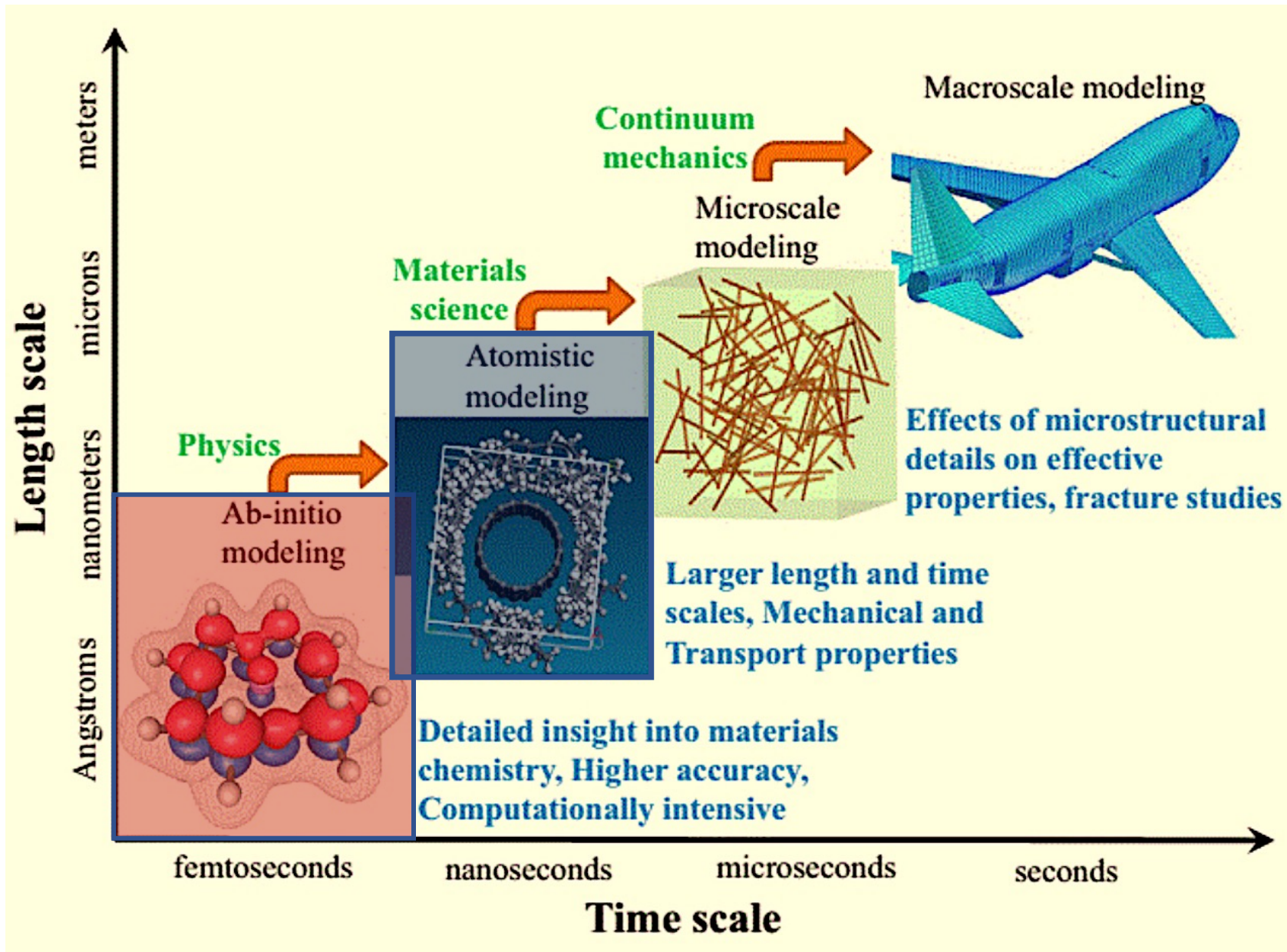


Dinâmica

Molecular



Primeiros Princípios → Mecânica Quântica

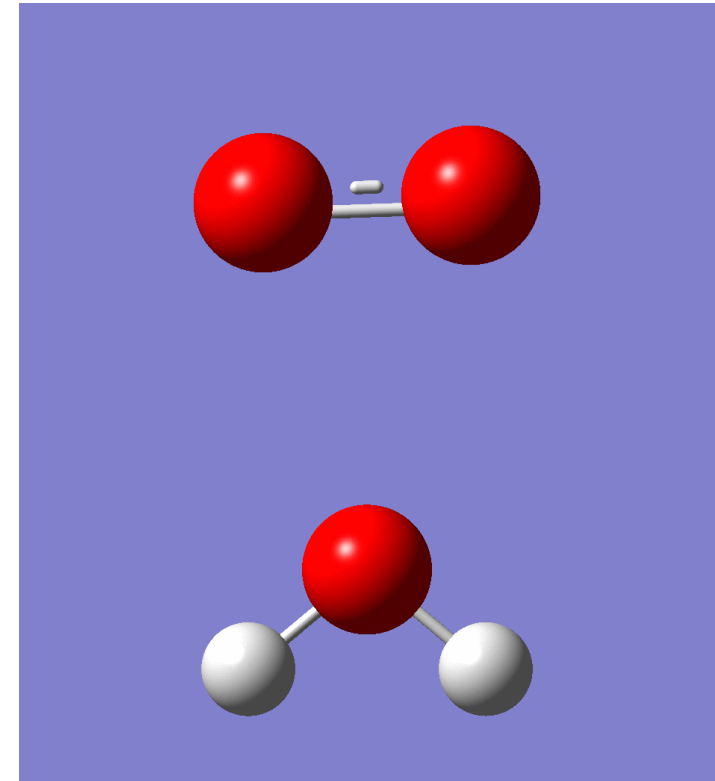
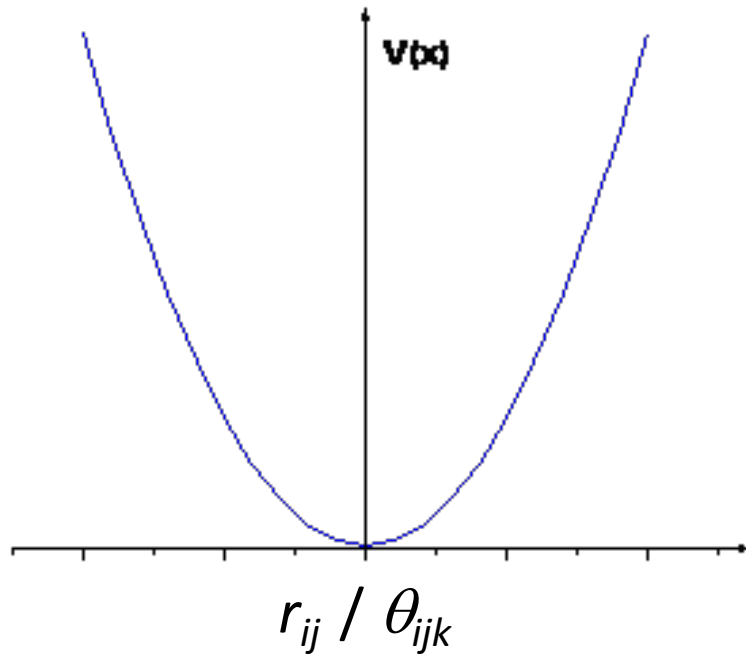
$$\hat{H}_{el}(R)\Psi_{el}(r;R) = E_{el}(R)\Psi_{el}(r;R)$$

Dinâmica Molecular (DM) → Física Clássica

$$U = U_{\text{intra}} + U_{\text{inter}}$$

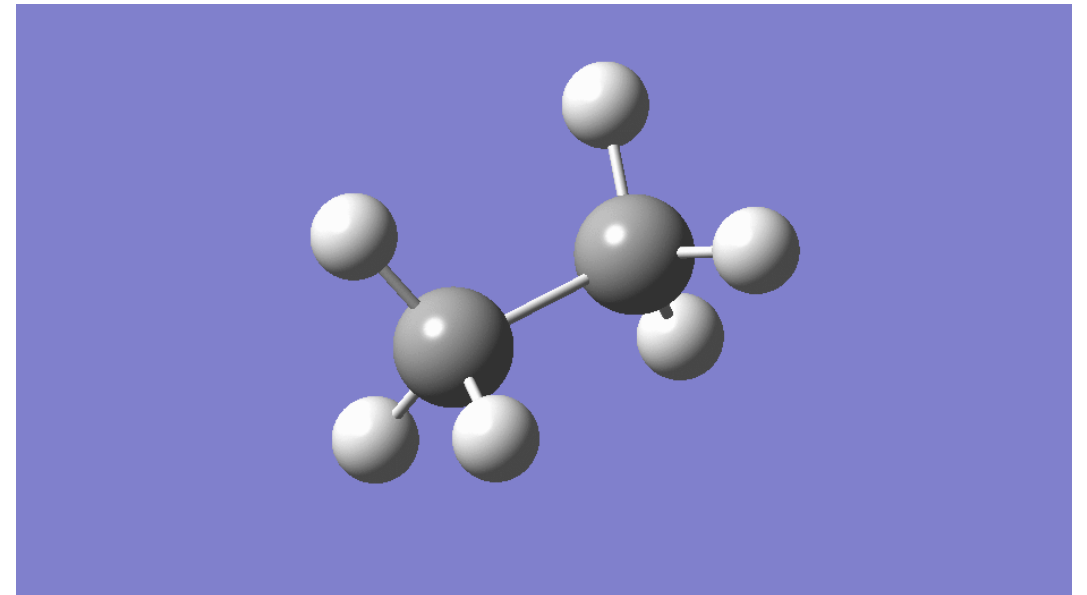
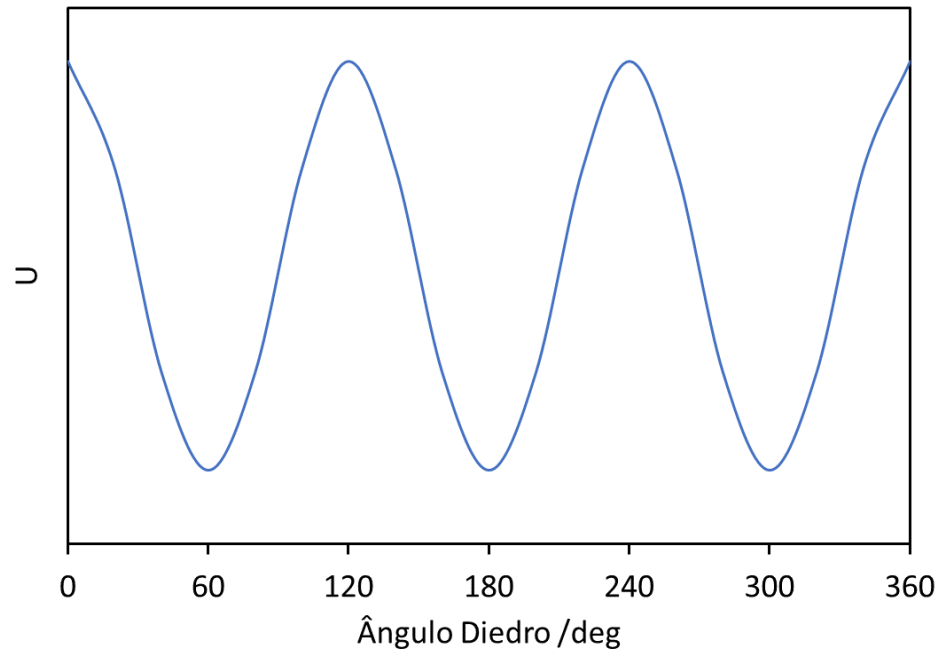
Campo de Forças $U = U_{\text{intra}} + U_{\text{inter}}$

