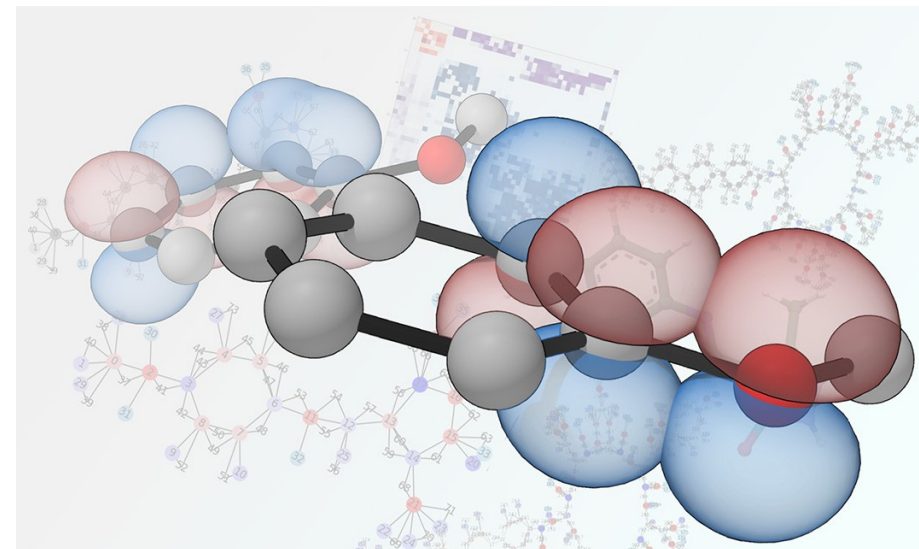


## Aula 06 – Dinâmica Molecular Ab Initio

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$$i\hbar \frac{\partial}{\partial t} |\Psi\rangle = \hat{H} |\Psi\rangle$$

$$|\Psi\rangle = |\psi\rangle e^{-iEt/\hbar}$$

$$\hat{H} |\psi\rangle = E |\psi\rangle$$

# Dinâmica Molecular Ab Initio

## Dinâmica de Born-Oppenheimer



Marx Born



Robert  
Oppenheimer

## Dinâmica de Car- Parrinello



Roberto Car



Michele  
Parrinello

# MD de Born-Oppenheimer (BOMD)

## Lagrangiana de Born-Oppenheimer

$$\mathcal{L}_{BO} = \frac{1}{2} \sum_{A=1}^M M_A \dot{\mathbf{R}}_A^2 - E_{KS}[\{\psi_i\}, \{\mathbf{R}_A\}]$$

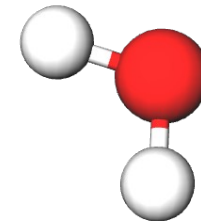
## Equações de movimento

$$M_A \ddot{\mathbf{R}}_A = -\nabla_A E_{KS}$$

## Equações de Kohn-Sham

$$\left[ -\frac{1}{2} \nabla^2 + V_{KS}(\mathbf{r}) \right] \psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r})$$

