Clase 9 M.Est. 09.oct.2020

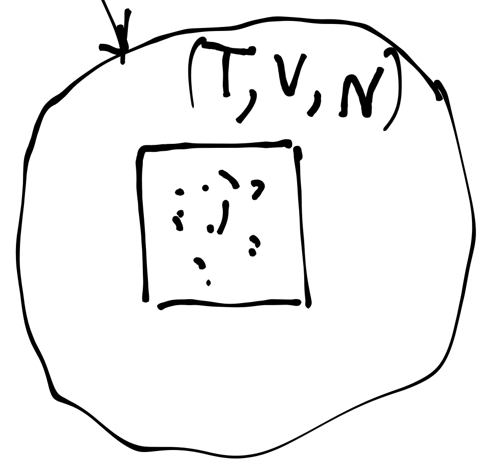
· Ensemble Canónico: (CONT')

$$\boxed{\rho(q,p) = \frac{e^{-\beta \mathcal{H}(q,p)}}{Z(\beta)} \; ; \quad \beta = \frac{1}{kT}}$$

$$\boxed{Z(\beta) = \int \frac{d^{3N}q \, d^{3N}p}{h^{3N} N!} \, e^{-\beta \mathcal{H}(q,p)}}$$

indist.

función partición canónica



· A partir de este ρ calculamos todos los observables físicos A:

$x = (q,p)$

$$\langle A \rangle = \int dx \; A(x) \, \rho(x) \; : \; dx = d\Gamma = \frac{d^{3N}q \, d^{3N}p}{\Lambda_N}$$

→ continuo.

$$\langle A \rangle = \sum_i A_i \, p_i \longrightarrow \text{discreto.}$$

donde $p_i = \dfrac{e^{-\beta \mathcal{H}(x_i)}}{Z(\beta)}$

$$Z(\beta) = \sum_i e^{-\beta \mathcal{H}(x_i)}$$

Ej: <u>Energía de un sistema:</u> $E = \langle \mathcal{H} \rangle$

$$E = \langle \mathcal{H} \rangle = \int dx\, \mathcal{H}(x)\, \rho(x)$$

$$E = \int \frac{d^{3N}q\, d^{3N}p}{\Lambda_N}\, \mathcal{H}(q,p)\, \frac{e^{-\beta \mathcal{H}(q,p)}}{Z(\beta)}$$

• esto es equivalente a

$$\boxed{E = -\frac{\partial}{\partial \beta} \ln Z}$$

<u>Dem:</u> $-\dfrac{\partial}{\partial \beta} \ln Z = -\dfrac{1}{Z} \displaystyle\int d\Gamma \frac{\partial}{\partial \beta} e^{-\beta \mathcal{H}}$

$$E = \frac{1}{Z} \int d\Gamma\, \mathcal{H}\, e^{-\beta \mathcal{H}}$$

Feynman: $\displaystyle\int dx\, a\, e^{za} = \frac{\partial}{\partial z} \int dx\, e^{za}$

• Obtengamos F : ecuación fundamental

$F = F(T, V, N)$: en. l. libre de Hemholtz.

Afirmación:

$$\boxed{F = -kT \ln Z} \quad \text{o} \quad F = -\frac{1}{\beta} \ln Z$$

o también $\boxed{Z = e^{-\beta F}}$

microcanónico

$$\Omega = e^{S/k_B}$$

Dem: Partimos de $S = -\frac{\partial F}{\partial T}$; pues $\overset{E = E(S,V,N)}{E}$, $F = E - T\overset{S = S(E,V,N)}{S}$

y $\frac{\partial}{\partial T} = \frac{\partial}{\partial \beta}\frac{\partial \beta}{\partial T} = \frac{\partial}{\partial T}\left(\frac{1}{k_B T}\right)\frac{\partial}{\partial \beta} = -\frac{1}{k_B T^2}\frac{\partial}{\partial \beta}$

$$\boxed{\frac{\partial}{\partial T} = -\frac{1}{T}\beta\frac{\partial}{\partial \beta}}$$

así:

$$S = \frac{1}{k_B T^2}\frac{\partial F}{\partial \beta}$$

y $\frac{\partial F}{\partial \beta} = \frac{\partial}{\partial \beta}\left(-\frac{1}{\beta}\ln Z(\beta)\right) = -\left(-\frac{1}{\beta^2}\ln Z - \frac{E}{\beta}\right)$

$$S = \frac{1}{T}\left(\beta\left[\frac{1}{\beta^2}\ln Z + \frac{E}{\beta}\right]\right)$$

$$TS = \frac{1}{\beta}\ln Z + E \Rightarrow TS = -F + E$$

$$\therefore \quad F = E - TS \quad \checkmark$$

luego: $$\boxed{F = -\frac{1}{\beta}\ln Z}$$

- Dos ejemplos: Gas ideal ; sist. 2 niveles

▷ <u>Gas ideal</u>:
$$\mathcal{H} = \sum \frac{p_i^2}{2m}$$

$$\rho = \frac{e^{-\beta\mathcal{H}}}{Z(\beta)}$$

$$Z(\beta) = \int \frac{d^{3N}q \, d^{3N}p}{h^{3N}\, N!} \, e^{-\beta \sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2m}}$$

