Introduction to molecular dynamics simulation

Institute of applied physics and computational mathematics

Han Wang (王涵)

- What is molecular dynamics simulation.
- The modeling of atomic interactions.
- The computation of atomic interactions

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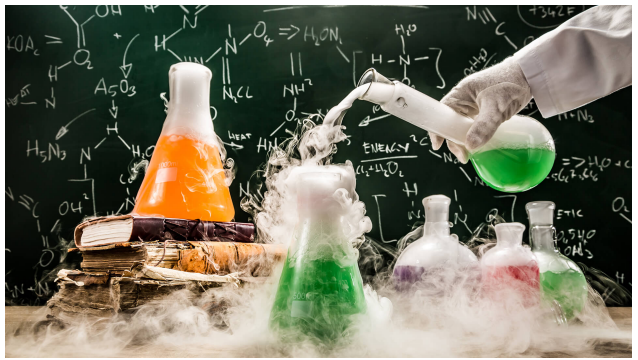
- The computation of atomic interactions

Introduction: what is molecular dynamics simulation

Real experiment in Lab.

1 准备样品



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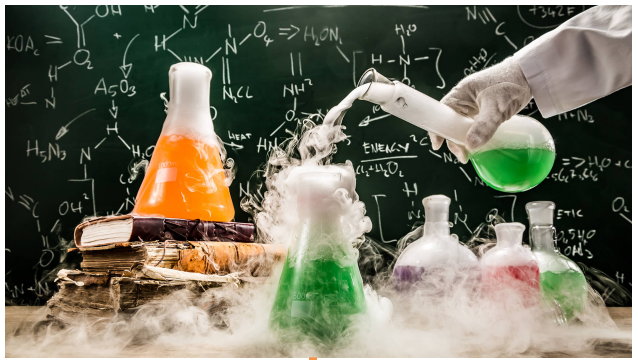

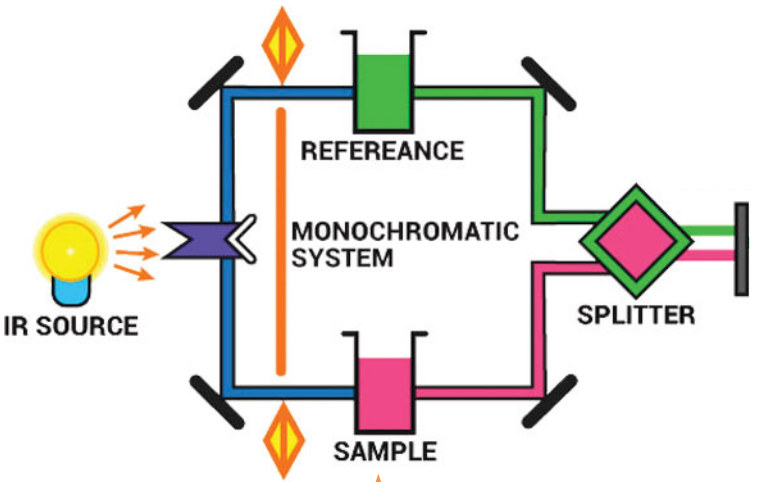

2 使用仪器进行分析

Introduction: what is molecular dynamics simulation

Real experiment in Lab.

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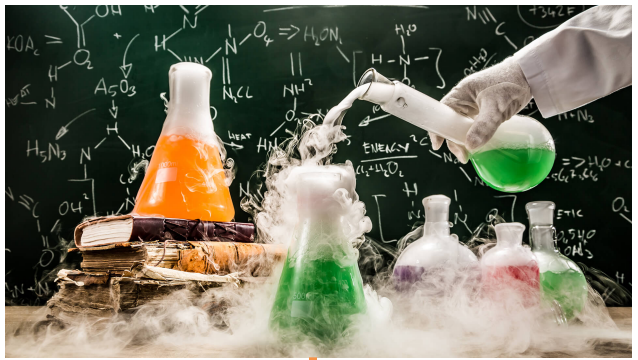
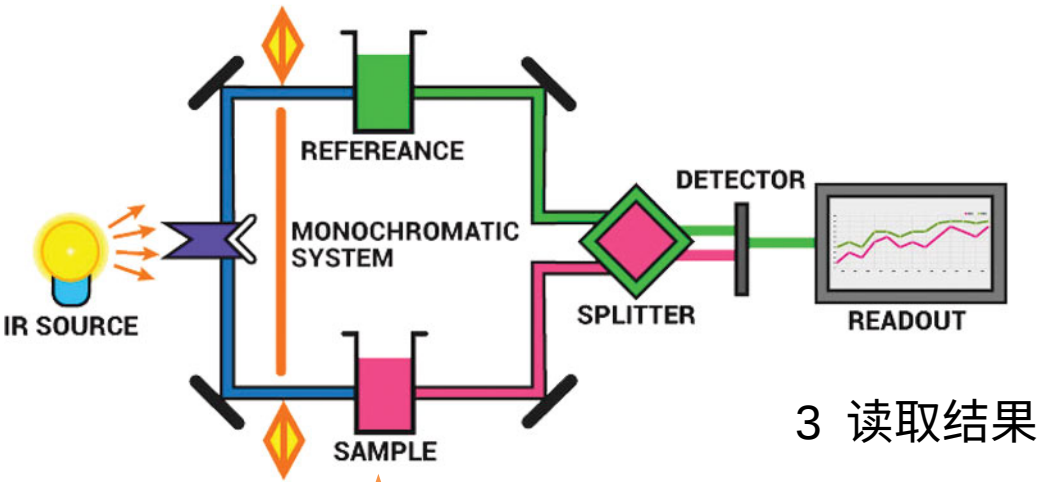




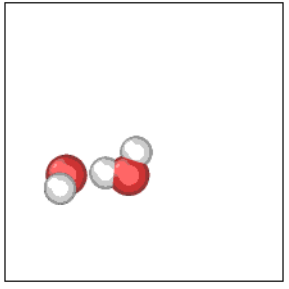
3 读取结果

2 使用仪器进行分析

Introduction: what is molecular dynamics simulation

Molecular dynamics simulation follows the same path as experiments

1 准备样品



Introduction: what is molecular dynamics simulation

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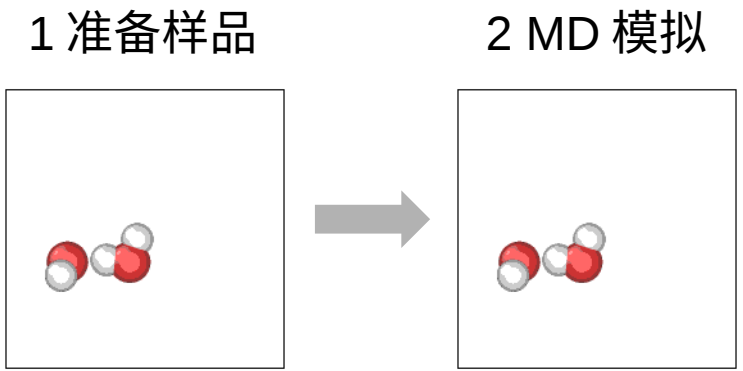

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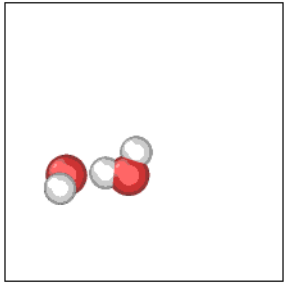
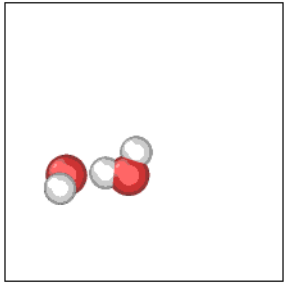


