International Spring School Statistical Thermodynamics, Santiago de Chile
Wednesday, November 29, 2017
Lecture 19

Treatment of electrostatic interactions and forces

Prof. Dr. Wilfred F. van Gunsteren
ETH Zürich, Switzerland

Treatment of periodic and non-periodic long-range interactions in MD simulation

1. **Introduction**
   - Concepts, classification of methods
2. **Methods: particles**
   1. All pairs
   2. Cut-off
   3. Cut-off + low frequency long-range
   4. Cut-off + multipoles
3. **Methods: particles-continuum**
   1. Poisson-Boltzmann reaction field
   2. Delayed plus stochastic reaction field
4. **Methods: particles-lattice sums**
   1. Ewald
   2. Particle-particle-particle-mesh: P^3M
   3. Particle-mesh-Ewald: PME
   4. Fast-multipole-method: FMM
   5. Artefacts due to periodicity
5. **Methods: particles-half periodic**
   1. Conducting boundary method: CBM

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Treatment of long-range forces

Interaction type	Energy U	Force $\vec{f}$	$U*r^2$	$f*r^2$
charge-charge	$\frac{1}{r}$	$\frac{1}{r^2}$	r	1
charge-dipole	$\frac{1}{r^2}$	$\frac{1}{r^3}$	1	$\frac{1}{r}$
dipole-dipole	$\frac{1}{r^3}$	$\frac{1}{r^4}$	$\frac{1}{r}$	$\frac{1}{r^2}$

Interaction energy summed over space: $U_{Total} = \int_0^\infty U(r) * 4\pi r^2 dr$

Converges (absolutely) if $U(r) \sim \frac{1}{r^\alpha}$ **with** $\alpha > 3$

Alternatives:
- Summation over a (periodic) lattice
- Cut-off plus reaction field due to continuum

Treatment of long-range forces

Concepts:

a. finite systems ⟷ **infinite** systems

boundary or **cut-off**

continuum: non-periodic

lattice: periodic

b. boundary between **particles** and **continuum**

1. Fixed boundary:

How to handle particles near boundary?

How to transfer particles over boundary?

Distortions near boundary

2. Moving boundary: sphere that **moves** with **(each) particle**

Advantage: particle for which force is calculated is always far from boundary.

Inconsistency: parts of system are treated as particles as well as continuum

c. periodic systems ⟷ **non-periodic** systems

finite: nearest or minimum image

infinite: all images, lattice sum

Artefacts for non-crystalline systems

finite: MI + spherical cut-off

infinite: continuum

Treatment of long-range forces

Concepts:

d. Force splitting $\vec{f}_i = \vec{f}_i^{\,sr} + \vec{f}_i^{\,lr}$

Force on particle is written as a **sum** of a **short-range force** and a **long-range force.**

Short-range force: particle-particle
nearest image periodic or non-periodic

Long-range force: variety of models and techniques or methods

Classification of methods: long-range forces $\vec{f}_i^{\,lr}$

1. Infinite periodic:

- Particles: Lattice sum
  - Ewald — $N^{3/2}$
  - FFT's: PPPM — $N \log N$
    PME — *or*
    SPME — N
  - Multipoles: FMM — N

2. Infinite non-periodic:

- Particles:
  - FFT's: Conducting boundary P^{3}M
  - Multipoles:
- Continuum:
  - Poisson-Boltzmann reaction field (RF)
  - Choice ε_{RF}
  - Heterogeneous environment ?

