Ensamble Gran Canónico

Lectura: M. Kardar Caps. 4; R. K. Pathria & D. Beale Cap. 5.

» El Ensamble Gran Canónico

En este caso, suponemos que el sistema puede intercambiar partículas, además de calor.

$$N + N_{\mathcal{R}} = N^0, (N/N^0) \ll 1$$

$$E_s + E_{\mathcal{R}} = E^0, (E_s/E^0) \ll 1$$

$$P(N,s) \propto \Omega_{\mathcal{R}}(N^0 - N, E^0 - E_s)$$

$$\ln \Omega_{\mathcal{R}}(N^0 - N, E^0 - E_s) = \ln \Omega_{\mathcal{R}}(N^0, E^0) + \left.\frac{\partial \ln \Omega_{\mathcal{R}}}{\partial N_{\mathcal{R}}}\right|_{N_{\mathcal{R}}=N^0}(-N) + \left.\frac{\partial \ln \Omega_{\mathcal{R}}}{\partial E_{\mathcal{R}}}\right|_{E_{\mathcal{R}}=E^0}(-E_s) + \cdots \simeq \ln \Omega_{\mathcal{R}} + \frac{\mu_{\mathcal{R}}}{k_B T_{\mathcal{R}}}N - \frac{E_s}{k_B T_{\mathcal{R}}}$$

$$P_{N,s} = \frac{e^{-\alpha N - \beta E_s}}{\sum_{r,s} e^{-\alpha N - \beta E_s}}, \qquad \alpha = -\mu/k_B T; \beta = 1/k_B T$$

» Gran Canónico (Cont.)

$$Z_{GC} = \sum_N e^{-\alpha N} \sum_{s|N} e^{-\beta E_s(N)}$$

$$= \boxed{\sum_N z^N Z(T, V, N)}$$

$$\langle N \rangle = -\frac{\partial}{\partial \alpha} \ln Z_{GC} = z \frac{\partial}{\partial z} \ln Z_{GC}$$

$$U = -\frac{\partial}{\partial \beta} \ln Z_{GC} \Big|_{\alpha}$$

¿Qué pasa con las fluctuaciones en N?

$$\sigma_N^2 \langle N^2 \rangle - \langle N \rangle^2 = \frac{1}{Z_{GC}} \frac{\partial^2 Z_{GC}}{\partial (\beta\mu)^2} - \left(\frac{\partial}{\partial \beta\mu} \ln Z_{GC} \right)^2 = \frac{\partial \langle N \rangle}{\partial (\beta\mu)}$$

$$\boxed{\frac{\sigma_N}{\langle N \rangle} \propto \frac{1}{\langle N \rangle^{1/2}}}$$

» Las fluctuaciones de N (Balescu)

$$\left\langle (N - \langle N\rangle)^2 \right\rangle = k_B T \frac{\partial \langle N\rangle}{\partial \mu}$$

$$\frac{\partial \langle N\rangle}{\partial \mu} = \left.\frac{\partial \langle N\rangle}{\partial p}\right|_{V,T} \left.\frac{\partial p}{\partial \mu}\right|_{V,T} = \left.\frac{\partial \langle N\rangle}{\partial p}\right|_{V,T} \left.\frac{\partial \langle N\rangle}{\partial V}\right|_{T,\mu}$$ (usando relación de Maxwell del Gran potencial Ω)

$$= \frac{\langle N\rangle}{V} \left.\frac{\partial \langle N\rangle}{\partial p}\right|_{V,T} = \langle N\rangle \frac{\partial}{\partial p} \left.\frac{\langle N\rangle}{V}\right|_{V,T} = \langle N\rangle^2 \left.\frac{\partial V^{-1}}{\partial p}\right|_{N,T} = -\frac{\langle N\rangle^2}{V^2} \left.\frac{\partial V}{\partial p}\right|_{N,T}$$

$$\frac{\sigma_N^2}{\langle N\rangle^2} \underset{\infty}{=} \frac{k_B T n}{\langle N\rangle} \chi_T$$ en el límite Termodinámico $N = N^* \simeq \langle N\rangle$

$$Z_{GC} = \lim_{\langle N\rangle \to \infty} \sum_{N=0}^{\infty} e^{\beta \mu N} Z(T,N) = e^{\beta \mu N^*} Z(T,N^*) \simeq e^{\beta \mu N^*} e^{-\beta F} = e^{-\beta(U - TS - \mu N)} = e^{-\beta \Omega}$$

NB: El gran potencial $\Omega = -pV$

» Las fluctuaciones de *E* (Pathria)

Como antes,

$$\langle E^2\rangle - \langle E\rangle^2 = -\left.\frac{\partial U}{\partial \beta}\right|_{z,V} = kT^2\left.\frac{\partial U}{\partial T}\right|_{z,V}$$

Pero z es medio "oscuro", pienso $N = N(z, T)$

$$\left.\frac{\partial U}{\partial T}\right|_{z,V} = \left.\frac{\partial U}{\partial T}\right|_{N,V} + \left.\frac{\partial U}{\partial N}\right|_{T,V}\left.\frac{\partial N}{\partial T}\right|_{z,V}$$

y además

$$\left.\frac{\partial N}{\partial \beta}\right|_{\alpha,V} = \left.\frac{\partial U}{\partial \alpha}\right|_{\beta,V} \quad\Rightarrow\quad \left.\frac{\partial N}{\partial T}\right|_{z,V} = \frac{1}{T}\left.\frac{\partial U}{\partial \mu}\right|_{T,V}$$

$$\sigma_E^2 = k_B T^2 C_v + k_B T\left.\frac{\partial U}{\partial N}\right|_{T,V}\left.\frac{\partial U}{\partial \mu}\right|_{T,V} \quad\Rightarrow\quad \sigma_E^2 = \left.\sigma_E^2\right|_{\text{canónico}} + \sigma_N^2\left(\left.\frac{\partial U}{\partial N}\right|_{T,V}\right)^2$$

» Los ensambles más frecuentes

Ensamble	Condiciones	Probabilidad	Termodinámica
Microcanónico	E, N, V ctes	$\frac{1}{\Omega(E,V,N)}$	$S = k_B \ln(\Omega)$ Entropía
Canónico	N, V, T ctes	$P(s) = \frac{e^{-\beta E_s}}{Z}$ $Z = \sum_s e^{-\beta E_s}$	$F(T,V,N) = -k_B T \ln Z(T,V,N)$ Energía libre de Helmholtz
Gran Canónico	μ, V, T ctes	$P(N, s_N) = \frac{e^{\beta\mu N} e^{-\beta E_s}}{Z_{GC}}$ $Z_{GC} = \sum_{N,s_N} e^{\beta\mu N} e^{-\beta E_s}$	$\Omega(\mu,T,V) = -k_B T \ln Z_{GC}$ $(\Omega = -pV)$ Gran potencial