2 MD 模拟



3 MD 结果分析

```
ITEM: TIMESTEP
0
ITEM: NUMBER OF ATOMS
6
ITEM: BOX BOUNDS xy xz yz pp pp pp
0.0000000000000000e+00 1.2000000000000000e+01 0.0000000000000000e+00
0.0000000000000000e+00 1.2000000000000000e+01 0.0000000000000000e+00
0.0000000000000000e+00 8.0000000000000000e+00 0.0000000000000000e+00
ITEM: ATOMS id type x y z fx fy fz
1 1 5.34607 4.5711 1.76 1.23427 4.89805 -0.0709105
2 1 2.65393 4.5711 1.76 -2.68941 -4.08063 0.0235947
3 2 5.66632 5.55412 1.74392 -1.35072 -4.69675 0.0760074
4 2 4.34418 4.66728 1.76493 1.40331 -0.000537707 -0.00857851
5 2 2.38369 3.99418 2.56104 0.706168 1.93915 -2.33251
6 2 2.38745 3.9908 0.960723 0.696387 1.94072 2.31239
ITEM: TIMESTEP
10
ITEM: NUMBER OF ATOMS
6
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0.0000000000000000e+00 1.2000000000000000e+01 0.0000000000000000e+00
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1 1 5.35366 4.57926 1.76615 -1.19579 -5.216 0.148149
2 1 2.63416 4.5683 1.75687 0.472865 3.21561 -0.23237
3 2 5.64045 5.38042 1.74236 2.17924 5.28926 -0.149619
4 2 4.37799 4.65016 1.7303 0.463678 0.191111 0.00996782
5 2 2.43651 4.08089 2.48826 -0.934825 -1.7258 3.11906
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Introduction: what is molecular dynamics simulation

Molecular dynamics simulation follows the same path as experiments

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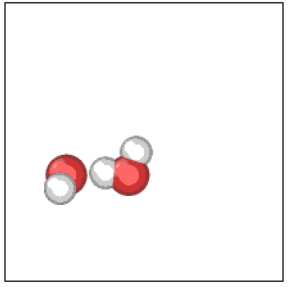

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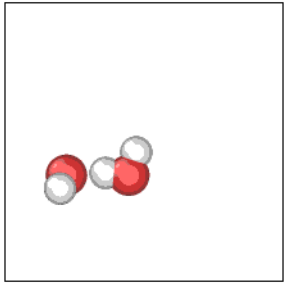

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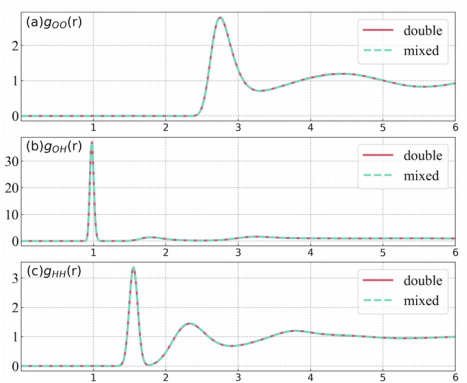

Introduction: what is molecular dynamics simulation

Translate in mathematical language

1 准备初条件 $x = (\underbrace{q_1, q_2, \ldots q_N}_{\text{坐标}}, \underbrace{p_1, p_2, \ldots, p_N}_{\text{动量}})$

Introduction: what is molecular dynamics simulation

Translate in mathematical language

1 准备初条件 $x = (q_1, q_2, \ldots q_N, p_1, p_2, \ldots, p_N)$

2 MD 模拟 $\dot{q}_i = \dfrac{\partial \mathcal{H}}{\partial p_i}$ $\dot{p}_i = -\dfrac{\partial \mathcal{H}}{\partial q_i}$

$$\mathcal{H} = \underbrace{\sum_{i=1}^{N} \frac{p_i^2}{2m_i}}_{\text{动能}} + \underbrace{E(q_1, \ldots, q_N)}_{\text{势能}}$$

注意 $F_i = -\dfrac{\partial E}{\partial q_i}$

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等价于牛顿运动定律 $m_i \ddot{q}_i = F_i$

Introduction: what is molecular dynamics simulation

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3 数值求解得到“轨道” $\{q_i(t),\, p_i(t)\}$

Introduction: what is molecular dynamics simulation

Translate in mathematical language

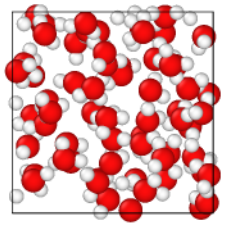
4 结果分析：物理可观测量可以写为坐标和动量 $\{q_i(t), p_i(t)\}$ 的函数

例如压力张量 $P = \frac{1}{T}\int_0^T \frac{1}{V}\sum_i \left(\frac{p_i(t)p_i(t)}{m_i} + r_i(t)F_i(t)\right)dt$

例如温度、密度、径向分布函数、扩散系数、粘性系数等

Introduction: what is molecular dynamics simulation

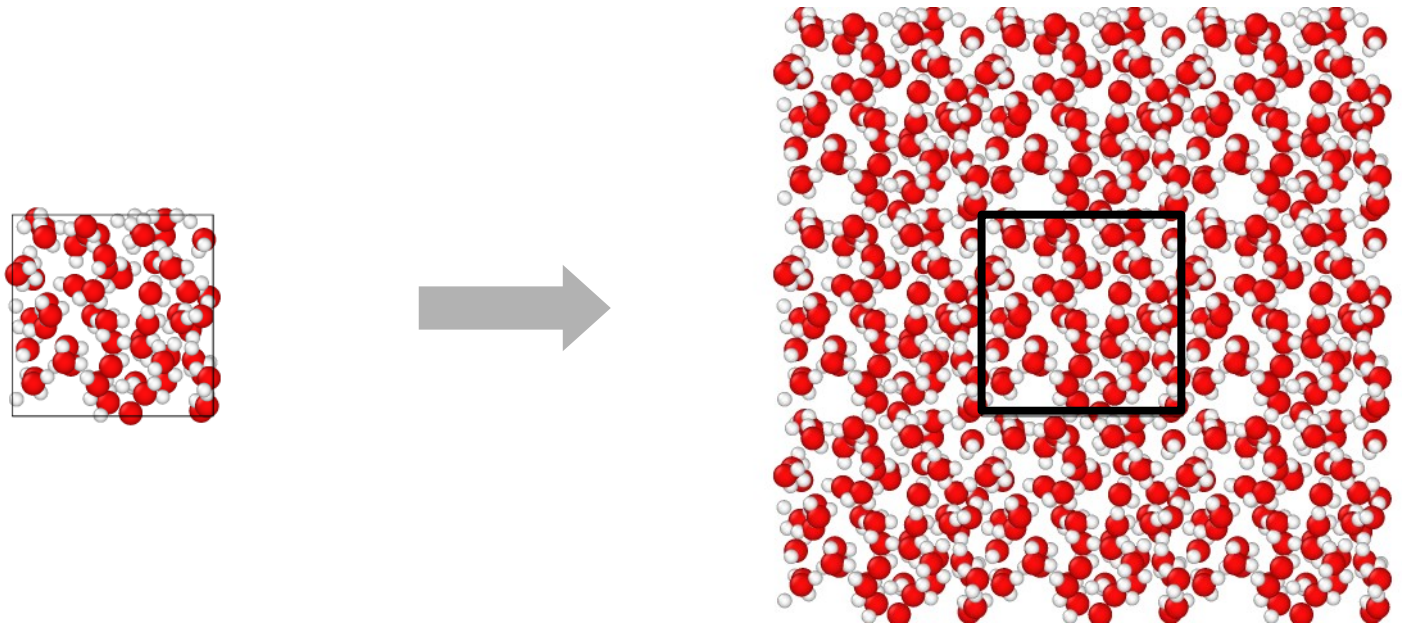
Periodic boundary condition



分子数 64 与宏观分子数 10^{23} 相差甚远

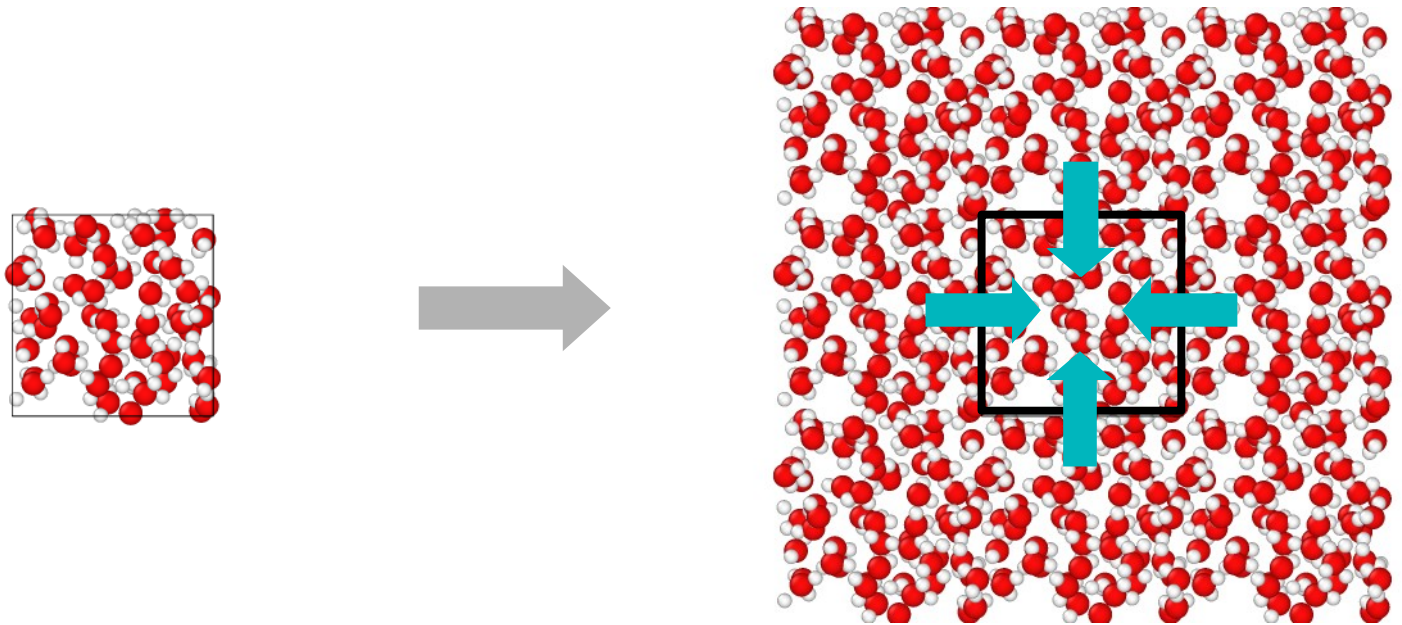
Introduction: what is molecular dynamics simulation

