Lecture 7

Review of micro-canonical ensemble

Phase-space density:

$$\rho(p, q, t) = \begin{cases} \rho_0 = \text{Constant for } E < H < E+\Delta \\ 0 \end{cases}$$

Microstates:

$$\Gamma(E) = \alpha \iint\limits_{E < H(p,q) < E+\Delta} d^{3N}p \, d^{3N}q$$

Here α is a constant

and $\alpha = \dfrac{\alpha^*}{h^{3N}} = \dfrac{1}{h^{3N} N!}$

→ Grainy structure of Phase space

→ Distinguishability

For normalized ~~density~~ density

$$\iint\limits_{E < H < E+\Delta} \rho_0 \, d^{3N}p \, d^{3N}q = 1$$

or

$$\rho_0 = \frac{1}{\iint d^{3N}p \, d^{3}q} = \frac{\alpha}{\alpha \iint d^{3N}p \, d^{3N}q} = \frac{\alpha}{\Gamma(E)} \quad \text{--- (1)}$$

<u>Three important quantities :</u>

$\Gamma(E) \longrightarrow$ Microstates between E and $E+\Delta$

$\Phi(E) \longrightarrow$ " " 0 and E

$$\Phi(E) = \alpha \iint\limits_{H(p,q) \leq E} d^{3N}p \, d^{3N}q$$

~~D(E)~~

$$\Gamma(E) = \phi(E+\Delta) - \phi(E) = \frac{\Delta\left[\phi(E+\Delta) - \phi(E)\right]}{\Delta}$$

a $$\Gamma(E) = \Delta \left.\frac{d\phi}{dE}\right|_{\Delta \to 0} = \Delta . D(E)$$

a $$D(E) = \left.\frac{\Gamma(E)}{\Delta}\right|_{\Delta \to 0} = \text{density of states (of energy)}$$

$S = k_B \ln \Gamma(E) \simeq k_B \ln \phi(E) \simeq k_B \ln D(E)$
when N is very high and Δ is finite and small

All three equations are the same in MC ensembles in the thermodynamic limit.

Ensemble Average in MC ensemble

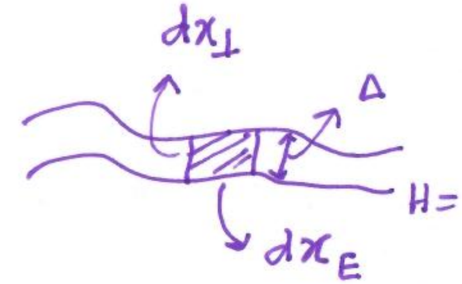
$$\langle F \rangle = \frac{\displaystyle\iint_{E<H<E+\Delta} d^{3N}p \, d^{3N}q \; F(p,q)}{\displaystyle\iint_{E<H<E+\Delta} d^{3N}p \, d^{3N}q}$$

[Check this!]

$$\boxed{\langle x \rangle = \int_a^b p(x)\, dx}$$

$$\simeq \frac{\alpha}{D(E)} \int_{H(p,q)=E} dx_E \, \frac{F(p,q)}{|\nabla H(p,q)|}$$

This definition is quite useful sometimes.



$d\Gamma = dx_\perp \, dx$

Equipartition of Theorem in MC ensembles

Mathematical statement:

$$\left\langle x_i \frac{\partial H}{\partial x_j} \right\rangle = k_B T \, \delta_{ij}$$

$x \equiv (p, q)$

Example: Let $x_i = p_i$ $\quad x_j = p_j$

$$\left\langle p_i \frac{\partial H}{\partial p_j} \right\rangle = k_B T \, \delta_{ij}$$

$$\text{a} \quad \langle p_i \dot{q}_j \rangle = k_B T . \delta_{ij}$$

a, $\boxed{\langle p_i \dot{q}_i \rangle = k_B T}$ $\qquad$ $\boxed{-\langle q_i \dot{p}_i \rangle = k_B T}$

Proof:

~~Since~~

By definition,

$$\left\langle x_i \frac{\partial H}{\partial x_j} \right\rangle = \iint\limits_{E < H < E+\Delta} \rho(p,q) \left(x_i \frac{\partial H}{\partial x_j} \right) d^{3N}p \, d^{3N}$$

$$= \frac{\displaystyle\iint\limits_{E<H<E+\Delta} d^{3N}p \, d^{3N}q \left(x_i \frac{\partial H}{\partial x_j} \right)}{\displaystyle\iint\limits_{E<H<E+\Delta} d^{3N}p \, d^{3N}q}$$ [check this!]

$$= \frac{\alpha \displaystyle\iint\limits_{E<H<E+\Delta} d^{3N}p \, d^{3N}q \left(x_i \frac{\partial H}{\partial x_j} \right)}{\alpha \displaystyle\iint\limits_{E<H<E+\Delta} d^{3N}p \, d^{3N}q}$$

$$= \frac{\alpha \displaystyle\iint_{E<H<E+\Delta} d^{3N}p\, d^{3N} \left(x_i \frac{\partial H}{\partial x_j} \right)}{\Gamma(E)} = \frac{\alpha \cdot \dfrac{\partial}{\partial E}\left[\displaystyle\iint_{H\le E} d^{3N}p\, d^{3N}q \left(x_i \frac{\partial H}{\partial x_j} \right)\right] \Delta}{\Gamma(E)} \qquad (7)$$

$$= \frac{\alpha \cdot \Delta}{\Gamma(E)} \cdot \frac{\partial}{\partial E}\left[\iint_{H\le E} d^{3N}p\, d^{3N}q \left(x_i \frac{\partial H}{\partial x_j} \right)\right]$$

$$= \frac{\alpha \cdot \Delta}{\Delta \cdot D(E)} \cdot \frac{\partial}{\partial E}\left[\iint_{H\le E} d^{3N}p\, d^{3N}q \left(x_i \frac{\partial H}{\partial x_j} \right)\right]$$

$$= \frac{\alpha}{D(E)} \frac{\partial}{\partial E}\left[\iint_{H\le E} d^{3N}p\, d^{3N}q \left(x_i \frac{\partial H}{\partial x_j} \right)\right]$$