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Methods to evaluate long-range electrostatic forces:

particles/discrete **non-periodic or periodic**

1. Inclusion all atom pairs:

Effort $\sim N^2$ too expensive

For periodic systems: minimum image cut-off ⟶ distortions

2. Spherical cut-off:

Effort $\sim NR_c^3$ expensive if cut-off radius R_c large

distortions even for large R_c

3. Cut-off plus low frequency update of long-range force f^{lr}

Effort $\sim N\left(R_{cl}^3 - R_c^3\right)$ times frequency of updates

4. Cut-off plus multipole expansion:

Fast multipole method: Effort $\sim N$

Efficient for large sparse systems (sets of stars or galaxies)

K. Esselink, PhD thesis, Groningen, The Netherlands, 1995

Treatment of long-range forces: methods

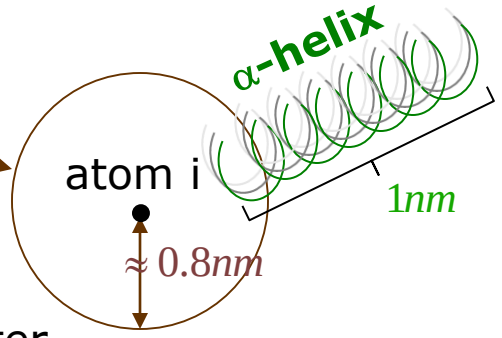
1. Inclusion of all atom pairs

Computing time $\sim N^2$ → too expensive

2. Cut-off radius

cut-off radius $R_c \approx 0.8nm$

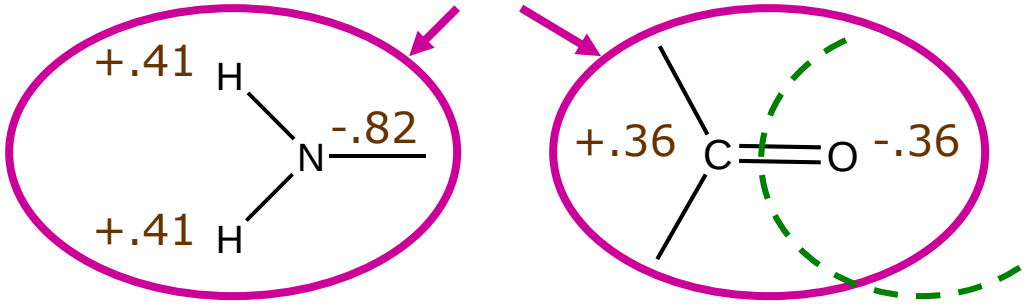
No interactions for distance $r_{ij} > R_c$



Error:

charge-charge	r^{-1}	shorter
charge-dipole	r^{-2}	range
dipole-dipole	r^{-3}	

Concept: use neutral groups of atoms: r^{-3}



cut-off radius does ***not*** split a group

3. Distance dependent dielectric

Use $\varepsilon_r = r(in\ Angstrom)$ → $V = \frac{1}{4\pi\varepsilon_0}\frac{1}{dr_{ij}}\frac{q_i q_j}{r_{ij}}$

$= d \cdot r$ → constant expressing units non-physical

Adaptation of a force field to a vacuum boundary condition

GROMOS force field: not vacuum

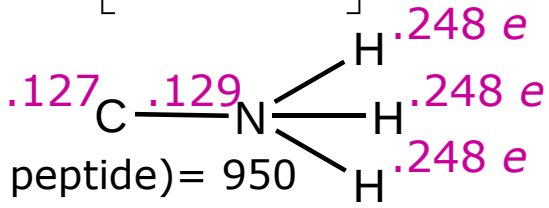
What to do when using it for *in vacuo* simulations?

solution parameters (37C4): **vacuo parameters**(37D4):

GROMOS: 43A1 (45A4, 53A6) 43B1 (45B4, 53B6)

neutralise charged groups retaining H-bond capacity

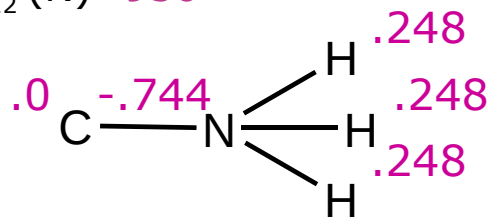
Lys: $C_{12}^{1/2}(N)=1500\left[\text{kcal/mol Å}^{12}\right]^{1/2}$