Periodic boundary condition



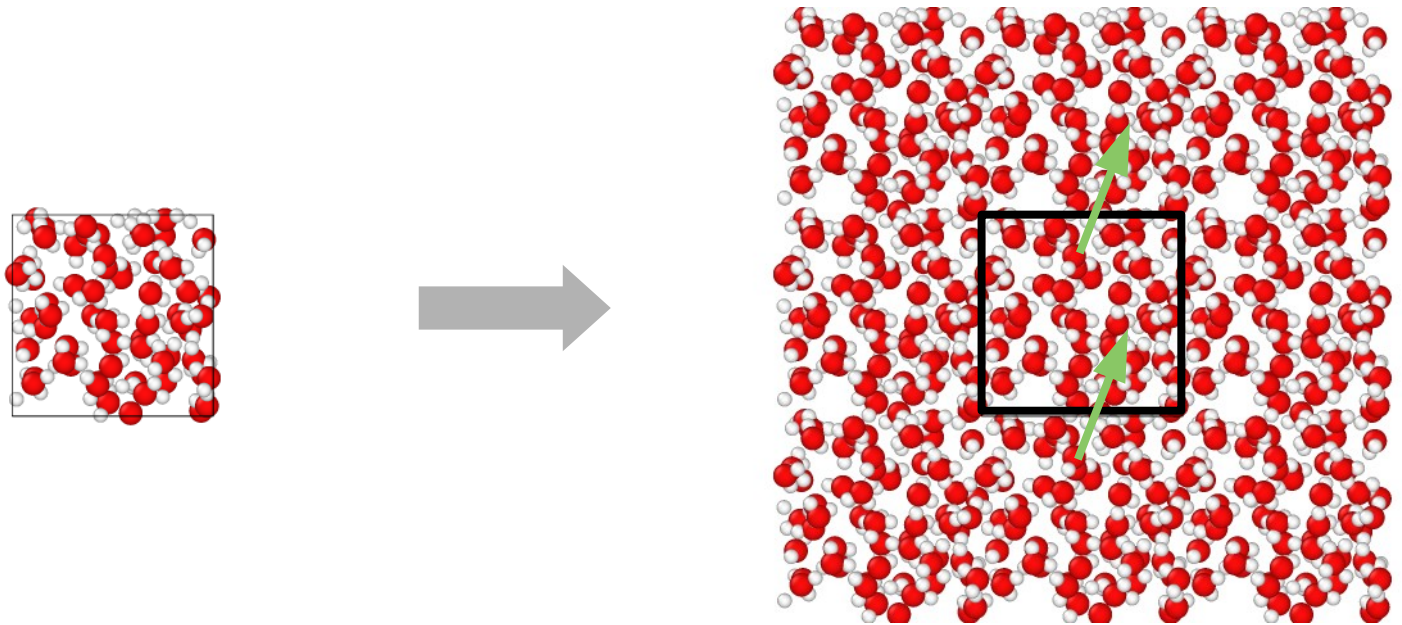
Introduction: what is molecular dynamics simulation

Periodic boundary condition



Introduction: what is molecular dynamics simulation

Periodic boundary condition



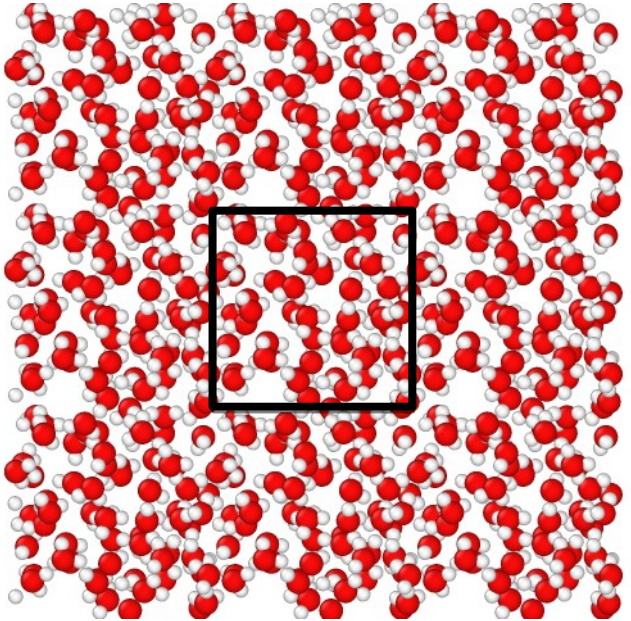
Introduction: what is molecular dynamics simulation

Periodic boundary condition

Periodic boundary condition

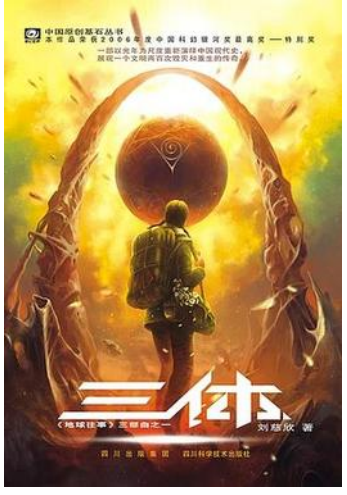
Mimic a bulk system

Finite size effect carefully checked



Introduction: the accuracy of MD

Accurate trajectory is impossible



MD: N-body problem

$$\dot{q}_i = \frac{\partial \mathcal{H}}{\partial p_i}$$

$$\dot{p}_i = -\frac{\partial \mathcal{H}}{\partial q_i}$$

Introduction: the accuracy of MD

What we need is not accurate trajectory, but accurate statistic.

$$P = \left\langle \frac{1}{V} \sum_i \left(\frac{p_i p_i}{m_i} + r_i F_i \right) \right\rangle \qquad \langle A \rangle = \int A(q,p)\rho(q,p)dqdp = \int A(x)\rho(x)dx$$

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$$\frac{1}{T} \int_0^T \frac{1}{V} \sum_i \left(\frac{p_i(t) p_i(t)}{m_i} + r_i(t) F_i(t) \right) dt$$

$$\{q_i(t),\ p_i(t)\}$$

采样分布

$$\rho(x)$$

Introduction: microcanonical ensemble

$$\dot{q}_i = \frac{\partial \mathcal{H}}{\partial p_i}$$
$$\dot{p}_i = -\frac{\partial \mathcal{H}}{\partial q_i}$$

$$\rho(x) = \delta(\mathcal{H}(x) - \mathcal{H}_0)$$
$$x = (q_1, q_2, \ldots q_N, p_1, p_2, \ldots, p_N)$$

遍历性假设下：采样微正则系综（ microcanonical ensemble ）

控制变量：原子数（ N ） 体积（ V ） 能量（ E ）

Introduction: canonical ensemble

$$\rho(x) = \frac{1}{Z} e^{-\beta \mathcal{H}(x)}$$

$$Z = \int e^{-\beta \mathcal{H}(x)} dx \quad \beta = \frac{1}{kT}$$

采样正则系综（ canonical ensemble ）

控制变量：原子数（ N ） 体积（ V ） 温度（ T ）

Introduction: canonical ensemble

$$\dot{q}_i = \frac{\partial \mathcal{H}}{\partial p_i}$$

$$\dot{p}_i = -\frac{\partial \mathcal{H}}{\partial q_i} - \gamma p_i + \sqrt{m_i}\sigma \dot{W}$$

$$\rho(x) = \frac{1}{Z} e^{-\beta \mathcal{H}(x)}$$

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采样正则系综（ canonical ensemble ）

控制变量：原子数（ N ） 体积（ V ） 温度（ T ）

Introduction: isothermo-isobaric ensemble

$$\rho(x) = \frac{1}{Z} e^{-\beta(\mathcal{H}(x)+PV)}$$

$$Z = \int e^{-\beta(\mathcal{H}(x)+PV)} dx$$

采样恒温恒压（ isothermo-isobaric ensemble ）

控制变量：原子数（ N ） 压强（ P ） 温度（ T ）

Introduction: isothermo-isobaric ensemble

$$\dot{q}_i = \frac{\partial \mathcal{H}}{\partial p_i} + \frac{p_V}{3M_V V} q_i$$

$$\dot{p}_i = -\frac{\partial \mathcal{H}}{\partial q_i} - \frac{p_V}{3M_V V} p_i - \gamma p_i + \sqrt{m_i}\sigma \dot{W}$$

$$\dot{V} = \frac{p_V}{M_V}$$

$$\dot{p}_V = P - P_0 - \gamma_V p_V + M_V^{\frac{1}{2}} \sigma_V \dot{W}$$

$$\rho(x) = \frac{1}{Z} e^{-\beta(\mathcal{H}(x)+PV)}$$

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采样恒温恒压（ isothermo-isobaric ensemble ）

控制变量：原子数（ N ） 压强（ P ） 温度（ T ）

Introduction: the accuracy of MD

Control params.	Dynamics	Ensemble
N,V,E	Newton	$p(\boldsymbol{x}) = \delta(\mathcal{H}(\boldsymbol{x}) - \mathcal{H}_0)$
