pi\frac{E}{\omega}$$

Thus $\Sigma = \frac{\sigma}{h}$.

The general prescription for a system with N degrees of freedom is $\Sigma = \frac{\sigma}{h^N}$ and

similarly $\Omega = \frac{\omega}{h^N}$,

where $\Omega = \Sigma'(E)\Delta$, $\omega = \sigma'(E)\Delta$.

This result is consistent with the uncertainty principle:

$$\Delta q \Delta p \gtrsim \hbar/2$$

It is not possible to specify a quantum state with greater precision. In fact, the volume associated with a single quantum state is $\Delta q \Delta p = h$ for a single degree of freedom.

Sums over quantum states get replaced by (coarse-grained) integrals over phase space in the classical limit:

$$\sum_n \longrightarrow \frac{1}{h^{3N}} \int d^{3N}q \int d^{3N}p$$