Métodos numéricos para escoamentos em nano e microescalas

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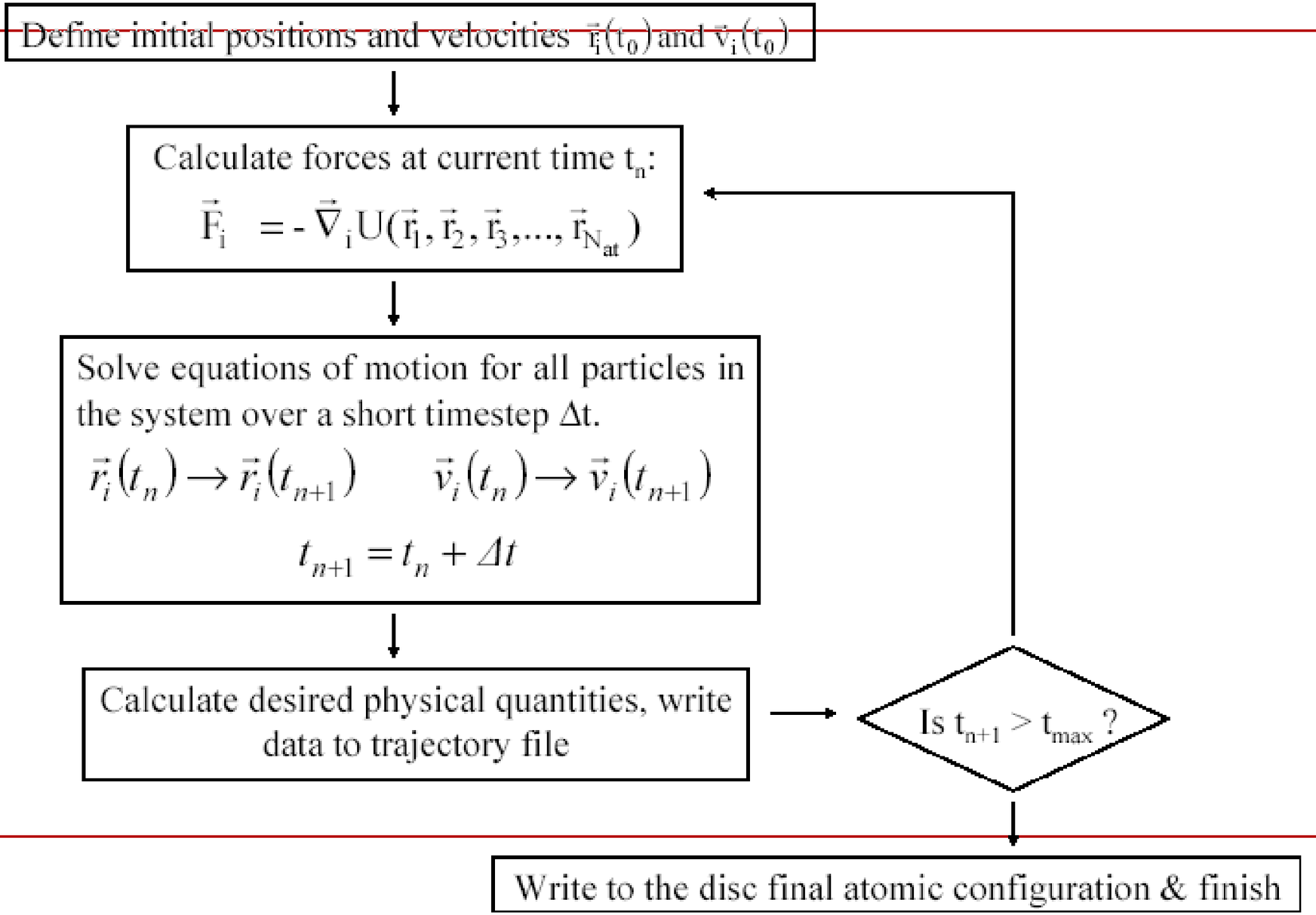
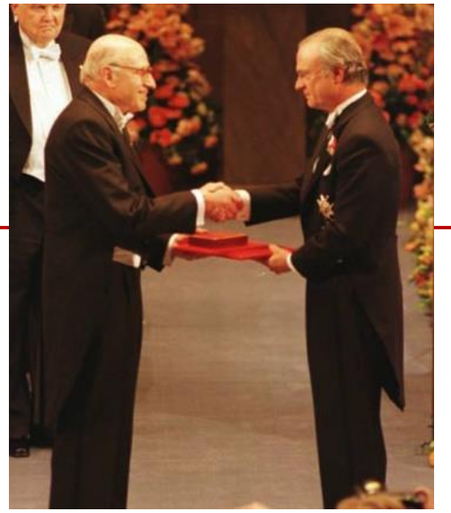
Schematic diagram of a basic MD code



Cálculos de primeiros princípios



Kohn - Nobel Prize 99

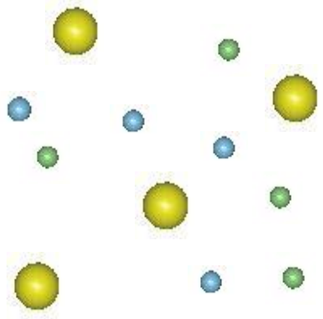
Resolve numericamente a equação de Schrödinger

Teoria do Funcional da Densidade (DFT)

Pseudopotenciais

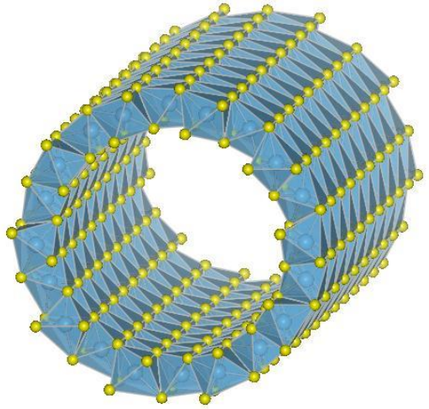
Quantum-Espresso, SIESTA, VASP and Gaussian

Composição



$$H\psi = E\psi$$

Estruturas



Propriedades

Thermodinâmica

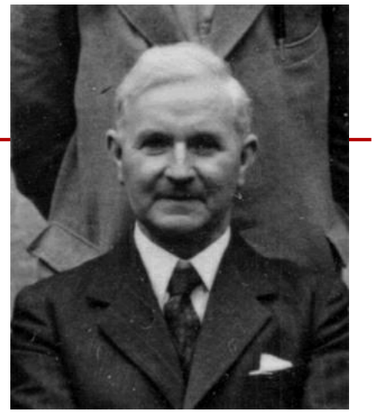
Parâmetro de rede

Constante elástica

Estrutura eletrônica

Cinética

Lennard-Jones:
modelo simples com 2 parâmetros



$$V(r) = \frac{A}{r^{12}} - \frac{B}{r^{6}}$$

$$\frac{V(r)}{\varepsilon} = \left[\left(\frac{\sigma}{r}\right)^{12} - 2\left(\frac{\sigma}{r}\right)^{6}\right]$$

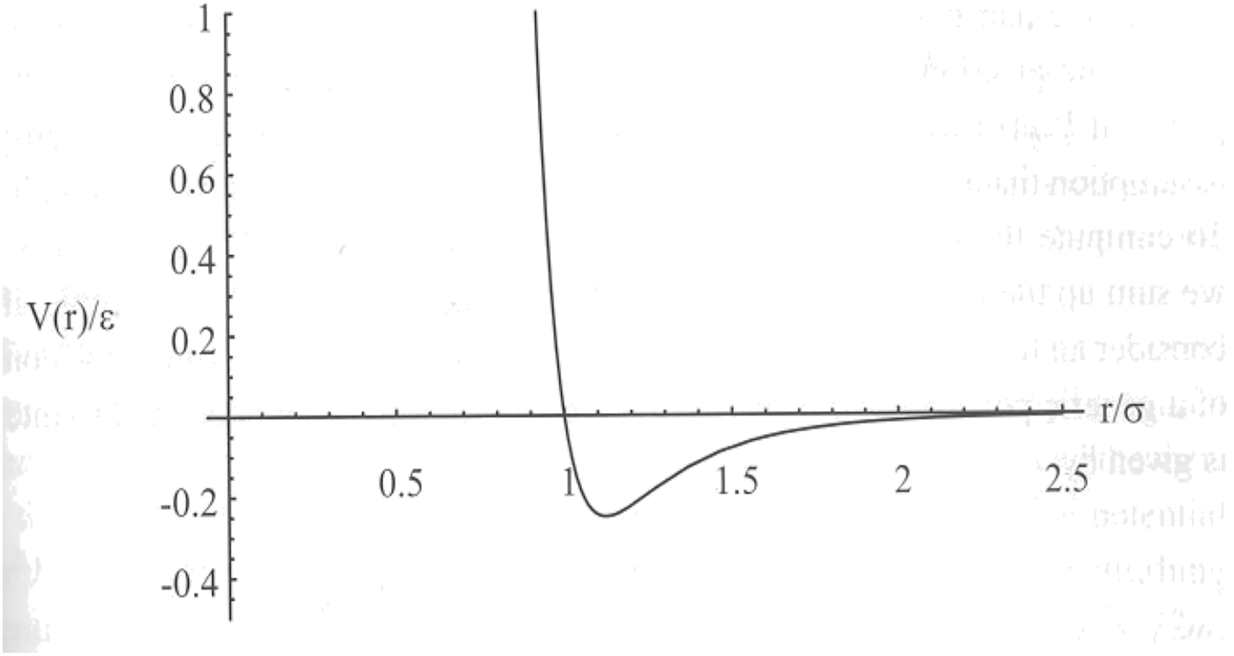
ε define a escala de energia
σ define a escala de comprimento

Todos os sistemas LJ são idênticos quando escrevemos a temperatura, pressão e densidade em unidades renormalizadas.

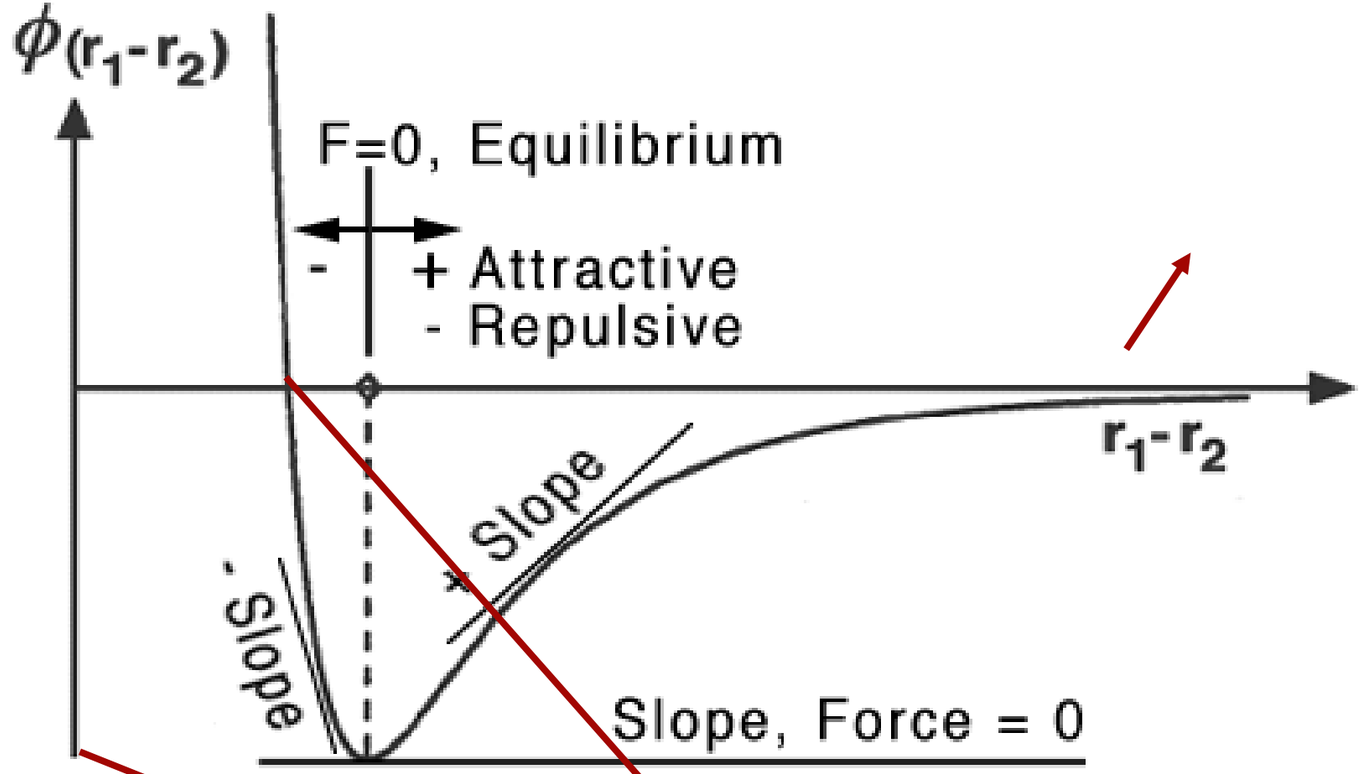
$$Temperature: \frac{\varepsilon}{k_B}$$

$$\text{Pr}\,essure: \frac{\varepsilon}{\sigma^3}$$

$$Density: \frac{1}{\sigma^3}$$



Potencial Lennard-Jones



$$u(r) = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^{6} \right]$$

Potencial Lennard-Jones

O Potencial LJ é uma aproximação. A forma do termo de repulsão não tem justificativa teórica.

A força de repulsão deve depender EXPONENCIALMENTE com a distância,

Mas o termo de repulsão da fórmula de LJ é mais conveniente pela facilidade e eficiência no cálculo do termo

r^{12} sendo o quadrado de r^6.

O Potencial atrativo de longo alcance, contudo, é derivado das interações de DISPERSÃO (London).

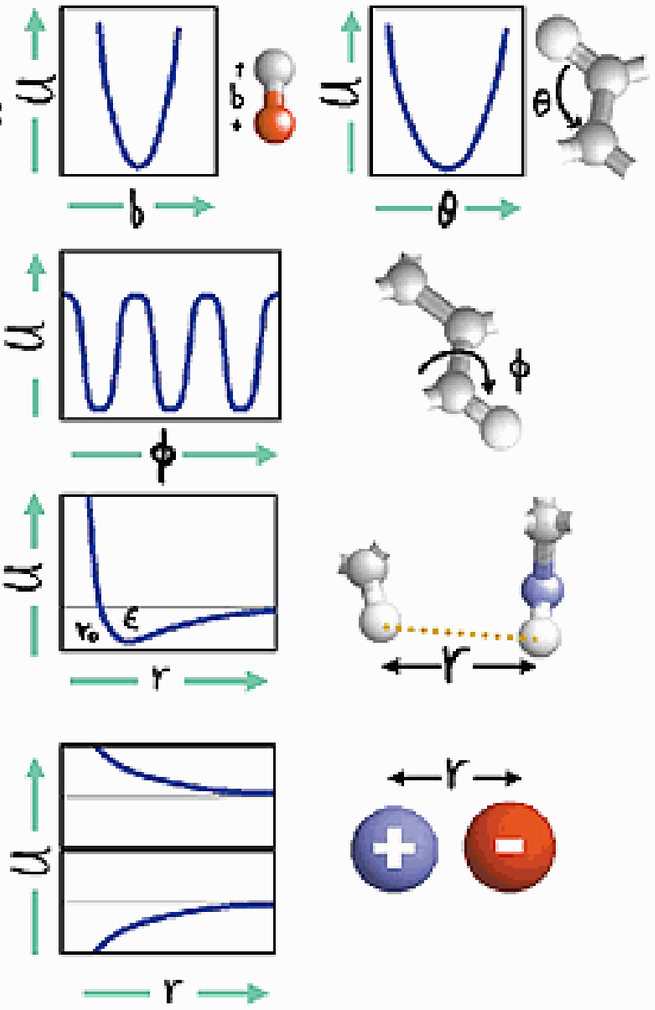
Potenciais para moléculas complexas

$$U = \sum_{\text{All Bonds}} \tfrac{1}{2} K_b (b - b_0)^2 + \sum_{\text{All Angles}} \tfrac{1}{2} K_\theta (\theta - \theta_0)^2$$