$$U_{\text{intra}} = \sum_{ij}^{\text{bonds}} \frac{k_{r,ij}}{2} (r_{ij} - r_{o,ij})^2 + \sum_{ijk}^{\text{angles}} \frac{k_{\theta,ijk}}{2} (\theta_{ijk} - \theta_{o,ijk})^2 + \sum_{ijkl}^{\text{dihedrals}} \sum_{n=1}^4 \frac{V_{n,ijkl}}{2} \left[1 + (-1)^n \cos(n\varphi_{ijkl}) \right]$$



Campo de Forças $U = U_{\text{intra}} + U_{\text{inter}}$

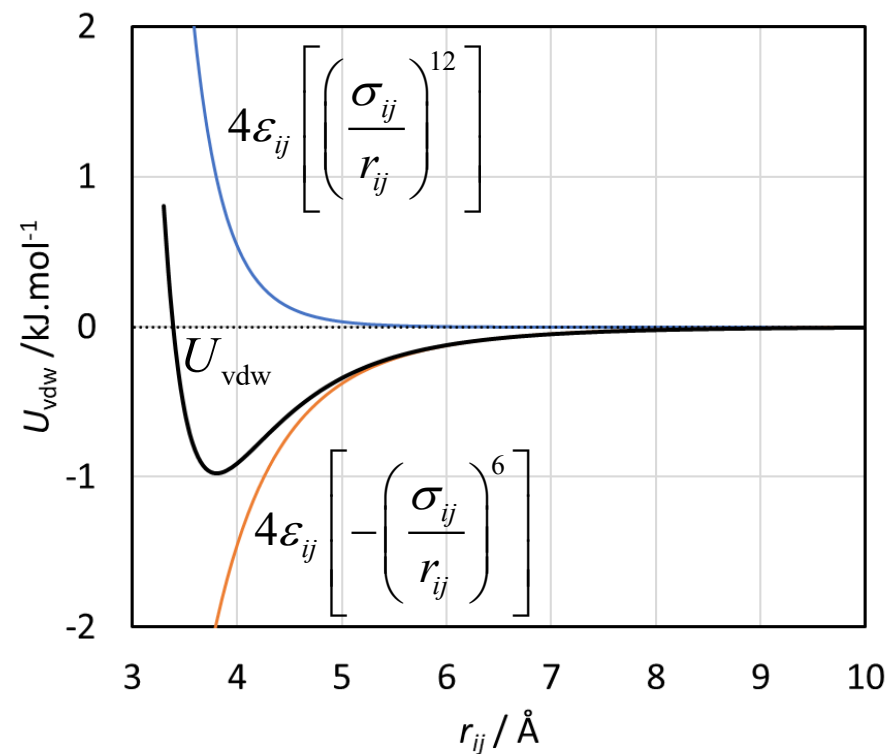
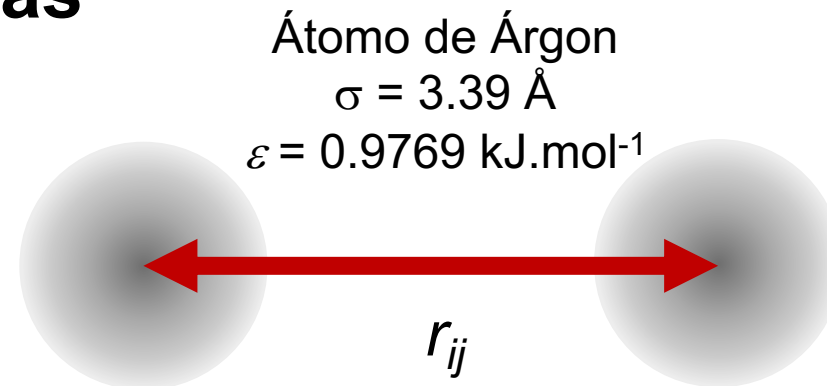
$$U_{\text{intra}} = \sum_{ij}^{\text{bonds}} \frac{k_{r,ij}}{2} (r_{ij} - r_{o,ij})^2 + \sum_{ijk}^{\text{angles}} \frac{k_{\theta,ijk}}{2} (\theta_{ijk} - \theta_{o,ijk})^2 + \sum_{ijkl}^{\text{dihedrals}} \sum_{n=1}^4 \frac{V_{n,ijkl}}{2} \left[1 + (-1)^n \cos(n\phi_{ijkl}) \right]$$



Campo de Forças

$$U_{\text{inter}} = U_{\text{vdw}} + U_{\text{coul}}$$

$$U_{\text{vdw}} = \sum_i \sum_{j>i} \left\{ 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] \right\}$$

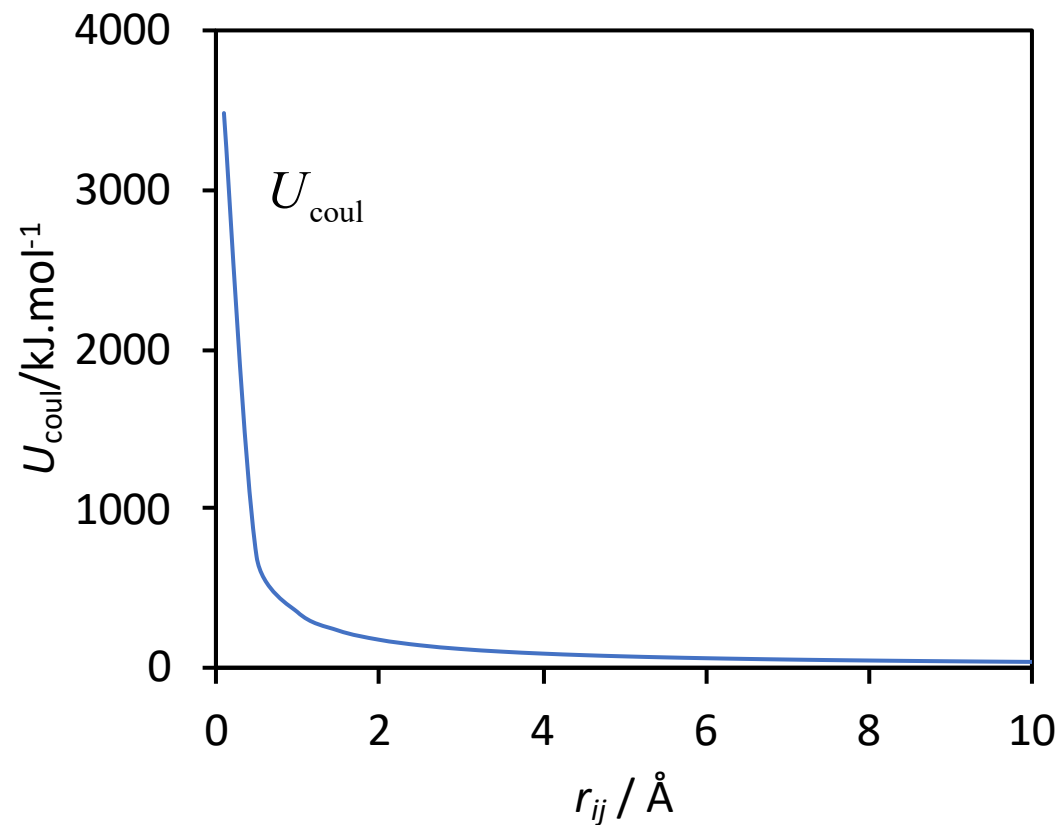
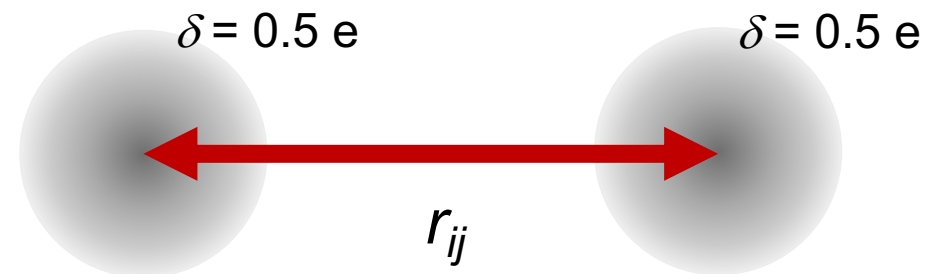