N,V,T	Nosé-Hoover, Langevin	$p(\boldsymbol{x}) = \frac{1}{Z} e^{-\beta \mathcal{H}(\boldsymbol{x})}$
N,P,T	MTTK, NPT-Langevin	$p(\boldsymbol{x}) = \frac{1}{Z} e^{-\beta(\mathcal{H}(\boldsymbol{x}) + PV)}$

The accuracy of Hamiltonian matters!

Introduction: the force field of MD

$$\mathcal{H} = \underbrace{\sum_{i=1}^{N} \frac{p_i^2}{2m_i}}_{\text{动能}} + \underbrace{E(q_1, \ldots, q_N)}_{\text{势能 (force field)}}$$

分子动力学模拟精度的关键是势能项的建模和计算

Introduction: other related mathematical problems

Prove that a certain dynamics asymptotically samples a certain ensemble

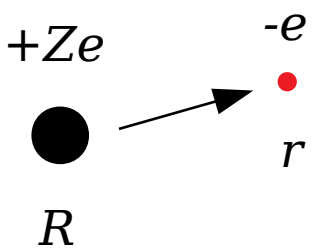
Design a numerical scheme for integrating the dynamics

Analyze the error introduced by the time discretization

Tuckerman, Statistical Mechanics: Theory and Molecular Simulation, 2010

- What is molecular dynamics simulation.
- The modeling of atomic interactions.
- The computation of atomic interactions

Wave function as a description of electron



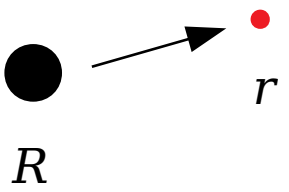
$$\Psi(\{r\};\{R\})$$

$$\rho(\{r\};\{R\}) = |\Psi(\{r\};\{R\})|^2$$

First principle: Schrodinger equation

$$\hat{H}(\{r\};\{R\})\Psi(\{r\};\{R\}) = E(\{R\})\,\Psi(\{r\};\{R\})$$

$$\hat{H} = -\sum_i \frac{\hbar^2}{2m_i}\nabla_i^2 - \sum_{i,I}\frac{Z_I}{|r_i - R_I|} + \sum_{i<j}\frac{1}{|r_i - r_j|}$$



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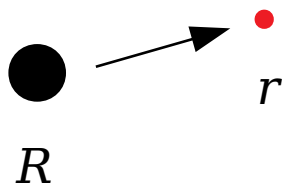

"... The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble. It therefore becomes desirable that approximate practical methods of applying quantum mechanics should be developed ..." [1]

[1] P. A. M. Dirac (1929), Proc. R. Soc. A, 123 (792): 714–733

The density functional theory

$$\hat{H}_{\mathrm{KS}}(r,\rho;\{R\})\psi(r;\{R\}) = E_{\mathrm{KS}}(\{R\})\psi(r;\{R\})$$

$$\hat{H}_{\mathrm{KS}} = -\frac{\hbar^2}{2m}\nabla^2 - \sum_I \frac{Z_I}{|r-R_I|} + \int \frac{\rho(r')}{|r-r'|}dr' + V_{\mathrm{xc}}[\rho](r)$$

$$\rho(r;\{R\}) = \sum_n f_n |\psi_n(r,\{R\})|^2$$

The density functional theory

$$\hat{H}_{\mathrm{KS}}(r,\rho;\{R\})\psi(r;\{R\}) = E_{\mathrm{KS}}(\{R\})\psi(r;\{R\})$$

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$$\rho(r;\{R\}) = \sum_n f_n |\psi_n(r,\{R\})|^2$$

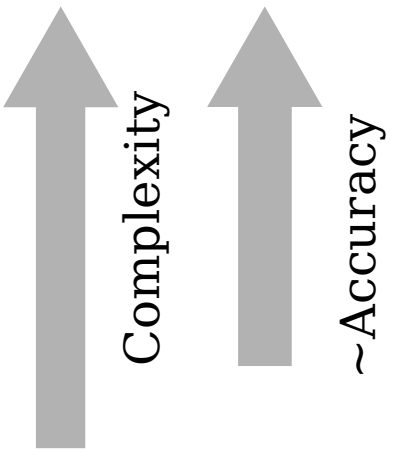
3 维非线性特征值问题：自洽求解。

$$\rho^{\mathrm{in}} \to \hat{H}_{\mathrm{KS}} \to \{\psi_n\} \to \rho^{\mathrm{out}} \to \text{a new } \rho^{\mathrm{in}} \to \dots$$

Other ab initio methods

Examples of “approximate practical methods”

Coupled cluster single double (triple) CCSD(T)	$O(N^7)$
Second order Moller-Plesset (MP2)	$O(N^5)$
Hartree-Fock (HF)	$O(N^4)$
Density functional theory (DFT)	$O(N^3)$



Computationally expensive: DFT ~100 atoms ~100 picoseconds

Empirical force fields

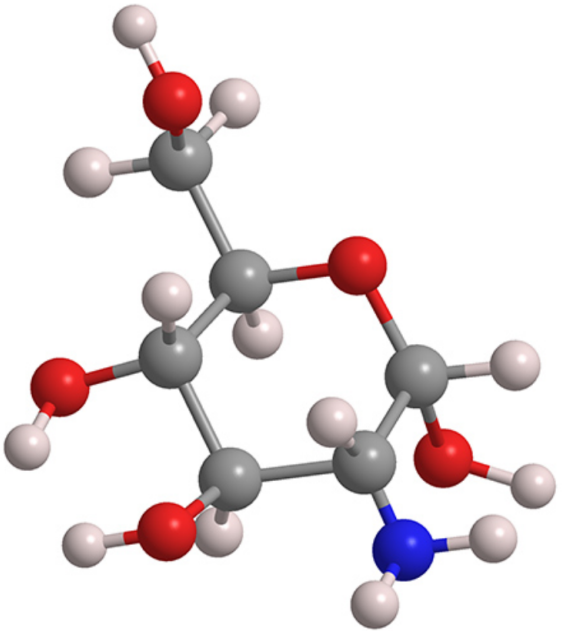
人为猜测势函数的函数形式，拟合其中的参数

$$E(r_1, r_2, \ldots, r_N)$$

难点：输入向量维度： $3N$

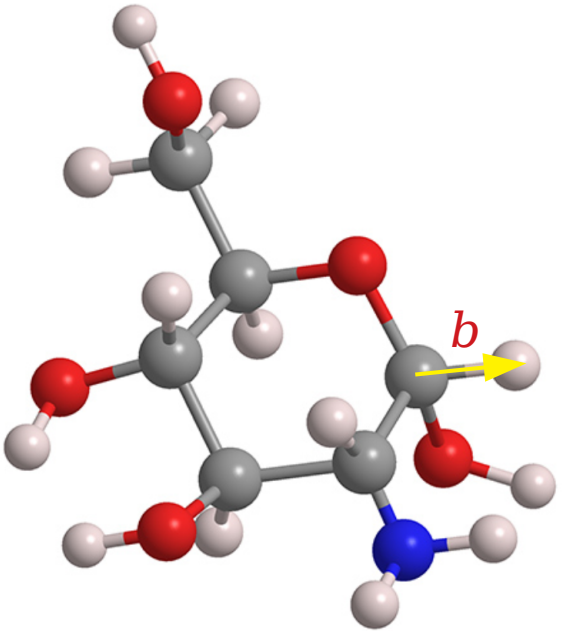
在特定的假设下，简化、分解高维问题为低维问题
例如 Charmm, Amber, Gromos, OPLS-AA 等

Empirical force field: example



$$E = E_{\text{bond}} + E_{\text{angle}} + E_{\text{dihedral}} + E_{\text{vdw}} + E_{\text{coulomb}}$$