$$= \frac{1}{h^{3N} N!}\left[\left(\int d\vec{r}_1 d\vec{p}_1 \, e^{-\beta\frac{\vec{p}_1^{\,2}}{2m}}\right) \times \left(\int d\vec{r}_2 d\vec{p}_2 \, e^{-\beta\frac{\vec{p}_2^{\,2}}{2m}}\right) \times (\quad) \times \dots \times \left(\int d\vec{r}_N d\vec{p}_N \, e^{-\beta\frac{\vec{p}_N^{\,2}}{2m}}\right)\right]$$

$$Z(\beta) = \frac{V^N}{h^{3N} N!} \left[\underbrace{\int d\vec{p}_i \, e^{-\beta \frac{\vec{p}_i^{\,2}}{2m}}} \right]^N$$

$$\left[\Bigg(\underbrace{\int_{-\infty}^{\infty} dp \, e^{-\beta \frac{p^2}{2m}}}_{\left(\frac{2m\pi}{\beta}\right)^{1/2}} \Bigg)^3 \right]^N$$

: ¡hacerlo!

$$\boxed{Z(\beta) = \frac{V^N}{h^{3N} N!} \left(\frac{2m\pi}{\beta} \right)^{\frac{3N}{2}}}$$

$$F = -\frac{1}{\beta} \ln Z \, , \quad y \quad S = -\frac{\partial F}{\partial T} :$$ Ec Sackur Tetrode.

¡Ej.!

N.B:

i) $\mathcal{H} = \sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2m} = \mathcal{H}_1 + \dots + \mathcal{H}_N$ con $\mathcal{H}_i = \frac{\vec{p}_i^{\,2}}{2m}$

partícula i

$$\mathcal{Z}(\beta) = \int \frac{dq^{3N}\, dp^{3N}}{h^{3N}\, N!}\, e^{-\beta \sum \frac{p_i^2}{2m}}$$

$$= \frac{1}{N!}\left(\int \frac{d^3q\, d^3p}{h^3}\, e^{-\beta \mathcal{H}} \right)^N ; \quad \mathcal{H} = \frac{\vec{p}^{\,2}}{2m}$$

$$\mathcal{Z}(\beta) = \frac{1}{N!} \cdot \left(Z_1 \cdot Z_2 \cdot Z_3 \cdots Z_N \right) = \frac{Z^N}{N!}$$

$$\boxed{\begin{array}{l} \text{Para sistema con hamiltoniano que es suma de subsistemas} \\ \mathcal{H} = \sum \mathcal{H}_i \qquad\qquad \text{multiplicación} \\ \qquad\qquad \mathcal{Z}(\beta) = \prod_i Z_i \end{array}}$$

- Ej: $\mathcal{H} = \sum_{i=1}^{N} \frac{p_i^2}{2m} + V(q_1 .. q_N)$

$$\mathcal{Z}(\beta) = Z_{cin} \cdot Z_{pot}$$

▷ <u>Sistema de 2 niveles</u>

$\uparrow\uparrow$: N partículas no interactuantes

—— ε

—— $-\varepsilon$

$$\mathcal{H} : \left\{ \begin{array}{ll} \text{—} & \varepsilon \\ \text{—} & -\varepsilon \end{array} \right. \quad ; \quad \mathcal{Z}(\beta) = \frac{z^N}{N!}$$

$$z(\beta) = \sum_{\{\text{estados}\}} e^{-\beta\mathcal{H}}$$

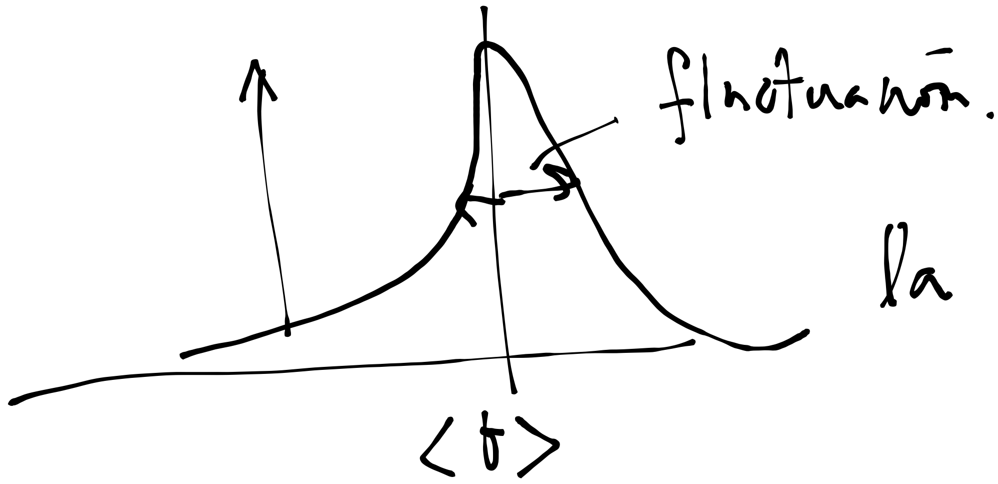
$$z(\beta) = e^{+\beta\varepsilon} + e^{-\beta\varepsilon} = 2\cosh\beta\varepsilon$$