Campo de Forças

$$U_{\text{inter}} = U_{\text{vdw}} + U_{\text{coul}}$$

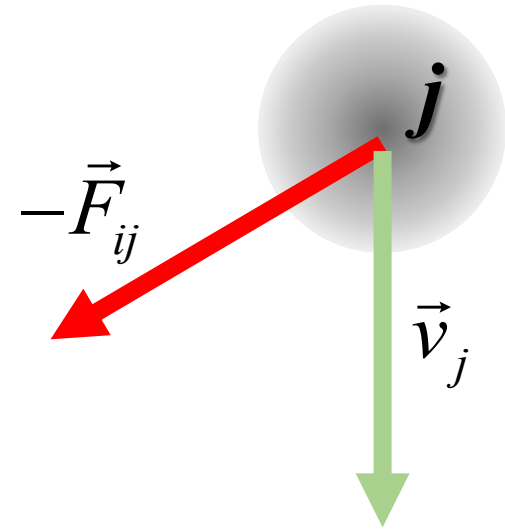
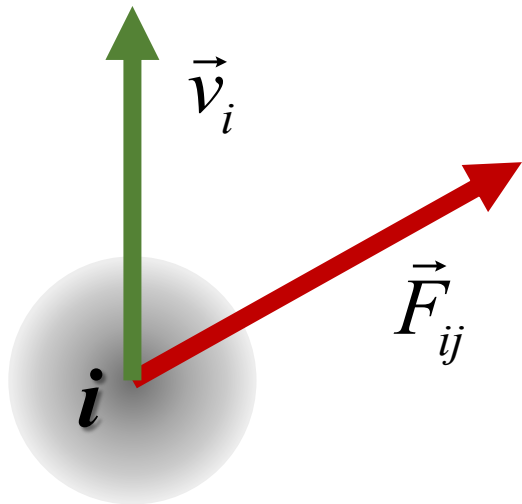
$$U_{\text{vdw}} = \sum_i \sum_{j>i} \left\{ 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] \right\}$$

$$U_{\text{coul}} = \sum_i \sum_{j>i} \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}}$$



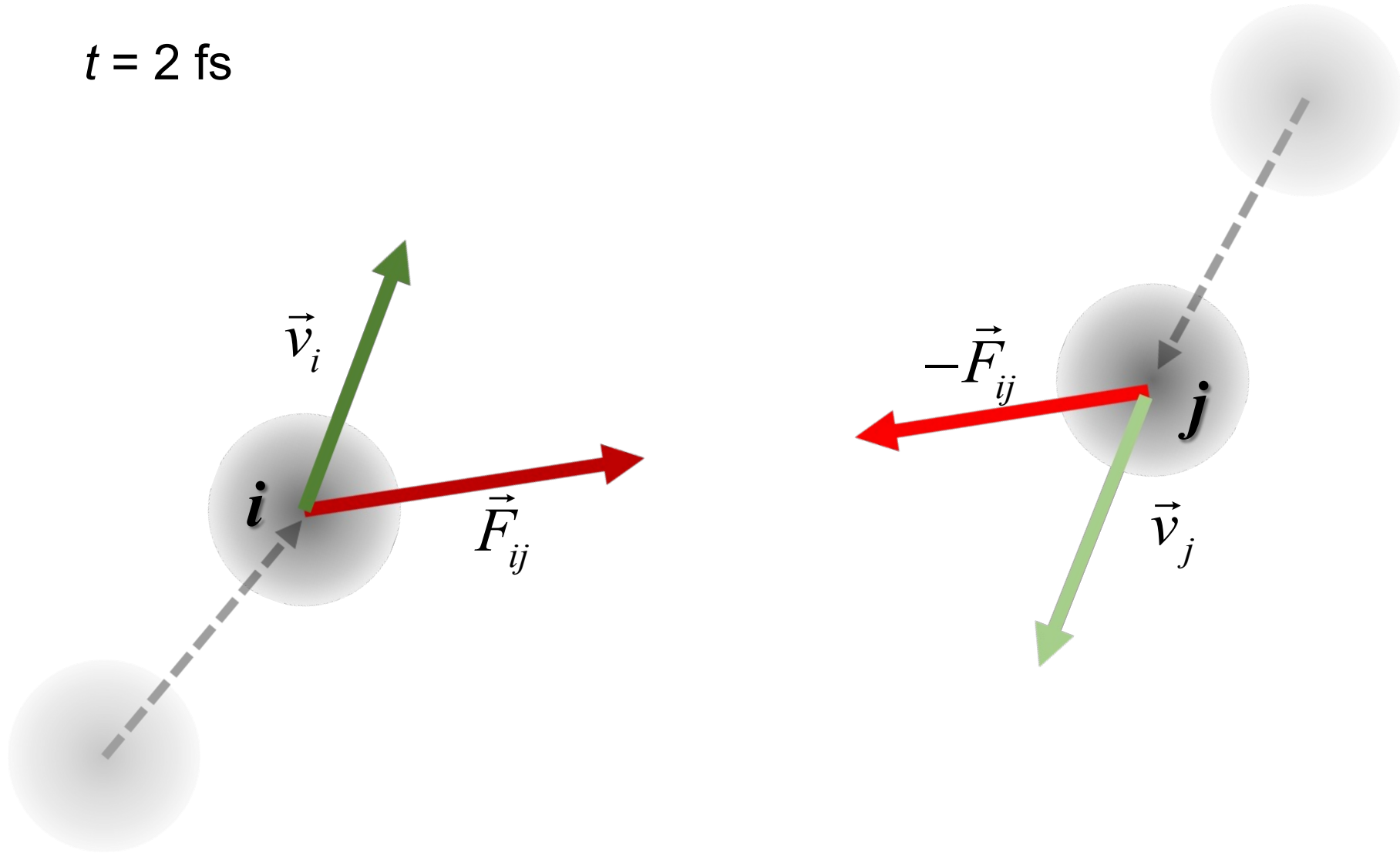
Dinâmica!!!

$t = 0$ fs



Dinâmica!!!

$t = 2 \text{ fs}$



Dinâmica!!!

Integração do movimento das moléculas (e.g. algoritmo Velocity Verlet - VV)

Assume que as posições, velocidades e forças de todos os átomos/partículas do sistema são conhecidas em cada passo.

1. Determina-se a velocidade das partículas em metade do tempo do passo:

$$\vec{v}(t + \frac{1}{2} \Delta t) \leftarrow \vec{v}(t) + \frac{1}{2} \Delta t \frac{\vec{F}(t)}{m}$$

2. Determina-se a posição após o tempo de passo:

$$\vec{r}(t + \Delta t) \leftarrow \vec{r}(t) + \Delta t \cdot \vec{v}(t + \frac{1}{2} \Delta t)$$

3. Determina-se a velocidade das partículas no final do passo:

$$\vec{v}(t + \Delta t) \leftarrow \vec{v}(t + \frac{1}{2} \Delta t) + \frac{1}{2} \Delta t \frac{\vec{F}(t + \Delta t)}{m}$$

Cálculo da Força

$$\vec{F}_{ij} = -\frac{1}{r_{ij}} \left[\frac{\partial}{\partial r_{ij}} U(r_{ij}) \right] \vec{r}_{ij}$$

$$U_{\text{vdw}} = \sum_i \sum_{j>i} \left\{ 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] \right\}$$

$$U_{\text{coul}} = \sum_i \sum_{j>i} \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}}$$

Caixa de Simulação



É impossível estudar um sistema molecular infinito.