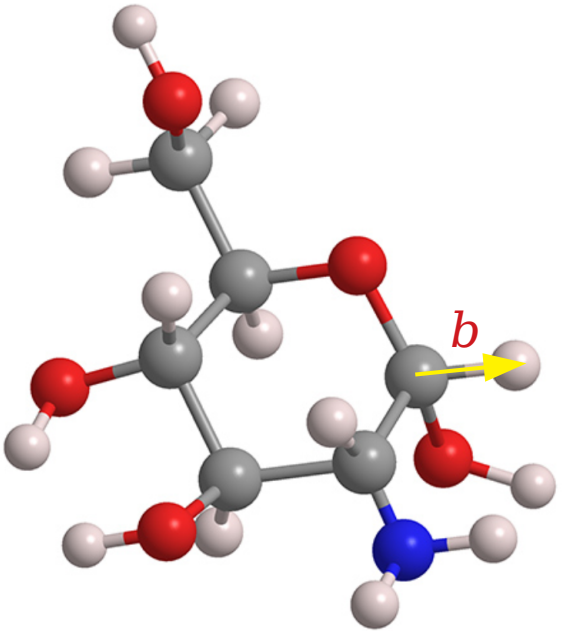
Empirical force field: example



$$E_{\text{bond}} = \sum_i E^i_{\text{bond}}$$

$$E^i_{\text{bond}} = \frac{1}{2} k_b (b^i - b^i_0)^2$$

Empirical force field: example



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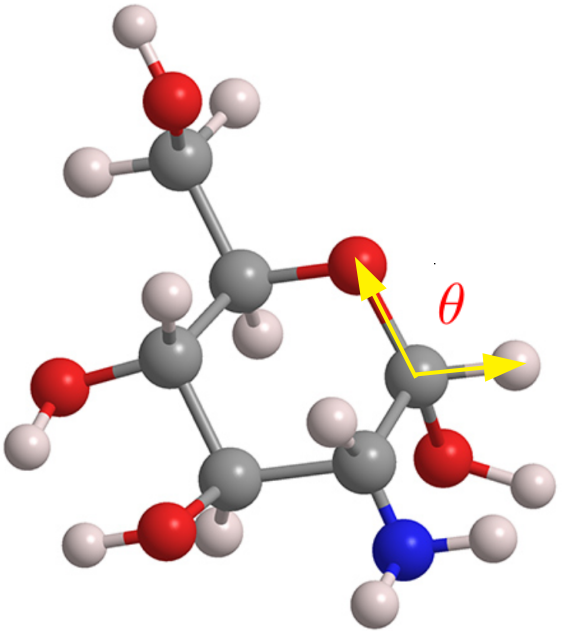
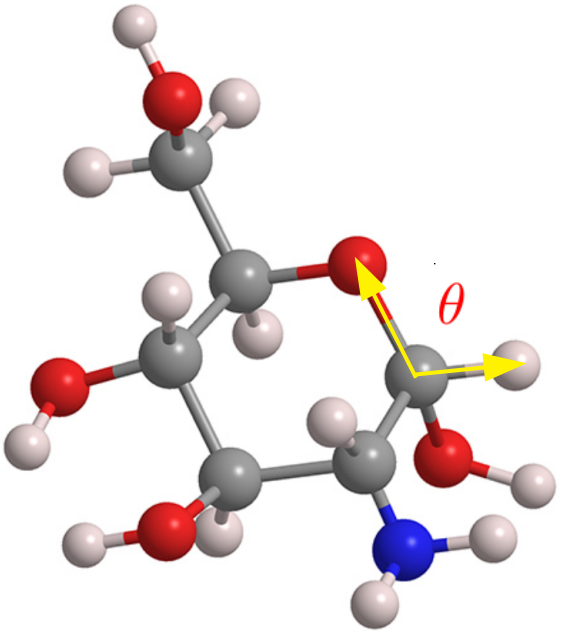


$$E_{\text{angle}} = \sum_i E^i_{\text{angle}}$$

$$E_{\text{angle}} = \frac{1}{2} k_\theta (\theta^i - \theta_0)^2$$

Empirical force field: example



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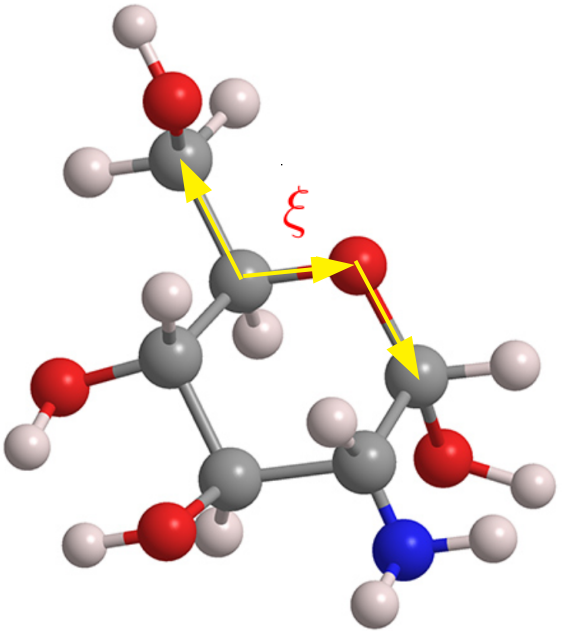
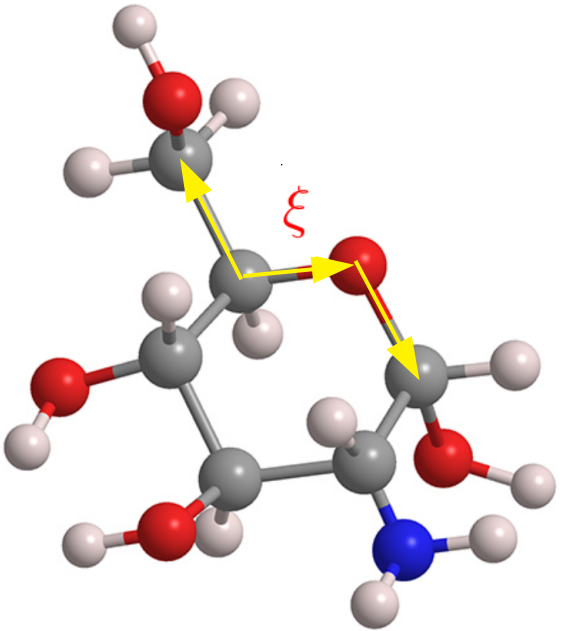


$$E_{\text{dihedral}} = \sum_i E^i_{\text{dihedral}}$$

$$E^i_{\text{dihedral}} = \frac{1}{2} k_\xi (\xi^i - \xi^i_0)^2$$

Empirical force field: example



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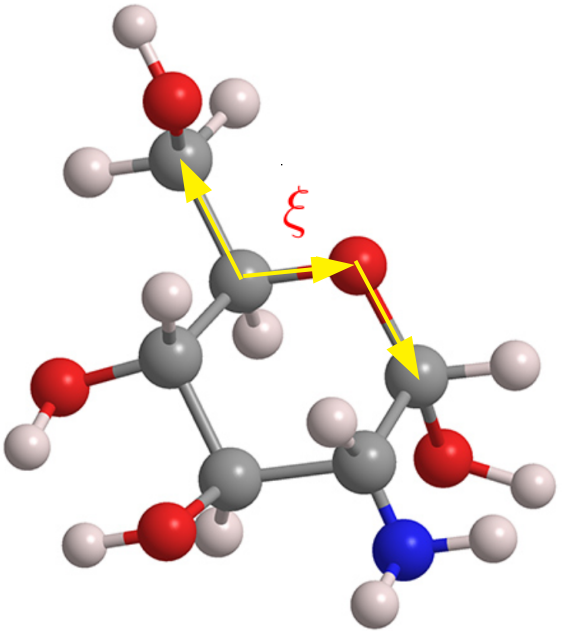
Empirical force field: example



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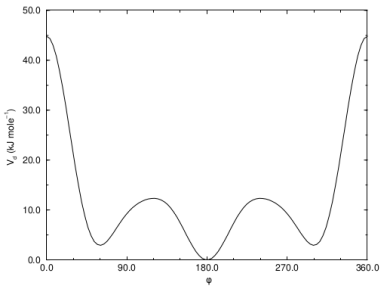
$$E_{\text{dihedral}} = \sum_{n=0}^{5} C_n \big(\cos(\xi - \pi) \big)^n$$



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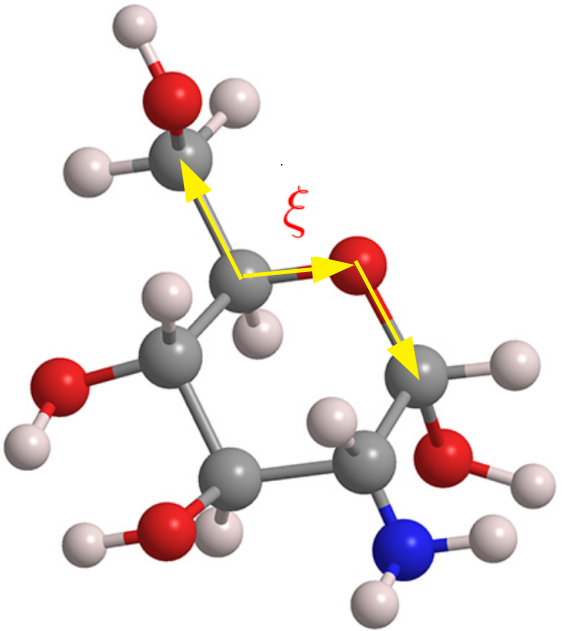

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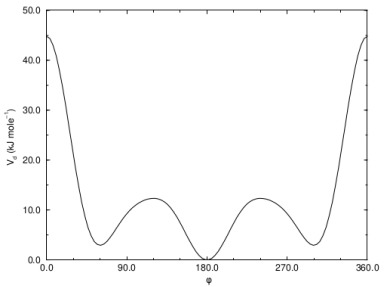
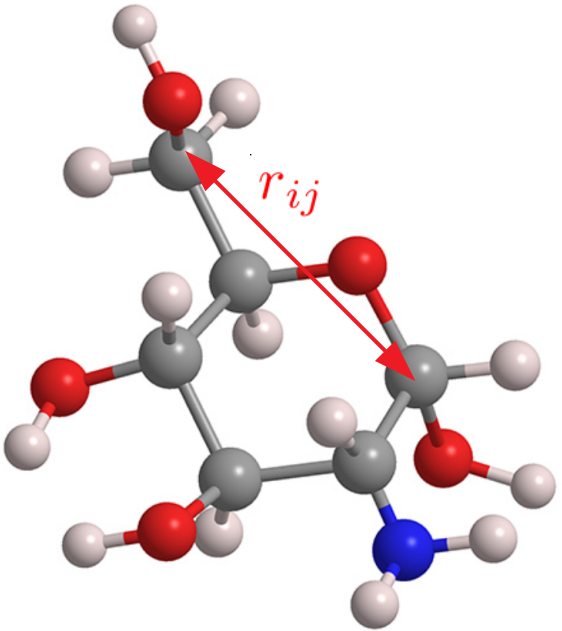


Empirical force field: example

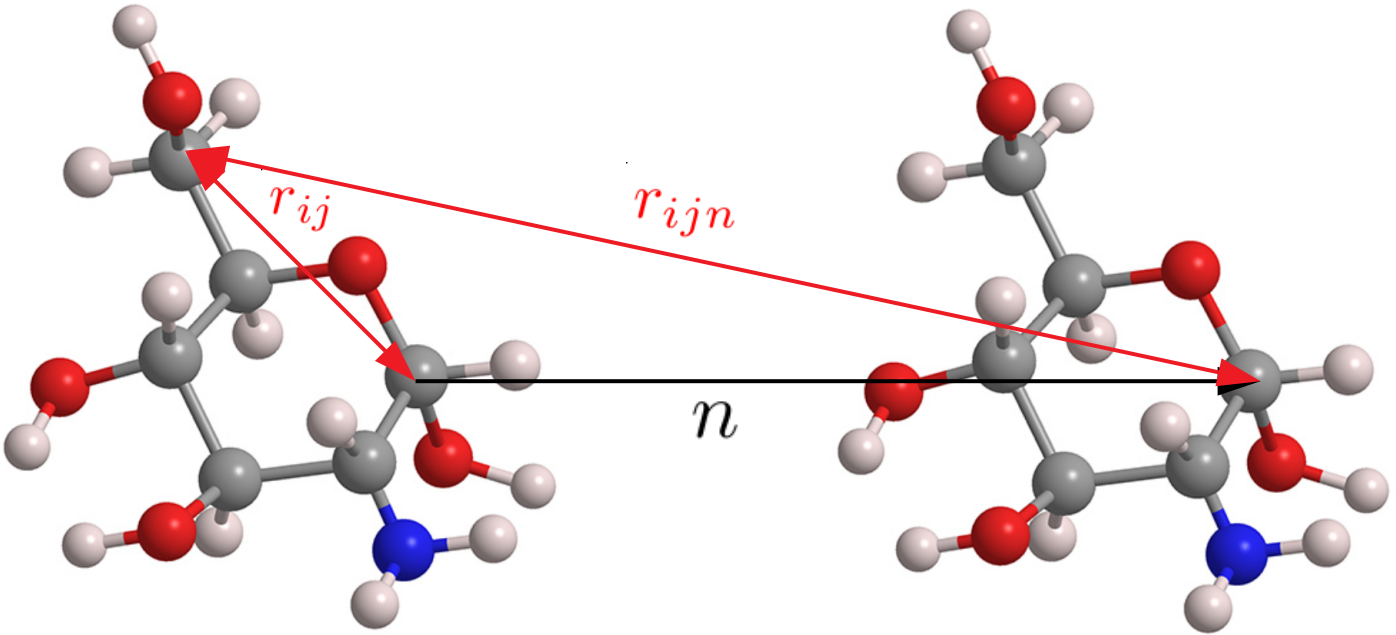


$$E_{\text{vdw}} = \sum_{ij} E_{\text{vdw}}^{ij}$$

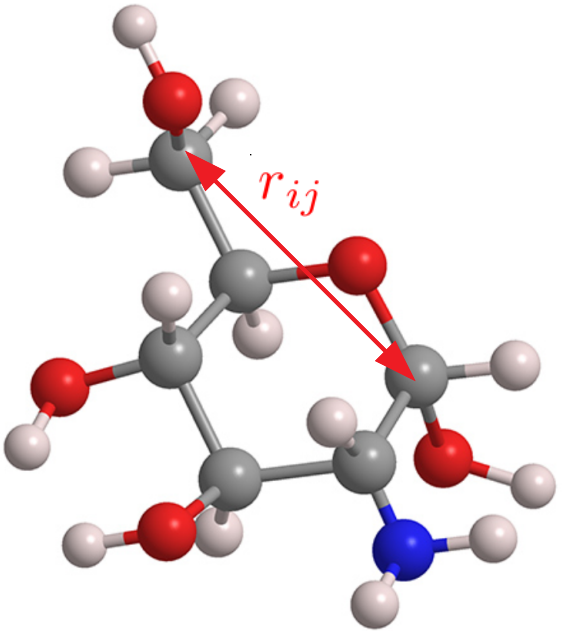
$$E_{\text{vdw}}^{ij} = 4\epsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^{6} \right]$$

$$r_{ij} = |r_i - r_j|$$

Empirical force field: example



Empirical force field: example



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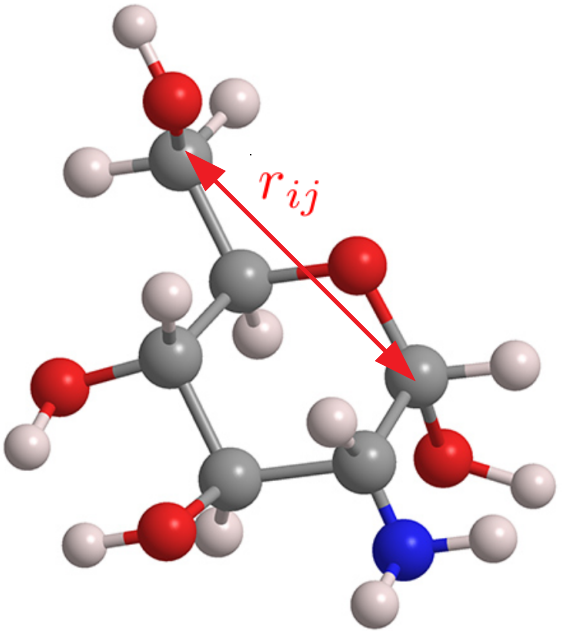
$$r_{ijn} = |r_i - r_j + n|$$

Empirical force field: example



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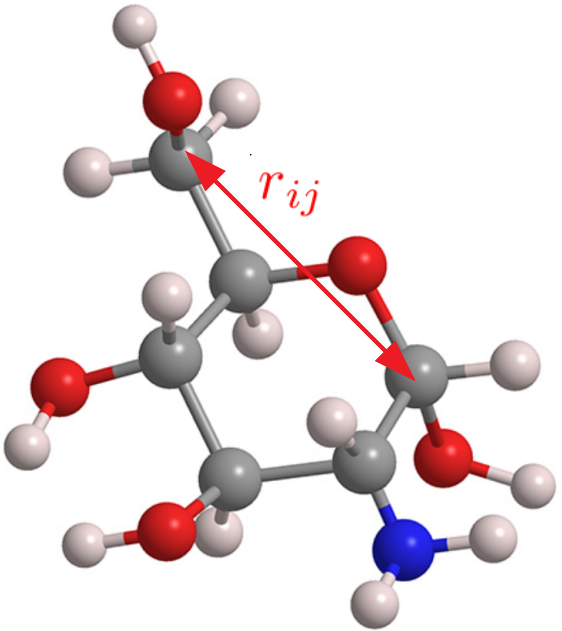

i, j 从 0 求和到 N-1 ， n 是无穷求和

$$E_{\mathrm{vdw}} = \sum_{ijn} E_{\mathrm{vdw}}^{ijn}$$

$$E_{\mathrm{vdw}}^{ijn} = 4\epsilon \left[\left(\frac{\sigma}{r_{ijn}} \right)^{12} - \left(\frac{\sigma}{r_{ijn}} \right)^{6} \right]$$

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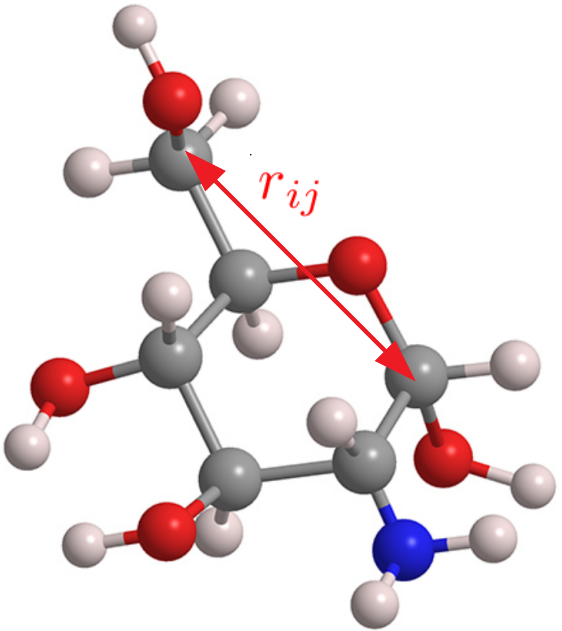
Empirical force field: example



$$E_{\text{coul}} = \sum_{ijn} E_{\text{coul}}^{ijn}$$

$$E_{\text{coul}}^{ijn} = \frac{1}{4\pi\epsilon_0} \frac{q_i q_j}{r_{ijn}}$$

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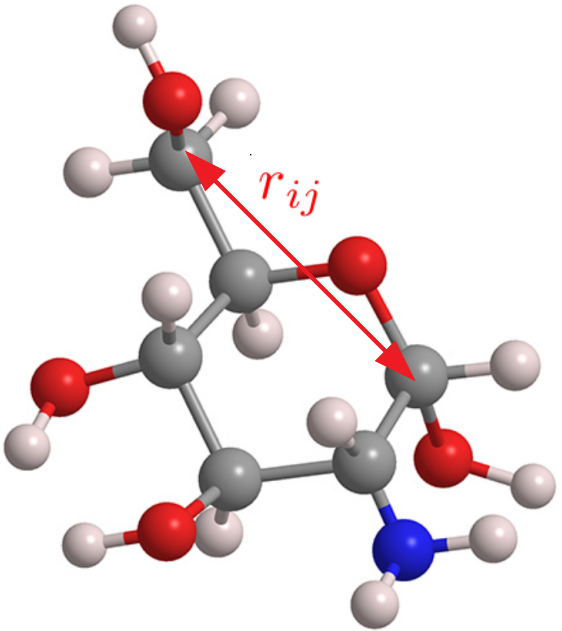
Empirical force field: example



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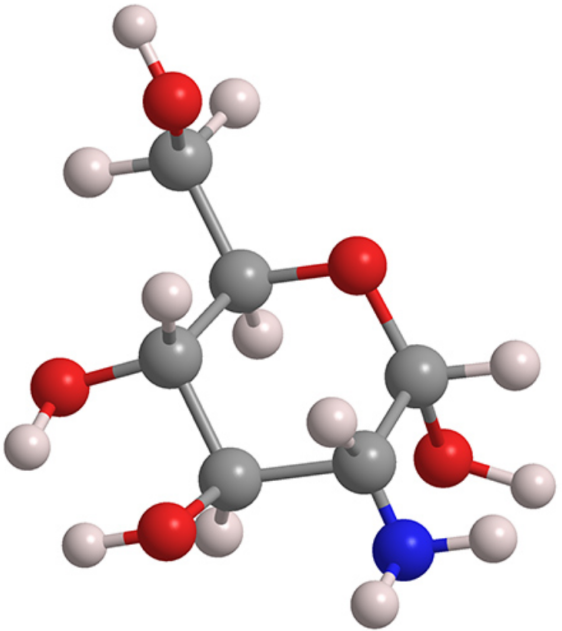
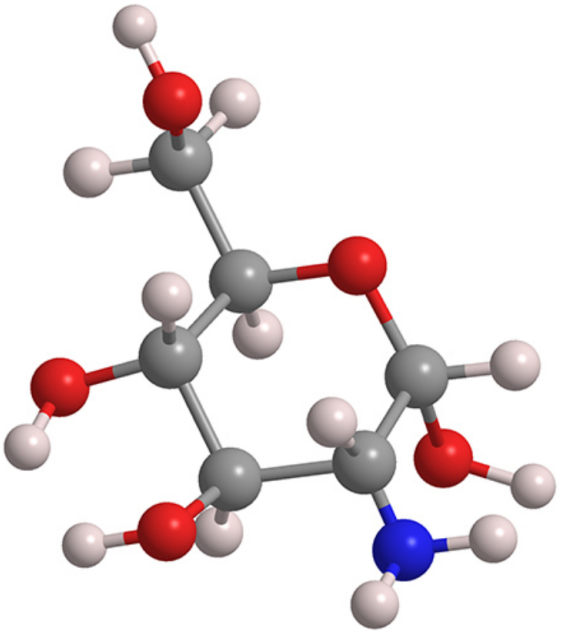


$$E = E_{\text{bond}} + E_{\text{angle}} + E_{\text{dihedral}} + E_{\text{vdw}} + E_{\text{coulomb}}$$

Tunable parameters

$$k_b, b_0,\ k_\theta, \theta_0,\ k_\xi, \xi_0,\ C_n,\ \epsilon,\ \sigma,\ q_i$$

Empirical force field: example



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Tunable parameters