$C_{12}^{1/2}$(N of peptide)= 950

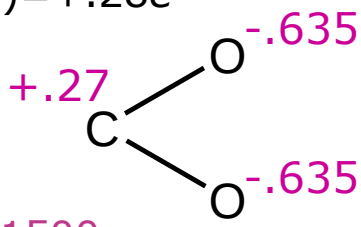
q(H of peptide)=+.28*e*

$C_{12}^{1/2}(N)=950$

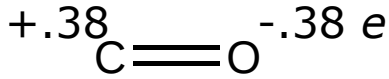


Asp:

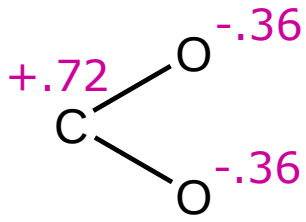
Glu:



$C_{12}^{1/2}(O) = 900/1500$



$C_{12}^{1/2}$(O of carbonyl) = 550



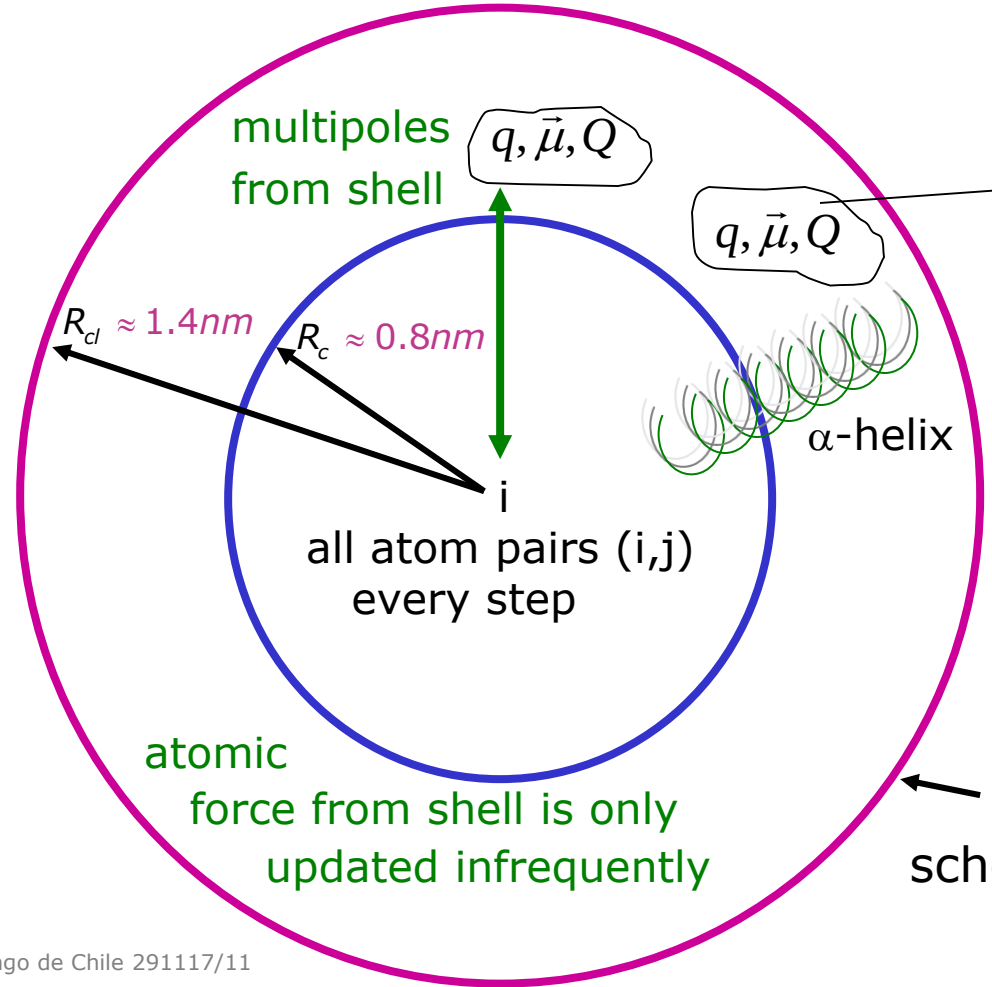
$C_{12}^{1/2}(O) = 550/550$

Arg, N-terminus, C-terminus: likewise

Treatment of long-range forces: methods

4. Cut-off (R_c)

- **plus low-frequency update** of $\vec{f}^{lr}$ **from shell**
- **plus multipole expansion**