$$+ \sum_{\text{All Torsion Angles}} K_\phi [1 - \cos(n\phi + \delta)]$$

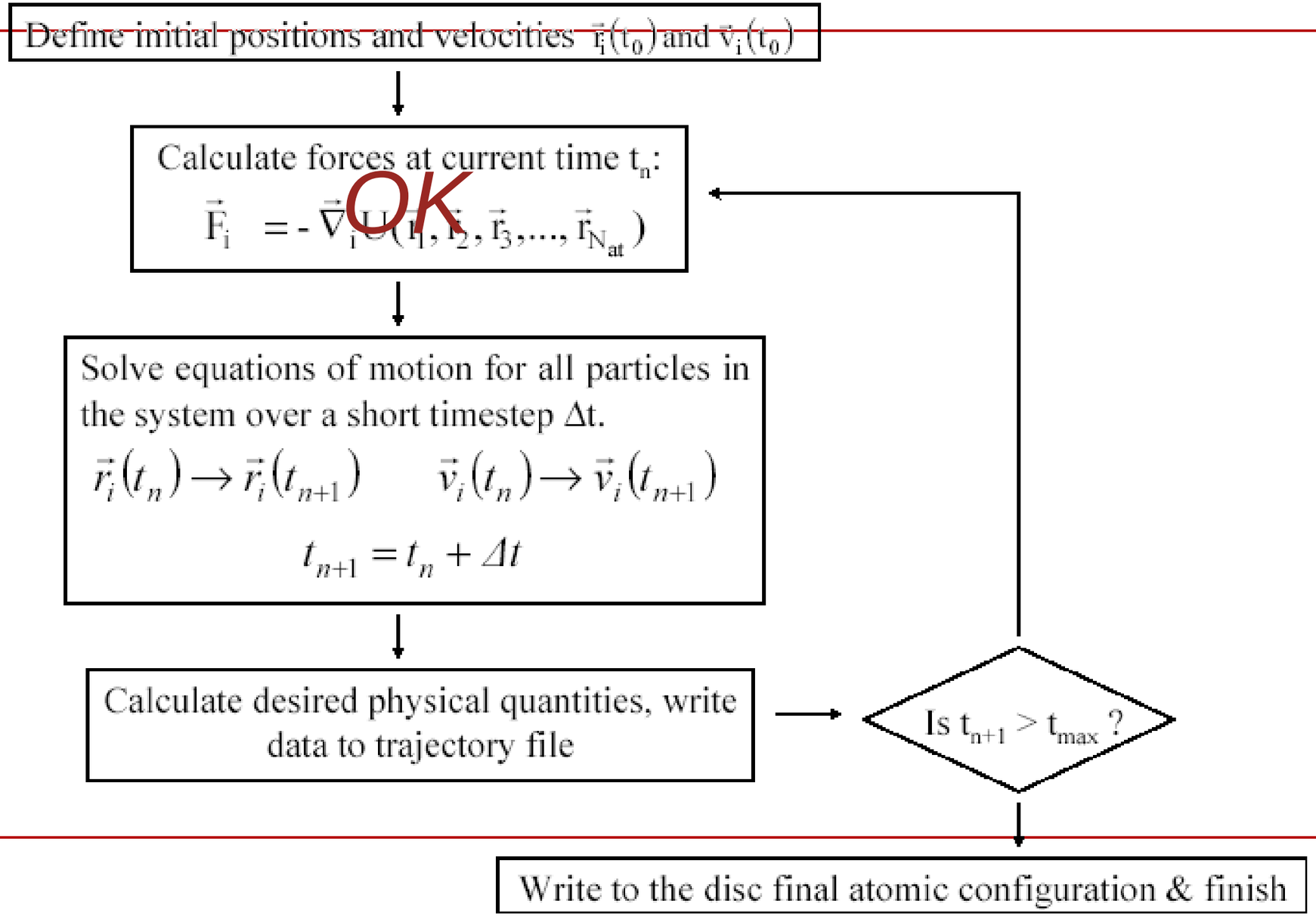
$$+ \sum_{\text{All nonbonded pairs}} \epsilon \left[(r_0/r)^{12} - 2(r_0/r)^6 \right]$$

$$+ \sum_{\text{All partial charges}} 332 q_i q_j / r$$



Michael Levitt, Nature Structural Biology 8, 392 - 393 (2001)
The birth of computational structural biology

Schematic diagram of a basic MD code



Parte 2 - Subrotina Init

O que é necessário ?

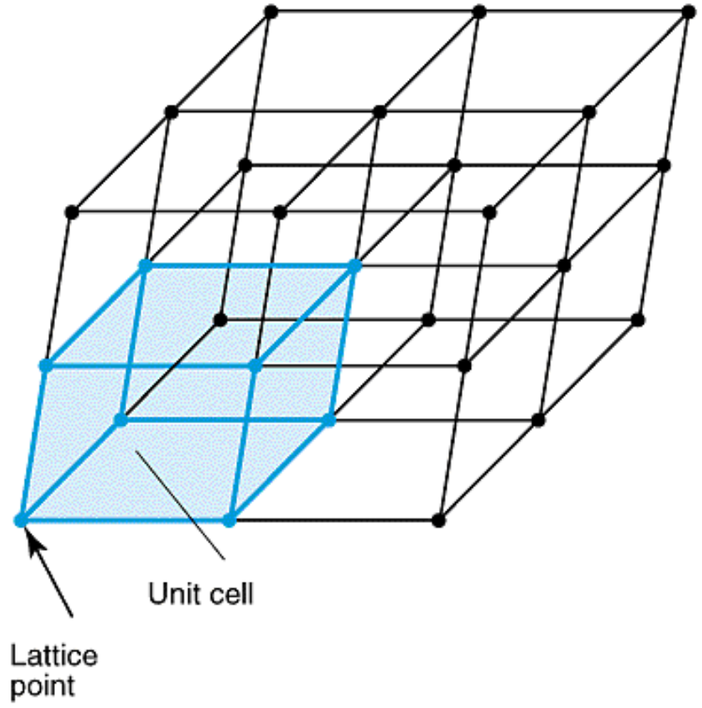
Definir: Condições: Temperatura, volume, número de átomos, ensemble

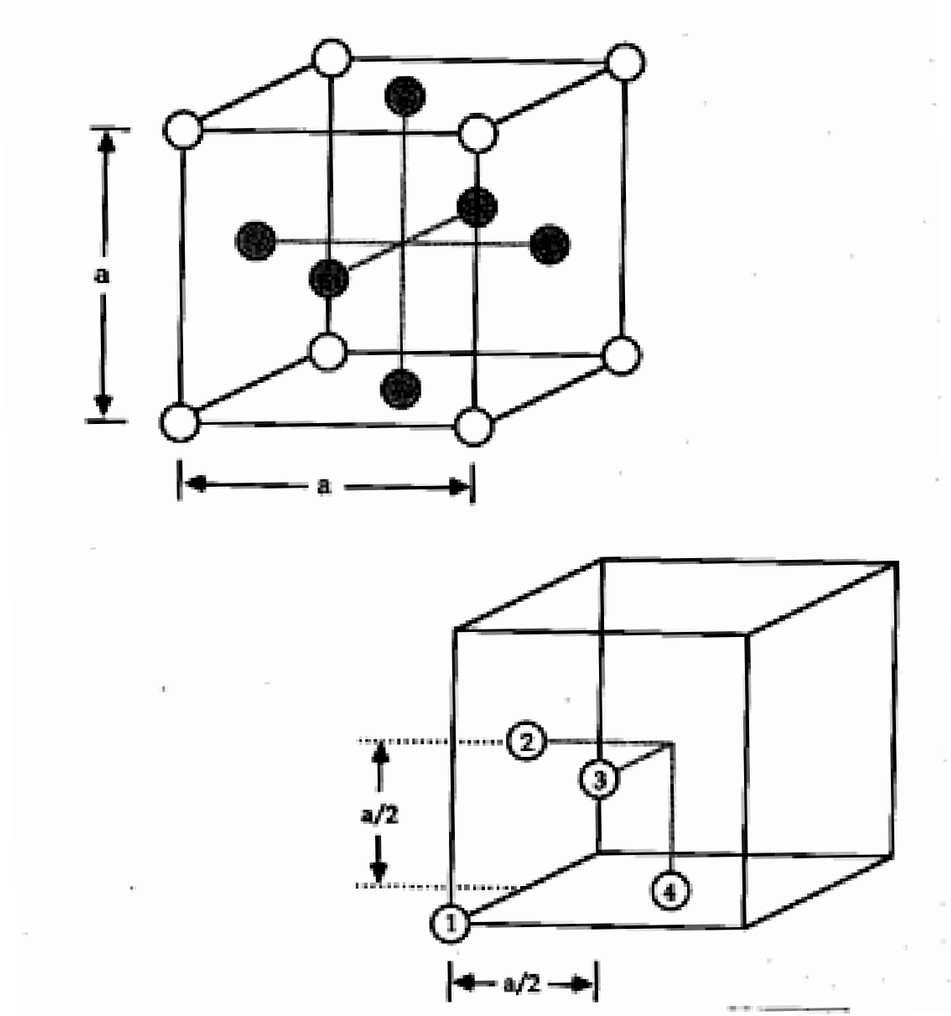
Coordenadas atômicas: Rede cristalina, minimização da energia, distribuição randômica, informação experimental, …

Velocidades: Distribuição de Maxwell-Boltzmann das velocidades
Fornece a temperatura média do sistema

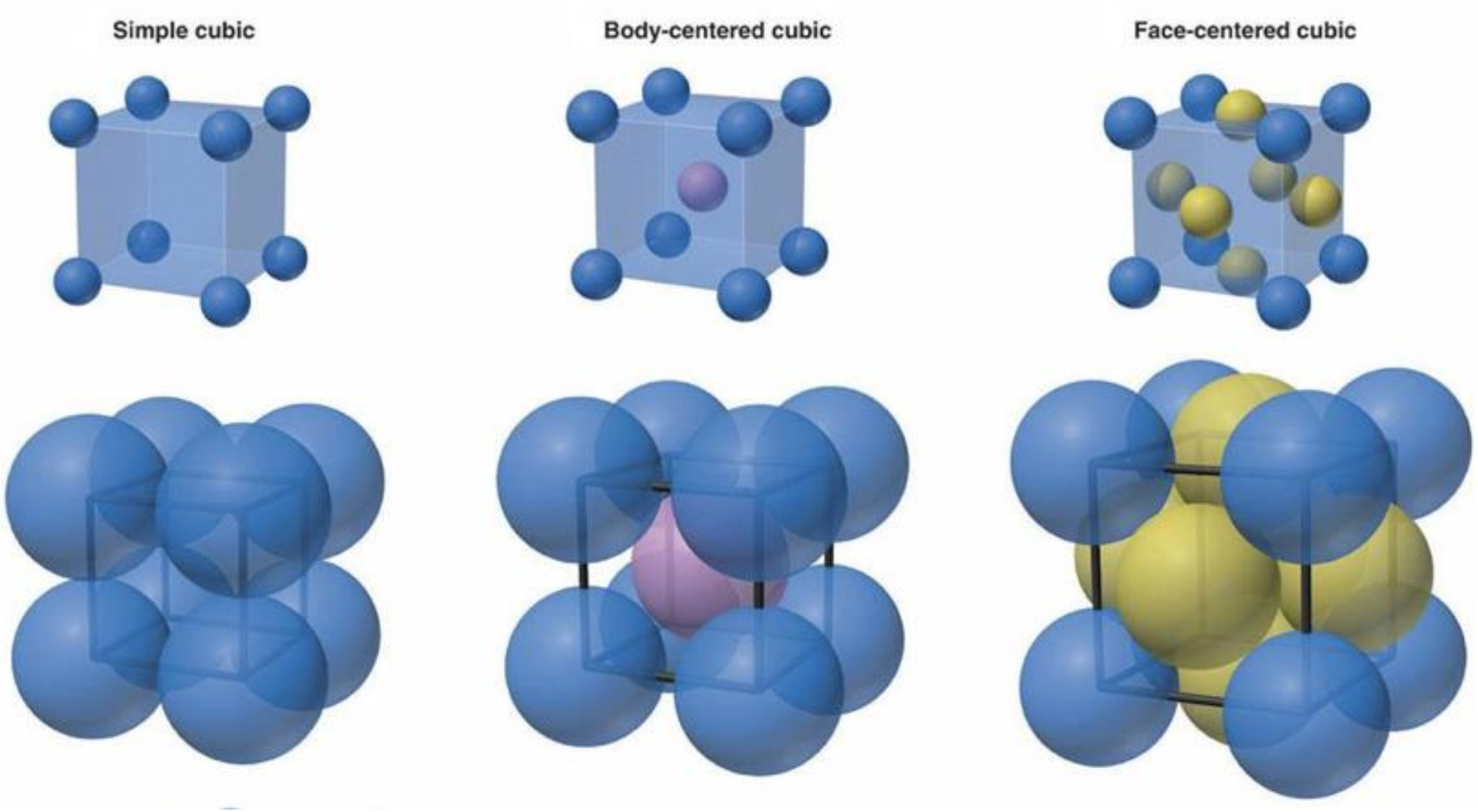
Acelerações: das forças das coordenadas atômicas iniciais

Posições iniciais

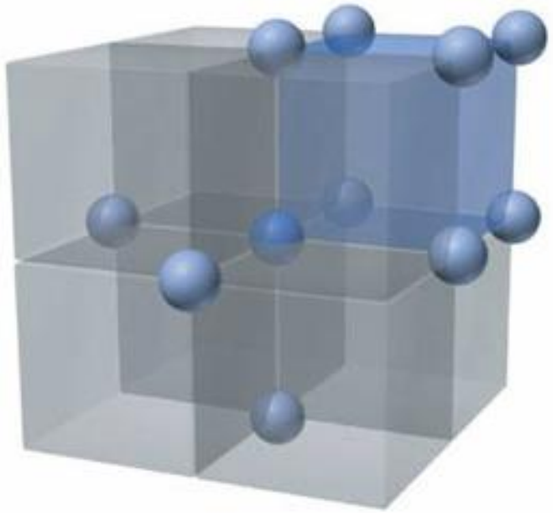




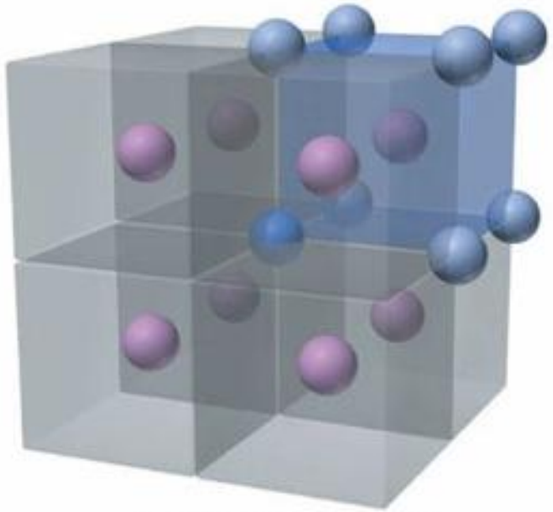
Posições iniciais



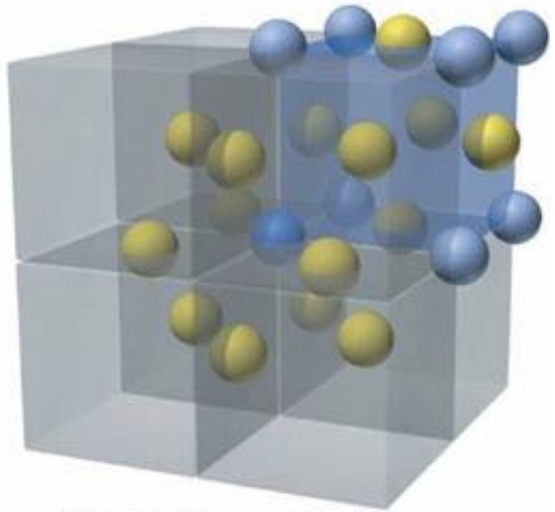
Posições iniciais



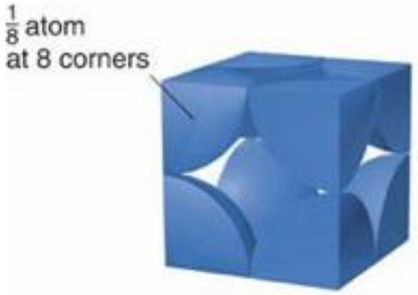
Coordination number = 6



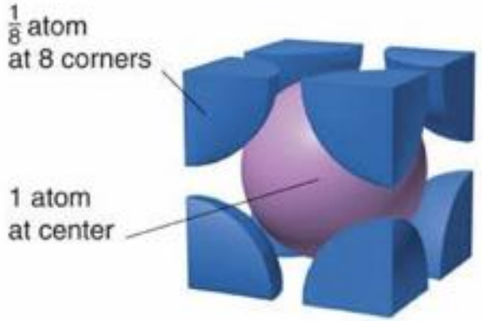
Coordination number = 8



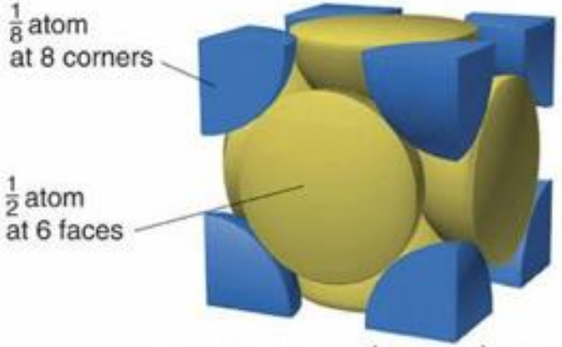
Coordination number = 12



Atoms/unit cell = $\frac{1}{8} \times 8 = 1$



Atoms/unit cell = $(\frac{1}{8} \times 8) + 1 = 2$



Atoms/unit cell = $(\frac{1}{8} \times 8) + (\frac{1}{2} \times 6) = 4$

Limitações da Dinâmica Molecular (III)

3) Limitações nas escalas de tempo e espaço

As limitações no tamanho da célula computacional de Dinâmica Molecular

Limitação do tempo de simulação

Limitações da Dinâmica Molecular (III)

3) Escala temporal

O passo **máximo** de integração em simulações e Dinâmica Molecular é definido pelo movimento mais rápido do sistema.