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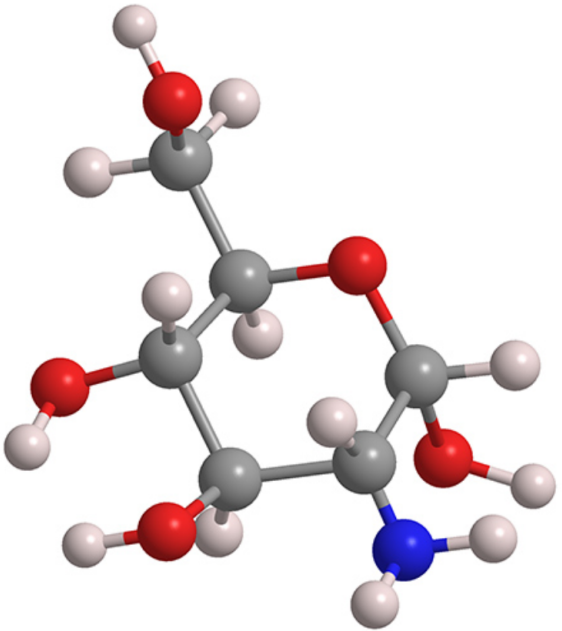
For each bond type

Empirical force field: example



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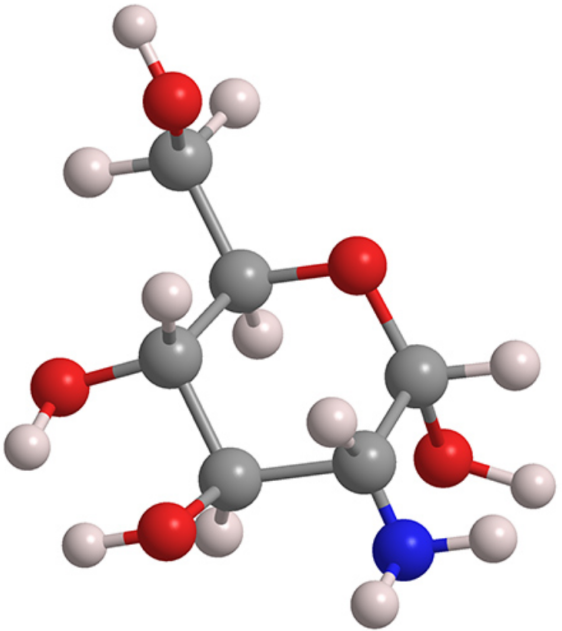
Tunable parameters

$$k_b, b_0,\ k_\theta, \theta_0,\ k_\xi, \xi_0,\ C_n,\ \underline{\epsilon,\ \sigma,}\ q_i$$

For each
non-bonded pair

Empirical force field: example



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Tunable parameters

$$k_b, b_0,\ k_\theta, \theta_0,\ k_\xi, \xi_0,\ C_n,\ \epsilon,\ \sigma,\ \underline{q_i}$$

For each atom

Investigating the accuracy

So we have models. How about their accuracy?

Investigating the accuracy

$$\dot{q}_i = \frac{\partial \mathcal{H}}{\partial p_i}$$
$$\dot{p}_i = -\frac{\partial \mathcal{H}}{\partial q_i} - \gamma p_i + \sqrt{m_i}\sigma \dot{W}$$

$$\rho(x) = \frac{1}{Z} e^{-\beta \mathcal{H}(x)}$$
$$Z = \int e^{-\beta \mathcal{H}(x)} dx \quad \beta = \frac{1}{kT}$$

Investigating the accuracy

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It is non-trivial to observe $\rho(x)$ in experiments

High dim of x

Investigating the accuracy

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Compute and compare with experimental observables

$$A = \langle A \rangle = \int A(x)\rho(x)dx \approx \frac{1}{T}\int_0^T A(x(t))dt$$

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Assume that we have long enough trajectories...

Investigating the accuracy

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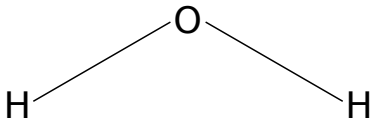
Compute and compare with experimental observables

$$A = \langle A \rangle = \int A(x)\rho(x)dx \approx \frac{1}{T}\int_0^T A(x(t))dt$$

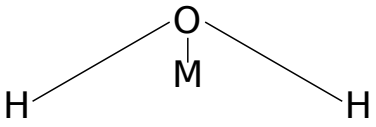
Density, pressure, radial distribution function, diffusion, viscosity...

Example: water models



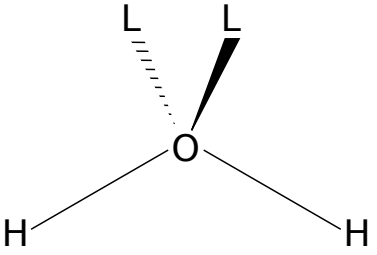
3-site

TIP3P, SPC, SPC/E



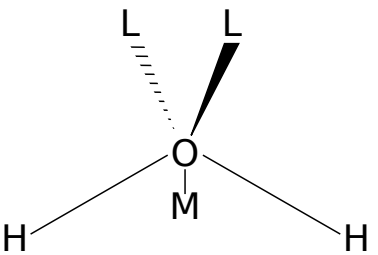
4-site

TIP4P, TIP4P/2005

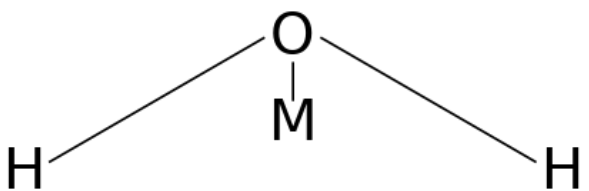


5-site

ST2, TIP5P



6-site



Partial charge: q_H=0.52 q_M=-1.04

vdw site: O

Example: accuracy of water models

Property	Expt	TIP3P	SPC/E	TIP4P	TIP4P/2005	TIP5P
Enthalpy of phase change/kcal mol^{-1}						
ΔH_{melt}	1.44	0.3	0.74	1.05	1.16	1.75
ΔH_{vap}	10.52	10.05	11.79	10.65	11.99	10.46
Critical point properties						
T_c/K	647.1	578	638.6	588	640	521
ρ_c/g cm^{-3}	0.322	0.272	0.273	0.315	0.31	0.337
p_c/bar	220.64	126	139	149	146	86
Surface tension/mN m^{-1}						
σ_{300K}	71.73	52.3	63.6	59	69.3	52.6
σ_{450K}	42.88	24.7	36.7	27.5	41.8	17.1
Melting properties						
T_m/K	273.15	146	215	232	252	274
ρ_{liq}/g cm^{-3}	0.999	1.017	1.011	1.002	0.993	0.987
ρ_{solid}/g cm^{-3}	0.917	0.947	0.95	0.94	0.921	0.967
dp/dT (bar K^{-1})	−137	−66	−126	−160	−135	−708
Orthobaric densities and TMD						
TMD/K	277	182	241	253	278	277
ρ_{298K}/g cm^{-3}	0.997	0.98	0.994	0.988	0.993	0.979
ρ_{400K}/g cm^{-3}	0.9375	0.868	0.916	0.895	0.93	0.859
ρ_{450K}/g cm^{-3}	0.8903	0.791	0.86	0.823	0.879	0.756