Elétrons relaxam em cada nova posição dos íons



# MD de Car-Parrinello

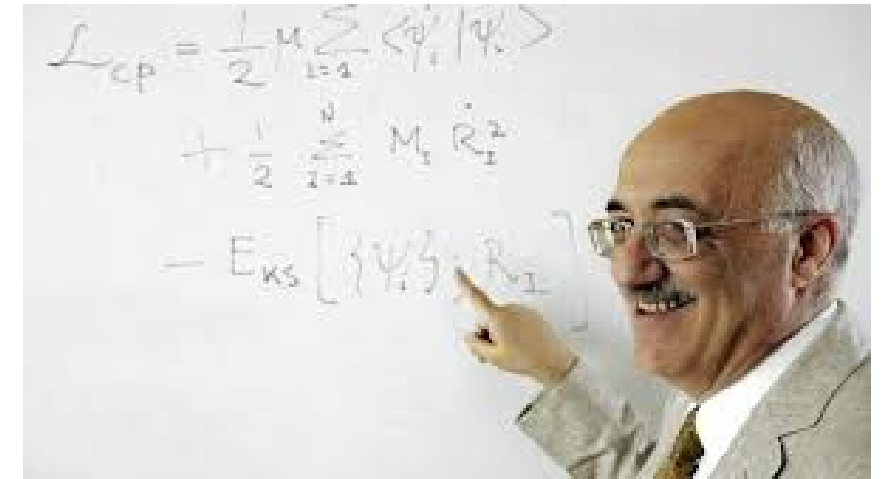
Lagrangiana de Car-Parrinello

$$\mathcal{L}_{CP} = \frac{1}{2} \sum_{A=1}^M M_A \dot{\mathbf{R}}_A^2 + \frac{1}{2} \mu \sum_{i=1}^N \langle \dot{\psi}_i | \dot{\psi}_i \rangle - E_{KS}[\{\psi_i\}, \{\mathbf{R}_A\}] + \sum_{i=1}^N \sum_{j \neq i}^N \Lambda_{ij} [\langle \psi_i | \psi_j \rangle - \delta_{ij}]$$

Ortogonalidade dos orbitais de Kohn-Sham

Evolução dos orbitais de Kohn-Sham.  
SCF somente para condição inicial.

$$\mu \ll M_A$$



Equações de movimento

$$M_A \ddot{\mathbf{R}}_A = -\nabla_A E_{KS}$$

$$\mu |\ddot{\psi}_i\rangle = -\underbrace{\frac{\delta E_{KS}}{\delta \langle \psi_i |}}_{\hat{H}_{KS}} + \sum_{j \neq i}^N \Lambda_{ij} |\psi_j\rangle$$

# Ensemble NVT

Distribuição de velocidades

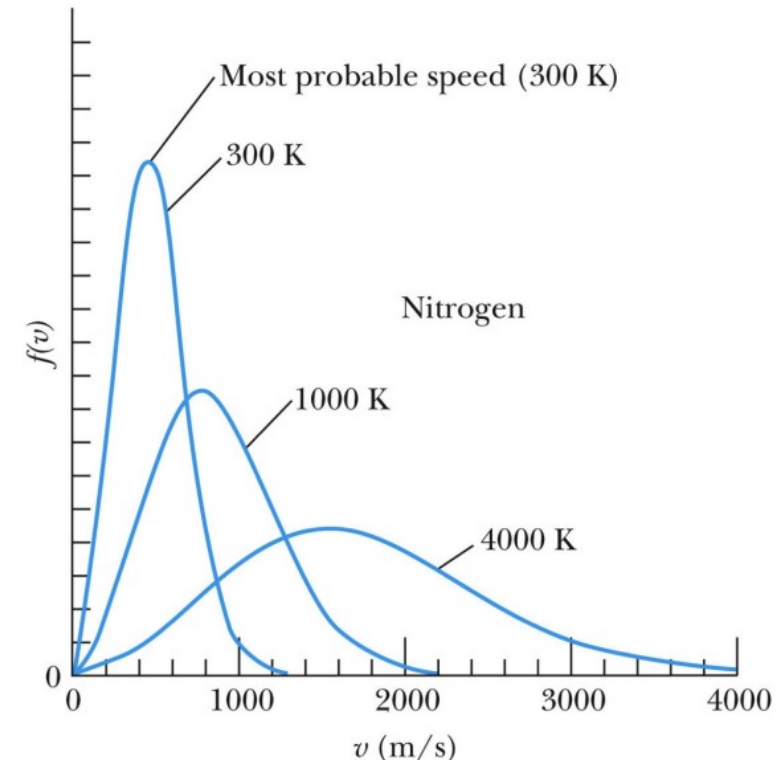
$$f(v_x) = \left( \frac{\beta}{2\pi m} \right)^{3/2} e^{-\beta \frac{mv_x^2}{2}} \longrightarrow$$