Frequências vibracionais em um sistema molecular são da ordem de 3000cm-1 (~10 femtosegundos)

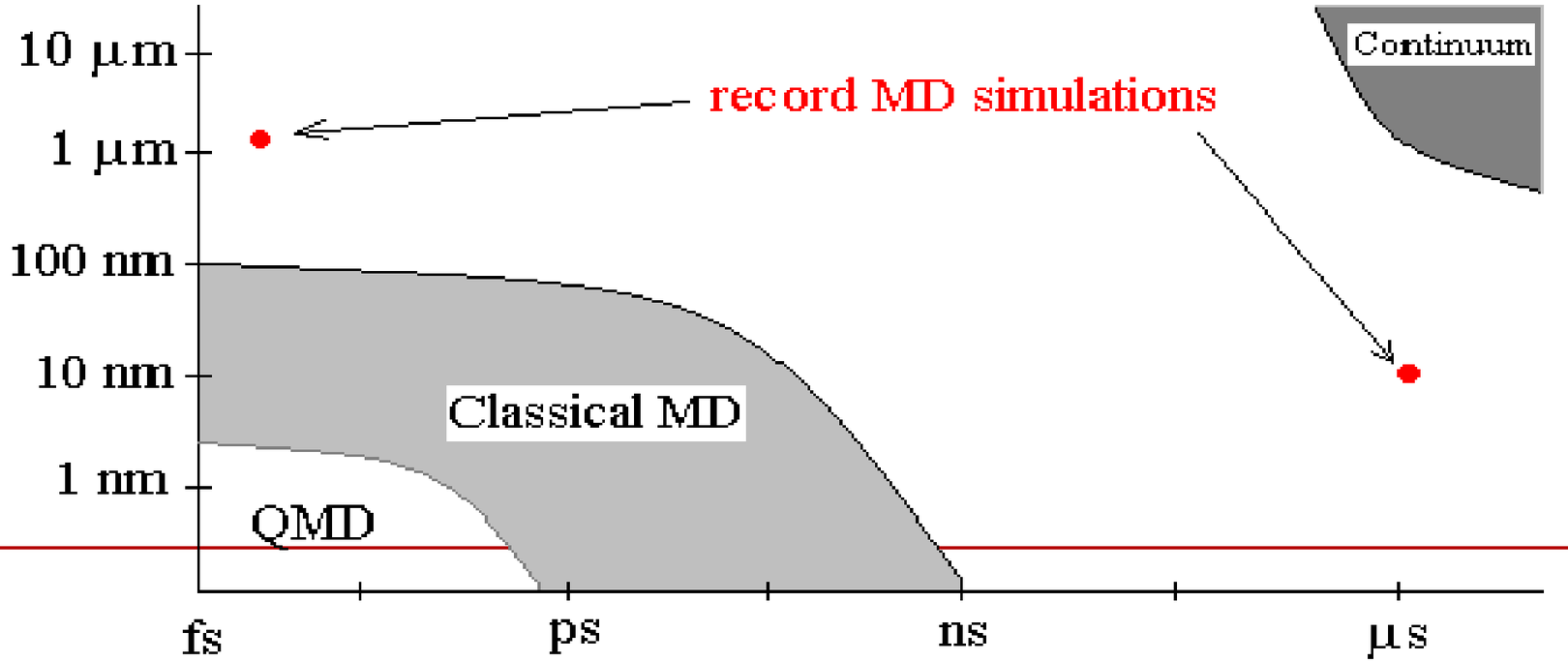
Frequências ópticas são da ordem de 10THz (período de 100fs)

Um típico passo de integração em Dinâmica Molecular é da ordem de FEMTONSEGUNDOS (10^-15s)

Length-scale:

The size of the computational cell is limited by the number of atoms that can be included in the simulation, typically $10^4 - 10^7$. This corresponds to the size of the computational cell on the order of **tens of nm**. Any structural features of interest and spatial correlation lengths in the simulation should be smaller than the size of the computational cell.

To make sure that the finite size of the computational cell does not introduce any artifacts into the simulation results, one can perform simulations for systems of different size and compare the measured properties.



Condições de contorno

A escala espacial em Dinâmica Molecular também é limitada:
Maior parte dos átomos que estão na superfície “sentem” a presença da superfície.

Como reproduzir as interações atômicas em uma célula computacional em Materiais ?

Condições de contorno (Livre)

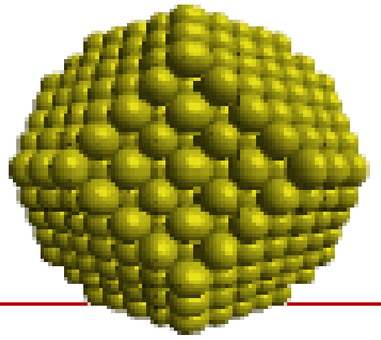
1. Free boundaries (or no boundaries). This works for a molecule, a cluster or an aerosol particle in vacuum. Free boundary condition can be also appropriate for ultrafast processes when the effect of boundaries is not important due to the short time-scale of the involved processes, e.g. fast ion/atom bombardment, etc.

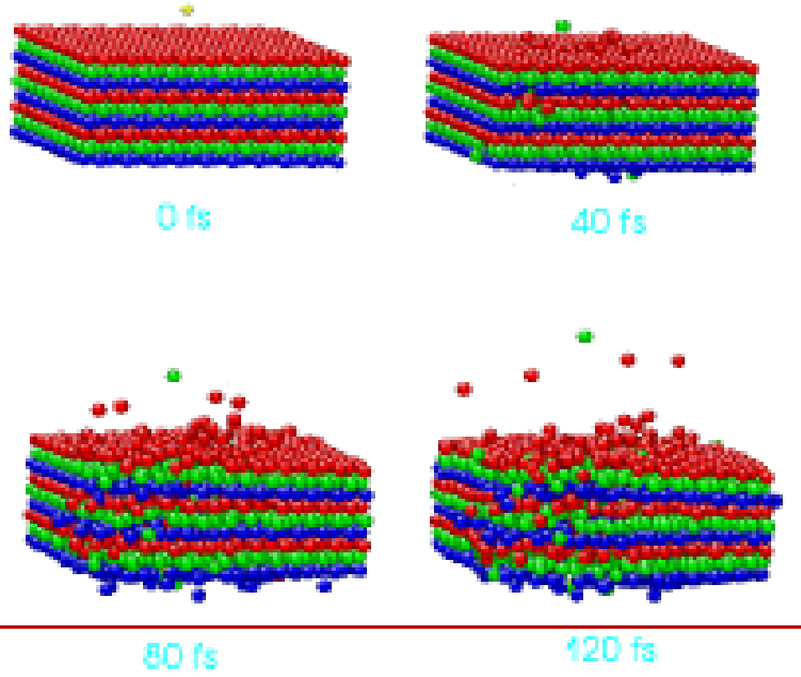
MD

Examples of free boundary conditions in MD:

Ultrafast process of sputtering

Free cluster





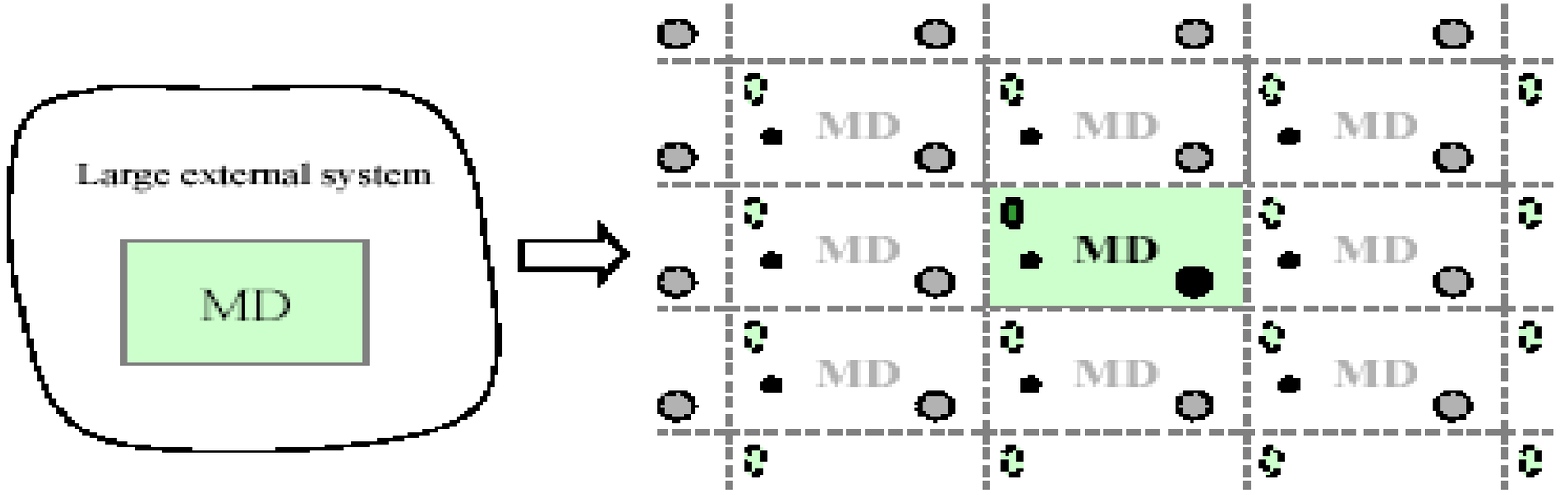
keV particle bombardment, by Barbara Garrison
http://galilei.chem.psu.edu/Research_bmb.html

Condições de contorno - Rígidas

2. Rigid boundaries (atoms at the boundaries are fixed). In most cases the rigid boundaries are unphysical and can introduce artifacts into the simulation results. Sometimes used in combination with other conditions (stochastic and periodic conditions, as discussed below).

Condições de contorno periódicas

3. Periodic boundary condition (eliminates surfaces – the most popular choice of boundary conditions). This boundary conditions are used to simulate processes in a small part of a large system.



All atoms in the computational cell (green box) are replicated throughout the space to form an infinite lattice. Than is, if atoms in the computational cell have positions r_i, the periodic boundary condition also produces mirror images of the atoms at positions defined as

$$\vec{r}_i^{\,image} = \vec{r}_i + l\vec{a} + m\vec{b} + n\vec{c}$$

where **a**, **b**, **c** are vectors that correspond to the edges of the box, l, m, n are any integers from $-\infty$ to $+\infty$.

Condições de contorno periódicas

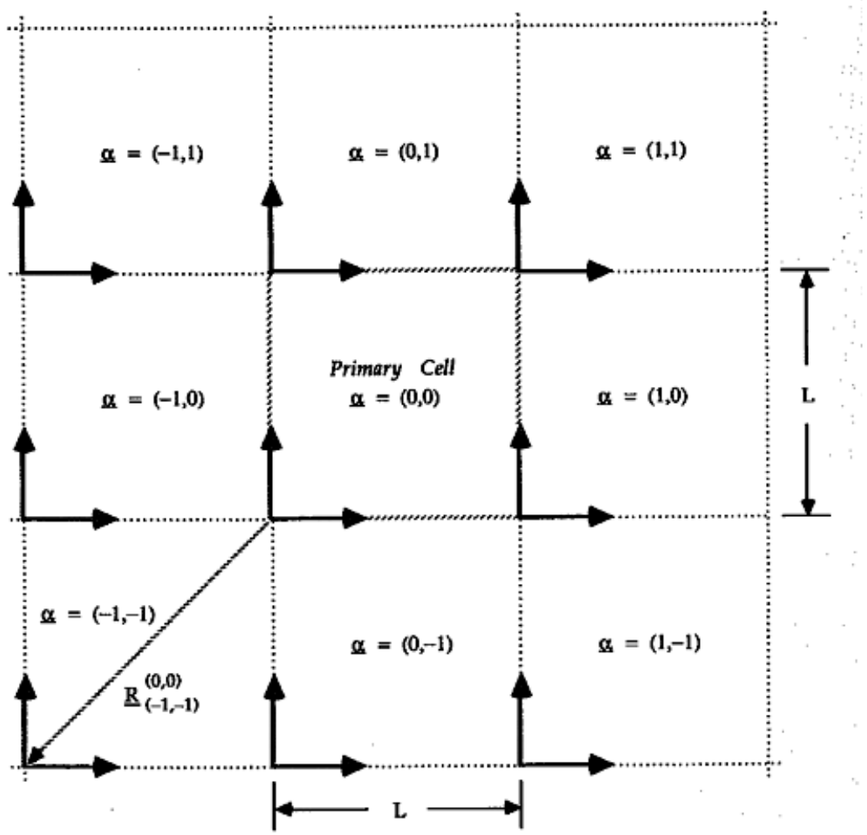
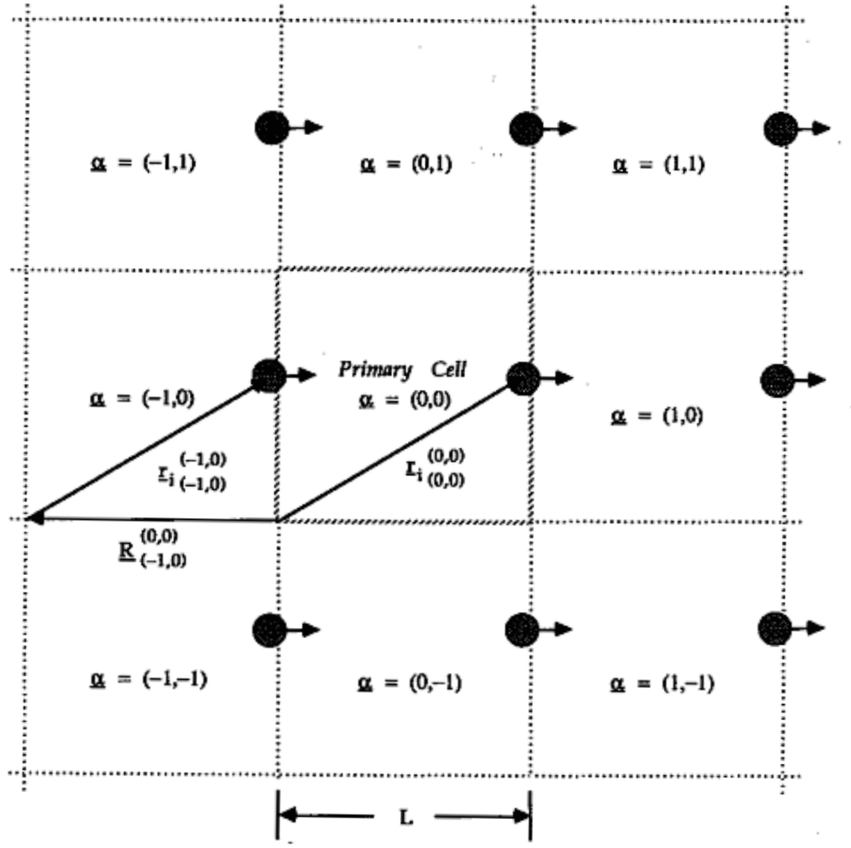
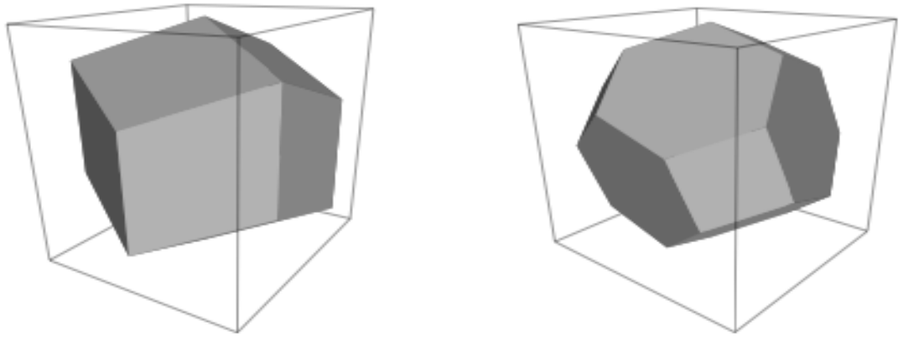


FIGURE 2.13 Periodic boundary conditions in two dimensions. The primary cell is surrounded by eight image cells and each cell is identified by a cell translation vector **α**. Each cell has a reference frame whose origin is the lower left corner of the cell. Each image frame is located wrt the primary frame by a vector **R**, such as the one shown here for cell $\boldsymbol{\alpha} = (-1, -1)$.



Condições de contorno periódicas

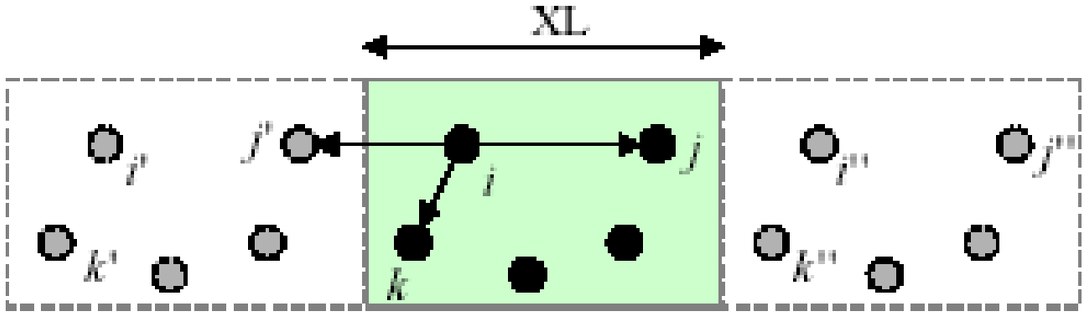


box type	image distance	box volume	box vectors			box vector angles		
			a	**b**	**c**	∠**bc**	∠**ac**	∠**ab**
cubic	d	d^3	d 0 0	0 d 0	0 0 d	90°	90°	90°
rhombic dodecahedron	d	$\frac{1}{2}\sqrt{2}\,d^3$ $0.707\,d^3$	d 0 0	0 d 0	$\frac{1}{2}\,d$ $\frac{1}{2}\,d$ $\frac{1}{2}\sqrt{2}\,d$	60°	60°	90°
truncated octahedron	d	$\frac{4}{9}\sqrt{3}\,d^3$ $0.770\,d^3$	d 0 0	$\frac{1}{3}\,d$ $\frac{2}{3}\sqrt{2}\,d$ 0	$-\frac{1}{3}\,d$ $\frac{1}{3}\sqrt{2}\,d$ $\frac{1}{3}\sqrt{6}\,d$	71.53°	109.47°	71.53°

Condições de contorno periódicas

Calculation of distances between atoms with periodic boundary conditions:

When the minimum image criterion is satisfied, a particle can interact only with the closest image of any other particle.