Isothermal compressibility (10^{-6}/bar)						
κ_T [1 bar; 298 K]	45.3	57.4	46.1	59	46	41
κ_T [1 bar; 360 K]	47	79.2	57.7	67.2	50.9	84

Vega and Abascal, PCCP, 13, (2011)

- What is molecular dynamics simulation.
- The modeling of atomic interactions.
- The computation of atomic interactions

The computation of force fields

Now we have force fields. How are they evaluated on computers?

The computation of force fields

Interaction	Complexity	Fast Algorithm
Bond	O(N)	no
Angle	O(N)	no
Dihedral	O(N)	no
van der Waals	infinity(?)	yes
Coulomb	infinity(?)	yes

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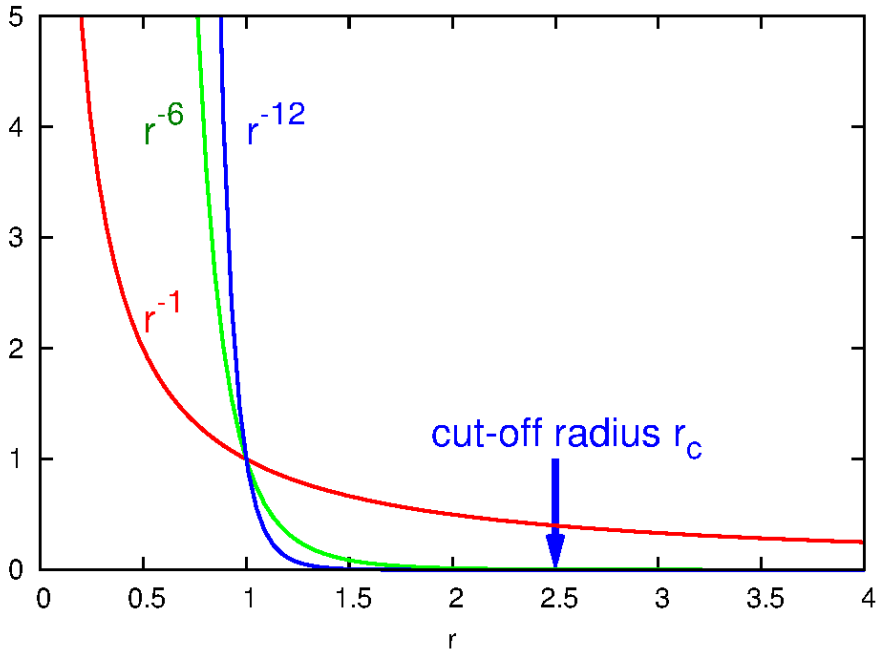
Short- and Long- range interactions

$$E_{\mathrm{vdw}}^{ijn} = 4\epsilon\left[\left(\frac{\sigma}{r_{ijn}}\right)^{12} - \left(\frac{\sigma}{r_{ijn}}\right)^{6}\right]$$

Short-range interaction, could be cutoff

$$E_{\mathrm{coul}}^{ijn} = \frac{1}{4\pi\epsilon_0}\frac{q_i q_j}{r_{ijn}}$$

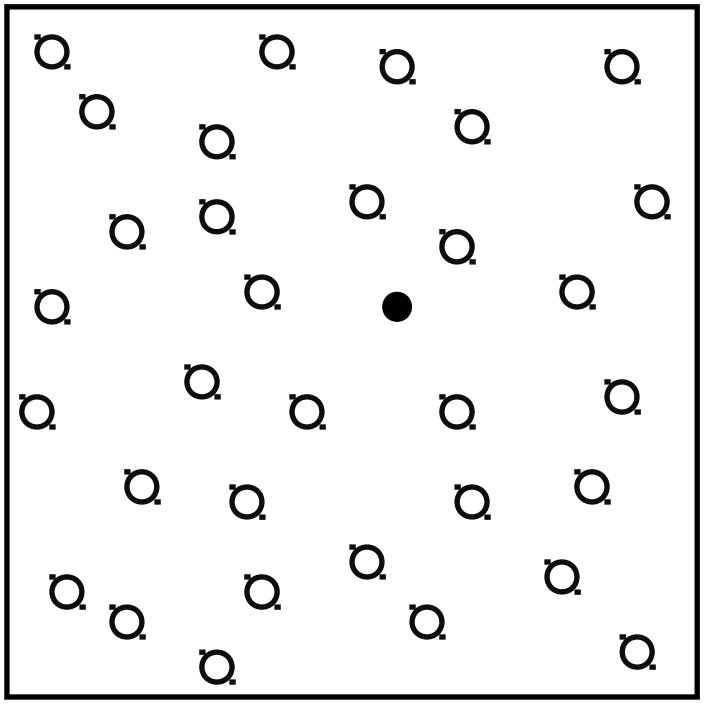
Long-range interaction, could not be cutoff



Short- and Long- range interactions

	Decay speed		Fast algorithms
Short-range interaction	$\frac{1}{r^\alpha}$	$\alpha > 3$	Cut-off method, Ewald for surface systems
Long-range interaction	$\frac{1}{r^\alpha}$	$\alpha \leq 3$	Ewald and its accelerated ver.

Cut-off method for short range interactions



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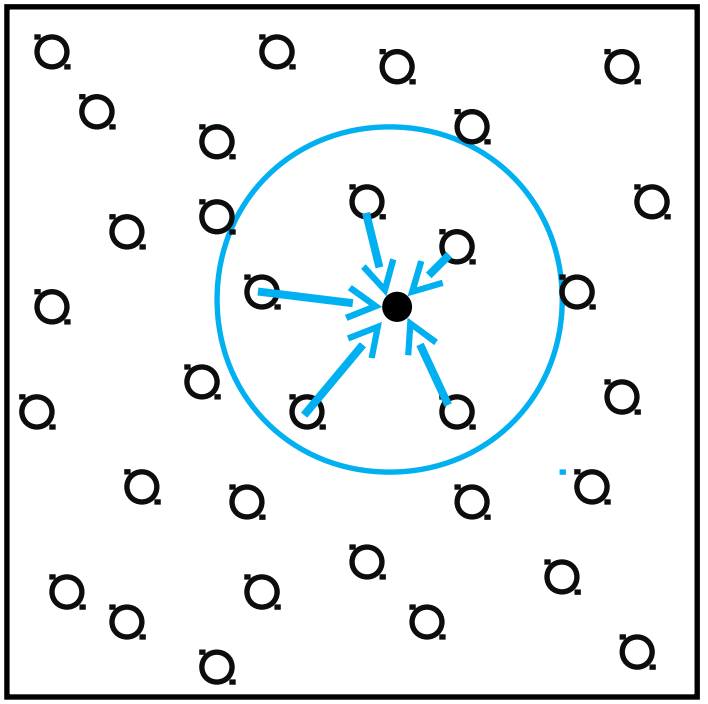
Cut-off method for short range interactions

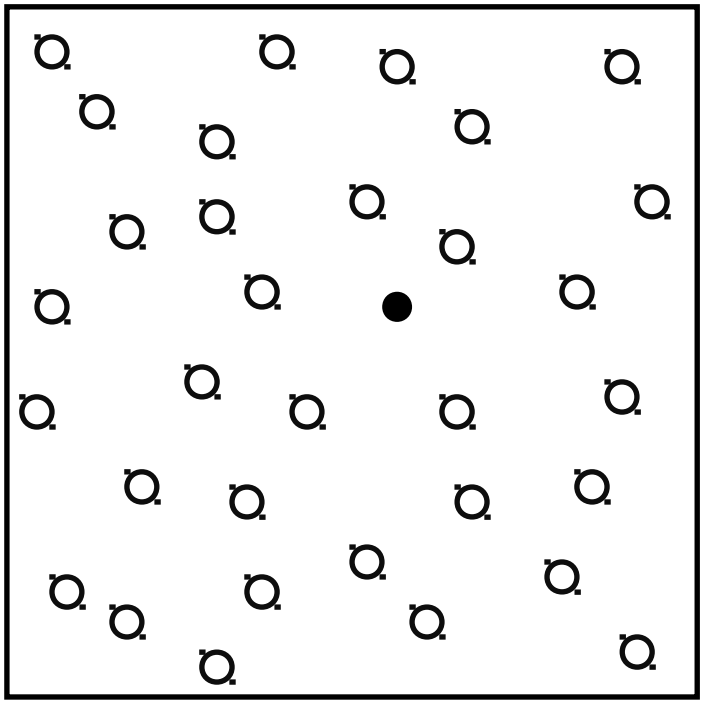


$$E_{\text{vdw}} = \sum_i E^i_{\text{vdw}} = \sum_i \sum_{j,n} E^{ijn}_{\text{vdw}}$$

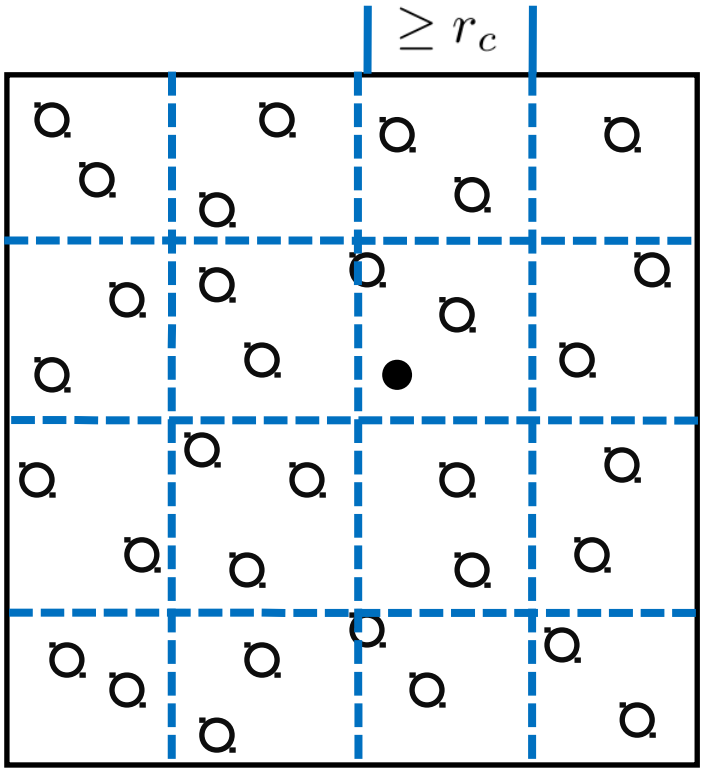
Computational cost:

Brute force neighbor search: $O(N^2)$

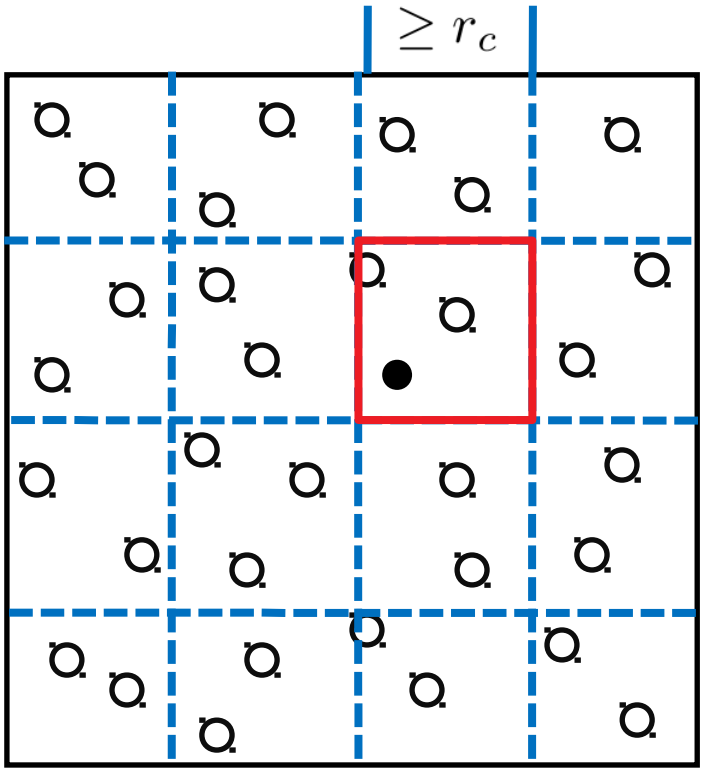
Cell division for short range interactions



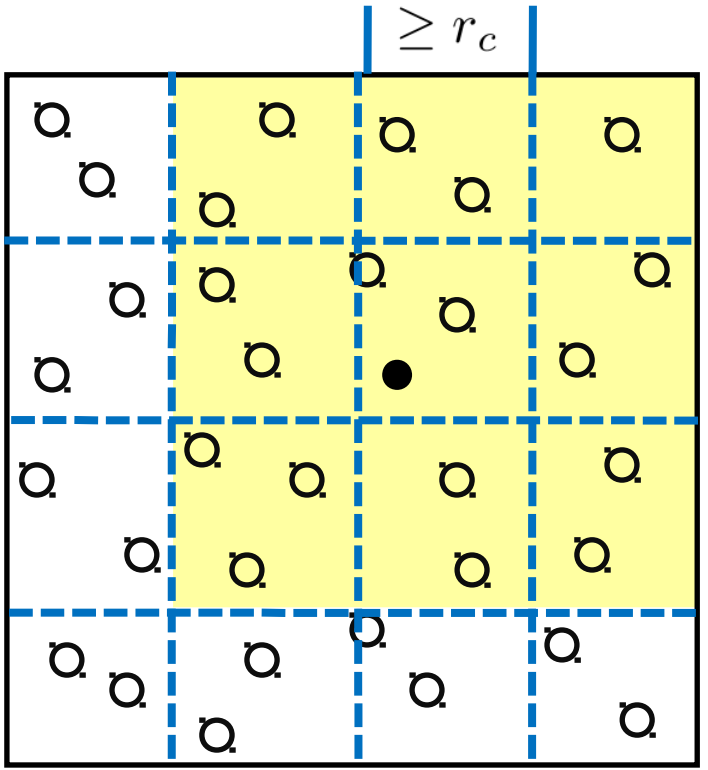
Cell division for short range interactions



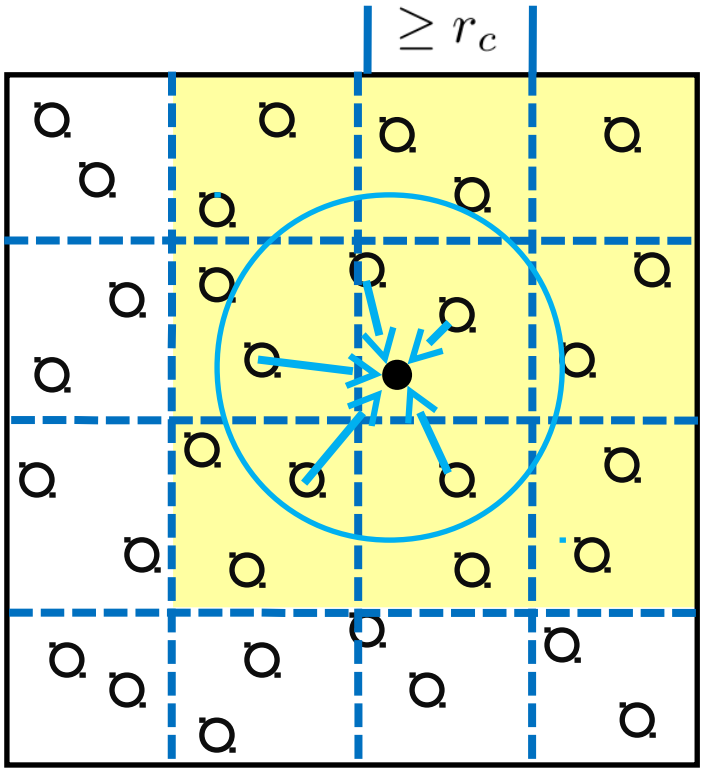
Cell division for short range interactions



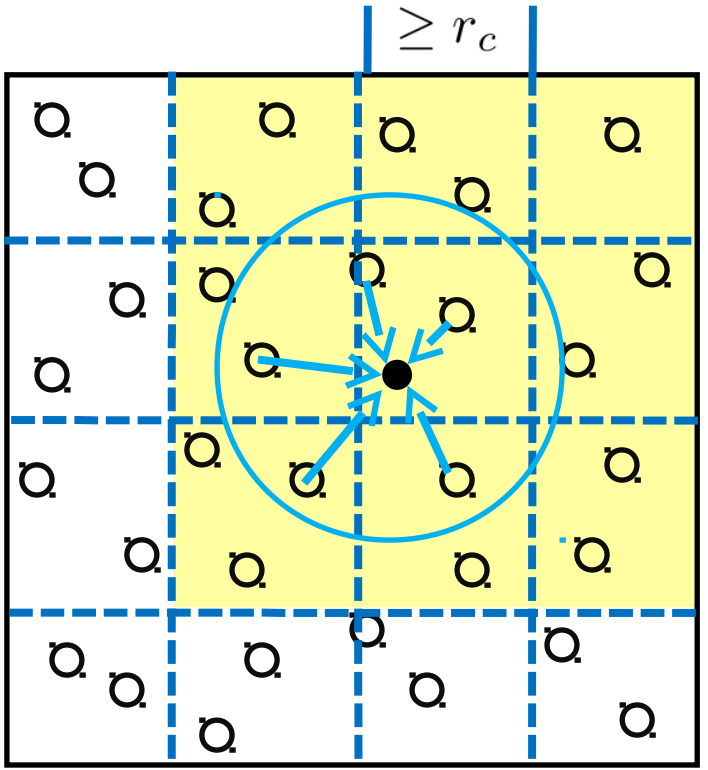
Cell division for short range interactions



Cell division for short range interactions



Cell division for short range interactions



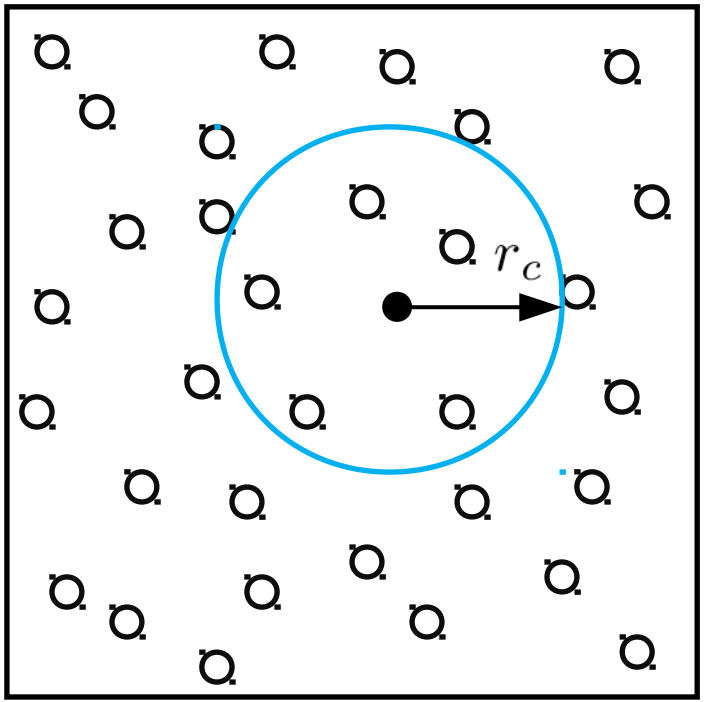
Computational cost:

Brute force neighbor search: $O(N^2)$

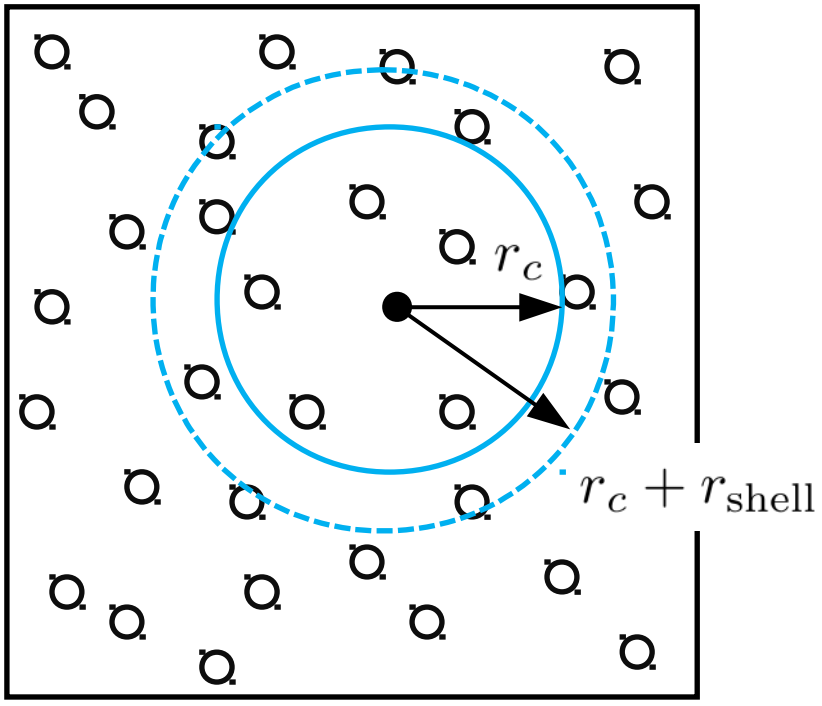
Cell division neighbor search: $O(N)$

Real neighbor / searched ~ 4 / 27

Verlet list for short range interactions



Verlet list for short range interactions



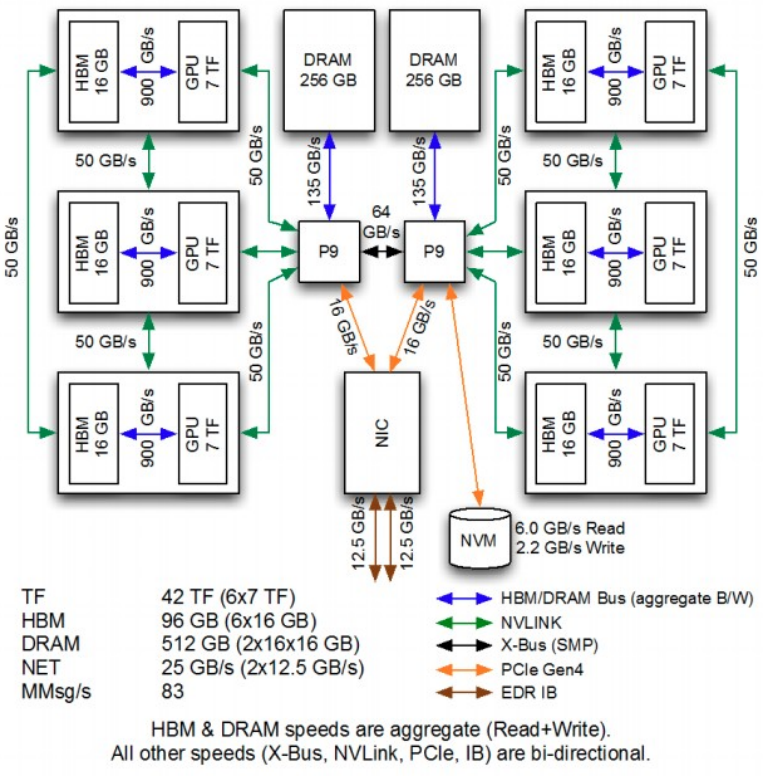
Neighbor list:
A list stores the indices of neighbor atoms

Neighbor list with cut-off $r_c + r_{\text{shell}}$

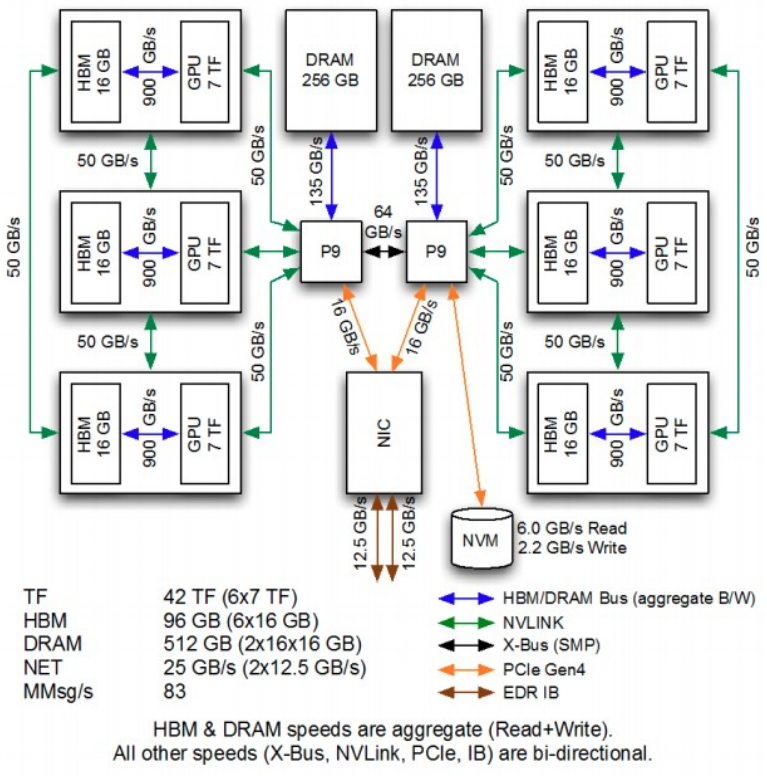
Neighbor list update only when the maximal displacement of atoms is larger than $0.5\, r_{\text{shell}}$

Parallelization of short-range interaction

Parallelization of short-range interaction

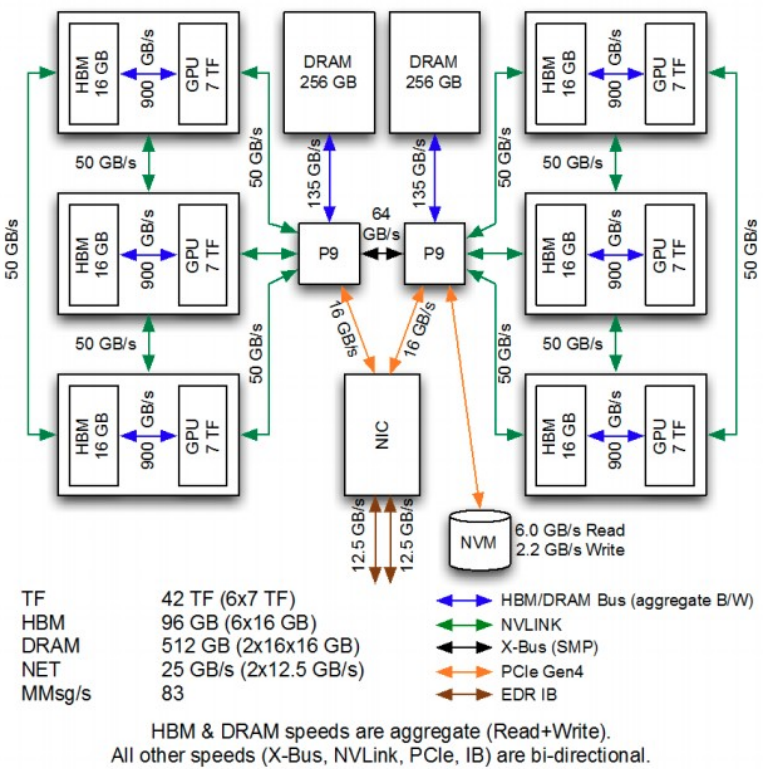


Parallelization of short-range interaction



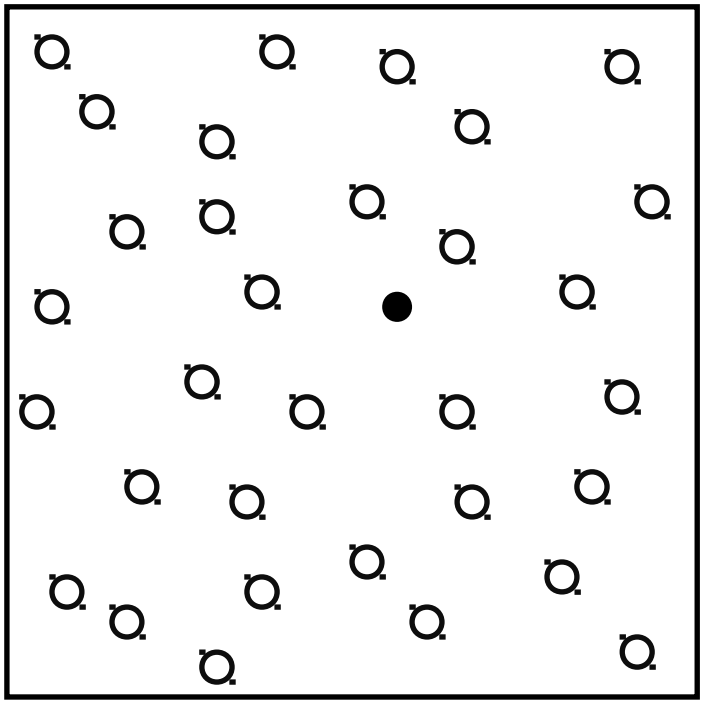
X 4560

Parallelization of short-range interaction

