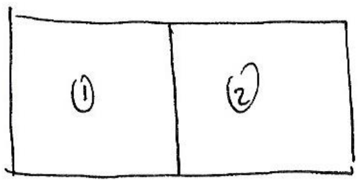
Distribuição de estados no ensemble gran-canônico

Sejam 2 membros de um ensemble em equilíbrio térmico e difusivo (flutuações da energia e do nº de constituintes)



$E = E_1 + E_2$ (energia)

$\mathcal{N} = \mathcal{N}_1 + \mathcal{N}_2$ (nº de constituintes)

hipótese (i): $P_{estado}(E, \mathcal{N})$ → probabilidade depende da energia e do nº de constituintes

hipótese (ii): $\dfrac{\partial P(E,\mathcal{N})}{\partial E} < 0$ $\left(\dfrac{\partial \ln P}{\partial E} < 0 \right)$ → estados com maior energia são menos prováveis

hipótese (iii): $P(E_1+E_2, \mathcal{N}_1+\mathcal{N}_2) = P_1(E_1,\mathcal{N}_1) \times P_2(E_2,\mathcal{N}_2)$ $(\ln P = \ln P_1 + \ln P_2)$ → independentes

$$\left\{ \begin{array}{l} \dfrac{\partial \ln P}{\partial E_1} = \dfrac{\partial \ln P}{\partial E} \overbrace{\left(\dfrac{\partial E}{\partial E_1}\right)}^{1} = \dfrac{\partial \ln P_1}{\partial E_1} \\[2ex] \dfrac{\partial \ln P}{\partial E_2} = \dfrac{\partial \ln P}{\partial E} \overbrace{\left(\dfrac{\partial E}{\partial E_2}\right)}^{1} = \dfrac{\partial \ln P_2}{\partial E_2} \end{array} \right.$$

$$\Longrightarrow \frac{\partial \ln P_1}{\partial E_1} = \frac{\partial \ln P_2}{\partial E_2} = \text{cte (negativa)} \; (-\beta)$$

(eq. térmico)

$$\left\{ \begin{array}{l} \dfrac{\partial \ln P}{\partial \mathcal{N}_1} = \dfrac{\partial \ln P}{\partial \mathcal{N}} \overbrace{\left(\dfrac{\partial \mathcal{N}}{\partial \mathcal{N}_1}\right)}^{1} = \dfrac{\partial \ln P_1}{\partial \mathcal{N}_1} \\[2ex] \dfrac{\partial \ln P}{\partial \mathcal{N}_2} = \dfrac{\partial \ln P}{\partial \mathcal{N}} \overbrace{\left(\dfrac{\partial \mathcal{N}}{\partial \mathcal{N}_2}\right)}^{1} = \dfrac{\partial \ln P_2}{\partial \mathcal{N}_2} \end{array} \right.$$

$$\Longrightarrow \frac{\partial \ln P_1}{\partial \mathcal{N}_1} = \frac{\partial \ln P_2}{\partial \mathcal{N}_2} = \text{cte} \; (\gamma)$$

(eq. difusivo)

$$\Longrightarrow \boxed{P_{estado}(E, \mathcal{N}) \sim e^{\gamma \mathcal{N} - \beta E}}$$

Função de partição gran-canônica

$$\sum_{\text{estado}} P(E,N) = 1 \text{ (normalização)} \Longrightarrow \begin{cases} P_{\text{estado}}(E,N) = \dfrac{e^{(\gamma N - \beta E)}}{Z_G} & \text{(distribuição gran-canônica)} \\[2ex] Z_G = \displaystyle\sum_{\text{estado}} e^{(\gamma N - \beta E)} & \text{(função de partição gran-canônica)} \end{cases}$$

Funções e leis da Termodinâmica

$$\langle E \rangle = U = \sum_{\text{estado}} E\, P(E,N) \quad \text{(energia interna)}$$

$$\frac{\partial Z_G}{\partial \beta} = -\sum E\, e^{\gamma N - \beta E} = -Z \sum E \overbrace{\left(\frac{e^{\gamma N - \beta E}}{Z_G} \right)}^{P(E,N)} = -Z_G \langle E \rangle$$

$$\boxed{U = \frac{1}{Z_G} \frac{\partial Z_G}{\partial \beta} = -\frac{\partial \ln Z_G}{\partial \beta}}$$

$$\begin{cases} P(E,N) = \dfrac{e^{+\gamma N - \beta E}}{Z_G} \\[2ex] \ln P(E,N) = \gamma N - \beta E - \ln Z_G \end{cases}$$

$$dU = \sum E\, dP + \sum P\, dE$$

$E(N, V, X)$ – depende do nº de constituintes, volume e outras variáveis como magnetização, ...