$\alpha =$ A constant $= \dfrac{1}{h^{3N} \cdot N!}$

$D(E) =$ Density of states at E (on the iso-surface, expressed in energy)

$$= \frac{\alpha}{D(E)} \cdot \frac{\partial}{\partial E} \Bigg[\iint\limits_{H \le E} d^{3N}p \, d^{3N}q \; \underbrace{x_i \frac{\partial}{\partial x_j} (H - E)} \Bigg] ; \quad \Bigg[\text{Since } \frac{\partial E}{\partial x_j} = 0 \Bigg]$$

Now consider the term

$$\frac{\partial}{\partial x_j} \Big[x_i (H - E) \Big] = \frac{\partial x_i}{\partial x_j} (H - E) + \overbrace{x_i \frac{\partial}{\partial x_j} (H - E)}$$

$$= \frac{\alpha}{D(E)} \cdot \frac{\partial}{\partial E} \Bigg[\iint\limits_{H \le E} d^{3N}p \, d^{3N}q \; \Bigg\{ \frac{\partial}{\partial x_j} \left(x_i H - x_i E \right) - \frac{\partial x_i}{\partial x_j} (H - E)$$

$$= \frac{\alpha}{D(E)} \cdot \frac{\partial}{\partial E} \Bigg[\iint\limits_{H \le E} d^{3N}p \, d^{3N}q \; \frac{\partial x_i}{\partial x_j} (E - H) \Bigg] + \frac{\partial}{\partial E} \Bigg[\iint\limits_{H \le E} d^{3N}p \, d^{3N}q \; \frac{\partial}{\partial x_j} \Big[x_i (H -$$

$$= \frac{\alpha}{D(E)} \cdot \frac{\partial}{\partial E} \Bigg[\iint\limits_{H \le E} d^{3N}x \; \frac{\partial x_i}{\partial x_j} (E - H) \Bigg] + \frac{\partial}{\partial E} \Bigg[\iint\limits_{H \le E} d^{3N}x \; \frac{\partial}{\partial x_j} \Big[x_i (H - E) \Big] \Bigg]$$

$$= \cancel{\frac{\alpha}{D(E)} \delta_{ij} \, \alpha \iint_E}$$

$$= \frac{\alpha \, \delta_{ij}}{D(E)} \iint_{H \leq E} d^{3N}x \; + \; \frac{\partial}{\partial E}\left[\int d^{3N-1}x \, . \, \underbrace{\int dx_j \frac{\partial}{\partial x_j}\left\{ x_i (H-E) \right\}}_{\downarrow} \right]$$

zero since
$H(\ldots x_j) = E$ for
all other $x_i \neq x_j$ remai[n]
fixed

$$= \frac{\alpha \, \delta_{ij}}{D(E)} \iint_{H \leq E} \underbrace{d^{3N}p \, d^{3N}q}_{= d^{3N}x}$$

$$= \frac{\phi(E)\,\delta_{ij}}{D(E)} = \frac{\delta_{ij}}{\frac{1}{\phi(E)} \cdot \frac{d\phi(E)}{dE}} = \frac{\delta_{ij}}{\frac{\partial}{\partial E}\left[\ln \phi(E)\right]} = \frac{\delta_{ij} \, k_B}{\frac{\partial}{\partial E}\left[k_B \ln \phi(E)\right]}$$

$$= \frac{\delta_{ij} \, k_B}{\left[\partial S / \partial E\right]_N} = \underline{\underline{\delta_{ij} \, k_B T}}$$

As stated earlier,

$$x_i = p_i \implies \left\langle p_i \frac{\partial H}{\partial p_j} \right\rangle = \boxed{\langle p_i \dot{q}_j \rangle = k_B T \, \delta_{ij}}$$

Similarly, $x_i = q_i \implies \left\langle \cancel{p}\, q_i \frac{\partial H}{\partial q_j} \right\rangle = \boxed{-\langle q_i \dot{p}_j \rangle = k_B T \delta}$

For $H(p, q) = \sum_i \frac{p_i^2}{2m} + V(\{q\})$

$$\dot{q}_j = \frac{\partial H}{\partial p_j} = \frac{1}{2m} \cdot \cancel{\delta_{ij}}\, 2 \frac{\partial p_i}{\partial p_j} \cdot p_i = \frac{p_i}{m} \cdot \delta_{ij}$$

$$\text{or} \quad \frac{\partial H}{\partial p_i} = \frac{p_i}{m} \implies \left\langle \frac{p_i^2}{m} \right\rangle = k_B T$$

$$\text{or} \quad \left\langle \frac{p_i^2}{2m} \right\rangle = \frac{1}{2} \cdot k_B T$$

$$\text{or} \quad \boxed{\langle T \rangle = \frac{1}{2} k_B T}$$

10

Similarly

$$\left\langle q_i \frac{\partial H}{\partial q_i} \right\rangle = K_B T$$

or $$\left\langle q_i \frac{\partial V}{\partial q_i} \right\rangle = K_B T$$

or $$\frac{1}{2} \left\langle q_i \frac{\partial V}{\partial q_i} \right\rangle = \frac{1}{2} K_B T = \langle T \rangle$$

or $$\boxed{\langle T \rangle = \frac{1}{2} \left\langle x_i \frac{\partial V}{\partial x_i} \right\rangle}$$ $\rightarrow$ Classical virial theorem