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UNIVERSIDADE FEDERAL
DO RIO DE JANEIRO

Aula 11 – Integração Termodinâmica

Parte 1

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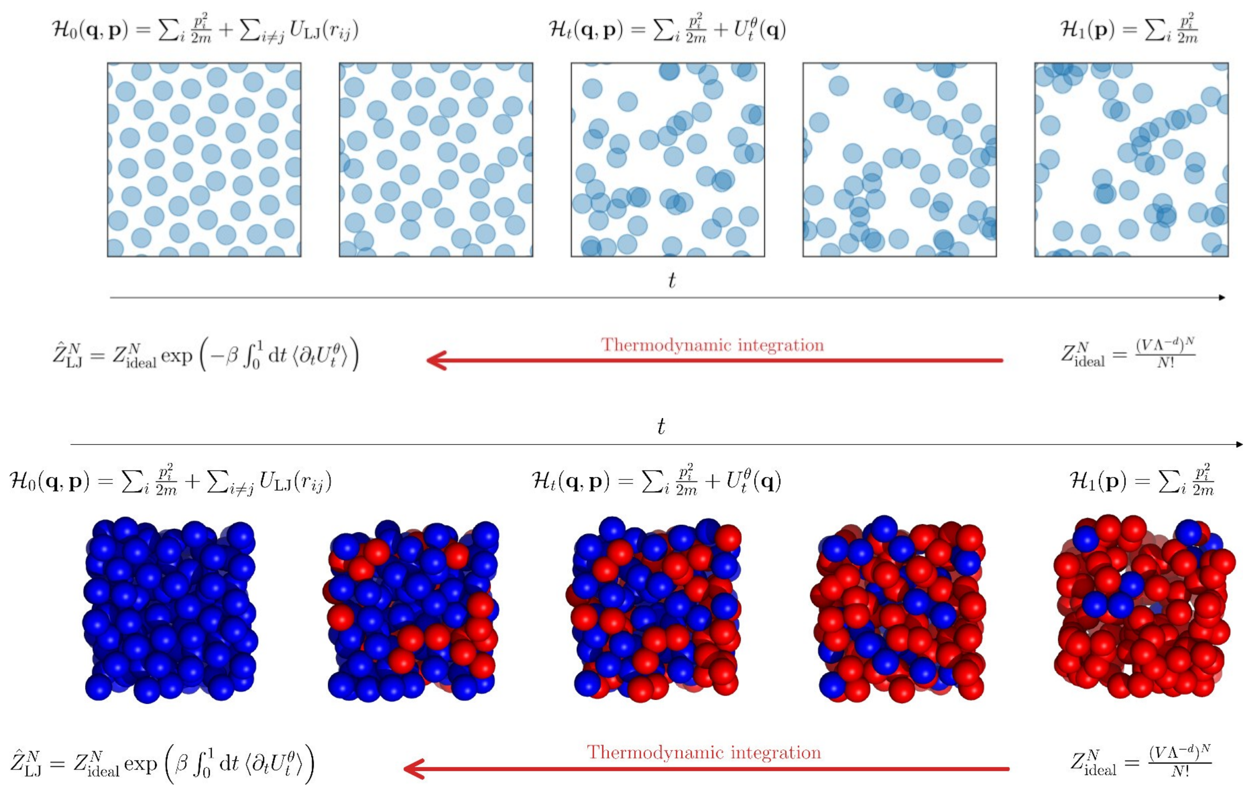

Imagens: Máté, B., Fleuret, F., & Bereau, T. (2024). Neural Thermodynamic Integration: Free Energies from Energy-Based Diffusion Models. The Journal of Physical Chemistry Letters, 15(45), 11395-11404.

Energia Livre e Simulação Molecular

- Hamiltoniano e Energia Total

$$H(\boldsymbol{q},\boldsymbol{p}) = \sum_{i=1}^{N} \frac{\boldsymbol{p}_i^2}{2m_i} + \sum_{j>i}\sum_{i=1}^{N} u(\boldsymbol{q}_{ij})$$

