Buenas Tardes!

Curso: MC + DM

La CoNGA physics

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Función de Aceptación de MC

- Como incorporar balance detallado en MC.

Unicidad

imponer en equil. (Boltzmann)

Balance detallado

$$\pi(x)\, P(x'|x) = \underline{\underline{\pi(x')}}\, P(x|x')$$

$$i \rightleftarrows j$$

b) La unicidad de $\pi(x)$ se garantiza con ergodicidad

c) Aperiodicidad de la cadena de Markov sobre su recorrido (no hay periodicidad)

— Si imponemos balance detallado

$$\pi(x) P(x'|x) = \pi(x') P(x|x')$$

$$\frac{P(x|x')}{P(x'|x)} = \frac{\pi(x')}{\pi(x)} \qquad \vec{X}_t, \ \vec{y}$$

Vamos a separar el proceso de Markov en 2 partes

$$\left.\begin{array}{ll} \text{Proposición:} & q(\overset{\text{nuevo edo}}{x'} | \overset{\text{edo actual}}{x}) \\ \text{Aceptación:} & \alpha(\underset{\text{propuesta}}{x'}, \underset{\text{actual}}{x}) \end{array}\right)$$

entonces → $P(x'|x) = q(x'|x)\,\alpha(x',x)$

$$\frac{q(x'|x)\,\alpha(x',x)}{q(x|x')\,\alpha(x,x')} = \frac{\pi(x')}{\pi(x)}$$

$$\frac{\alpha(x',x)}{\alpha(x,x')} = \frac{\pi(x')\,q(x|x')}{\pi(x)\,q(x'|x)} \nearrow 1$$

$\alpha(x,x')$ si x es mejor que x'

$$\alpha(x,x') = 1 \qquad \longrightarrow$$

$$\alpha(x',x) < 1$$

$$\alpha(x',x) = \frac{\pi(x')\, q(x|x')}{\pi(x)\, q(x'|x)} < 1$$

$$\alpha(x',x) = \min\left(1,\ \frac{\pi(x')\, q(x|x')}{\pi(x)\, q(x'|x)}\right)$$

si $\alpha < 1$

$\Rightarrow$ comparo con un # unif

$U \in [0,1] \longleftarrow$ movidas exploratorias

$\alpha < U$

Distintos ensembles:

Binder (libro)

$$Z = \text{función de partición}$$

$$= \sum_{\substack{\text{estados}\\ \text{accesibles}}} e^{-\beta \mathcal{H}} \quad , \quad \beta = \frac{1}{k_B T}$$

$$P_\mu = \frac{e^{-\beta \mathcal{H}(\mu)}}{\cancel{Z}} \longleftarrow \sum_\mu P_\mu = \frac{Z}{Z} = 1$$

edo

F (energía libre Helmholtz)

$$= -k_B T \ln Z \rightsquigarrow \text{canónica}$$

$$(N, V, T)$$

$$\downarrow \ \downarrow \ \downarrow$$

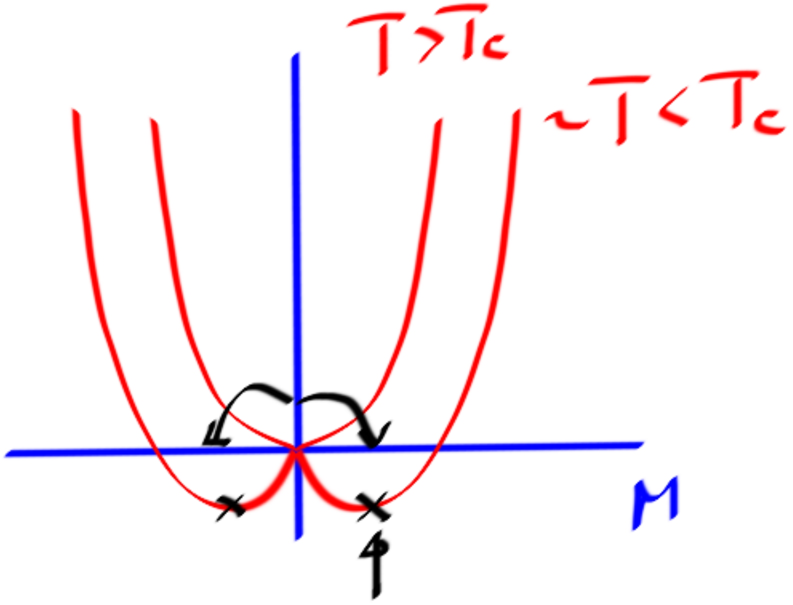
$$F = U - TS \ \leftarrow$$

$$dF = dU - TdS - SdT$$

$$= T\cancel{dS} - PdV + HdM - \cancel{TdS} - SdT$$

$$= -PdV + HdM - SdT = 0$$

$$dF = 0$$



Transición de fase

$$P = -\left(\frac{\partial F}{\partial V}\right)_{M,T} \qquad H = \left(\frac{\partial F}{\partial M}\right)_{V,T}$$

$$U = -T^2 \frac{\partial}{\partial T}\left(\frac{F}{T}\right) \rightarrow EU = F + TS$$