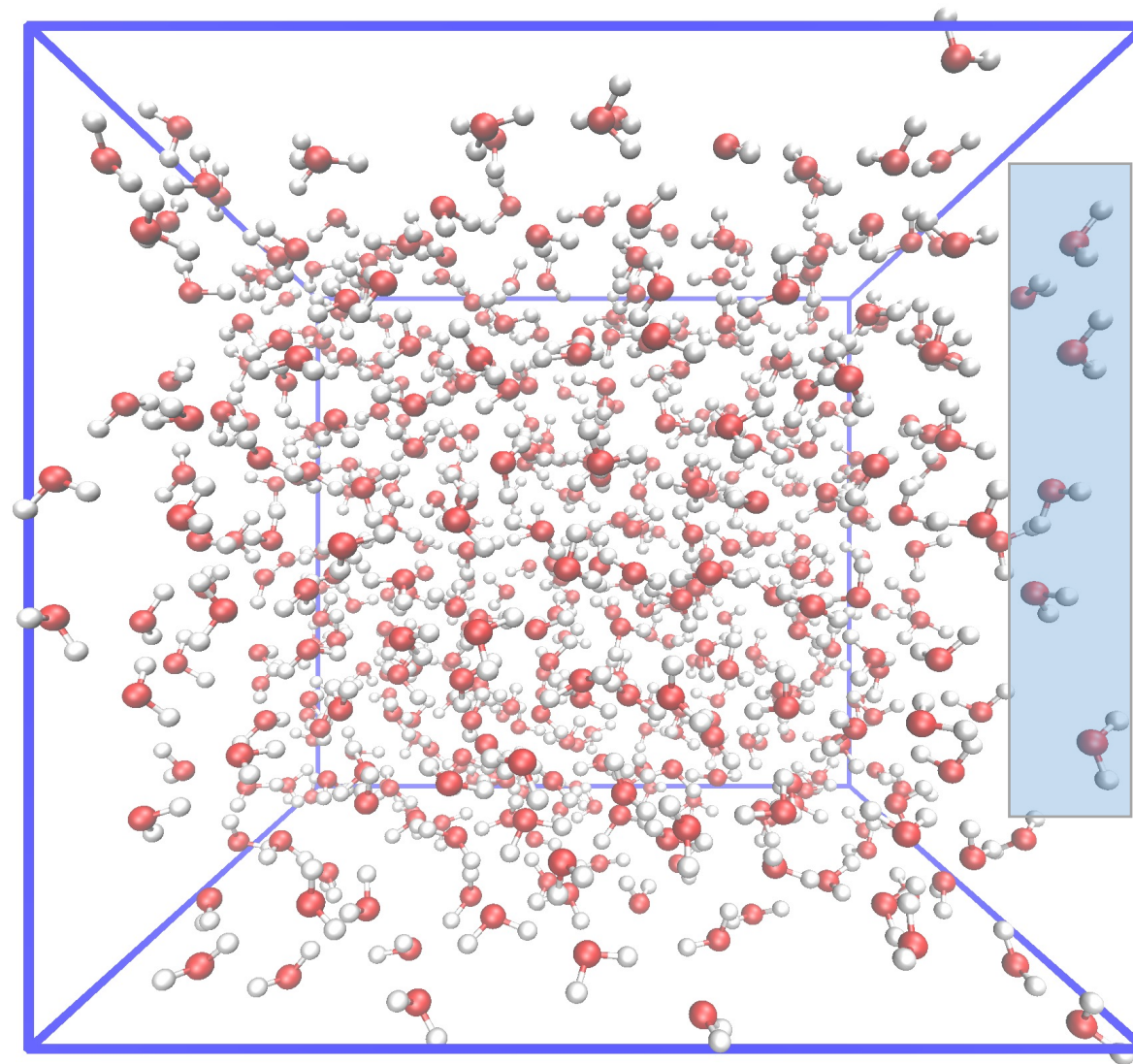


Caixa com 100 nm → ~45 000 000 átomos → 3 meses de cálculo

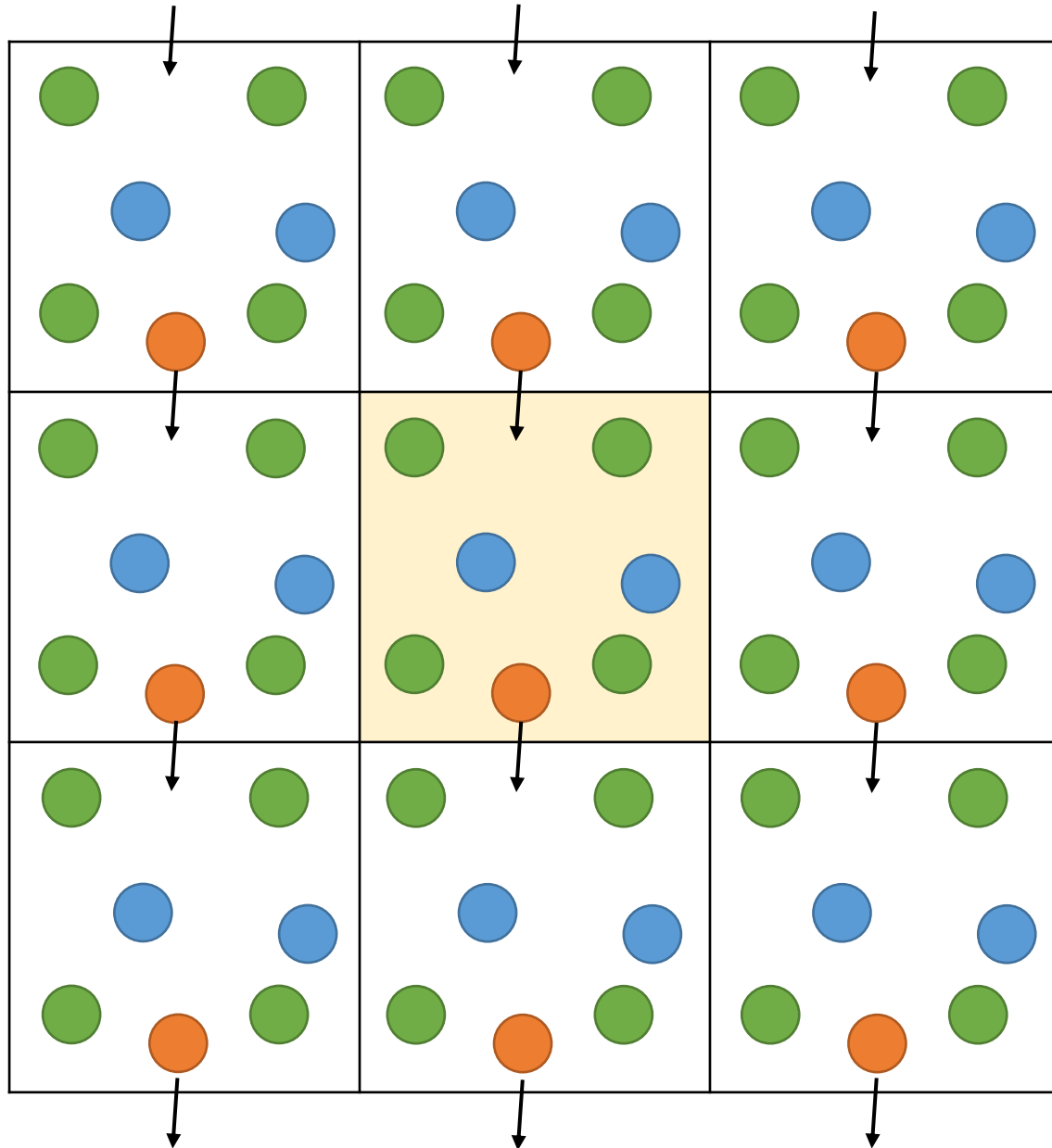


Esta deve ser ajustada às propriedades que se pretendem estudar.

