

Ensamble Gran Canónico

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» El Ensamble Gran Canónico

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

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

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

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

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

$$P_{N,s} = \frac{e^{-\alpha N - \beta E_s}}{\sum_{r,s} e^{-\alpha N - \beta E_s}},$$

$$\alpha = -\mu/k_B T; \beta = 1/k_B T$$

» Gran Canónico (Cont.)

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

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

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

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

¿Qué pasa con las fluctuaciones en N ?

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

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

» Las fluctuaciones de N

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

$$\begin{aligned} \frac{\partial \langle N \rangle}{\partial \mu} &= \left. \frac{\langle N \rangle}{\partial p} \right|_{V,T} \left. \frac{\partial p}{\partial \mu} \right|_{V,T} = \left. \frac{\partial \langle N \rangle}{\partial p} \frac{\partial \langle N \rangle}{\partial V} \right|_{T,\mu} \\ &= \left. \frac{\langle N \rangle}{V} \frac{\partial \langle N \rangle}{\partial p} \right|_{V,T} = \left. \langle N \rangle \frac{\partial}{\partial p} \left(\frac{\langle N \rangle}{V} \right) \right|_{V,T} = \left. \langle N \rangle^2 \frac{\partial V^{-1}}{\partial p} \right|_{N,T} = - \left. \frac{\langle N \rangle^2}{V^2} \frac{\partial V}{\partial p} \right|_{N,T} \end{aligned}$$

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

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

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

» Las fluctuaciones de E

Como antes,

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

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

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

y además

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

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

» Gas Ideal

» 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