**Dist. de Maxwell-Boltzmann**

$$f(v) = f(v_x)f(v_y)f(v_z)$$

## Termostatos

- Velocity-rescaling
- Berendsen
- Andersen
- Nosé-Hoover (cadeia)
- **Langevin**

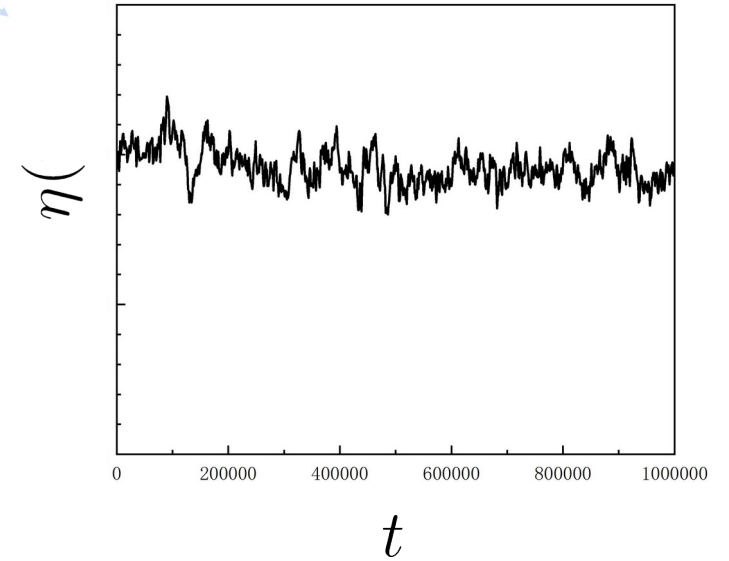
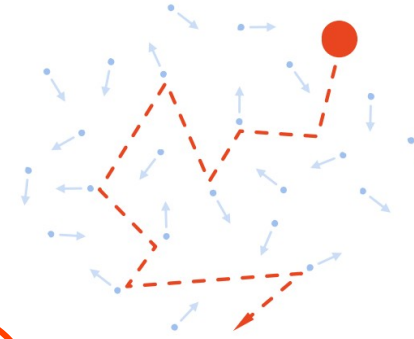


# Termostato de Langevin

Equações de Langevin

$$\frac{d\mathbf{R}}{dt} = \frac{\mathbf{P}}{M} \quad \text{e} \quad \frac{d\mathbf{P}}{dt} = -\nabla U - \gamma \mathbf{P} + \sigma \boldsymbol{\eta}$$

Força  
estocástica



Propriedades do termo estocástico

$$\langle \eta(t) \rangle = 0 \quad \text{e} \quad \langle \eta(t_1) \eta(t_2) \rangle = \delta(t_1 - t_2)$$

Sem potencial externo  $U = 0$

Equipartição de Energia

$$\left\langle \frac{\mathbf{P}^2}{2M} \right\rangle = \frac{3}{2} k_B T$$

Flutuação-Dissipação

$$\sigma = \sqrt{2\gamma m k_B T}$$

# Termostatos implementados no VASP

The following combinations of thermostats and barostats is possible:

	Thermostat					
Ensemble	Andersen	Nosé-Hoover	Langevin	Nosé-Hoover chain	CSVR	Multiple Andersen
Microcanonical (NVE)	MDALGO=1, ANDERSEN_PROB=0.0					
Canonical (NVT)	MDALGO=1	MDALGO=2	MDALGO=3	MDALGO=4	MDALGO=5	MDALGO=13
	ISIF=2	ISIF=2	ISIF=2	ISIF=2	ISIF=2	ISIF=2
Isobaric-isothermal (NpT)	not available	not available	MDALGO=3	not available	not available	not available
			ISIF=3			
Isoenthalpic-isobaric (NpH)	MDALGO=3, ISIF=3, LANGEVIN_GAMMA=LANGEVIN_GAMMA_L=0.0					