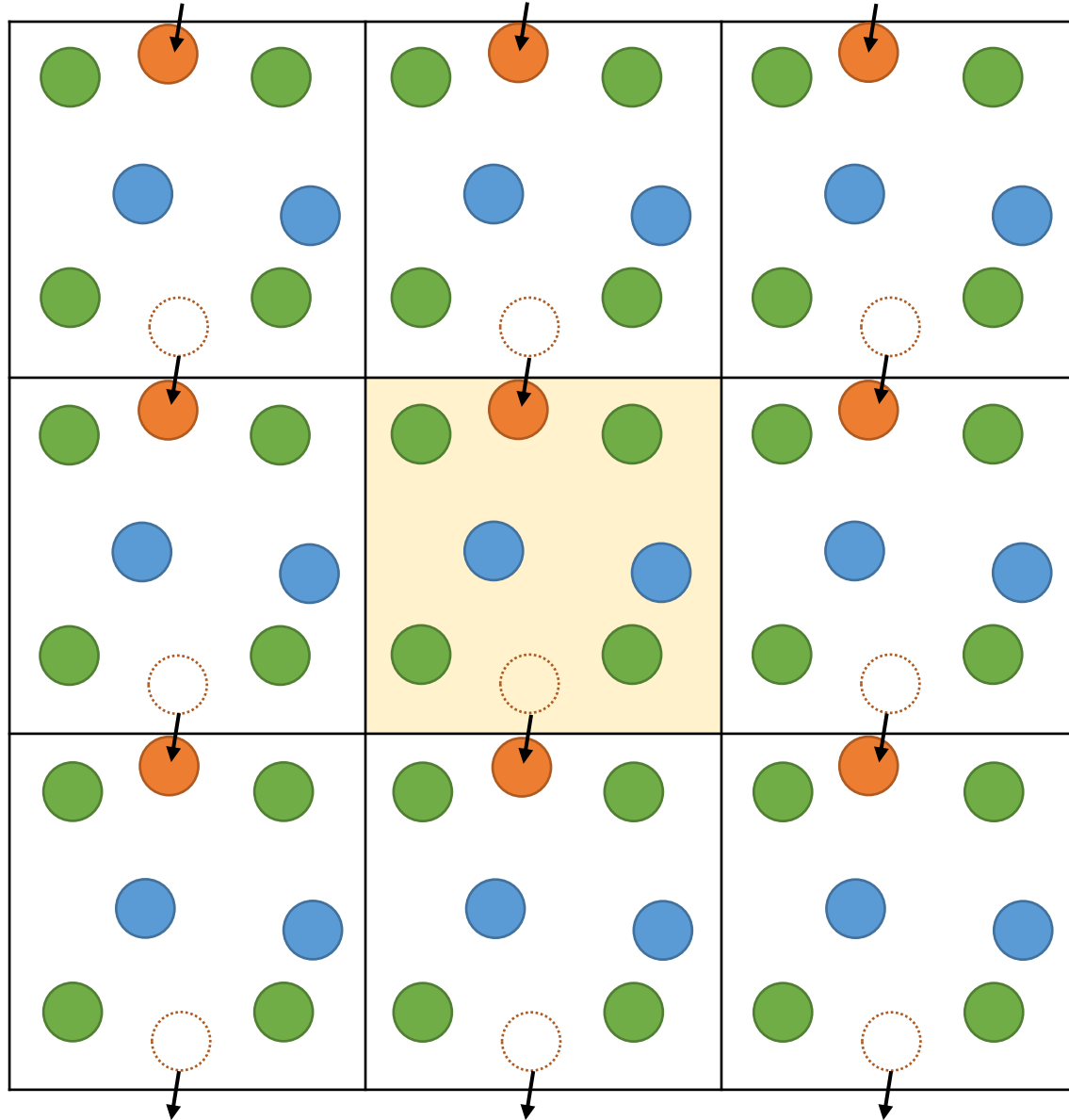
Caixa de Simulação



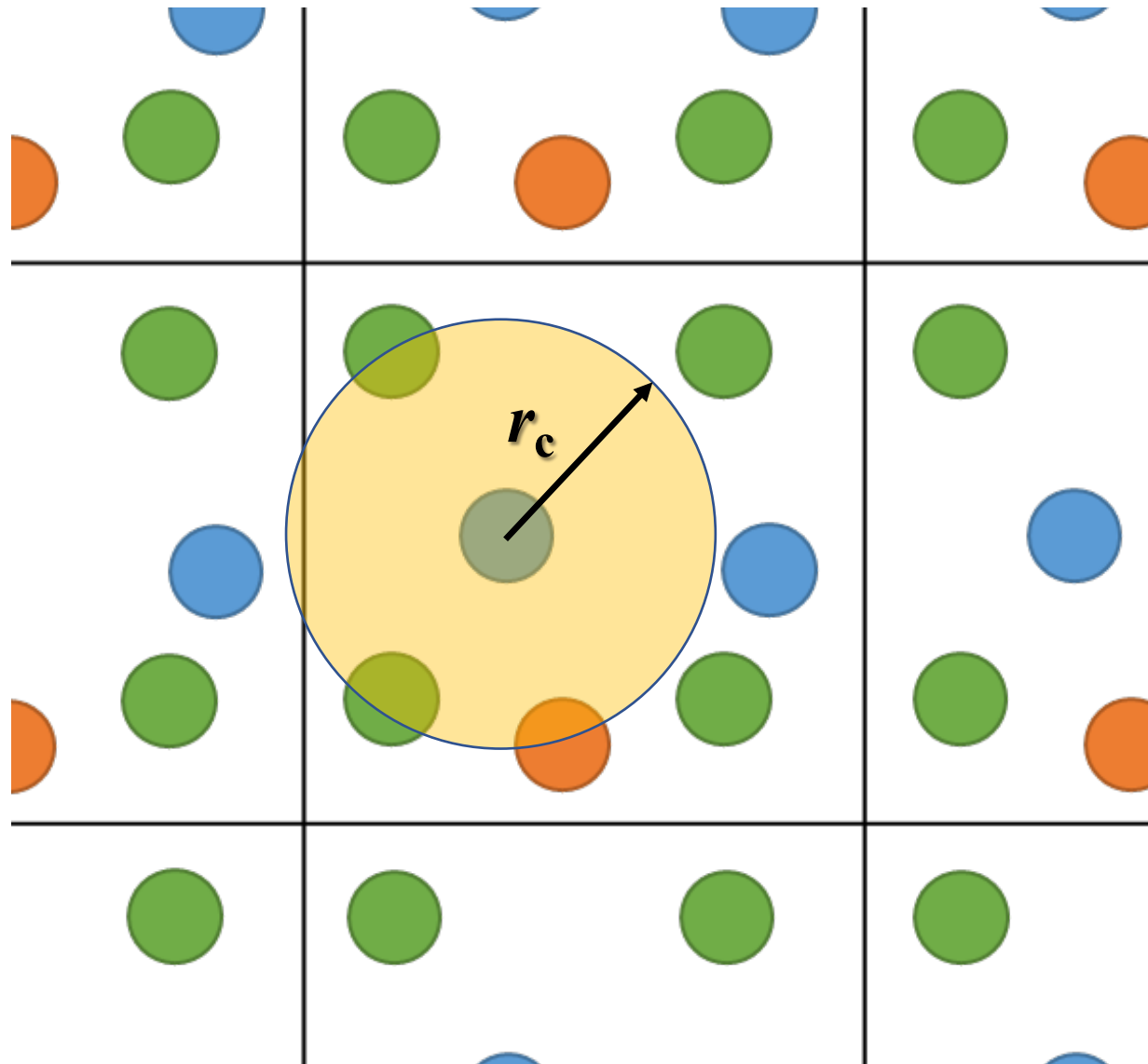
Condições Fronteira



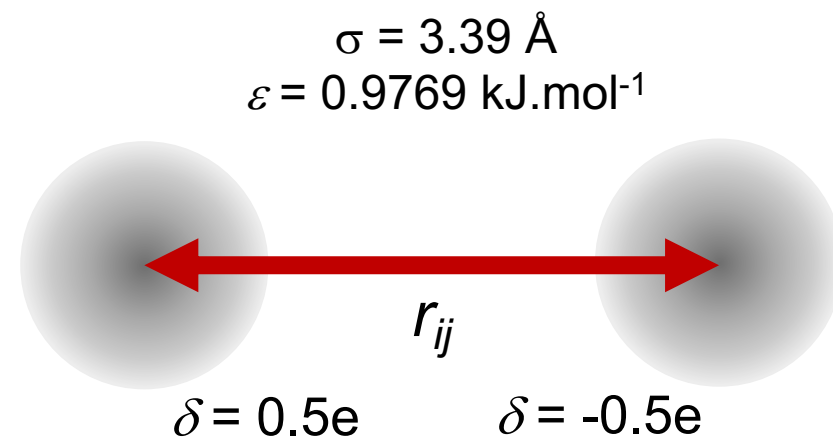
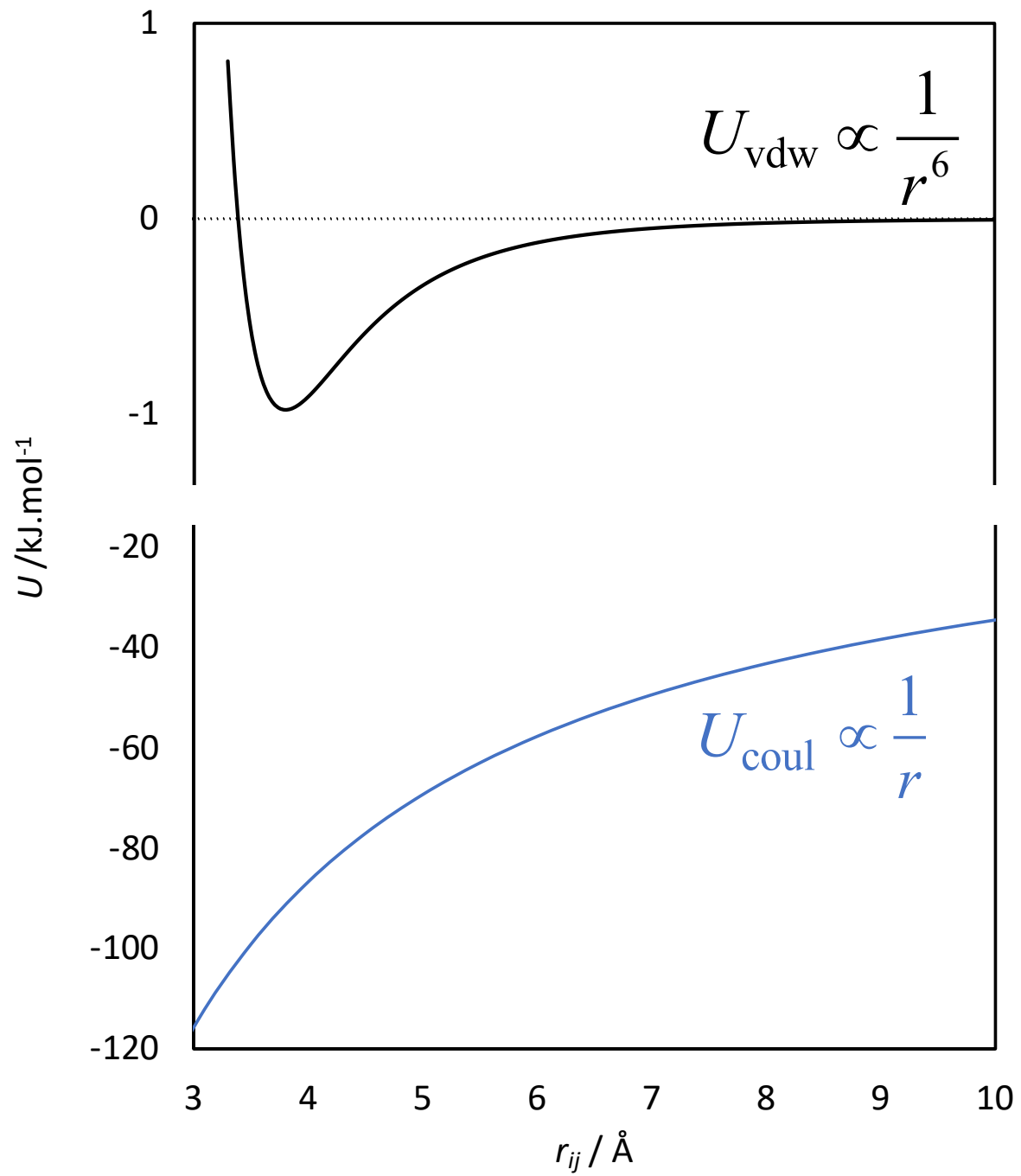
Condições Fronteira