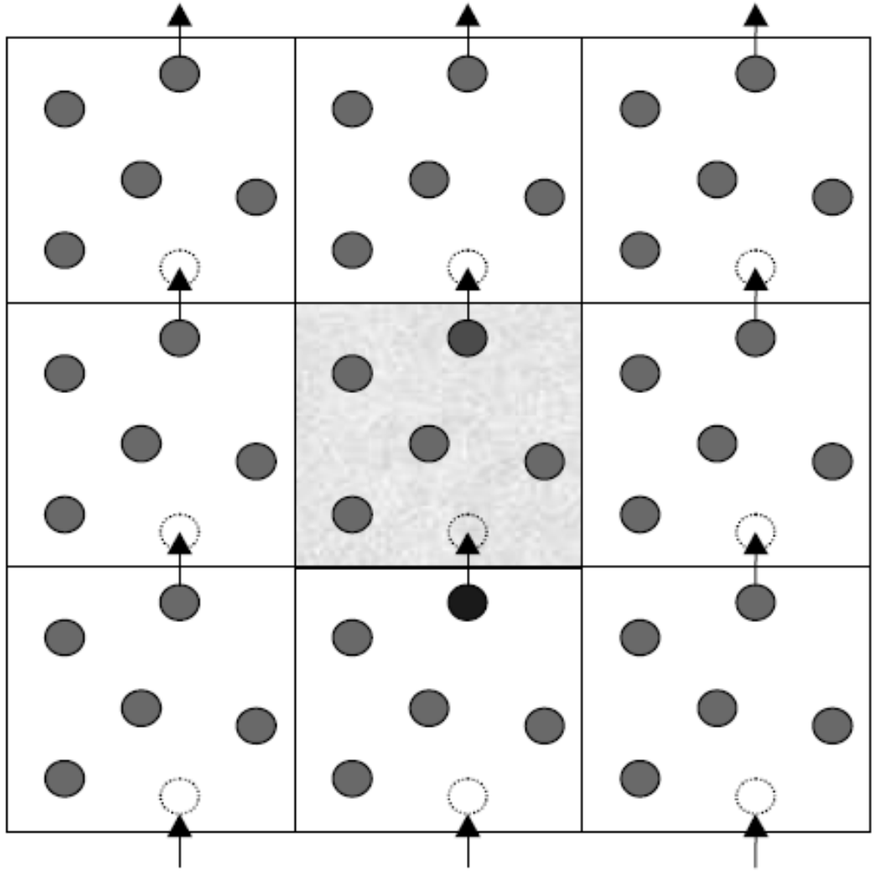
The closest image may or may not belong to the computational cell. Therefore, in the code, if a particle j is beyond the range of interaction with particle i ($R_{ij} > R_{cut}$), we have to check the closest images. For example, in MSE524-MD code, an algorithm for checking the closest image is:

```
IF(LIDX.EQ.1) THEN
   IF(DX.GT.XLHALF) DX=DX-XL
   IF(DX.LT.-XLHALF) DX=DX+XL
ENDIF
```

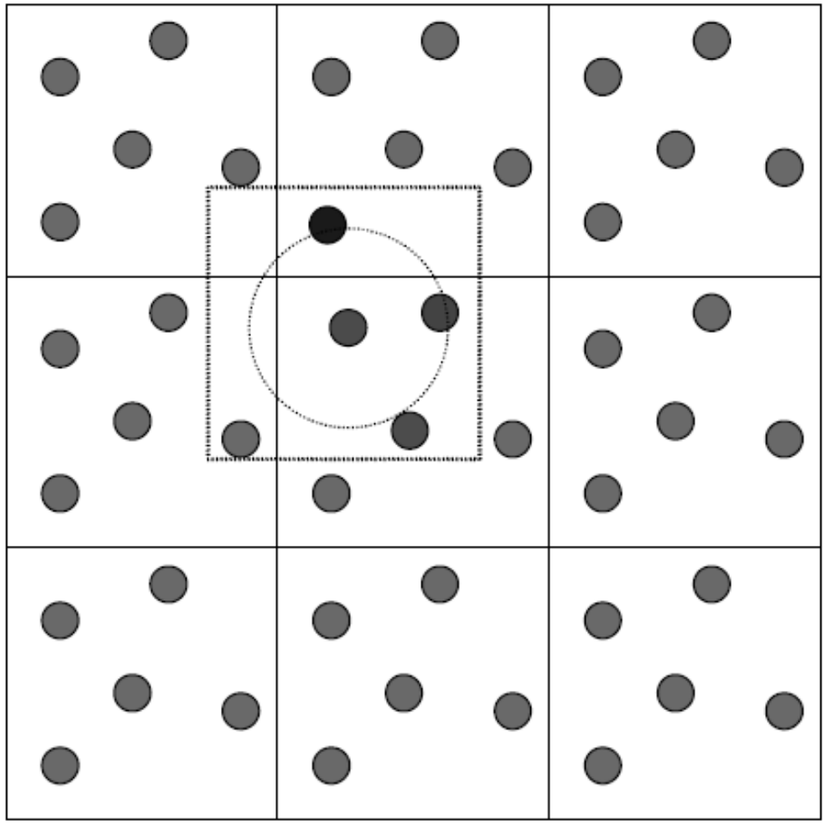
where $DX = X_j - X_i$

XLHALF = XL/2

Critério da imagem mínima



Condições Periódicas de Contorno



Critério da imagem mínima

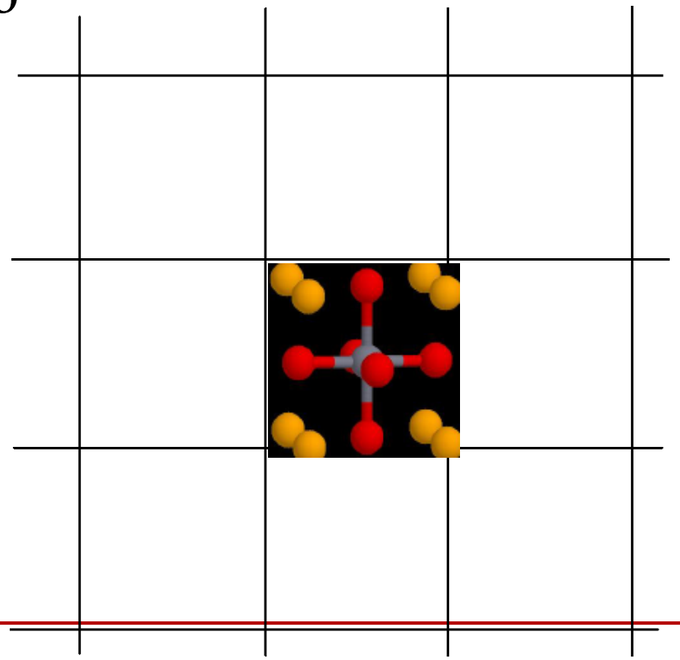
Tamanho do sistema e condições de contorno

Sistema finito (ex. molécula ou cluster)

Sem problemas; -> simplesmente use todos os átomos

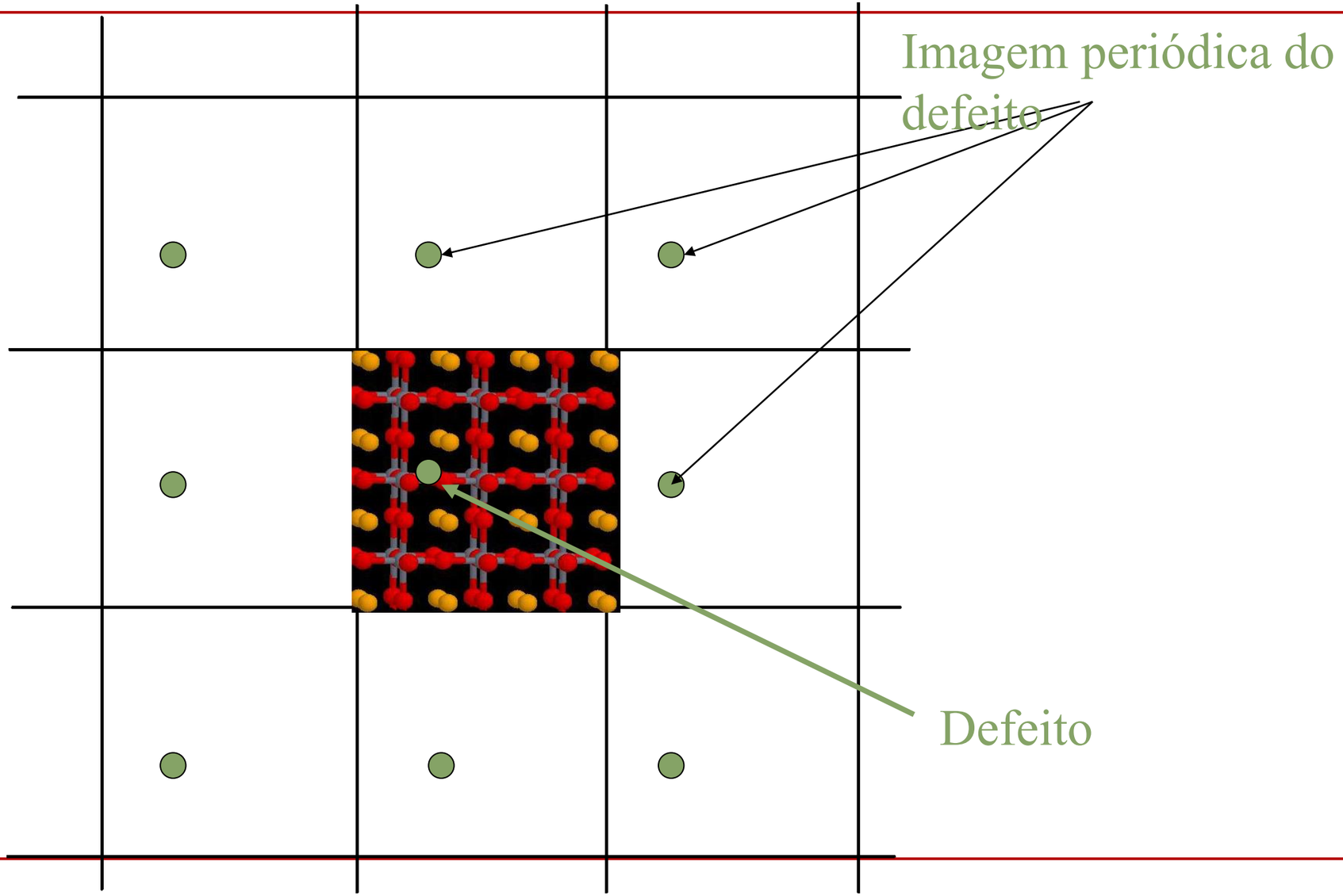
Sistema infinito (ex. sólidos/líquidos)

Não podemos aproximar como sistema finito -> uso das Condições Periódicas de Contorno

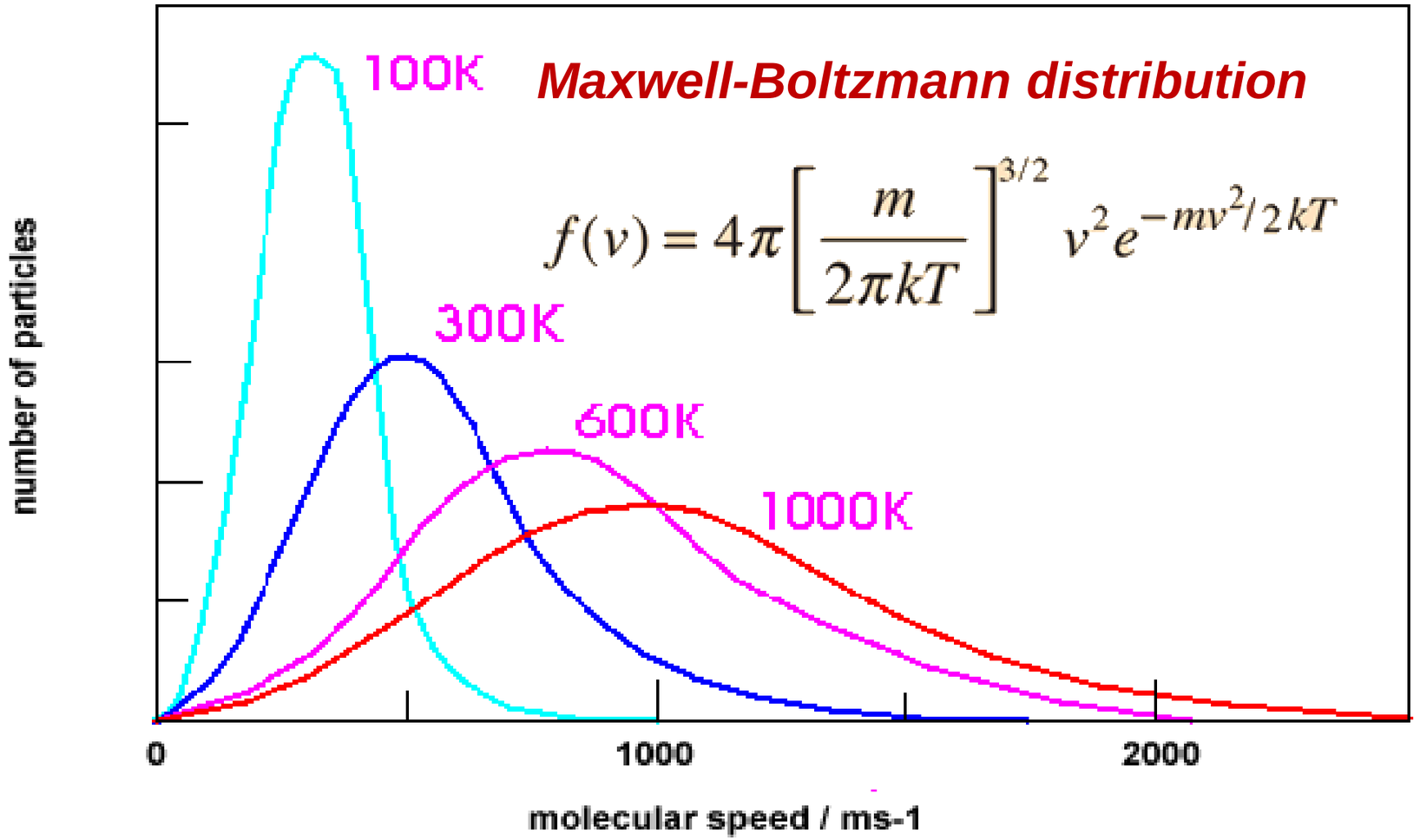


$BaTiO_3$

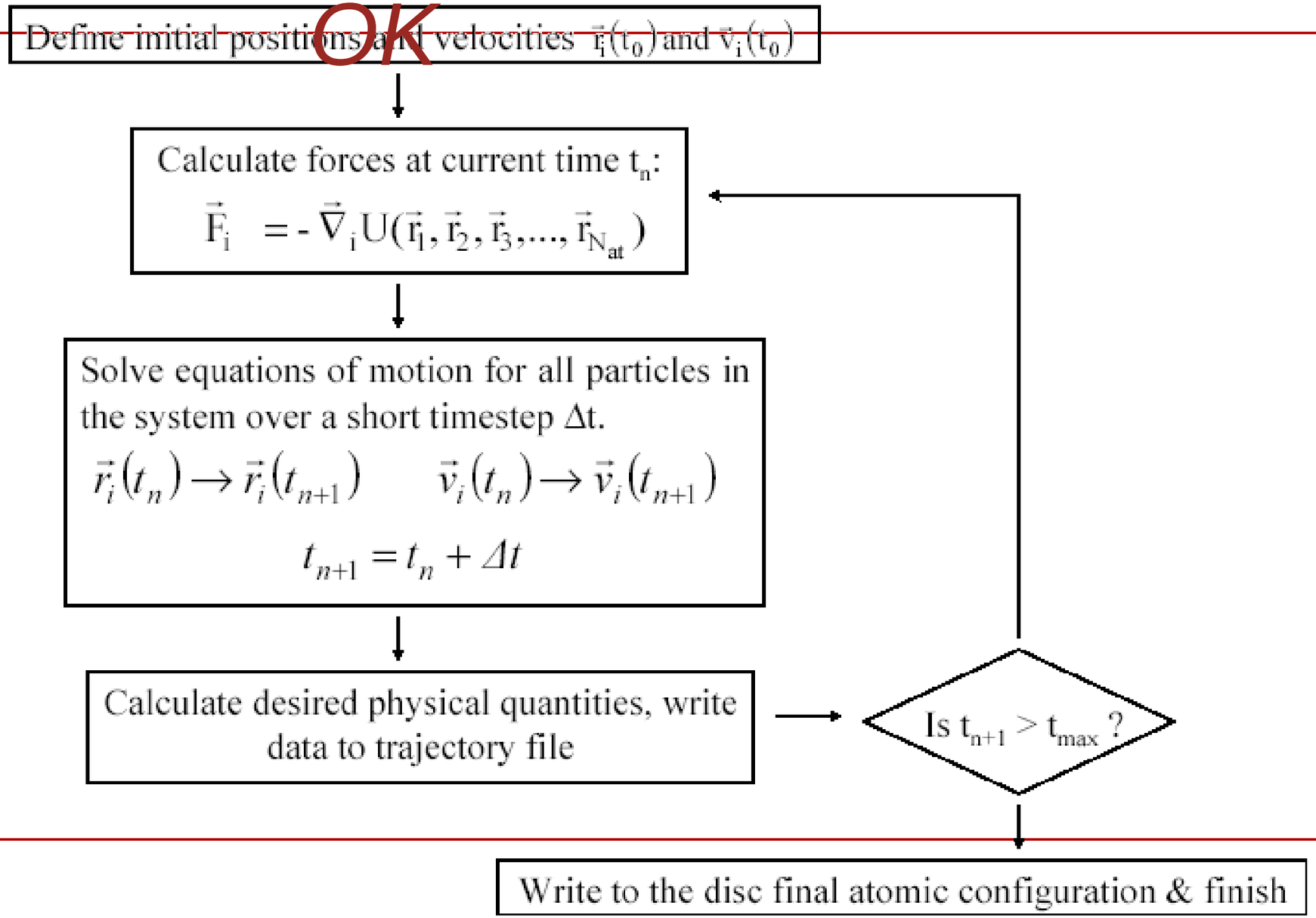
Como tratar defeitos ?