$$\frac{1}{\beta}(\gamma N - \ln P - \ln Z_G) \qquad \underbrace{\frac{\partial E}{\partial N}}_{\gamma/\beta} dN + \frac{\partial E}{\partial V} dV + \frac{\partial E}{\partial X} dX$$

$$\ln P = \gamma N - \beta E - \ln Z_G$$

$$dU = \underbrace{\frac{\gamma}{\beta}\sum N dP}_{\frac{\gamma}{\beta}\left[\underbrace{d\left(\sum N P\right)}_{d\langle N\rangle} - \cancel{\sum P dN}\right]} - \frac{1}{\beta}\underbrace{\sum (\ln P)\, dP}_{d\left(\underbrace{\sum P \ln P}_{\langle \ln P\rangle}\right) - \underbrace{\sum P\, d\ln P}_{\sum dP = 0}} - \cancel{\frac{1}{\beta}\ln Z_G \underbrace{\sum dP}_{d\left(\sum P\right) = 0}} + \cancel{\frac{\gamma}{\beta}\sum P dN} + \underbrace{\sum P\left(\frac{\partial E}{\partial V}\right)}_{\left\langle \frac{\partial E}{\partial V}\right\rangle} dV + \underbrace{\sum P\left(\frac{\partial E}{\partial X}\right)}_{\left\langle \frac{\partial E}{\partial X}\right\rangle} dX$$

analogia de Gibbs

$$\begin{cases} dU = \dfrac{d\langle -\ln P\rangle}{\beta} + \left\langle \dfrac{\partial E}{\partial V}\right\rangle dV + \left\langle \dfrac{\partial E}{\partial X}\right\rangle dX + \dfrac{\gamma}{\beta} d\langle N\rangle \\ dU = T dS - P dV + Y dX + \mu dN \end{cases} \Rightarrow \begin{cases} \beta = \dfrac{1}{kT} \quad S = -k\langle \ln P\rangle \quad \gamma = \beta\mu \\ P = -\left\langle \dfrac{\partial E}{\partial X}\right\rangle \quad Y = \left\langle \dfrac{\partial E}{\partial X}\right\rangle \quad \gamma = \dfrac{\mu}{kT} \end{cases}$$

$$E = -\frac{1}{\beta}\ln P - \frac{1}{\beta}\ln Z_G + \overbrace{\left(\frac{\gamma}{\beta}\right)}^{\mu} N \Rightarrow \underbrace{\langle E\rangle}_{U} - \underbrace{\frac{\langle -\ln P\rangle}{\beta}}_{TS} - \mu \underbrace{\langle N\rangle}_{N} = \boxed{-kT\ln Z_G = \Omega}$$

(potencial gran-canônico)

$$\boxed{Z_G = \sum_{\text{stado}} e^{(\mu N - E)/kT}}$$

$$\begin{cases} G = \mu N = U - TS - PV \\ \Downarrow \\ -PV = U - TS - \mu N = \Omega \end{cases}$$

$$
\begin{cases}
dU = T\,dS - P\,dV + Y\,dX + \mu\,dN & U(S,N,V,X) \\
d(\underbrace{U - TS - \mu N}_{\Omega}) = -S\,dT - P\,dV - N\,d\mu \; + Y\,dX & \Omega(T,\mu,V,X) = -k \ln Z_G = -PV
\end{cases}
$$

$$
\begin{cases}
S = -\left(\dfrac{\partial \Omega}{\partial T}\right)_{V,X,\mu} = k \dfrac{\partial}{\partial T}\left(T \ln Z_G\right)\Big|_{V,X,\mu} \\[2ex]
N = -\left(\dfrac{\partial \Omega}{\partial \mu}\right)_{T,V,X} = kT\left(\dfrac{\partial \ln Z_G}{\partial \mu}\right)_{T,V,X} \\[2ex]
P = -\left(\dfrac{\partial \Omega}{\partial V}\right)_{T,\mu,X} = kT\left(\dfrac{\partial \ln Z_G}{\partial V}\right)_{T,\mu,X} \\[2ex]
U = -\left(\dfrac{\partial \ln Z_G}{\partial \beta}\right)_{V,N,X} = kT^2\left(\dfrac{\partial \ln Z_G}{\partial T}\right)_{V,N,X}
\end{cases}
$$

$$
Z_G = \sum_{\text{states}} e^{-\beta(E - \mu N)}
$$

No ensemble gran-canônico as propriedades termodinâmicas derivam da função de partição gran-canônica.