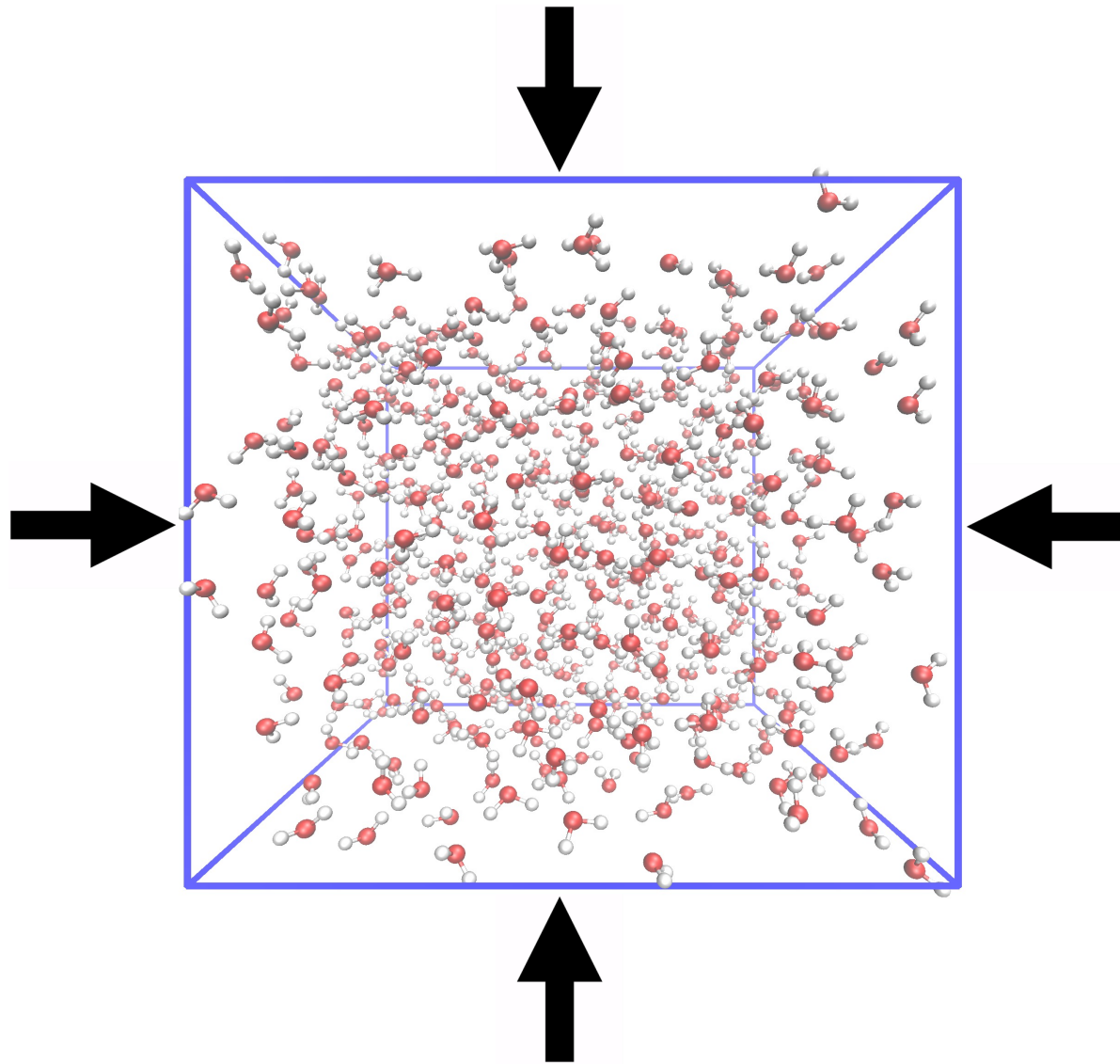
Raio de Corte



$$r_c < \frac{l_{caixa}}{2}$$

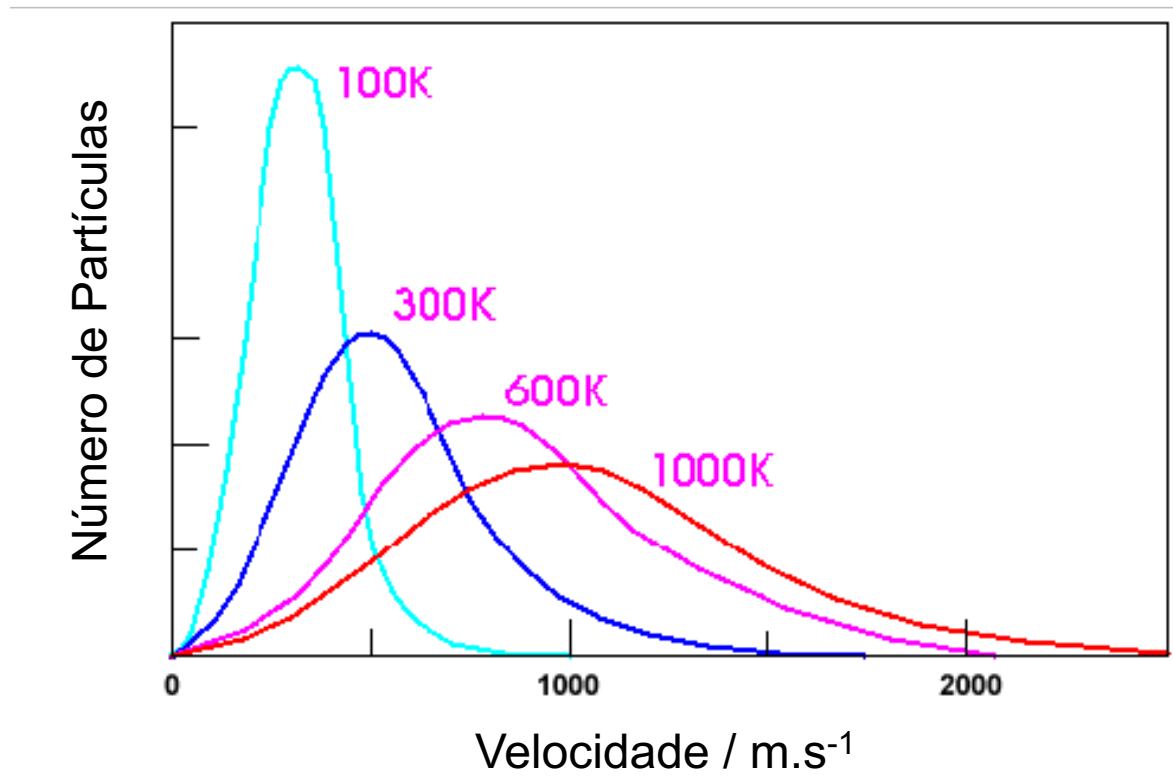


Baróstatos e Termostatos

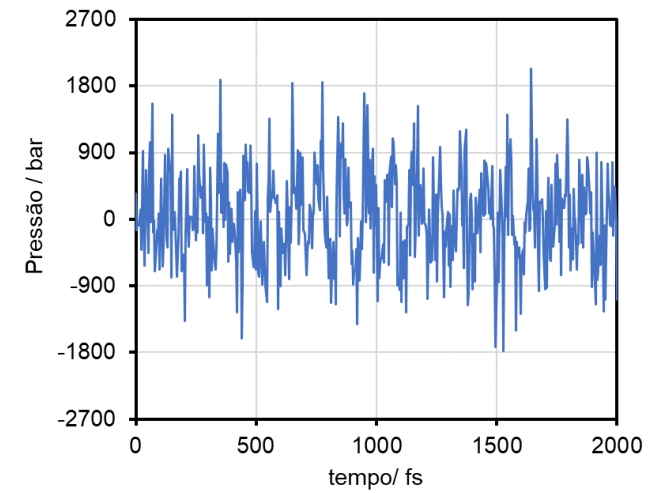
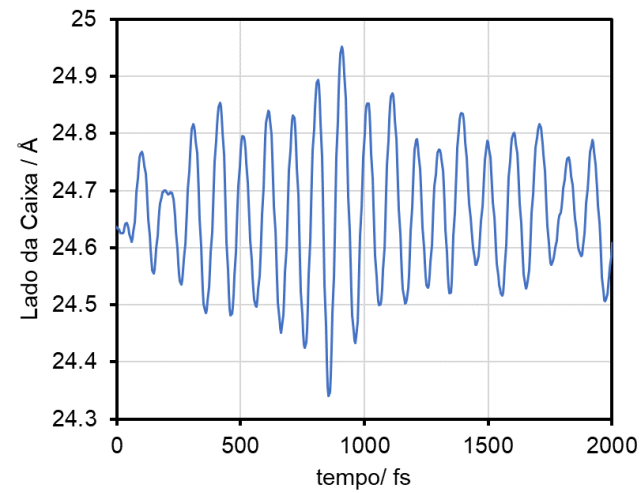
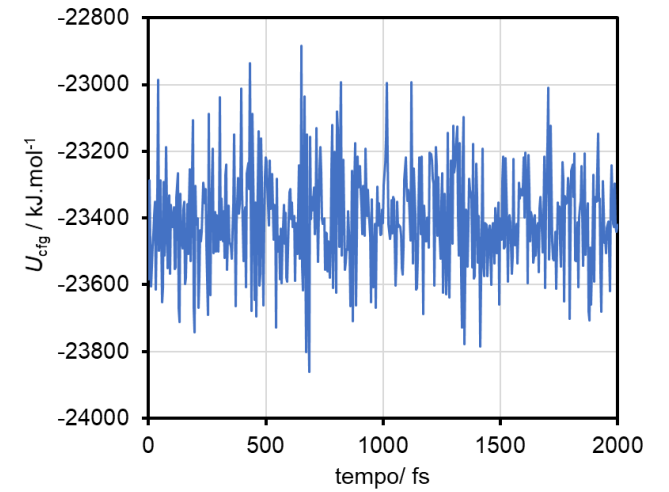
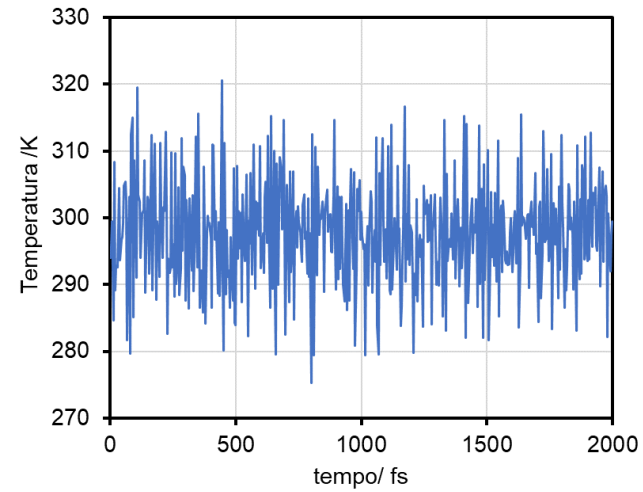


Baróstatos e Termostatos

$$T = \frac{E_k}{k_b} \quad E_k = \frac{1}{2}mv^2$$



Propriedades Médias



Validação de Campos de Força

1. Comparação de dados volumétricos (por exemplo, densidade de líquidos ou de sólidos)

$$\rho = \frac{m}{V}$$

2. Dados de energia de rede ou coesão (por exemplo, energia de sublimação ou vaporização)

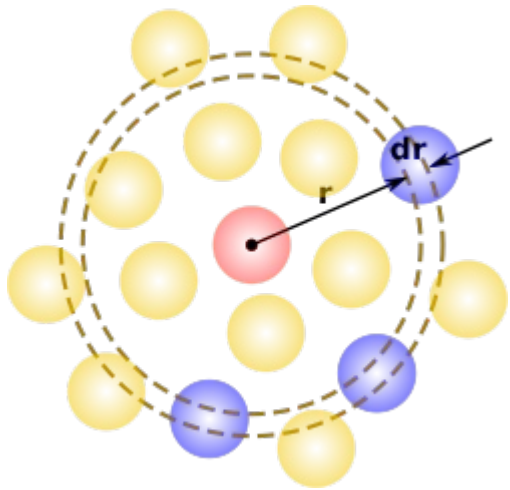
$$A(\text{cr/l}) \rightarrow A(\text{g})$$
$$\Delta_{\text{sub/vap}} U = U(\text{g}) - U(\text{cr/l})$$

3. Dados espectroscópicos (por exemplo, espectros de infravermelhos e de NMR)

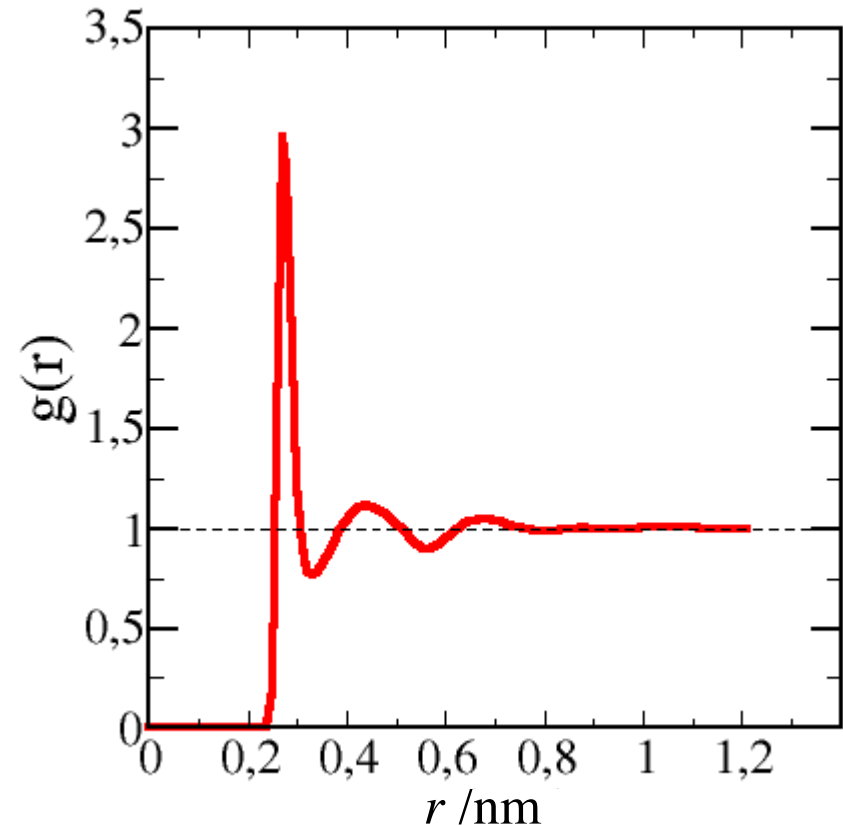
Analise conformacional de Moléculas

Que tipo de Estudos se Podem Fazer com DM

1. Determinação de propriedades estáticas: estrutura de substâncias e matérias, previsão de propriedades energéticas, e **Funções de Distribuição Radiais (RDFs)**