Velocidades iniciais



Schematic diagram of a basic MD code



Escolhendo o integrador e codificando-o

O Que é importante ?

1) **Trajetórias exatas**
2) **Satisfazer as conservações de momento e energia**

Seria também bom que …

Computacionalmente rápido

Requer pouca memória

Reversível no tempo e permite usar valores grandes para dt

Opções:

Verlet,Velocity-Verlet, Leapfrog, Predictor Corrector, …

Parte 3 - Vamos pegar o caso mais simples

Expansão em Taylor

$$f(x_0 + \Delta x) = \sum_{n=0}^{\infty} \frac{1}{n!} \frac{d^n f(x_0)}{dx^n} \Delta x^n$$

$$f(x_0 - \Delta x) = \sum_{n=0}^{\infty} \frac{(-1)^n}{n!} \frac{d^n f(x_0)}{dx^n} \Delta x^n$$

Parte 3 - Vamos pegar o caso mais simples

Futuro

$$\mathbf{r}_i(t+dt) = \mathbf{r}_i(t) + \mathbf{v}_i(t)dt + \frac{\mathbf{F}_i(t)}{2m}dt^2 + \ldots$$

Passado

$$\mathbf{r}_i(t-dt) = \mathbf{r}_i(t) - \mathbf{v}_i(t)dt + \frac{\mathbf{F}_i(t)}{2m}dt^2 - \ldots$$

Parte 3 - Vamos pegar o caso mais simples

$$\mathbf{r}_i(t+dt) = \mathbf{r}_i(t) + \mathbf{v}_i(t)dt + \frac{\mathbf{F}_i(t)}{2m}dt^2 + \dots$$

$$+$$

$$\mathbf{r}_i(t-dt) = \mathbf{r}_i(t) - \mathbf{v}_i(t)dt + \frac{\mathbf{F}_i(t)}{2m}dt^2 - \dots$$

Parte 3 - Vamos pegar o caso mais simples

$$\mathbf{r}_i(t+dt) = \mathbf{r}_i(t) + \mathbf{v}_i(t)dt + \frac{\mathbf{F}_i(t)}{2m}dt^2 + \dots$$

$$+$$

$$\mathbf{r}_i(t-dt) = \mathbf{r}_i(t) - \mathbf{v}_i(t)dt + \frac{\mathbf{F}_i(t)}{2m}dt^2 - \dots$$

$$=$$

$$\mathbf{r}_i(t+dt) + \mathbf{r}_i(t-dt) \simeq 2\mathbf{r}_i(t) + \frac{\mathbf{F}_i(t)}{m}dt^2$$

Parte 3 - Vamos pegar o caso mais simples

$$\mathbf{r}_i(t+dt) + \mathbf{r}_i(t-dt) \simeq 2\mathbf{r}_i(t) + \frac{\mathbf{F}_i(t)}{m}dt^2$$

Ótimo !! Temos tudo que precisamos :

$$\mathbf{r}_i(t+dt) \simeq 2\mathbf{r}_i(t) - \mathbf{r}_i(t-dt) + \frac{\mathbf{F}_i(t)}{m}dt^2$$

$$\mathbf{v}_i(t) = \frac{\mathbf{r}_i(t+dt) - \mathbf{r}_i(t-dt)}{2dt}$$

Parte 3 - Vamos pegar o caso mais simples

Subroutine Integrator

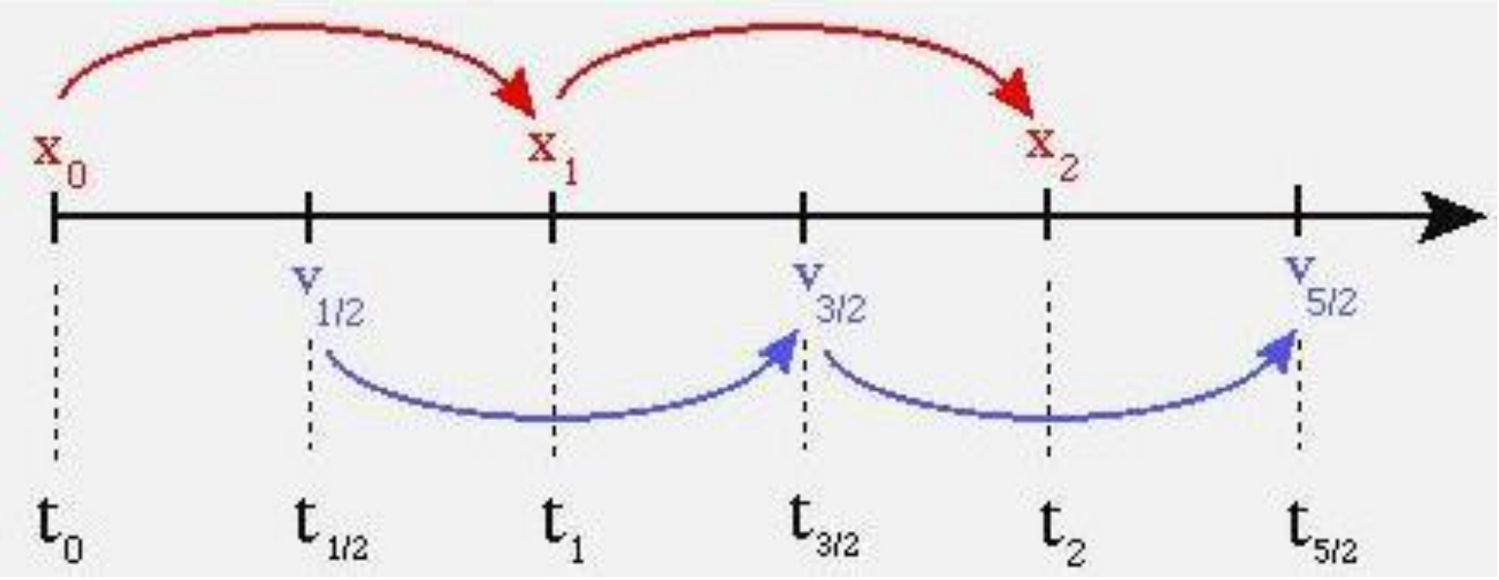
```
Do i = 1, N_particles

    fm          =     fx(i) * dt **2 / m
    x_new       =      2 * x_now(i) - x_old(i) + fm
    velx(i)     =     (x_new - x_old(i)) / (2*dt)
    x_old(i)    =     x_now(i)
    x_now(i)    =     x_new

Enddo

return
end
```

Outros métodos de integração

Leapfrog (pulo da rã)

$$v_{x,n+\frac{1}{2}} = v_{x,n-\frac{1}{2}} + \Delta t\, a_x(x_n, y_n, t)$$
$$x_{n+1} = x_n + \Delta t\, v_{n+\frac{1}{2}}$$

$$v_{x,\frac{1}{2}} = v_0 + \frac{\Delta t}{2} a_x(x_0, y_0, 0) + \left(\frac{\Delta t}{2}\right)^2 \frac{\partial a_x}{\partial x}|_{(x_0,y_0,0)}$$



Outros métodos de integração

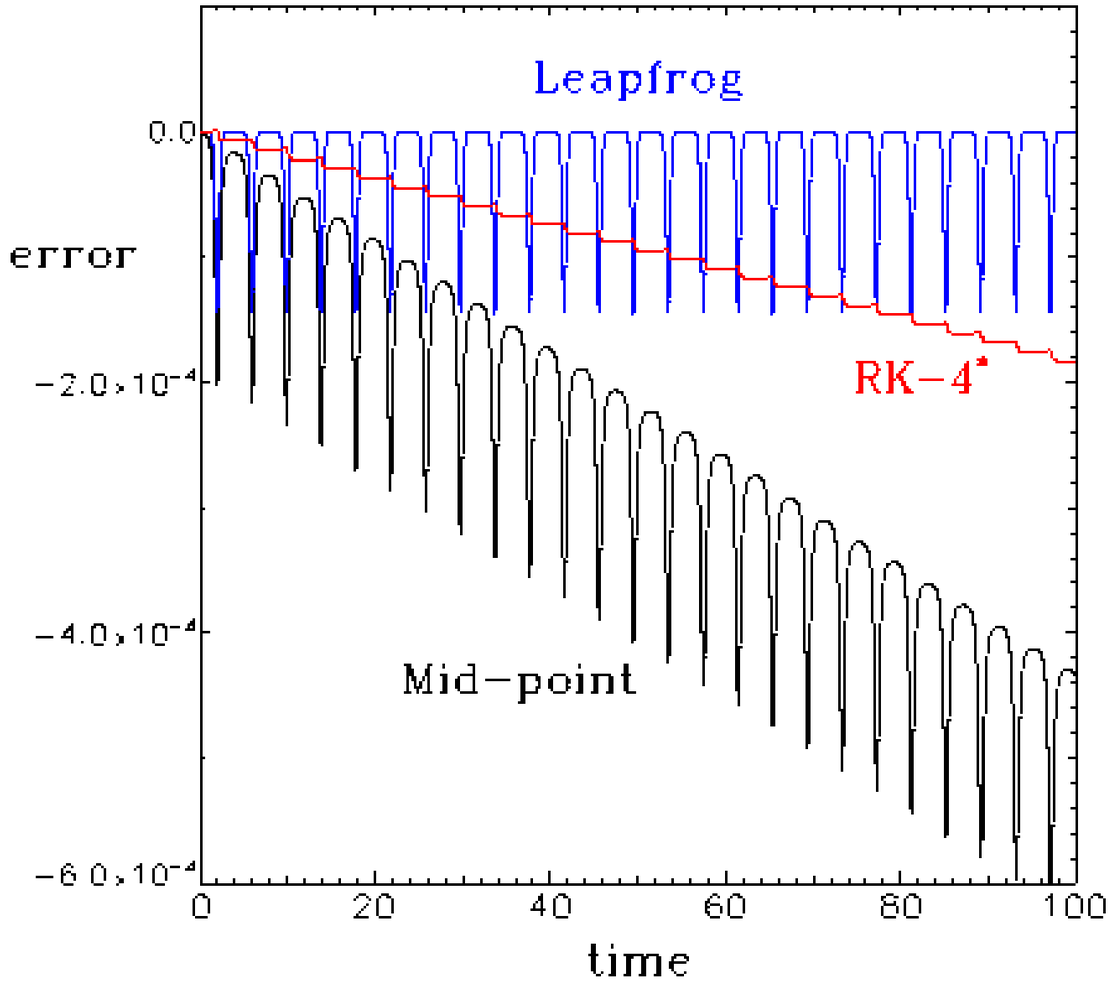
Leapfrog

$$r(t+\delta t) = r(t) + v\left(t+\frac{1}{2}\delta t\right)\delta t$$

$$v\left(t+\frac{1}{2}\delta t\right) = v\left(t-\frac{1}{2}\delta t\right) + a(t)\delta t$$

$$v(t) = \frac{1}{2}\left[v\left(t-\frac{1}{2}\delta t\right) + v\left(t+\frac{1}{2}\delta t\right)\right]$$

Outros métodos de integração



Outros métodos de integração

Leapfrog

Esse método requer apenas um grau de custo computacional adicional que o método de Euler, mas o ERRO é de terceira ordem.

Esse método utiliza derivada no ponto médio de cada passo
(Velocidades são obtidas no mesmo tempo que o passo)

Isso requer apenas um passo adicional para mover a velocidade meio-passo adiante da posição.

Devido a sua melhor acurácia enquanto mantém o custo computacional baixo, o método de “Leapfrog” é normalmente o método padrão em Dinâmica Molecular (default)

Outros métodos de integração

Predição-correção

Let us take the often used 6-value predictor-corrector algorithm [10] as an example. We start out with $6 \times 3N$ storage: $\mathbf{x}^{3N(0)}(t_0)$, $\mathbf{x}^{3N(1)}(t_0)$, $\mathbf{x}^{3N(2)}(t_0), \ldots, \mathbf{x}^{3N(5)}(t_0)$, where $\mathbf{x}^{3N(k)}(t)$ is defined by,

$$\mathbf{x}_i^{(k)}(t) \equiv \left(\frac{\mathrm{d}^k \mathbf{x}_i^{(t)}}{\mathrm{d}t^k}\right)\left(\frac{(\Delta t)^k}{k!}\right). \tag{29}$$

The iteration consists of prediction, evaluation, and correction steps:

Outros métodos de integração

Etapa de Predição

$$
\begin{aligned}
\mathbf{x}_i^{(0)} &= \mathbf{x}_i^{(0)} + \mathbf{x}_i^{(1)} + \mathbf{x}_i^{(2)} + \mathbf{x}_i^{(3)} + \mathbf{x}_i^{(4)} + \mathbf{x}_i^{(5)}, \\
\mathbf{x}_i^{(1)} &= \mathbf{x}_i^{(1)} + 2\mathbf{x}_i^{(2)} + 3\mathbf{x}_i^{(3)} + 4\mathbf{x}_i^{(4)} + 5\mathbf{x}_i^{(5)}, \\
\mathbf{x}_i^{(2)} &= \mathbf{x}_i^{(2)} + 3\mathbf{x}_i^{(3)} + 6\mathbf{x}_i^{(4)} + 10\mathbf{x}_i^{(5)}, \\
\mathbf{x}_i^{(3)} &= \mathbf{x}_i^{(3)} + 4\mathbf{x}_i^{(4)} + 10\mathbf{x}_i^{(5)}, \\
\mathbf{x}_i^{(4)} &= \mathbf{x}_i^{(4)} + 5\mathbf{x}_i^{(5)}.
\end{aligned}
$$

The general formula for the above is

$$
\mathbf{x}_i^{(k)} = \sum_{k'=k}^{M-1} \left[\frac{k'!}{(k'-k)!k!} \right] \mathbf{x}_i^{(k')}, \quad k = 0, \ldots, M-2, \tag{31}
$$

with $M = 6$ here. The evaluation must proceed from 0 to $M - 2$ sequentially.

Outros métodos de integração

Avaliação

Cálcula as forças f^{3N} usando as novas posições $x^{3N(0)}$.