Energia Térmica

$$\beta = 1/k_B T$$

- Função de Partição Canônica

$$Z = \frac{1}{N!h^{3N}} \int \cdots \int e^{-\beta H(\boldsymbol{q},\boldsymbol{p})} \mathrm{d}\boldsymbol{q}^N \mathrm{d}\boldsymbol{p}^N = \frac{Z_{\text{ideal}}^N}{V^N} \left[\int e^{-\beta \sum_{j>i} \sum_{i=1}^{N} u(\boldsymbol{q}_{ij})} \mathrm{d}\boldsymbol{q}^N \right]$$

$$Z_{\text{ideal}}^N = \frac{V^N}{N!h^{3N}} \left[\int e^{-\beta \sum_{i=1}^{N} \frac{\boldsymbol{p}_i^2}{2m_i}} \mathrm{d}\boldsymbol{p}^N \right] = \frac{V^N \Lambda^{-3N}}{N!}$$

Energia Livre de Helmholtz (NVT)

$$F = -k_B T \ln Z$$

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References

Integração Termodinâmica (IT)

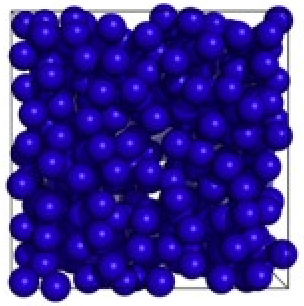
- Generalizando Interação soluto e solvente

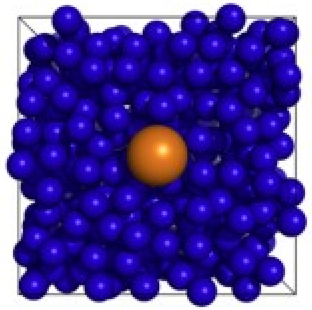
$$U_\lambda = U_A + U_B + U_{AB}^{\lambda}$$

$$U_{AB}^{\lambda=0} = 0 \qquad U_{AB}^{\lambda=1} = U_{AB}$$

$$U_0 = U_A + U_B$$

$$U_1 = U_A + U_B + U_{AB}$$





- Diferença de energia livre

$$\Delta F_{0\to 1} = \int_0^1 \frac{\partial F}{\partial \lambda} \mathrm{d}\lambda = -k_B T \int_0^1 \frac{\partial \ln Z_\lambda}{\partial \lambda} \mathrm{d}\lambda$$

$$= \int_0^1 \frac{1}{Z_\lambda} \frac{\partial}{\partial \lambda} \left[\int e^{-\beta U_\lambda(x)} \mathrm{d}x \right] \mathrm{d}\lambda$$

$$= \int_0^1 \frac{1}{Z_\lambda} \left[\int e^{-\beta U_\lambda(x)} \frac{\partial U_\lambda(x)}{\partial \lambda} \mathrm{d}x \right] \mathrm{d}\lambda$$

Integração Termodinâmica

$$\Delta F_{0\to 1} = \int_0^1 \left\langle \frac{\partial U_\lambda(x)}{\partial \lambda} \right\rangle_\lambda \mathrm{d}\lambda$$

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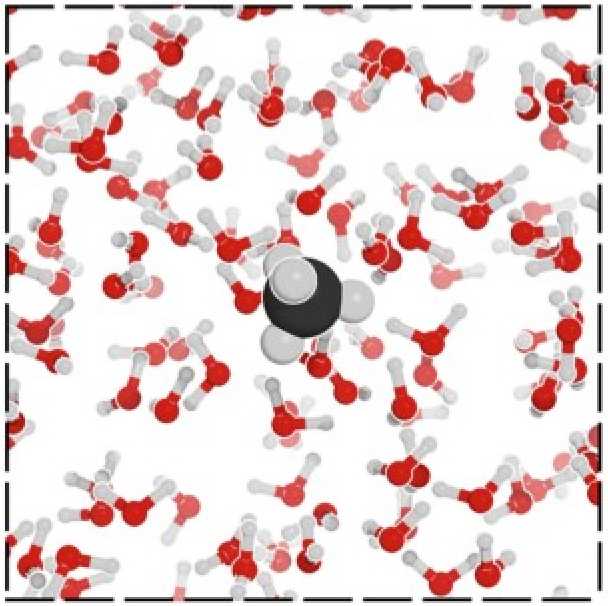
Ref: Kirkwood, J. G. (1935). Statistical mechanics of fluid mixtures. The Journal of chemical physics, 3(5), 300-313.

IT na Dinâmica Molecular

$$\Delta F_{0\to 1} = \frac{1}{N_\lambda} \sum_{\lambda_i} \left\langle \frac{\partial U_\lambda(x)}{\partial \lambda} \right\rangle_{\lambda_i}$$

$$\lambda_i \in \{0, 1/N_\lambda, 2/N_\lambda, \ldots, (N_\lambda - 1)/N_\lambda\}$$



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