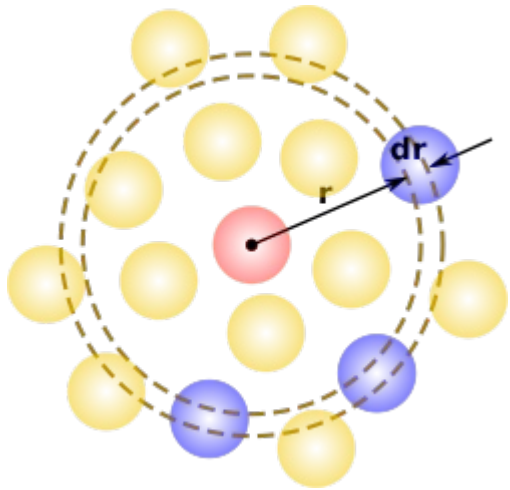


$$g(r) = \frac{1}{N} \frac{dn(r)}{4\pi^2 dr \rho}$$

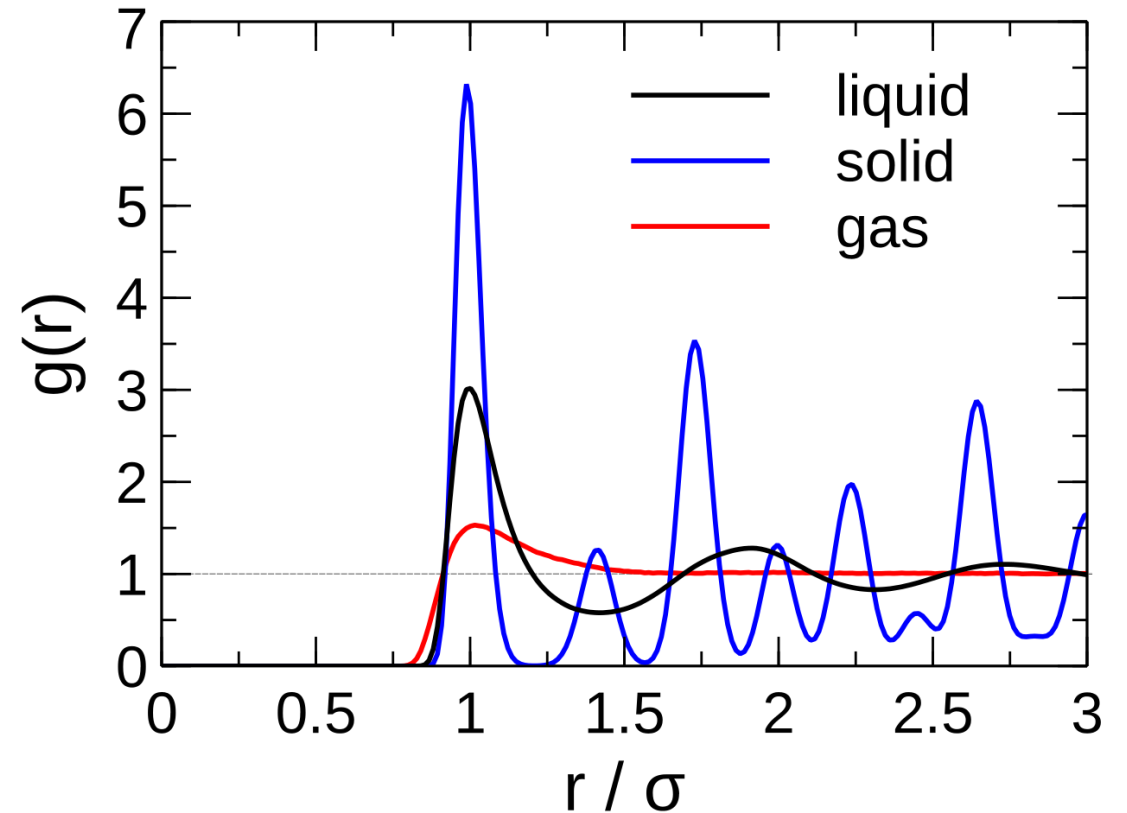


Que tipo de Estudos se Podem Fazer com DM

1. Determinação de propriedades estáticas: estrutura de substâncias e matérias, previsão de propriedades energéticas, e **Funções de Distribuição Radiais (RDFs)**



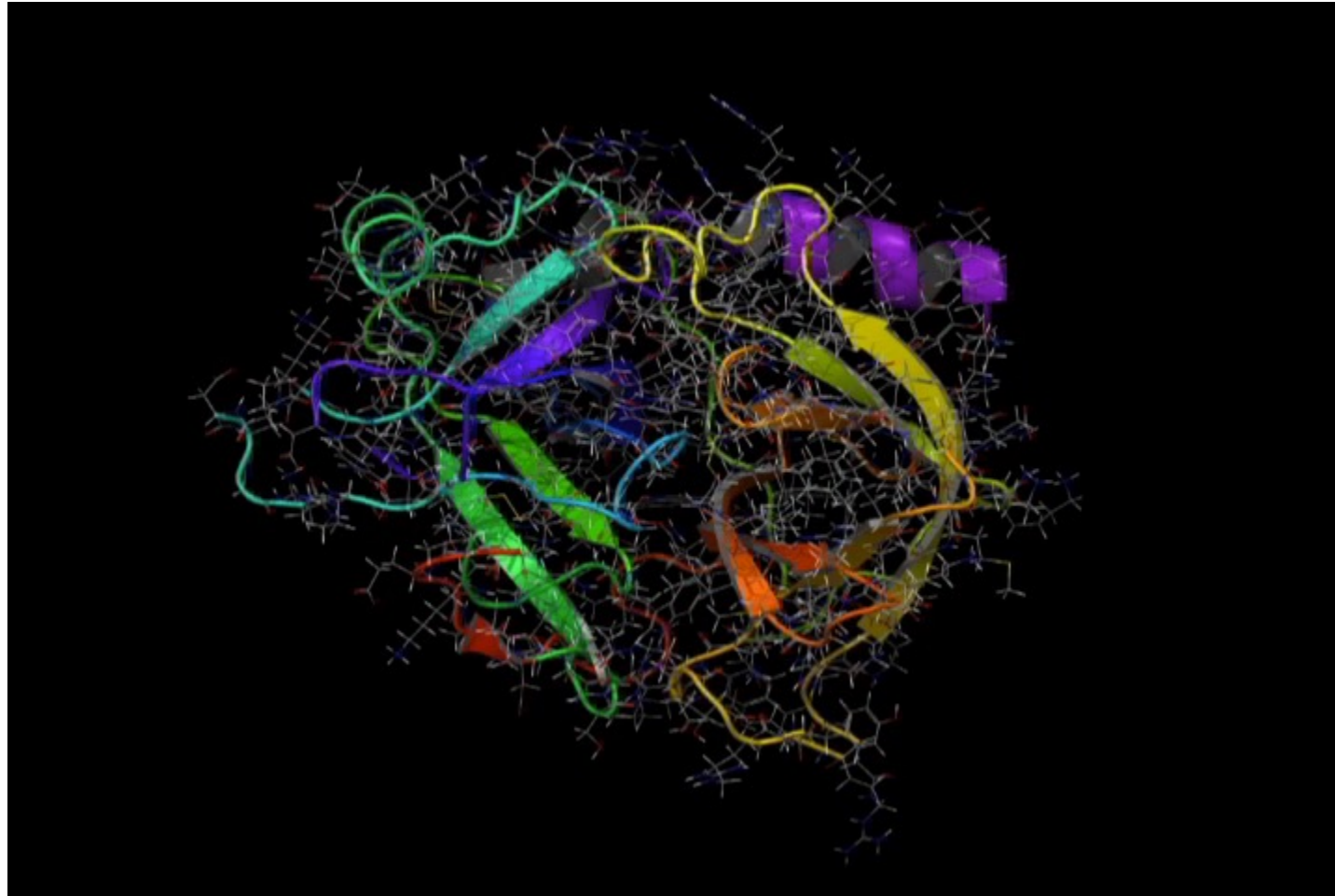
$$g(r) = \frac{1}{N} \frac{dn(r)}{4\pi^2 dr \rho}$$



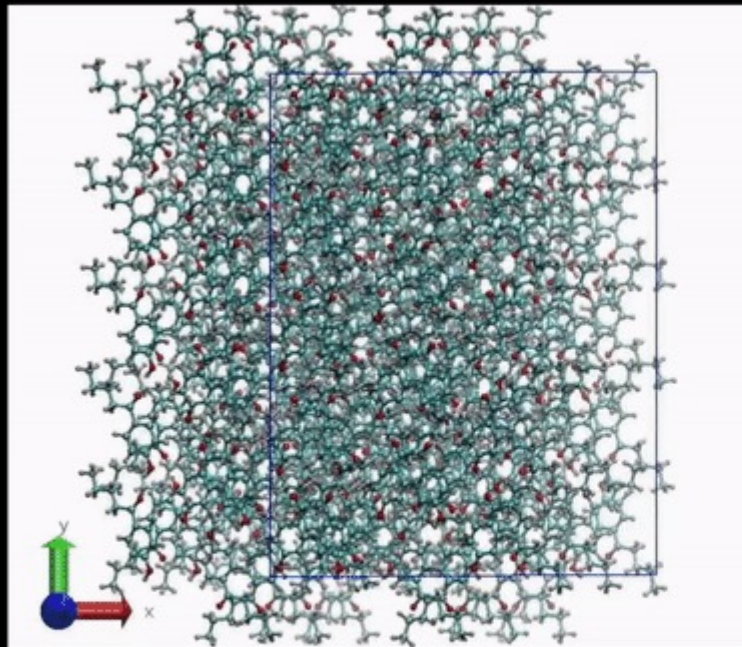
Que tipo de Estudos se Podem Fazer com MD

1. Determinação de propriedades estáticas: estrutura de substâncias e matérias, previsão de propriedades energéticas.
2. Determinação de propriedades dinâmicas usando funções de autocorrelação, como por exemplo, de velocidades (coeficientes de difusão) e de tensão (viscosidades).
3. Estudar o comportamento da matéria.