Correção

$$\mathbf{e}_i \equiv \mathbf{x}_i^{(2)} - \left(\frac{\mathbf{f}_i}{m_i}\right)\left(\frac{(\Delta t)^2}{2!}\right).$$

Aplica-se as correções,

$$\mathbf{x}_i^{(k)} = \mathbf{x}_i^{(k)} - C_{Mk}\mathbf{e}_i, \qquad k = 0, \ldots, M-1,$$

onde C_{Mk} são constantes conhecidas (ver próximo slide)

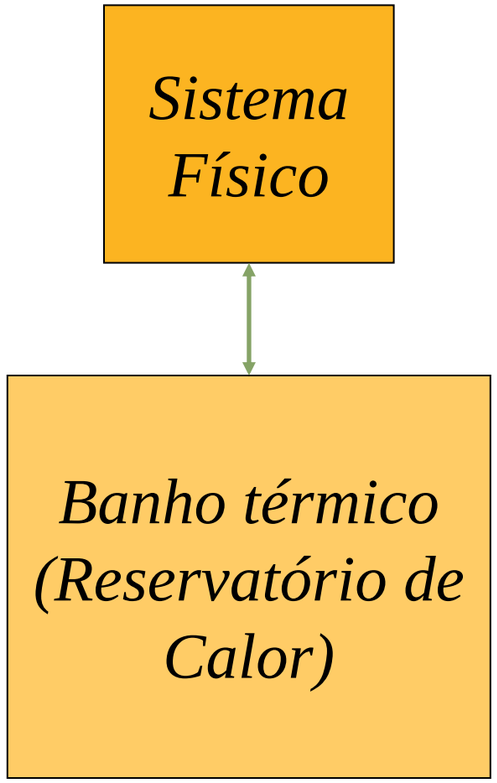
Outros métodos de integração

Gear Predictor-Corrector Coefficients

Table 2. Gear predictor-corrector coefficients

C_{Mk}	$k=0$	$k=1$	$k=2$	$k=3$	$k=4$	$k=5$	$k=6$	$k=7$
$M=4$	1/6	5/6	1	1/3				
$M=5$	19/120	3/4	1	1/2	1/12			
$M=6$	3/20	251/360	1	11/18	1/6	1/60		
$M=7$	863/6048	665/1008	1	25/36	35/144	1/24	1/360	
$M=8$	1925/14112	19087/30240	1	137/180	5/16	17/240	1/120	1/2520

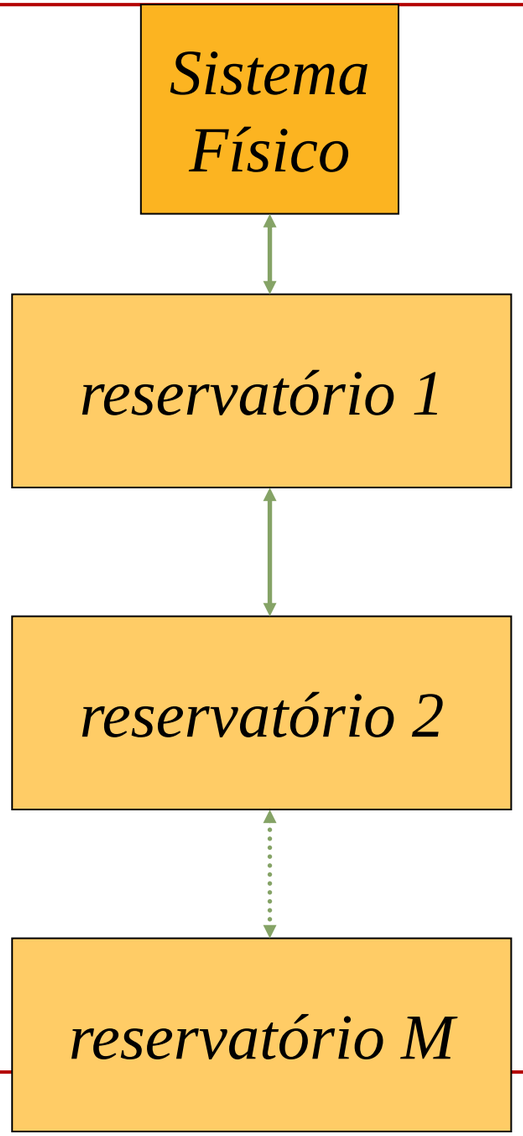
Dinâmica de Nosé-Hoover



$$H = V(\vec{r}_1, \vec{r}_2, ..., \vec{r}_N) + \sum_{i=1}^{N} \frac{p_i^{\,2}}{2m_i} + \frac{p_\eta^{\,2}}{2Q} + Nk_B T\eta$$

Nosé JCP 1984 and Hoover PRA 1985

Massive Nosé-Hoover Chain Dynamics



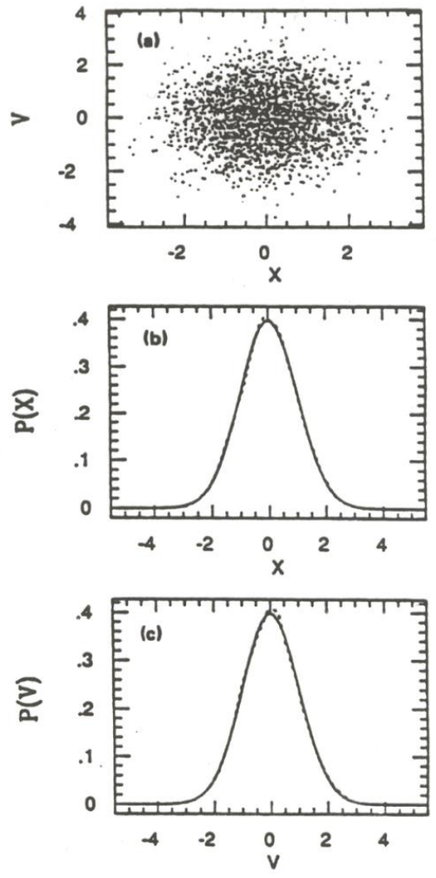
$$H = V(\vec{r}_1, \vec{r}_2, ..., \vec{r}_N) + \sum_{i=1}^{N} \frac{p_i^{\,2}}{2m_i} + \sum_{j=1}^{M} \frac{p_{\eta_j}^{\,2}}{2Q_j} +$$

$$Nk_BT\eta_1 + \sum_{j=2}^{M} k_BT\eta_j$$

Martyna, Klein, and Tuckerman, JCP 1992

Oscilador Harmônico unidimensional

Massive Nosé-Hoover Chain,
Usando 2 reservatórios



Métodos numéricos para escoamentos em nano e microescalas

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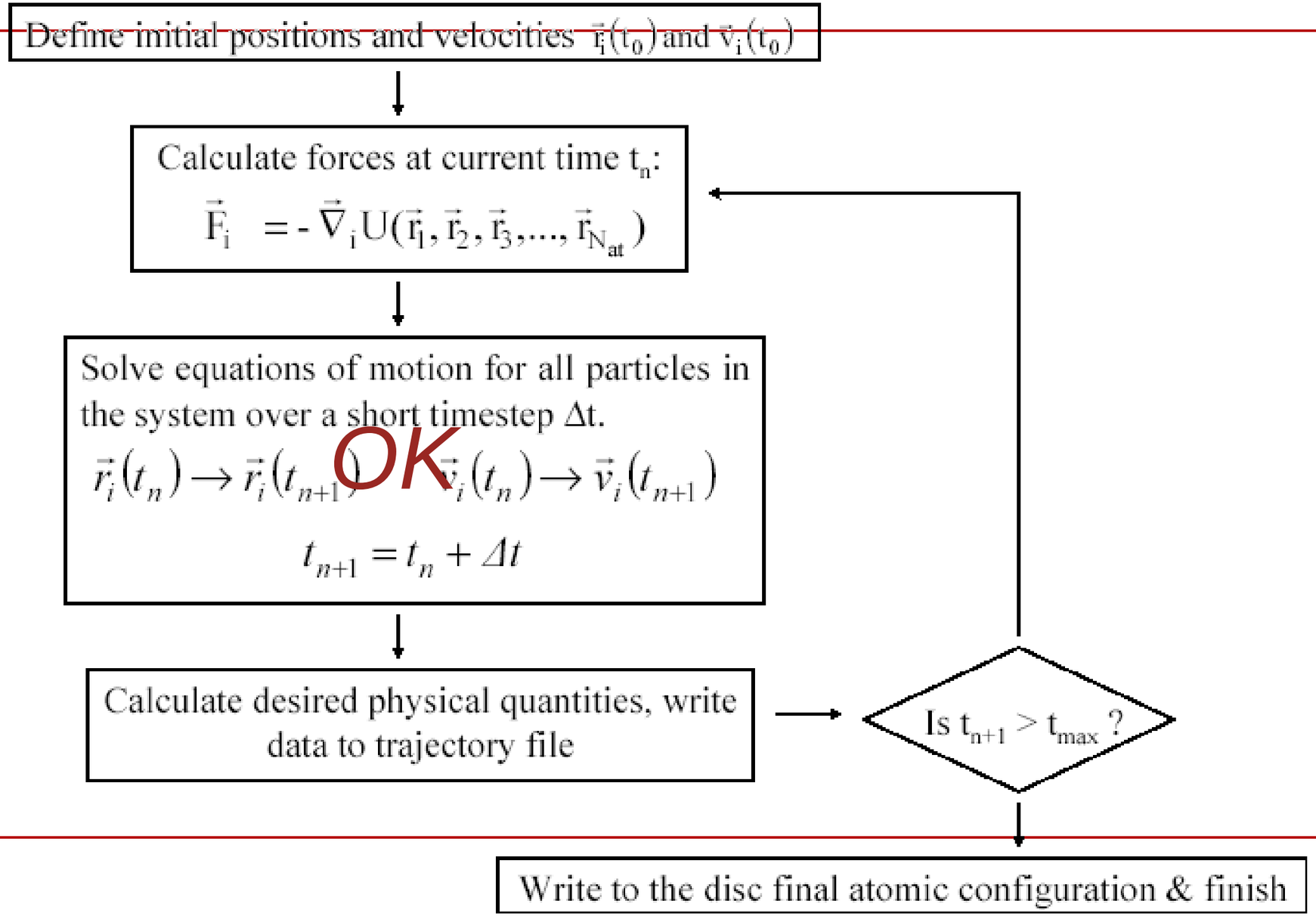
Schematic diagram of a basic MD code



Part 4 - Subrotina Sample

O que “sample” faz ?

Acumula os parâmetros relevantes durante a simulação (energias total, cinética e potencial, posições, velocidades, pressão, densidade, …)

Valor de equilíbrio é a média temporal

Propriedades no equilíbrio

Variáveis termodinâmicas

Seja: a variável dinâmica A(t)

$$A(t) = f\left(\mathbf{r}_1(t), \ldots, \mathbf{r}_N(t), \mathbf{v}_1(t), \ldots, \mathbf{v}_N(t)\right)$$

Precisão: a imagem microscópica de A(r,p) (energia potencial, cinética, temperatura e pressão)

Para casa passo de integração temporal, nós calculamos A

Experimento

Experimento: observação (medida) de valores médios

(propriedade macroscópica é a média da microscópica)

Valor médio

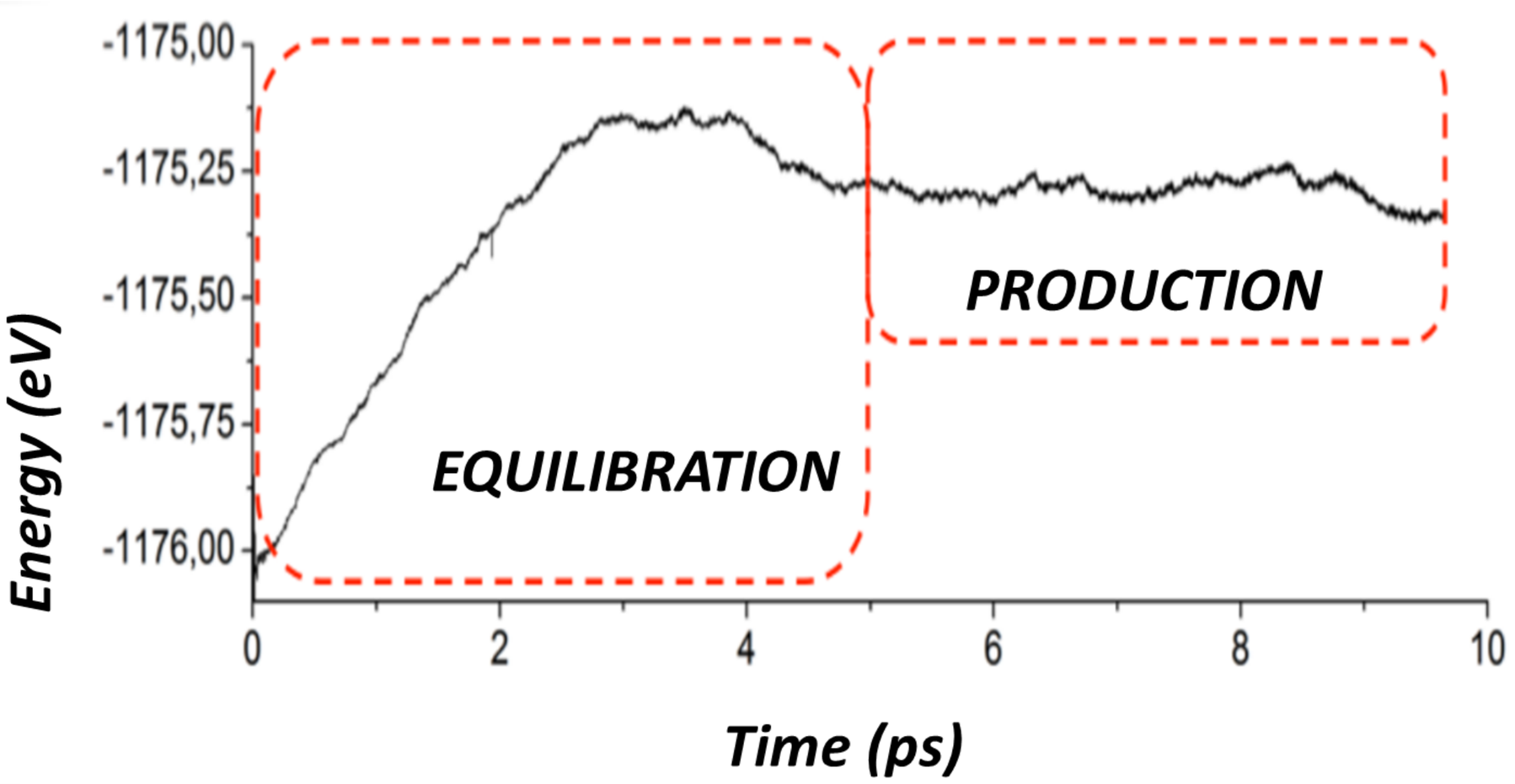
O Valor médio é a média temporal !!

$$\langle A \rangle = \frac{1}{N_T} \sum_{t=1}^{N_T} A(t)$$

Part 4 - Subrotina Sample

```
subroutine sample
somupot = somupot + upot
somecin = somecin + ecin
sometot = sometot + etotal
somtemp = somtemp + temp
sompres = sompres + press
nsim = nsim + 1
medupot = somupot/nsim
medecin = somecin/nsim
medetot = sometot/nsim
medtemp = somtemp/nsim
medpres = sompres/nsim
return
end
```

Propriedades de equilíbrio



Propriedades do equilíbrio

Energia Potencial

$$V(t) = \sum_i \sum_{j>i} \phi\left(|\mathbf{r}_i(t) - \mathbf{r}_j(t)|\right)$$

Energia Cinética

$$K(t) = \frac{1}{2} \sum_i m_i [v_i(t)]^2$$

Temperatura

Pressão

Difusão

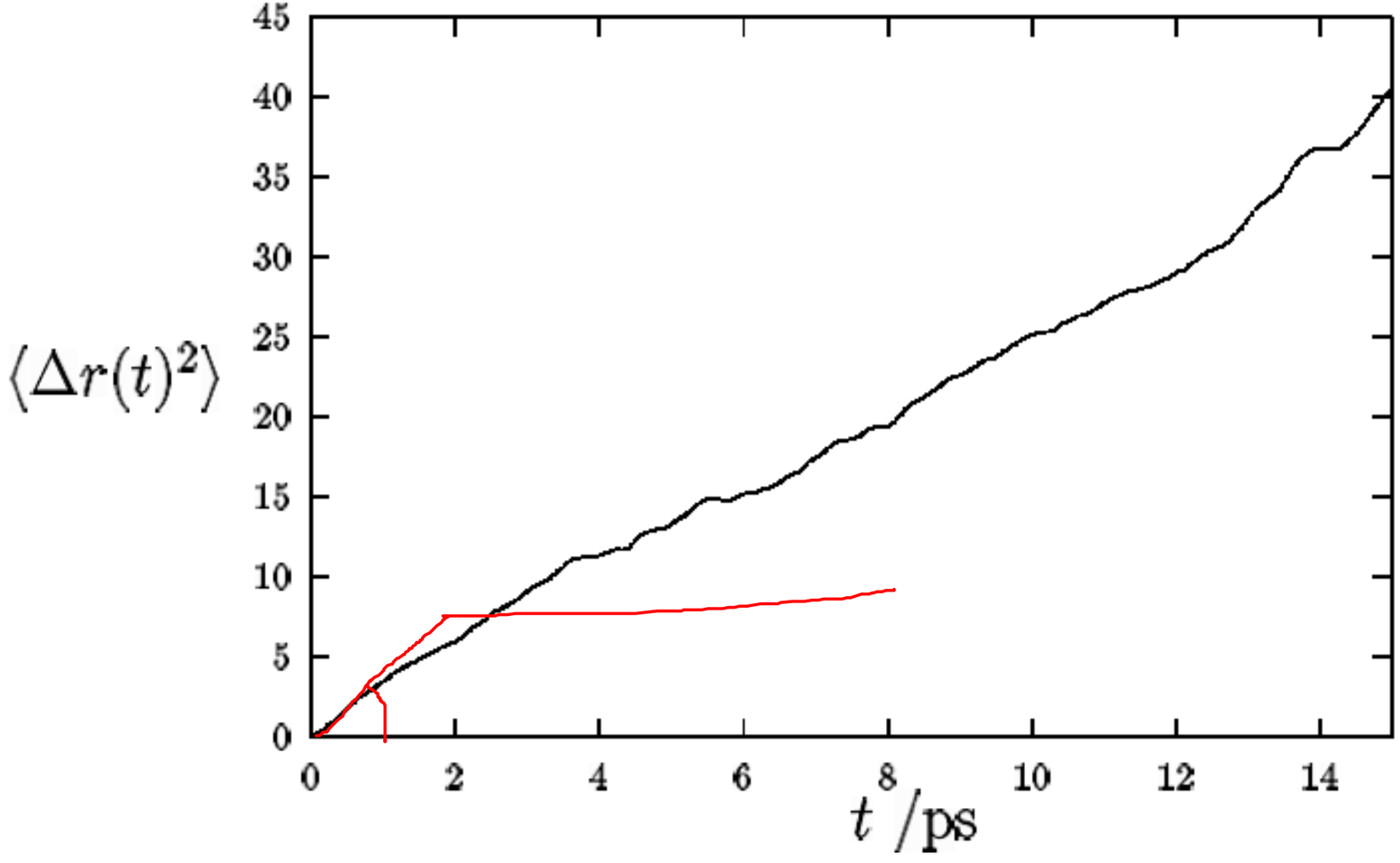
Relação de Einstein (t longo)

$$\left\langle \Delta r(t)^2 \right\rangle = 6Dt$$

Deslocamento Quadratico médio

$$\left\langle \Delta r(t)^2 \right\rangle = \frac{1}{N} \sum_{i=1}^{N} \left(\mathbf{r}_i(t) - \mathbf{r}_i(0) \right)^2$$