Potenciales termodinámicos:

$$F = U - TS$$ Helmholtz

$$H = U + PV$$ Entalpía

$$G = U - TS + PV$$ Gibbs

$$Z(N,V,T) = \sum_{\mu} e^{-\beta \mathcal{H}(\mu)}$$ Canónica

$$Y(\mu,V,T) = \sum_{N=0}^{\infty} \underline{\underline{e^{\beta\mu N}}}\, \underline{Z(N,V,T)}$$

$$P_{\mu V T} = \frac{e^{\beta \mu N} e^{-\beta H}}{\mathcal{Y}}$$

$$P_{NVT} = \frac{e^{-\beta H}}{Z}$$

$$\Psi(P,T) = \sum_{V} e^{-\beta P V} Z(V,T)$$

$$P_{P,T} = e^{-\beta P V} Z(V,T) / \Psi$$

$$\vec{J} \cdot \vec{\alpha} = [\text{Energia}]$$

$$-PV \, , \quad \mu N \, , \quad \underline{HM}$$

$$p(\vec{J}, \vec{\alpha}) = \frac{e^{-\beta H(\alpha) + \beta \vec{J} \cdot \bar{\alpha}}}{Z}$$

$$Z = \sum_{\text{edos } \mu} e^{\beta \vec{J} \cdot \bar{\alpha} - \beta H(\mu)} \quad //$$

Fluctuaciones

$\langle U \rangle$ = energia interna

$$= \langle \mathcal{H}(\mu) \rangle = \sum_{\mu} \mathcal{H}(\mu) P_{\mu}$$

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

$$\langle U^2 \rangle = \sum_{\mu} \frac{e^{-\beta \mathcal{H}(\mu)}}{Z} \cdot \mathcal{H}^2(\mu)$$

Ed

$\sim$ extensiva $\propto N$

$$\mathrm{Var}(U) = \langle U^2 \rangle - \langle U \rangle^2 = k_B T^2 C_V$$

$$\rightarrow \frac{\mathrm{Var}(U)}{\langle U \rangle^2} \propto \frac{N}{N^2} \sim \frac{1}{N} \leftarrow$$

Promedios dominan a las fluctuaciones

límite tendiendo $N \to \infty$

Fluctuaciones de Magnetización

$$\langle M^2\rangle - \langle M\rangle^2 = k_B T \chi \propto N$$

detalles μ-scopicos

Canónico

$$\frac{Var(M)}{\langle M\rangle^2} \propto (\,)\frac{1}{N} \qquad ||$$

$$\Rightarrow \quad P(U) = \frac{1}{\sqrt{2\pi\sigma^2}}\, e^{-\frac{(U-\langle U\rangle)^2}{2 k_B T^2 C_V}}$$

Gaussiana

$$P(M) = \frac{1}{(2\pi k_B T \chi)^{1/2}} e^{-\frac{(M - \langle M \rangle)^2}{2 k_B T \chi}}$$

Conexión con el equilibrio

Fluctuaciones dependen del ensamble

$$\langle (\Delta U)^2 \rangle_{NVT} \sim k_B T^2 C_V$$

$$\langle (\Delta U)^2 \rangle_{NPT} \sim k_B T^2 C_V - \left[T \left(\frac{\partial P}{\partial T} \right)_V - P \right]^2 \times k_B T \left(\frac{\partial V}{\partial P} \right)_T$$

$$\langle (\Delta S)^2 \rangle_{NVT} = k_B C_p$$

$$\langle (\Delta P)^2 \rangle_{NVT} = -k_B T \left(\frac{\partial P}{\partial V}\right)_S \propto \frac{1}{V} \,/\, \frac{1}{N}$$

permits checking your MC function

$$\langle \Delta S \Delta P \rangle_{NVT} = 0$$

$$\Big\downarrow$$

$$k_S = V \left(\frac{\partial P}{\partial V}\right)_S$$

$$\frac{\langle (\Delta P)^2 \rangle^{\propto 1/N}}{\langle P \rangle^2 \to N^0} \propto \frac{1}{N} \leftarrow \;\; ||$$

Problemas de escala / escalamiento,
finito L