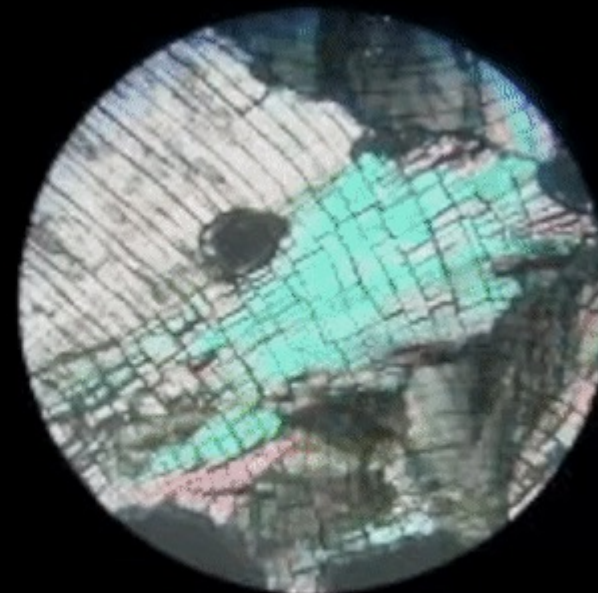
Que tipo de Estudos se Podem Fazer com DM



Que tipo de Estudos se Podem Fazer com DM



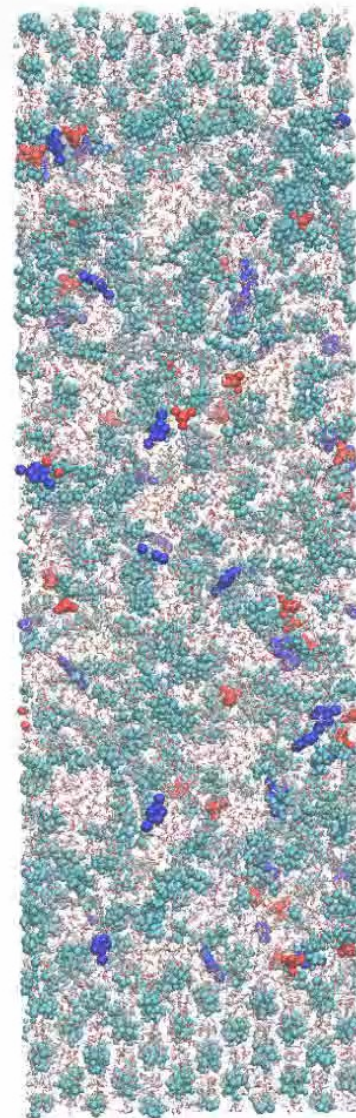
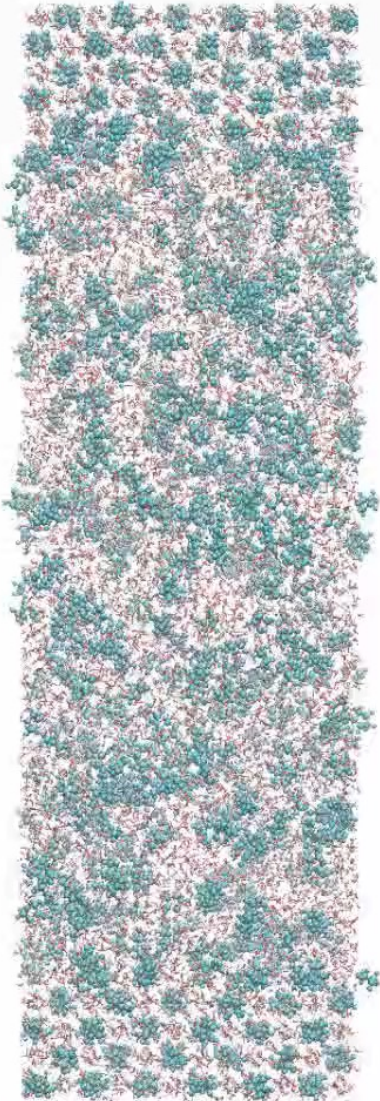
THEORY



244.630 K

EXPERIMENT

Que tipo de Estudos se Podem Fazer com DM



0.0 μS

GROMACS

FAST. FLEXIBLE. FREE.

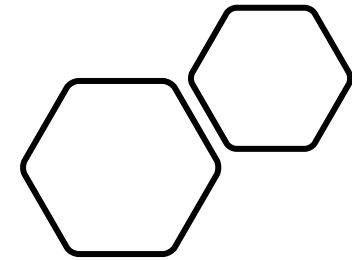


Tabela 1. Parâmetros dos modelos SPC/E (“Simple Point Charge/Extended”) e TIP3P (“Transferable Intermolecular Potentials with 3 Points”) para a água.

Interação	$\sigma_{\text{oo}} / \text{\AA}$	$\varepsilon_{\text{oo}} / \text{kJ}\cdot\text{mol}^{-1}$	$r_{\text{OH}} / \text{\AA}^a$	$\theta_{\text{HOH}} / \text{deg}^b$	q_{O} / e	q_{H} / e
SPC/E						
O–O	3.166	0.650	1.00	109.47	–0.8476	+0.4238
O–H	0.0	0.0				
H–H	0.0	0.0				
TIP3P						
O–O	3.1507	0.6364	0.9572	104.52	–0.834	+0.417
O–H	0.0	0.0				
H–H	0.0	0.0				

^a comprimento da ligação O–H da molécula de água. ^b ângulo H–O–H da molécula de água. Para comparação, os valores experimentais do comprimento de ligação O–H e do ângulo H–O–H da molécula isolada (monómero no gás) são, respetivamente, 0.9572 Å e 104.52°.

Ficheiros de Input do GROMACS

Ficheiro de Coordenadas

SCPE

1500

```
1h2o_s OWE 1 2.088 2.023 0.899 0.2100 -0.0045 -0.4466
1h2o_s HWE 2 1.988 2.026 0.911 -0.0045 -1.0858 -1.7268
1h2o_s HWE 3 2.132 2.061 0.980 -1.2329 -0.4541 0.5925
2h2o_s OWE 4 2.170 2.276 2.403 -0.4659 -0.2750 0.2514
2h2o_s HWE 5 2.122 2.344 2.457 -0.0947 0.1043 0.1147
2h2o_s HWE 6 2.111 2.197 2.388 -1.2760 0.4519 -0.4728
3h2o_s OWE 7 1.129 0.960 1.098 -0.4827 0.0868 -0.0531
3h2o_s HWE 8 1.084 0.923 1.179 -1.6371 0.0556 -0.6871
3h2o_s HWE 9 1.221 0.920 1.089 -0.1212 0.4974 1.5223
```

.....

```
499h2o_s OWE 1495 2.382 0.275 2.353 -0.0572 -0.3585 0.2819
499h2o_s HWE 1496 2.475 0.279 2.387 -0.2517 -1.2074 0.9430
499h2o_s HWE 1497 2.374 0.202 2.285 -0.3357 -0.5711 0.5401
500h2o_s OWE 1498 0.809 2.151 0.162 0.0165 -0.1365 -0.4896
500h2o_s HWE 1499 0.906 2.173 0.153 -0.3709 1.4959 -0.9270
500h2o_s HWE 1500 0.757 2.197 0.089 -1.0220 -1.5051 -0.6578
2.46088 2.46088 2.46088
```

Ficheiros de Input do GROMACS

Ficheiro de Topologia

```
[ defaults ]
; nbfunc  comb-rule  gen-pairs  fudgeLJ fudgeQQ
1         2         yes         0.5000 0.5000

[ atomtypes ]
; name  at.num  mass  charge  ptype  sigma  epsilon
OWE     8 15.99900 -0.84760  A 0.31660 0.65314
HWE     1 1.00800  0.42380  A 0.00000 0.00000

[ moleculetype ]
; Name      nrexcl
h2o_spcE    3

[ atoms ]
;  nr  type  resnr  residue  atom  cgnr  charge  mass
  1  OWE   1  h2o_spcE  OWE   1 -0.84760 15.99900
  2  HWE   1  h2o_spcE  HWE   2  0.42380  1.00800
  3  HWE   1  h2o_spcE  HWE   3  0.42380  1.00800
```

```
[ constraints ]
;  at1  at2  funct    ro
   1    2    1 0.10000000
   1    3    1 0.10000000
   2    3    1 0.16329800

[ system ]
; Name
H2O

[ molecules ]
; Compound      #mols
h2o_spcE        500
```

Ficheiros de Input do GROMACS

Ficheiro de Controlo

```
; Run parameters
integrator          = md
nsteps             = 100000
dt                = 0.002

; Output control
nstxout-compressed = 100
nstenergy         = 100
nstlog           = 100
nstcomm          = 5000

; Bond parameters
continuation       = yes
constraint_algorithm = lincs
constraints        = H-bonds
lincs_iter        = 1
lincs_order       = 4

; Neighborssearching
cutoff-scheme     = Verlet
ns_type           = grid
nstlist           = 10
rcoulomb          = 1.0
rvdw              = 1.0

; Electrostatics & Dispersion correction
coulombtype       = PME
vdw-type          = Cut-off
fourierspacing    = 0.10
pme_order         = 4
ewald-rtol        = 1e-7
ewald-geometry    = 3d
epsilon-surface   = 0
DispCorr          = EnerPres

; Temperature coupling for production
tcoupl            = nose-hoover
tc-grps           = System
tau_t             = 5.0
ref_t             = 298.15

; Pressure coupling for production
ref_p             = 1.0
pcoupl            = Parrinello-Rahman
pcoupltype        = isotropic
tau_p             = 20.0
compressibility   = 4.5e-5
refcoord_scaling  = com

; Periodic boundary conditions
pbc               = xyz

; Velocity generation
gen_vel           = no
gen_temp          = 300
gen_seed          = 123456
```