Metano - líquido 150K e 1000bar

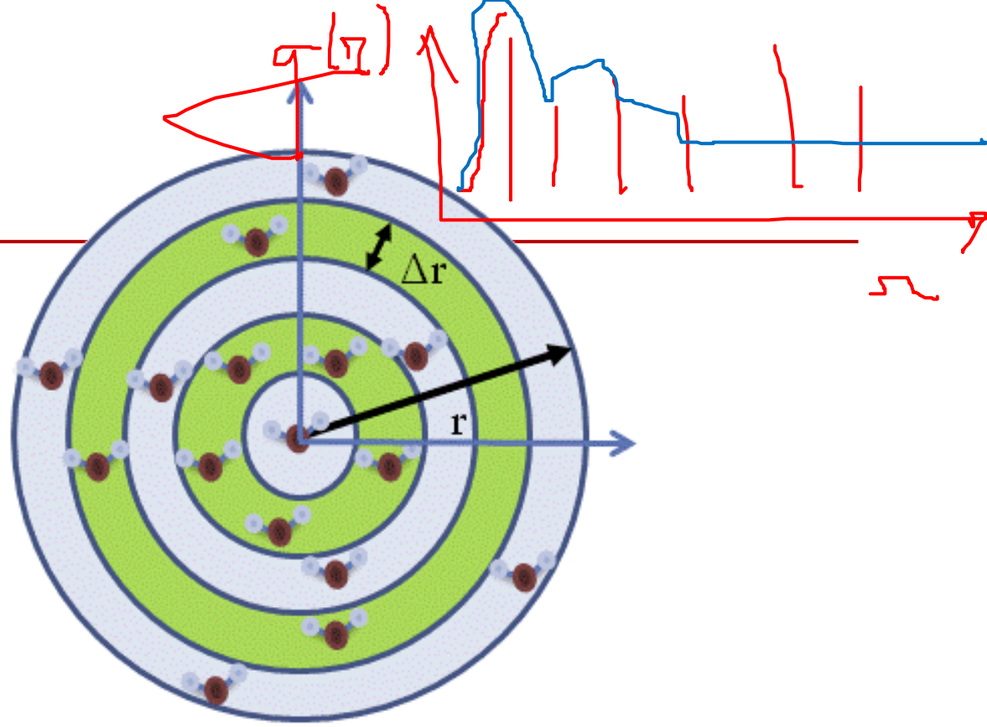


Molecular Dynamics

Structural and thermodynamic properties

- **Radial distribution**
- **Diffusion coeficient**

$$g_{ij}(r) = \frac{N_{ij}(r, r + \Delta r)}{4\pi r^2 \Delta r \rho_j}$$

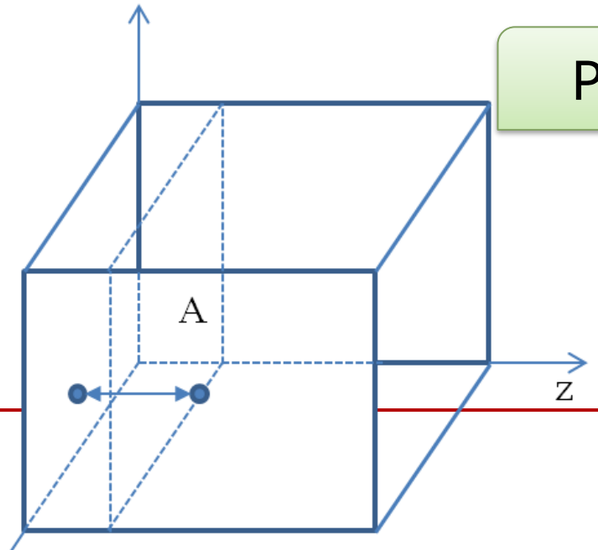


$$DMQ(t) = \langle |r_i(t) - r_i(0)|^2 \rangle \qquad D = \frac{1}{6} \lim_{t\to\infty} \frac{1}{N} \sum_{i=1}^{N} \frac{DMQ(t)}{t}$$

Surface tension

L_x, L_y e L_z

$$\gamma = \int_{-L}^{L} dz (p_N(z) - p_T(z)), \qquad \gamma = L_z \langle\, p_N(z) - p_T(z) \,\rangle$$



Pressure and stress

$$\boldsymbol{P} = -\langle \boldsymbol{\sigma} \rangle. \qquad \boldsymbol{P} = \langle \frac{1}{3V} \left(\sum_i^N \frac{\boldsymbol{p}_i^2}{m_i} + \sum_i^N \boldsymbol{r}_i \boldsymbol{F}_i \right) \rangle$$

$$-\sigma_z = \frac{1}{L_z} \int_0^{L_z} \frac{1}{A} \left\{ \frac{1}{\delta t} \sum_{z_i \le z,\, z_i + v_{zi}\delta t \ge z} 2 m_i v_{zi} + \sum_{i,j} \lfloor f_{ij} \rfloor_z \right\},$$

Função de correlação

Definition **Scalar product average of a dynamical variable A(0) in the time origin t=0 with the dynamical variable B(r) at time t.**

$$C(t) = \langle \mathbf{A}(0) \cdot \mathbf{B}(t) \rangle$$

t	$A(t)$	$B(t)$
0	2	4
1	3	2
2	1	3
3	5	5

C(0) = 2.4 + 3.2 + 1.3+5.5=42 nc=4

- *Correlations at same time*

C(1) = 3.4 + 1.2 + 5.3 =29 nc=3

Correlations at dt

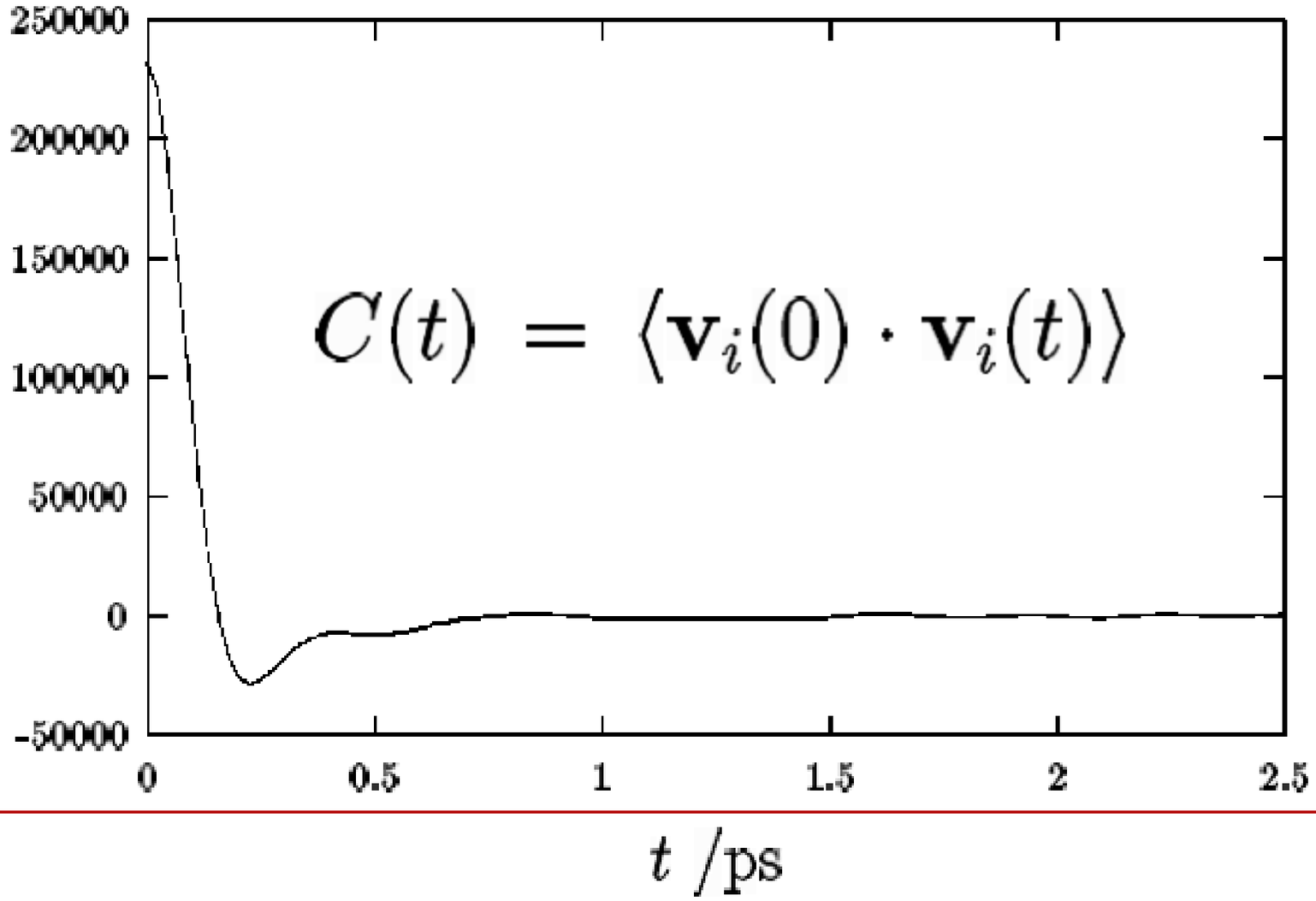
C(2) = 1.4 + 5.2 =14nc=2

Correlations at 2dt

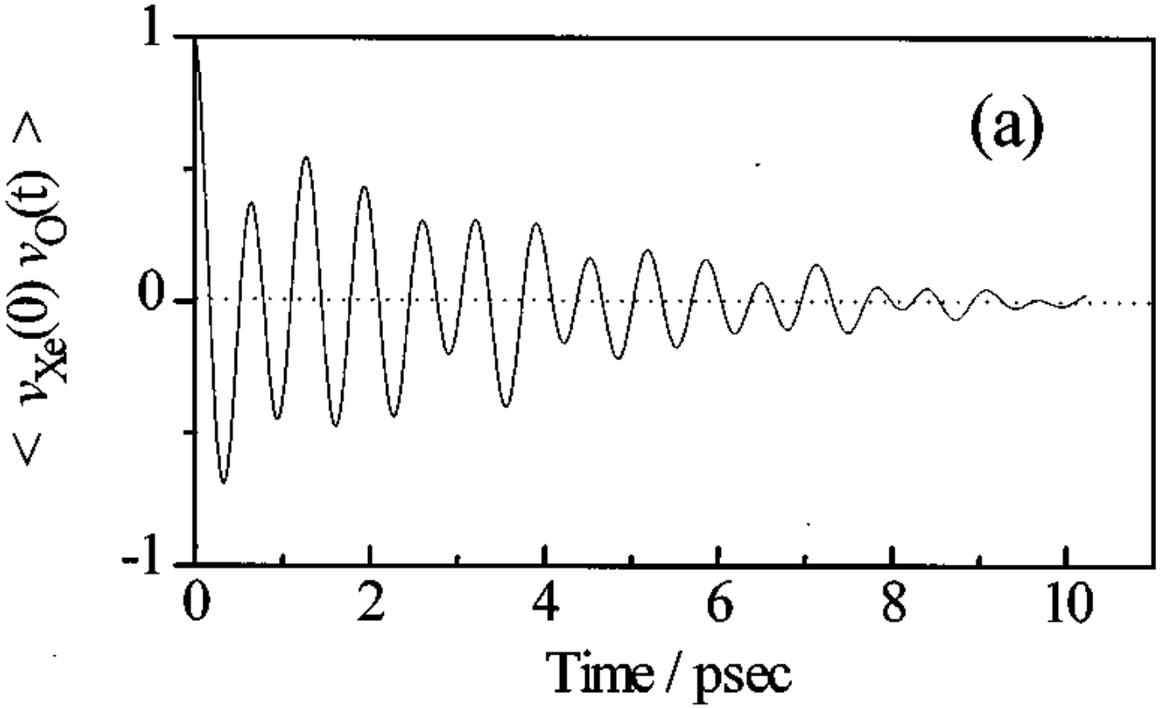
- C(0)=42/4; C(1)=29/3; C(2)=14/2

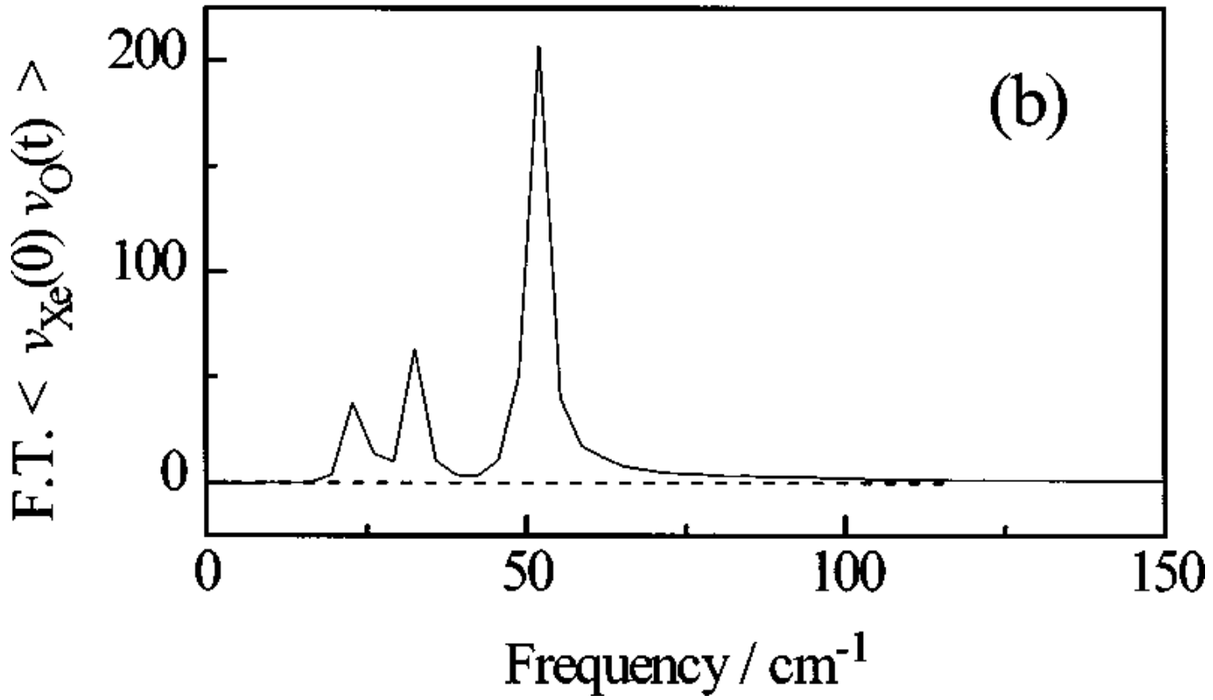
Velocity-Velocity autocorrelation function

Calculates the correlation function with Velocity



Vel-vel correlation function





Transport properties

Diffusion coefficient

$$D = \frac{1}{3} \int_0^\infty \langle \mathbf{v}_i(0) \cdot \mathbf{v}_i(t) \rangle \, dt$$

- **Viscosity**

$$\eta = \frac{1}{V k_B T} \int_0^\infty \langle \sigma_{xy}(0) \cdot \sigma_{xy}(t) \rangle \, dt$$

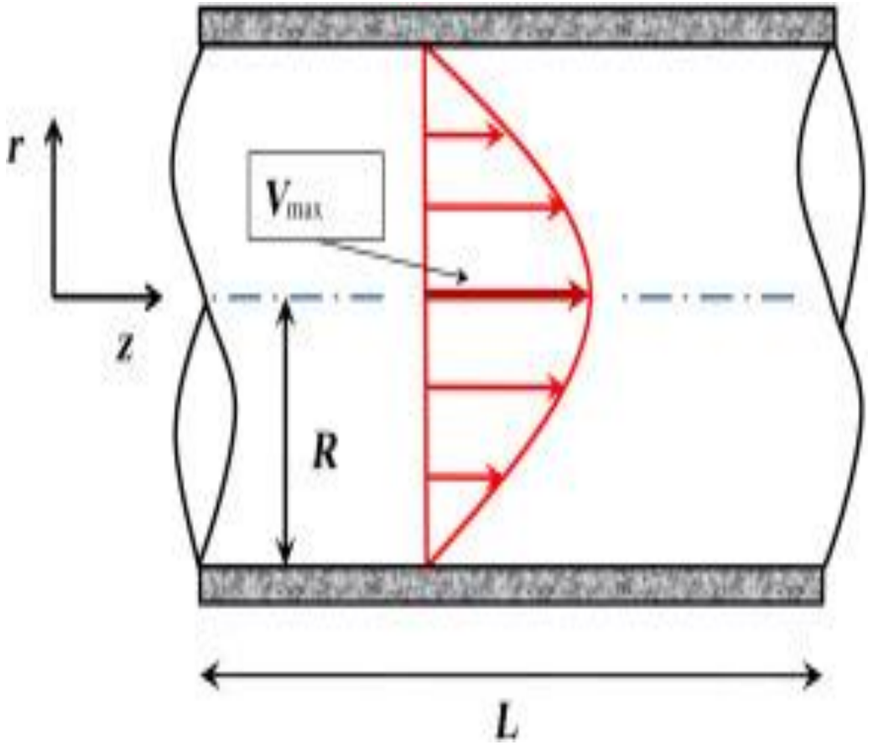
$$\sigma_{xy} = \sum_{i=1}^{N} m v_{i,x} v_{i,y} + \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} r_{i,x} F_{i,y}$$