$q =$ charge
$\vec{\mu} =$ dipole
$Q =$ quadrupole

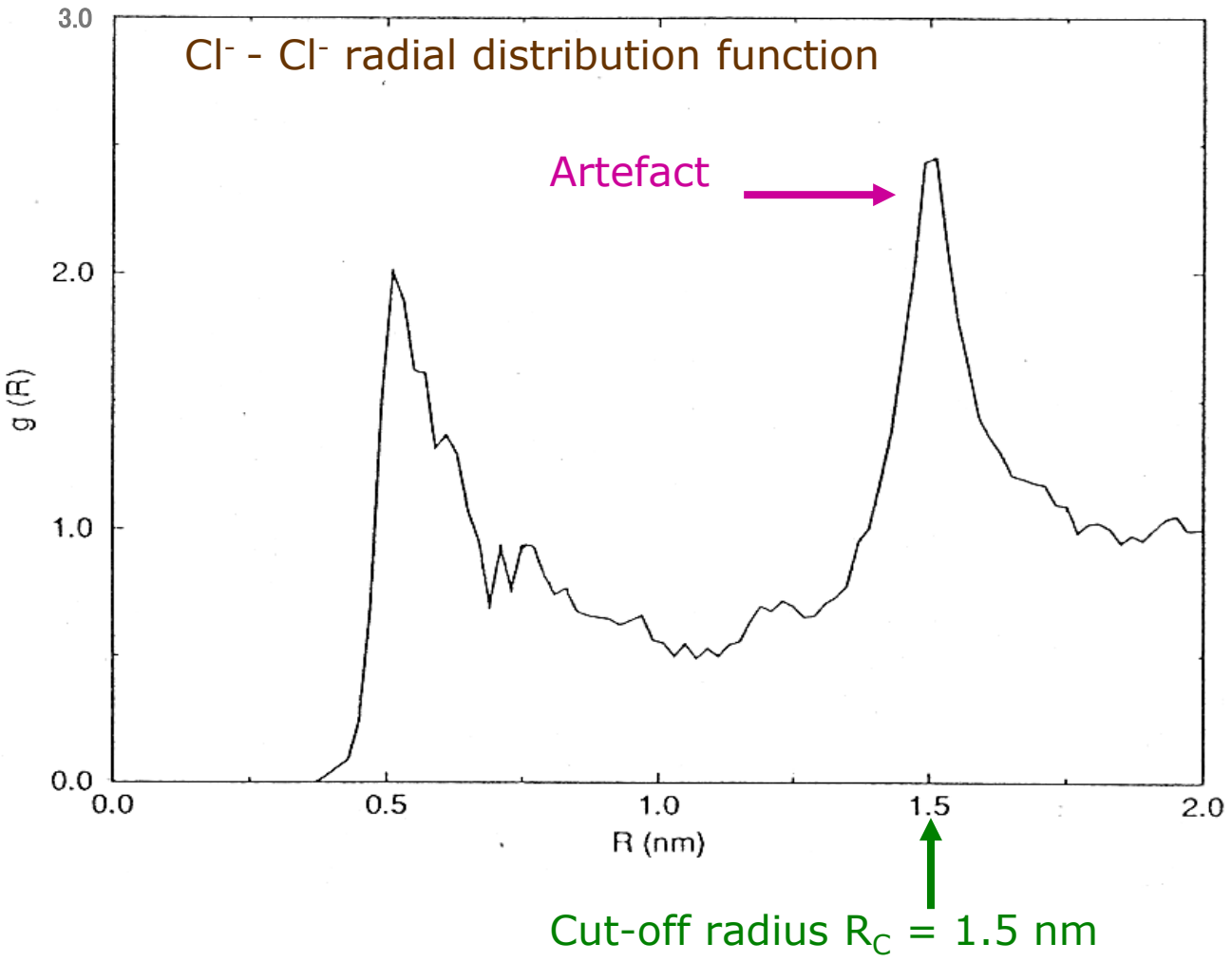
α-helix

Multiple time step scheme in GROMOS (since ≈ 1984)

MD simulation of 40 Na^+Cl^- in 2127 H_2O

Cubic periodic box: edge length = 4.05 nm

Cut-off distortion



Cut-off distortion is present, even for long cut-off distances

Treatment of long-range (electrostatic) forces

Use of (neutral) charge groups

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When applying cut-offs or boundaries, use centre of dipole for distance cut-off
Aqvist + Hansson, *J. Phys. Chem.* B102 (1998) 3837

Disadvantage charge groups: Additional derivative terms
(interaction depends on additional, virtual site)

Interaction energy summed over space: $U_{total} = \int_0^\infty U(r) 4\pi r^2 dr$

Converges if $U(r) \sim \frac{1}{r^\alpha}$ with $\alpha > 3$

Alternatives: - Summation over a (periodic) lattice
- Cut-off plus reaction field due to continuum

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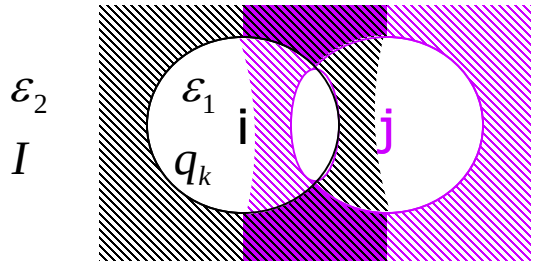
Methods to evaluate long-range electrostatic forces:

particles/continuum

non-periodic or periodic

Moving spherical boundary

1. Poisson-Boltzmann reaction field