$$\therefore \boxed{\mathcal{Z}(\beta) = \frac{2^N \cosh^N \beta\varepsilon}{N!}} \therefore$$

$$E = -\frac{\partial}{\partial\beta}\ln\mathcal{Z} := \ldots\ldots\ldots //.$$

∘ $\boxed{\text{Fluctuaciones}}$

En equilibrio, las cantidades físicas corresponden de valores de expectación: $\mathcal{O}(q,p)$: $\langle \mathcal{O} \rangle$



Ej: en el canónico la $E = \langle \mathcal{H} \rangle$

y hay fluctuación en torno a ese valor: ΔE

• Ej:

$$C_V = \frac{1}{k_B T^2} \left\langle \left(E - \mathcal{H}(q,p)\right)^2 \right\rangle$$

$$\frac{\partial \langle \mathcal{H} \rangle}{\partial T} = C_V = \frac{1}{k_B T^2} \left[\langle (\mathcal{H})^2 \rangle - \langle \mathcal{H} \rangle^2 \right]$$

Dem: $\langle \mathcal{H} \rangle = -\frac{\partial}{\partial \beta} \ln Z$

¿$\langle \mathcal{H}^2 \rangle$? : $\langle \mathcal{H}^2 \rangle = \int dx \, \mathcal{H}^2 \, \rho(x)$

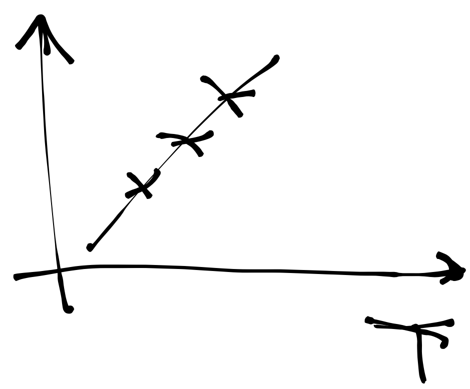
$$\frac{\partial^2}{\partial \beta^2} e^{-\beta \mathcal{H}} = \mathcal{H}^2 e^{-\beta \mathcal{H}} \Big/ \int \frac{d\Gamma}{Z}$$

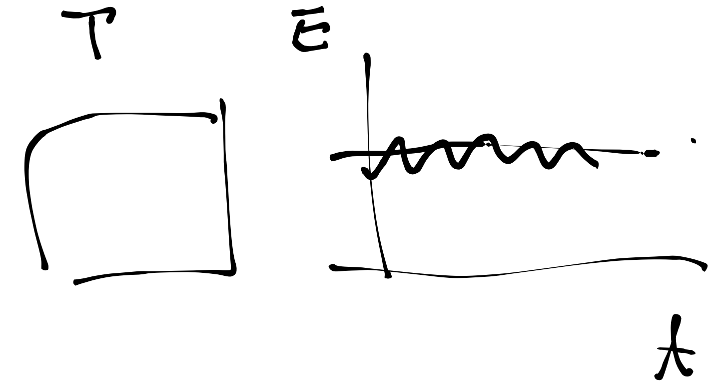
$$\int \frac{d\Gamma}{Z(\beta)} \frac{\partial^2}{\partial \beta^2} e^{-\beta \mathcal{H}} = \langle \mathcal{H}^2 \rangle$$

$$\frac{\partial^2}{\partial \beta^2} \ln Z = \frac{\partial}{\partial \beta} \left[\frac{1}{Z} \int dx \, (-\mathcal{H}) \, \underline{e^{-\beta \mathcal{H}}} \right]$$

$$= \left(\frac{\partial}{\partial\beta}\frac{1}{Z}\right)\int dx\,(-\mathcal{H})\,e^{-\beta\mathcal{H}} + \frac{1}{Z}\int dx\,\mathcal{H}^2 e^{-\beta\mathcal{H}}$$

C_V / $\frac{dE}{dT}$;





formula de fluctuación.

Caso ejemplo Green

relación de Kubo.

: funciones respuesta como fluctuación en torno al equilibrio. // gr.

$\boxed{\text{PRUEBA}}$

$$c_v = \frac{1}{N} C_V \; :$$

• Ej: Demostrar teo. de equipartición — Kardar, Greiner, Huang.

$$\langle \mathcal{O} \rangle = \int dx\, \mathcal{O}(x)\, \rho(x)$$

$$\rho(x) = \frac{e^{-\beta\mathcal{H}(x)}}{Z(\beta)}$$