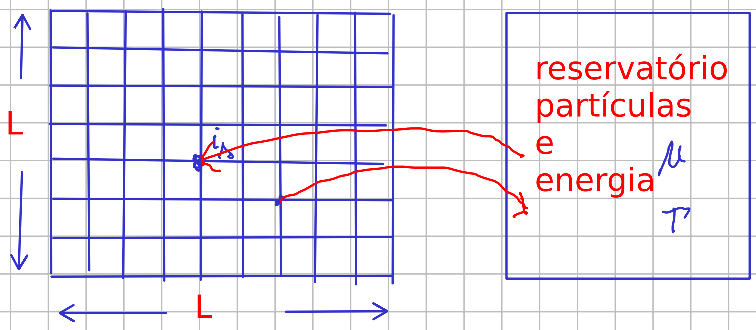
exercicio 36



a) $V = n^{\underline{o}}$ total de sítios $= L^2$

Algoritmo de Metropolis genérico

p_A = probabilidade de aceitar x' partindo de x

$$= \min\left(1, \frac{Q(x|x')}{Q(x'|x)} \frac{P_{st}(x')}{P_{st}(x)}\right)$$

Adição

$x' = \{n_{i \neq i_s}, n_{i_s} + 1\}$ $\quad i_s \equiv$ sítio específico

$x = \{n_{i \neq i_s}, n_{i_s}\}$

$$Q(x'|x) = \frac{1}{V} \qquad Q(x|x') = \frac{1}{N+1}$$

$$P_{st}(\{n_i\}) = \frac{e^{-\beta(E - \mu N)}}{Z_{GC}}$$

$E = 0$

$$P_{st}(x') = \frac{e^{+\beta\mu(N+1)}}{Z_G}$$

$$\frac{P_{st}(x')}{P_{st}(x)} = e^{\beta\mu}$$

$$P_{st}(x) = \frac{e^{\beta\mu N}}{Z_G}$$

$$p_A = \min\left(1, \frac{1/_{N+1}}{1/_V} \frac{e^{\beta\mu(N+1)}}{e^{\beta\mu N}}\right) = \min\left(1, \frac{V}{N+1} e^{\beta\mu}\right)$$

Remoção

$$x' = \{n_{i \neq i_1}, n_{i_s} - 1\} \qquad Q(x|x') = \frac{1}{V}$$

$$x = \{n_{i \neq i_n}, n_{i_n}\} \qquad Q(x'|x) = \frac{1}{N}$$

$$\frac{P_{st}(x')}{P_{st}(x)} = \frac{e^{\beta\mu(N-1)}}{e^{\beta\mu N}} = e^{-\beta\mu}$$

$$P_A = \min\left(1, \frac{1/V}{1/N} e^{-\beta\mu}\right) = \min\left(1, N/V\, e^{-\beta\mu}\right)$$

$$\langle N \rangle = \sum_s N_s \frac{e^{-\beta(E_s - \mu N_s)}}{Z_{GC}}, \quad Z_{GC} = \sum_s e^{-\beta(E_s - \mu N_s)}$$

$$\frac{\partial Z_{GC}}{\partial \mu} = \sum_s \beta N_s e^{-\beta(E_s - \mu N_s)}$$

$$= \frac{1}{\beta} \frac{\frac{\partial Z_{GC}}{\partial \mu}}{Z_{GC}} = \frac{1}{\beta} \frac{\partial}{\partial \mu} \ln Z_{GC}$$

$E_s = 0$

Calculo da função de partição no ensemble Grande-Canónico

$$Z_{GC} = \sum_{n_1=0}^{1} \sum_{n_2=0}^{1} \cdots e^{\beta\mu N}, \quad N = \sum_i n_i$$

$$= \sum_{n_1=0}^{1} e^{\beta\mu n_1} \sum_{n_2=0}^{1} e^{\beta\mu n_2} \cdots$$

$$= \left(1 + e^{\beta\mu}\right)\left(1 + e^{\beta\mu}\right) \cdots$$

$$= \left(1 + e^{\beta\mu}\right)^V$$

$$\langle N\rangle = \frac{1}{\beta}\frac{\partial}{\partial\mu}\ln Z_{GC} = \frac{1}{\beta}\frac{\partial}{\partial\mu}\left[V\ln\left(1+e^{\beta\mu}\right)\right]$$

$$= \frac{V}{\cancel{\beta}}\frac{\cancel{\beta}e^{\beta\mu}}{1+e^{\beta\mu}} \Rightarrow \boxed{\bar{\rho} = \frac{\langle N\rangle}{V} = \frac{e^{\beta\mu}}{1+e^{\beta\mu}}}$$

$$\sigma_N^2 = \langle N^2\rangle - \langle N\rangle^2$$, Variancia.

$$\langle N^2\rangle = \langle N\rangle^2 + \frac{1}{\beta}\frac{\partial\langle N\rangle}{\partial\mu}$$

$$\sigma_N^2 = \frac{1}{\beta}V\frac{\beta e^{\beta\mu}\left(1+e^{\beta\mu}\right) - e^{\beta\mu}\beta e^{\beta\mu}}{\left(1+e^{\beta\mu}\right)^2} = V\frac{e^{\beta\mu} + \cancel{e^{2\beta\mu}} - \cancel{e^{2\beta\mu}}}{\left(1+e^{\beta\mu}\right)^2}$$

$$\boxed{\sigma_N^2 = V\frac{e^{\beta\mu}}{\left(1+e^{\beta\mu}\right)^2}}$$

N pelo teorema do limite central é uma variável aleatória Gaussiana

$$N = \sum_{i=1}^{V} n_i \Rightarrow P_N(N) = \frac{1}{\sqrt{2\pi\sigma_N^2}}e^{-\frac{(N-\langle N\rangle)^2}{2\sigma_N^2}}$$

$$\rho = \frac{N}{V} \qquad \bar{\rho} = \frac{\langle N\rangle}{V} \qquad \sigma_\rho^2 = \frac{1}{V^2}\sigma_N^2$$

$$P(\rho) = \frac{1}{\sqrt{2\pi\sigma_\rho^2}}\exp\left(-\frac{(\rho-\bar{\rho})^2}{2\sigma_\rho^2}\right)$$

n_i segue uma distribuição de Bernoulli

$$p(n_i) = \begin{cases} p = \dfrac{e^{\beta\mu}}{1+e^{\beta\mu}} & \text{se } n_i = 1 \\[2ex] 1-p = \dfrac{1}{1+e^{\beta\mu}} & \text{se } n_i = 0 \end{cases}$$

$$P_{st}(\{n_i\}) = \prod_{i=1}^{V} p^{n_i}(1-p)^{1-n_i}$$

Probabilidade do número de partículas ser N

$$P(N) = \binom{V}{N} p^N (1-p)^{V-N}, \quad p = \frac{e^{\beta\mu}}{1+e^{\beta\mu}}$$

é uma distribuição binomial

$$P(N) = \frac{V!}{N!(V-N)!} \frac{e^{\beta\mu N}}{(1+e^{\beta\mu})^V}$$

a distribuição de Gauss é uma boa aproximação desta distribuição
numa gama grande de valores do potencial químico