- **Heat Transport**

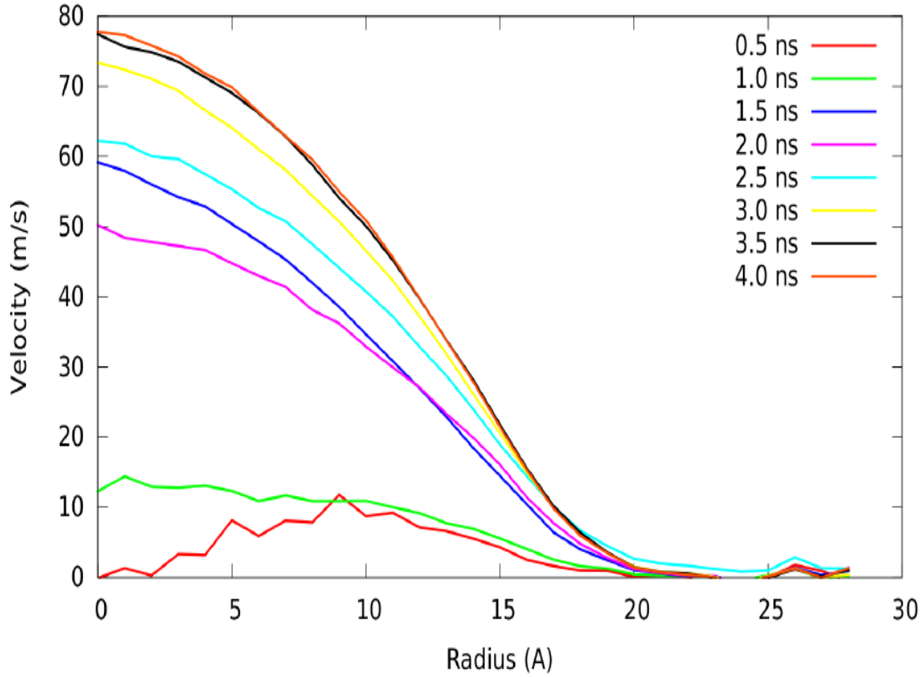
$$\lambda_T = \frac{1}{V k_B T^2} \int_0^\infty \langle j_x(0) \cdot j_x(t) \rangle \, dt$$

$$j_x = \frac{d}{dt} \sum_{i=1}^{N} r_{i,x} \left(E_i - \langle E_i \rangle \right)$$

Equação de Hagen–Poiseuille



$$u(x) = \frac{3g\left[(d/2)^2 - (x - x_{max})^2\right]}{2(\tau - 1/2)}$$



Applied acceleration

$$\eta = -\frac{\vec{a}\rho}{\left(\frac{d^2 v(\vec{r})}{dr^2}\right)},$$

Density, constant region has to be taken

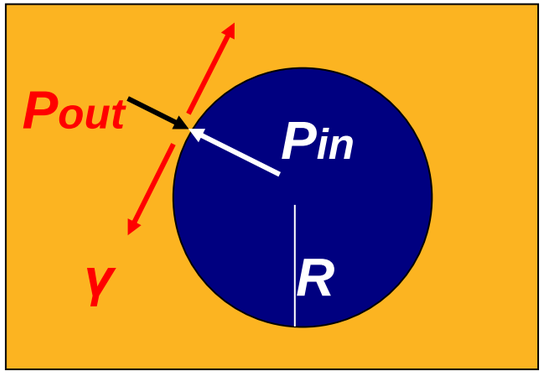
Second derivative of the parabolic velocity profile

Interfaces fluído-fluído e fluído-sólido

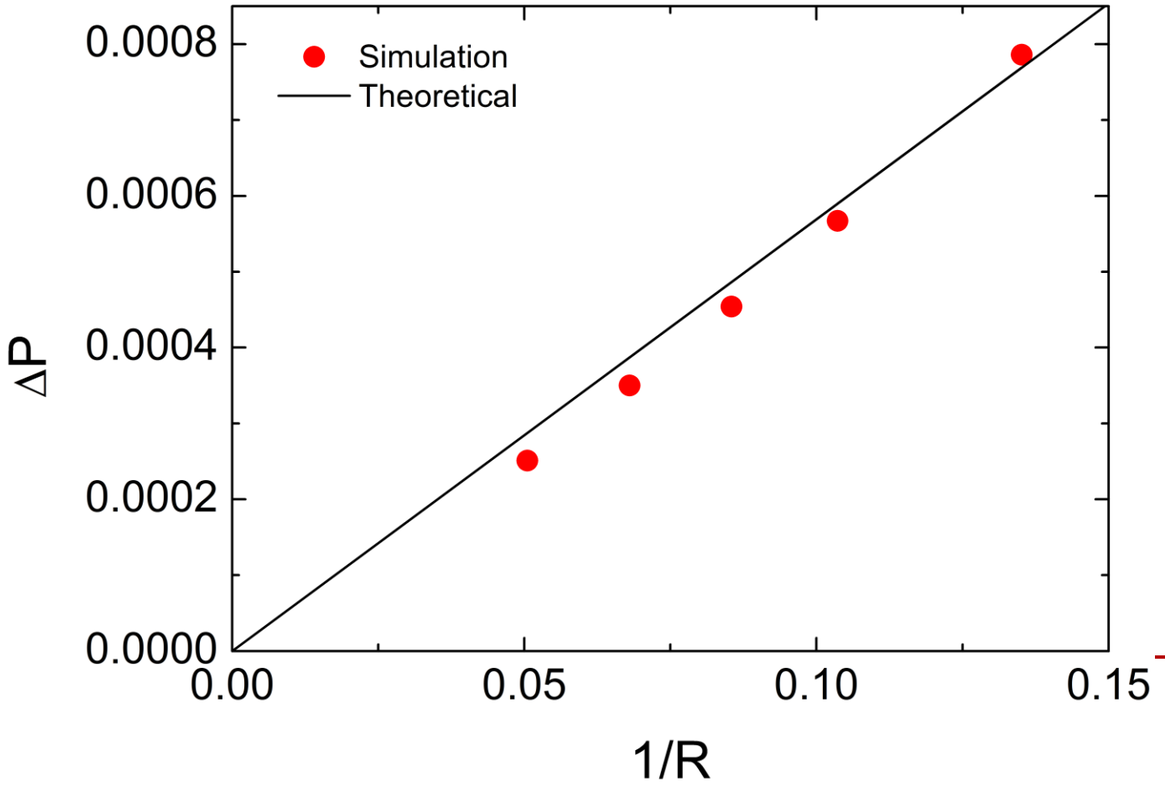
Laplace's Law:

$$\Delta P = \frac{2\gamma}{R},$$

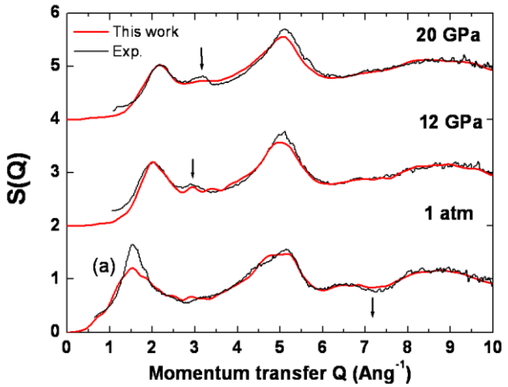
$\Delta P = P_{in} - P_{out}$



The *Laplace's law* indicates that dP is linear with respect to the curvature of bubbles or drops

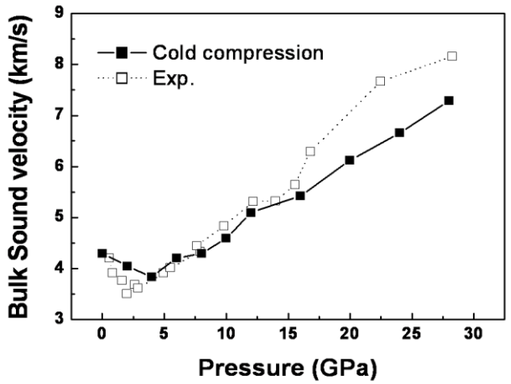


Que tipo de informação podemos obter ?

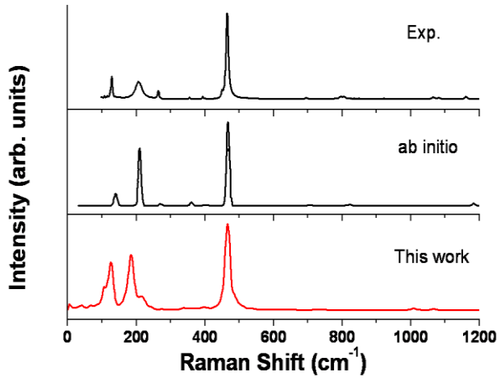


Propriedades estruturais
(Raio-X e neutron)

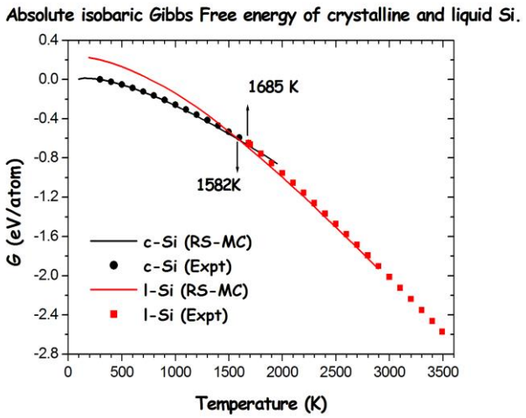
Simulações Atomísticas



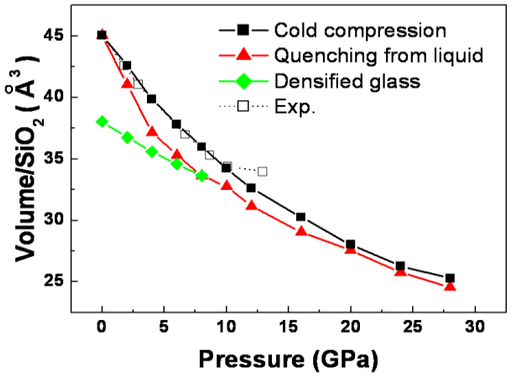
Propriedades elásticas
(ondas sísmicas)



Espectróscopia
(Infrared, Raman & NMR)



Termodinâmica
(calorimetria)

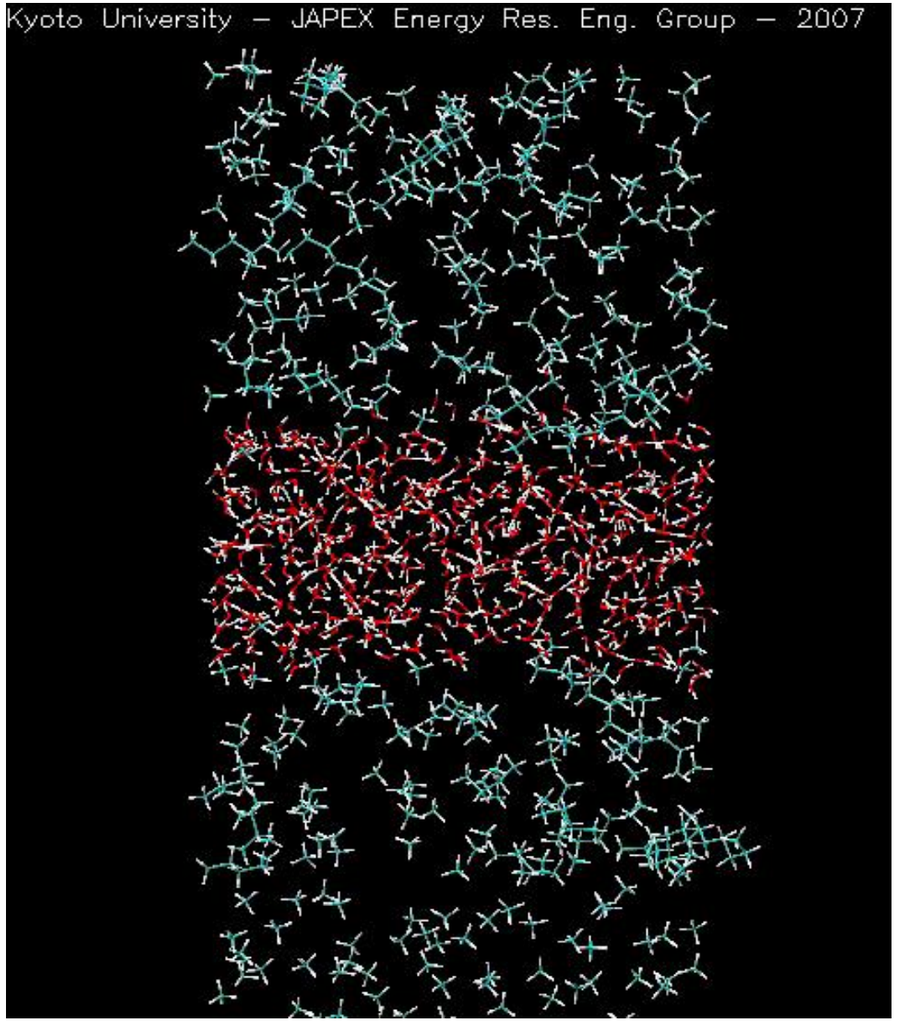


Estabilidade de fases
(Experimentos em altas pressões)

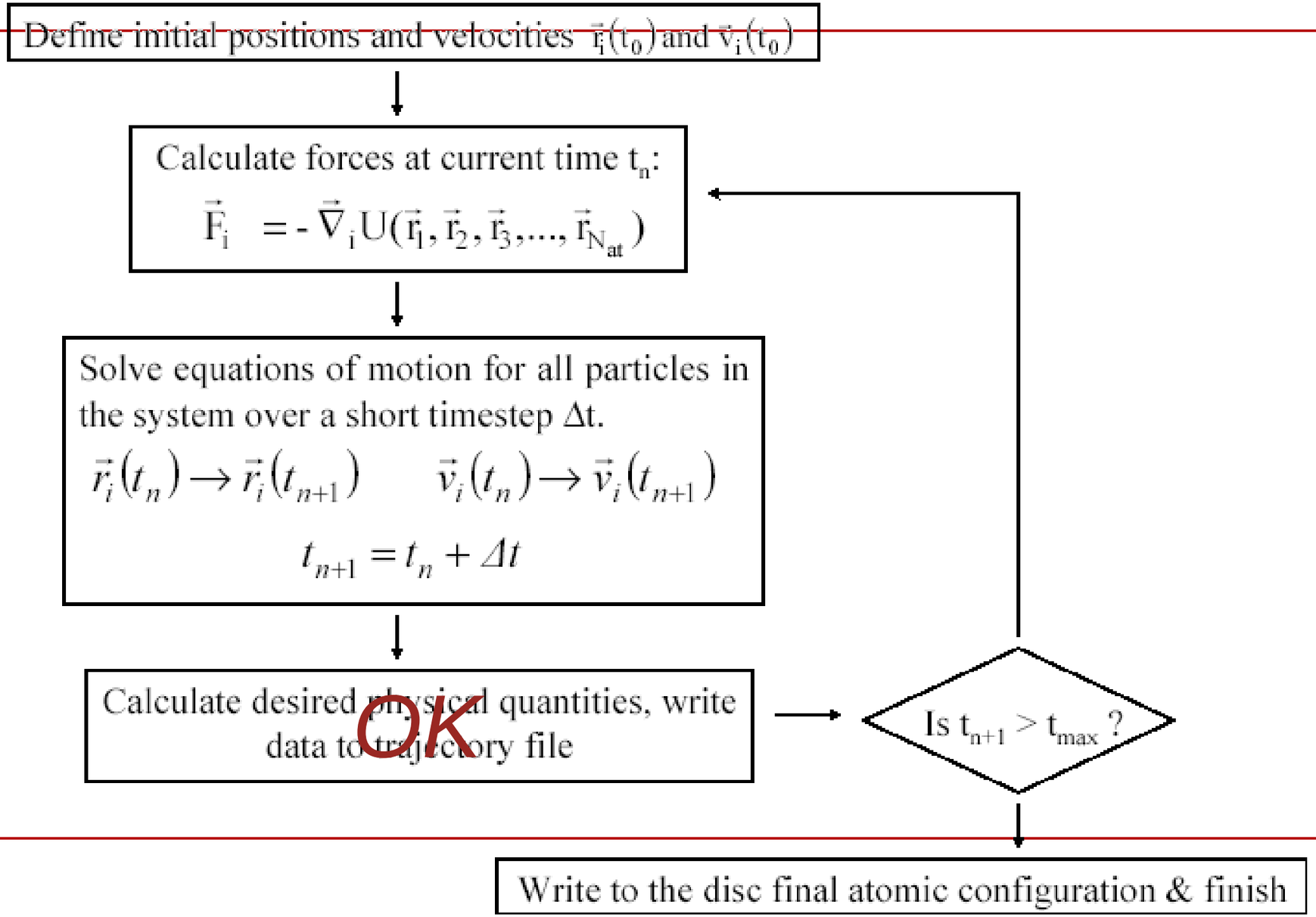
Water - oil interface

- ✓ Realistic models of crude oil
- ✓ Water, CO_2 and N_2
- ✓ Diffusion
- ✓ Viscosity
- ✓ Interface free energy tension
- ✓ Thermodynamics

  (T and P database)



Schematic diagram of a basic MD code



https://www.virtualbox.org/

Espelho da máquina virtual

https://github.com/Sampa-USP/mne2020