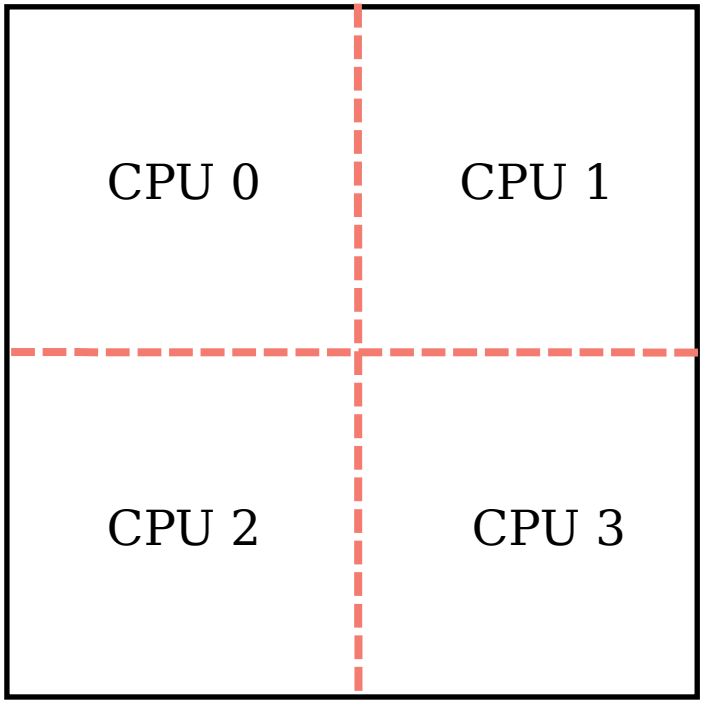


X 4560 =

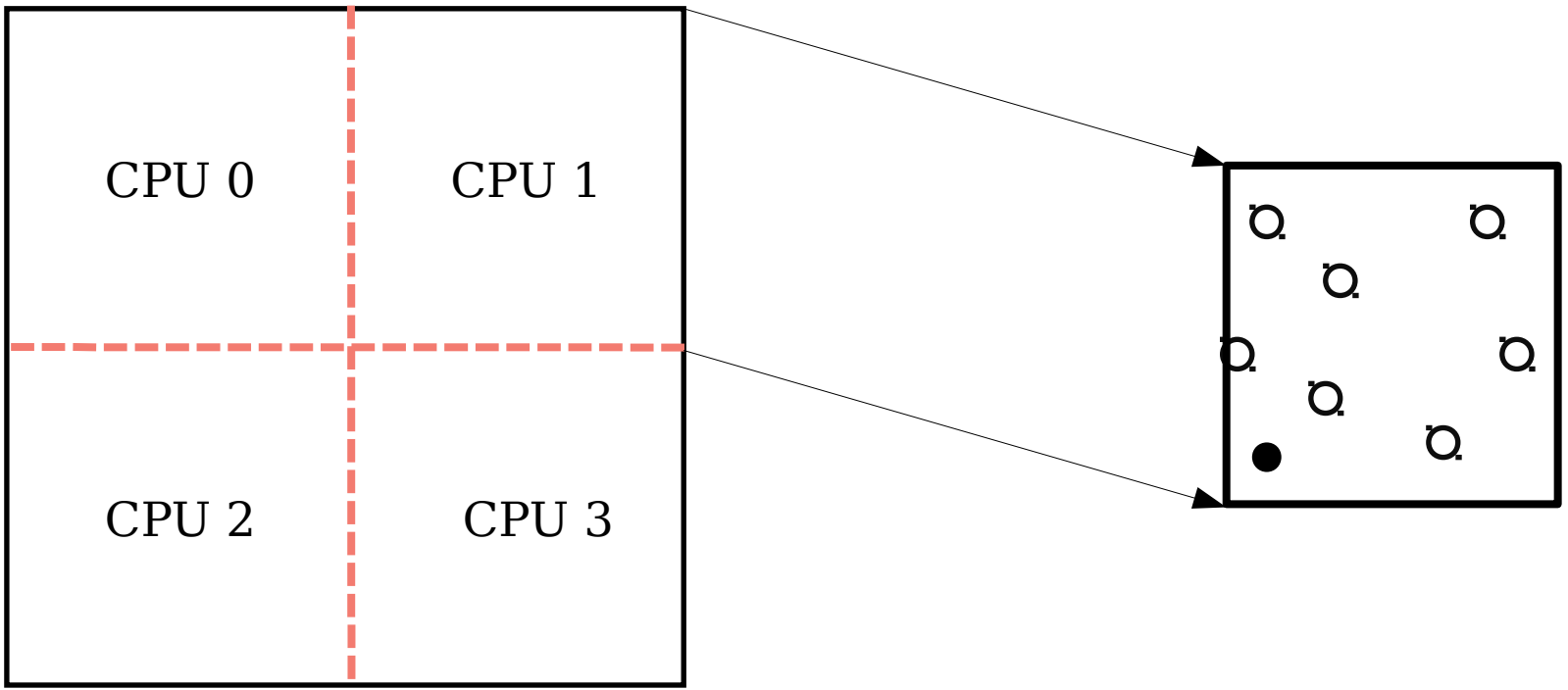
Parallelization of short-range interaction



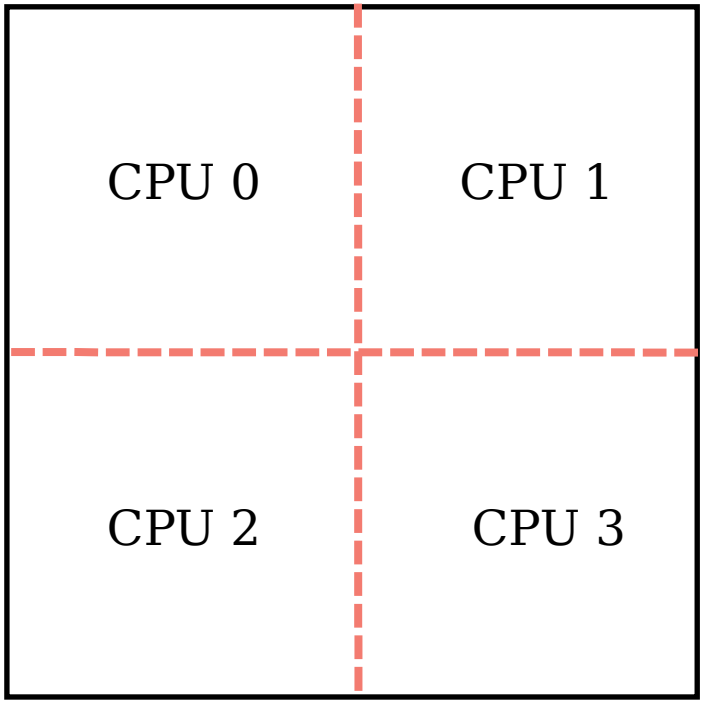
Parallelization of short-range interaction

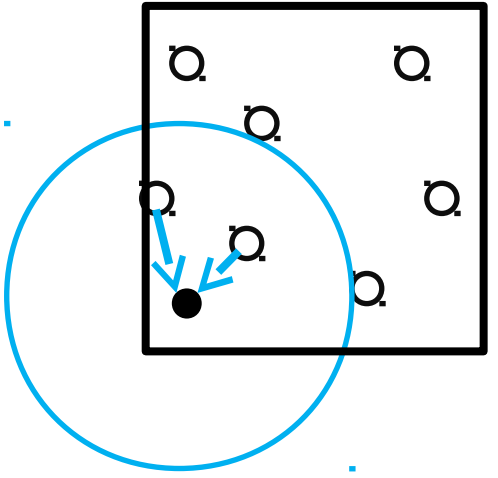


Parallelization of short-range interaction



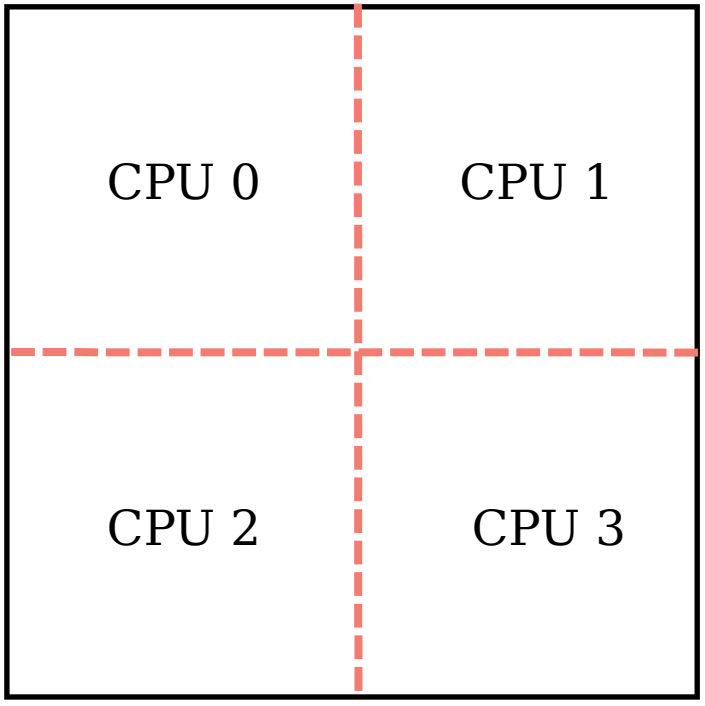
Parallelization of short-range interaction

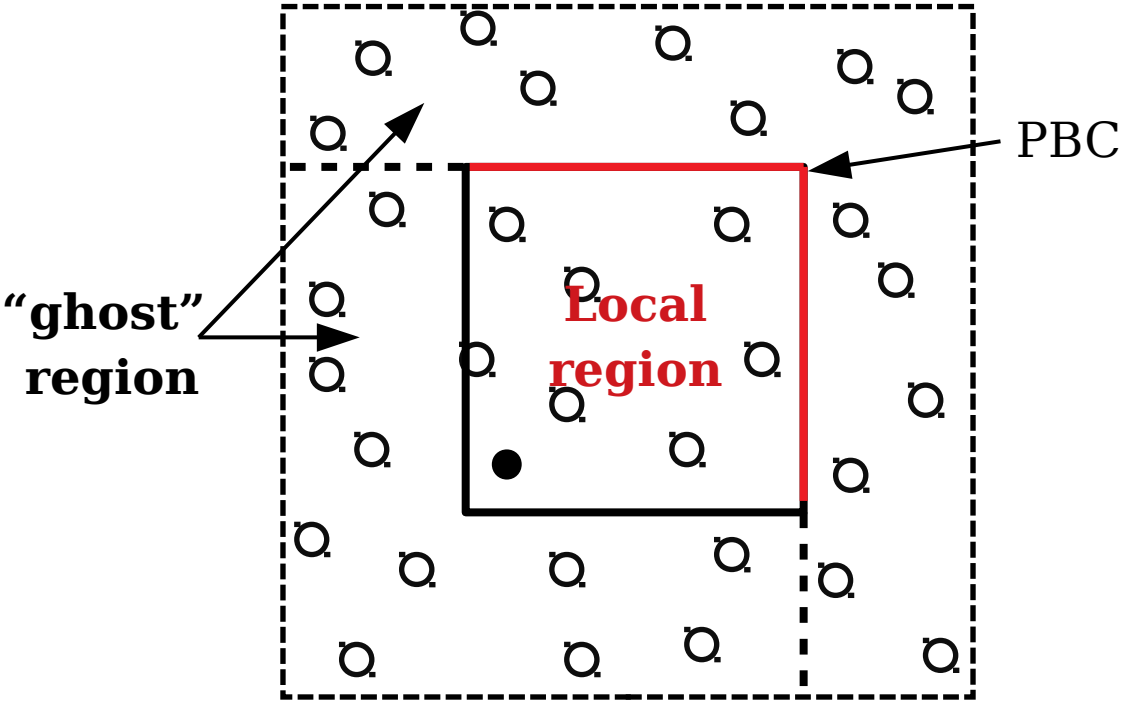




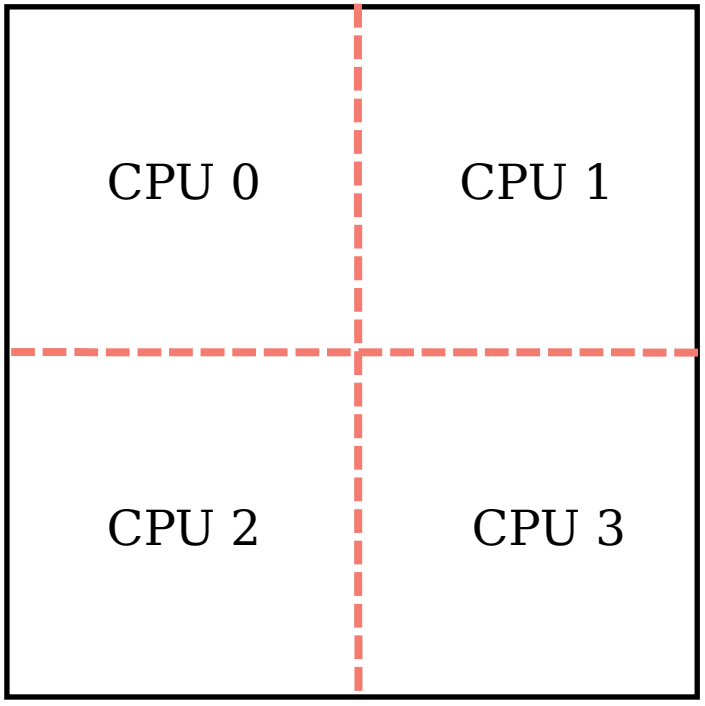
Some neighbors are missing!
They are held by other CPUs

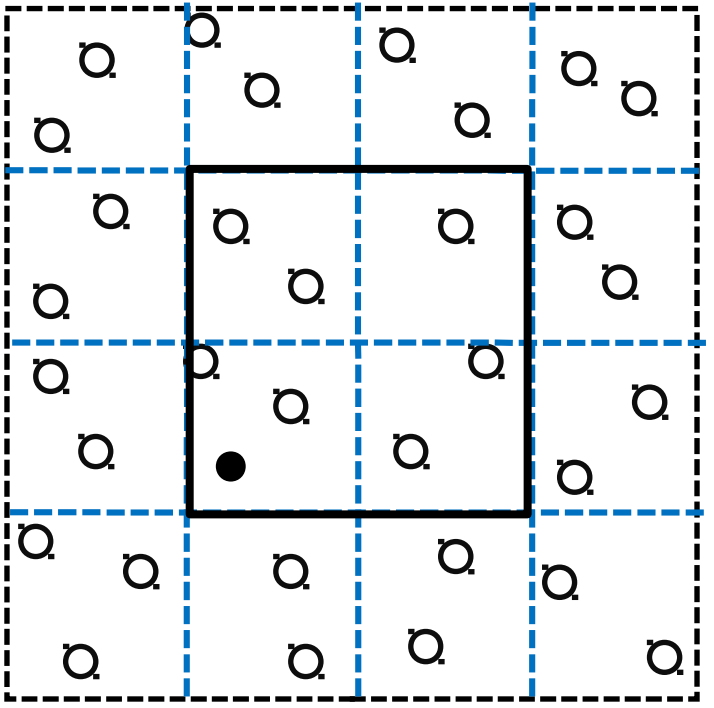
Parallelization of short-range interaction



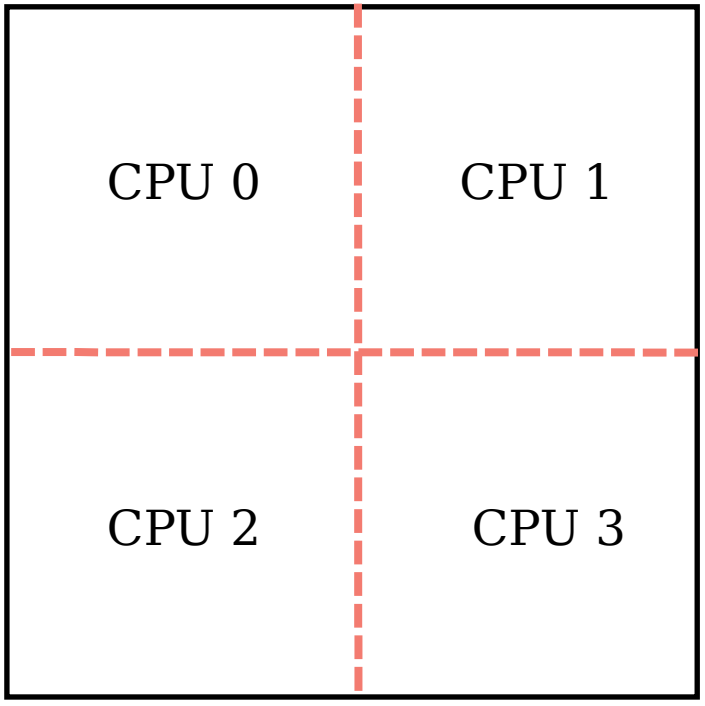


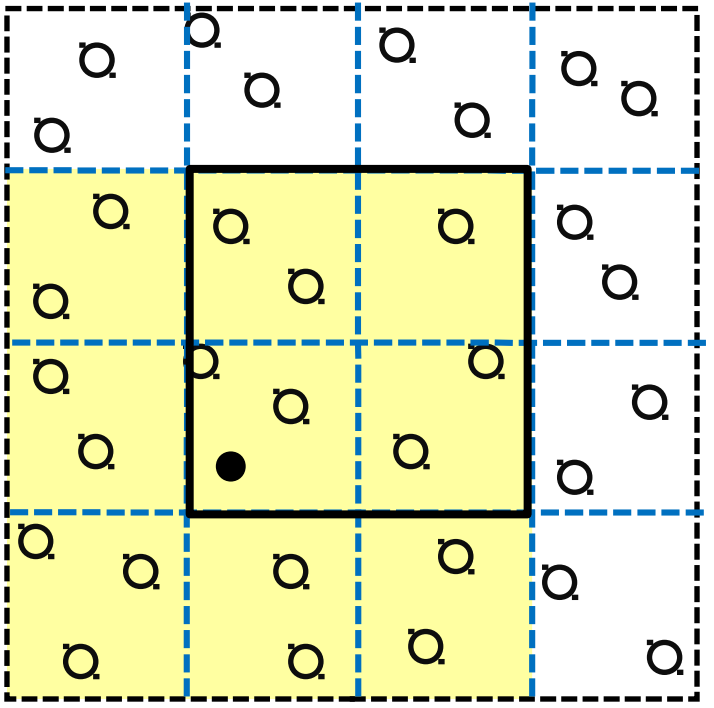
Parallelization of short-range interaction



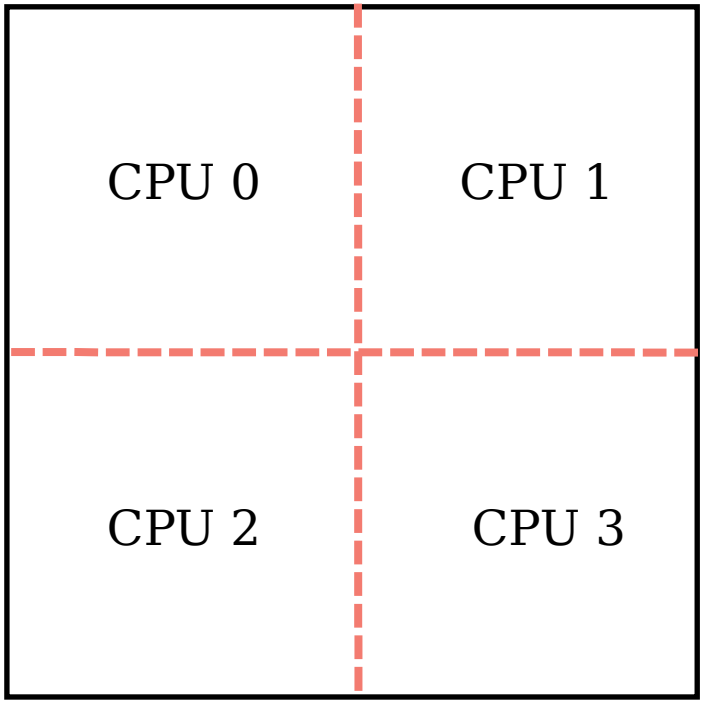


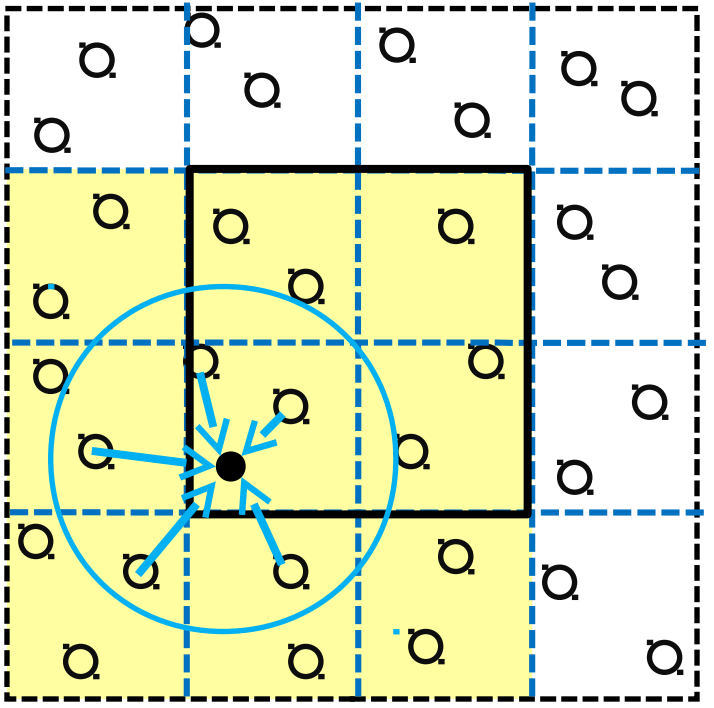
Parallelization of short-range interaction



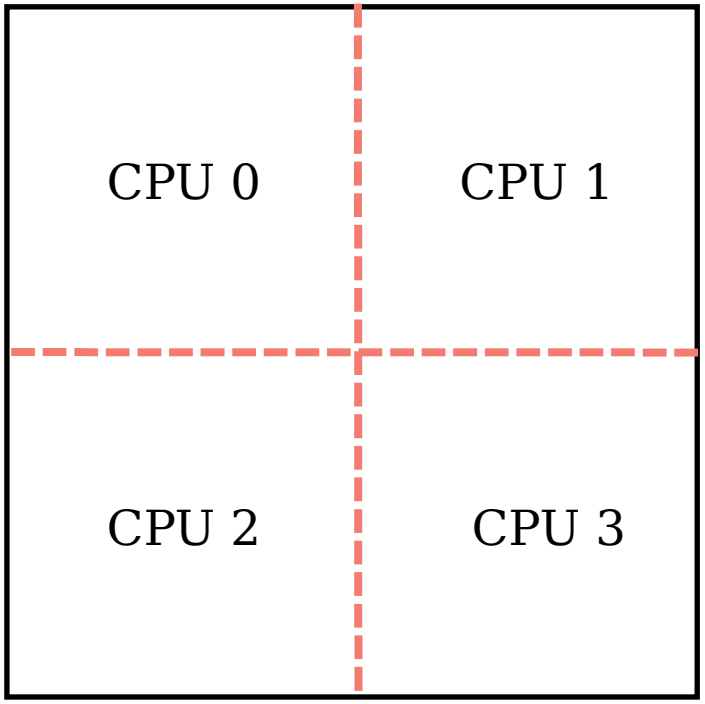


Parallelization of short-range interaction





Parallelization of short-range interaction



Communication pattern:

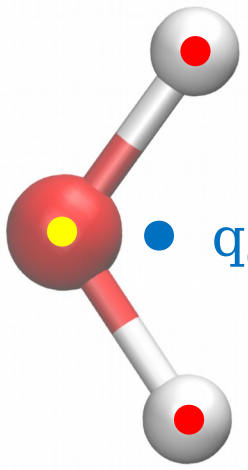
Neighboring processors need communicate

Data transferred / Number of nodes
= constant

Easily scalable on modern supercomputers

Long-range interaction

TIP4P model



$q_H = 0.52$ e

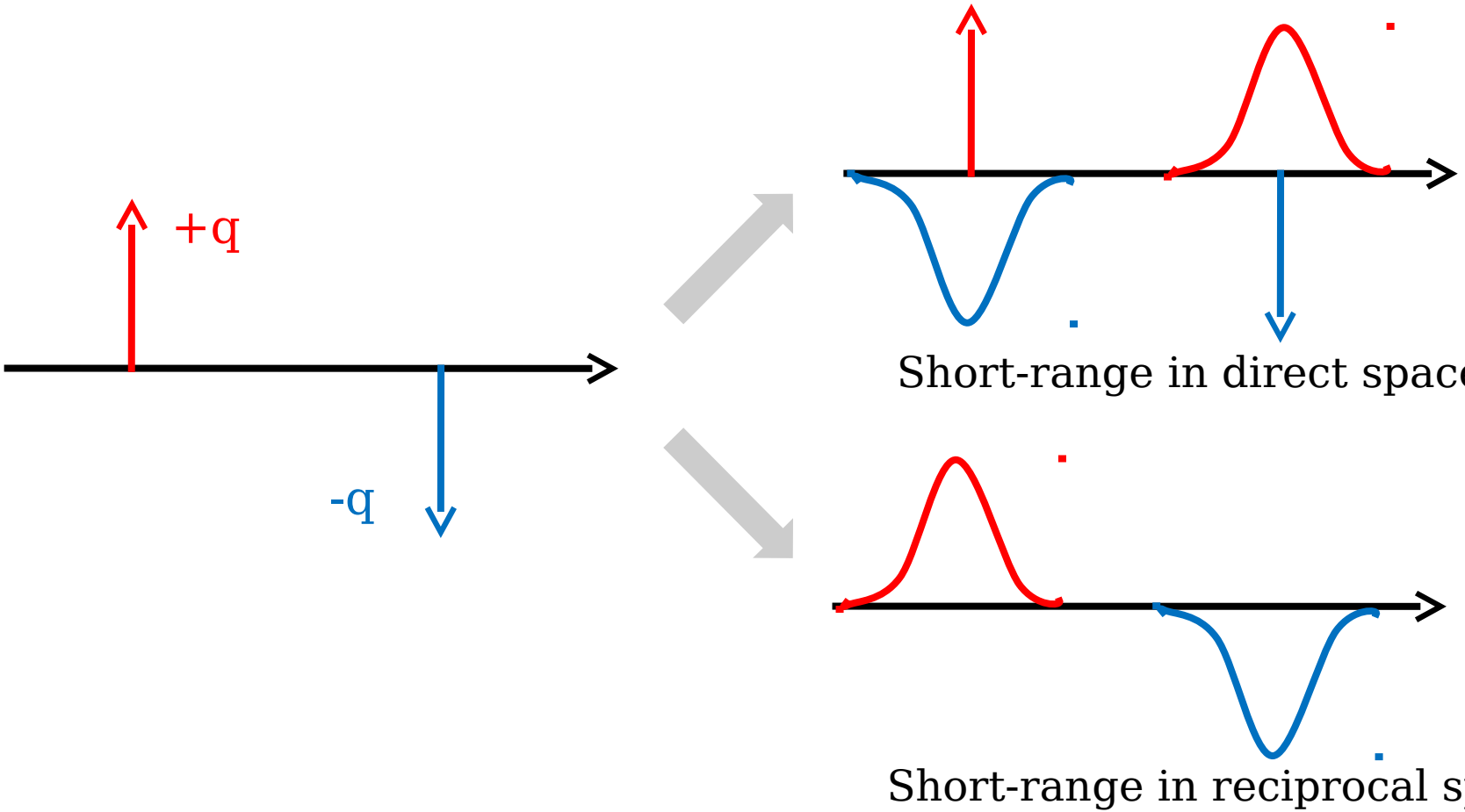
$q_O = -1.04$ e

$$E_{\text{coul}} = \sum_{ijn} E_{\text{coul}}^{ijn}$$

$$E_{\text{coul}}^{ijn} = \frac{1}{4\pi\epsilon_0} \frac{q_i q_j}{r_{ijn}}$$

$$r_{ijn} = |r_i - r_j + n|$$

Long-range interaction: Ewald summation



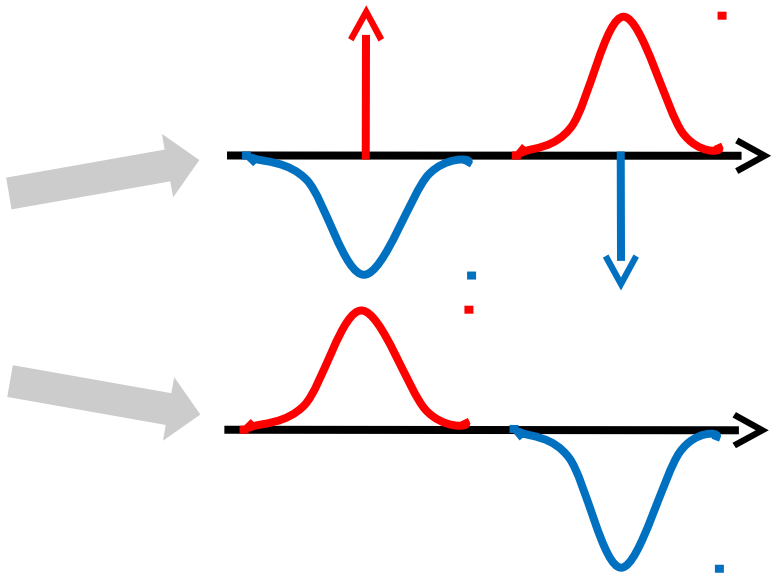
Long-range interaction: Ewald summation

$$U_{\mathrm{ele}} = U_{\mathrm{dir}} + U_{\mathrm{rec}} + U_{\mathrm{corr}}$$

$$U_{\mathrm{dir}} = \frac{1}{2} \sum_{\mathbf{n}}^{*} \sum_{i,j=1}^{N} \frac{q_i q_j \,\mathrm{erfc}(\beta|\mathbf{r}_{ij} + \mathbf{n}|)}{|\mathbf{r}_{ij} + \mathbf{n}|}$$

$$U_{\mathrm{rec}} = \frac{1}{2\pi V} \sum_{\mathbf{m} \neq 0} \frac{\exp(-\pi^2 \mathbf{m}^2 / \beta^2)}{\mathbf{m}^2} S(\mathbf{m}) S(-\mathbf{m})$$

$$U_{\mathrm{corr}} = -\frac{\beta}{\sqrt{\pi}} \sum_{i=1}^{N} q_i^2$$



Fast algorithm of Ewald: Particle mesh Ewald Darden et.al. JCP (1993)

The computational cost of models

Interaction	Complexity	Fast Algorithm
Bond	O(N)	no
Angle	O(N)	no
Dihedral	O(N)	no
van der Waals	O(N)	yes
Coulomb	O(NlogN)	yes

The software for MD simulation

First principle

- Abinit (abinit.org)
- Quantum-Espresso (quantum-espresso.org)
- VASP (www.vasp.at)
- CP2K (www.cp2k.org)
- CONQUEST (www.order-n.org)
- Siesta (departments.icmab.es/leem/siesta)
- Castep (castep.org)

Empirical force fields

- Lammps (lammps.sandia.gov)
- Gromacs (www.gromacs.org)
- Amber (ambermd.org)
- Charmm (www.charmm.org)
- NAMD (www.ks.uiuc.edu/Reseach/namd)
- OpenMM (openmm.org)
- Tinker (dasher.wustl.edu/tinker)

Take home messages

All you need for an accurate MD is an accurate potential

First principle potentials: expensive and accurate

Empirical force fields: fast but inaccurate

Cut-off method for short-range interaction

Thank you! Questions?