Instantaneous response of environment outside cut-off sphere

Cut-off distortions largely resolved

cheap, easy to implement

2. Delayed plus stochastic reaction field

- Response of environment is delayed
- Environment produces fluctuating field

⟹ Connected via fluctuation-dissipation theorem

Better physical model

Expensive (spatial correlation)

Continuum methods for electrostatic interactions

Divide system in 2 parts:

1. Inner region: explicit charges q_i — dielectric ε_1
2. Outer region: continuum — dielectric ε_2; ionic strength I

Potential:

1. Inner region $\varphi_1\left(\vec{r}\right) = \varphi_C\left(\vec{r}\right) + \varphi_R\left(\vec{r}\right)$

Coulomb *reaction*

$$\varphi_C\left(\vec{r}\right) = \frac{1}{4\pi\varepsilon_0\varepsilon_1}\sum_{i=1}^{N}\frac{q_i}{\left|\vec{r}-\vec{r}_i\right|} \longrightarrow \textbf{Poisson equation: } \vec{\nabla}^2\varphi\left(\vec{r}\right) = \frac{-1}{\varepsilon_1}\sum_{i=1}^{N} q_i\delta\left(\vec{r}-\vec{r}_i\right)$$

$$\varphi_R\left(\vec{r}\right) = \longrightarrow \textbf{Laplace equation: } \vec{\nabla}^2\varphi\left(\vec{r}\right) = 0$$

2. Outer region $\varphi_2\left(\vec{r}\right) = \longrightarrow$ ***Poisson-Boltzmann equation:*** $\vec{\nabla}^2\varphi\left(\vec{r}\right) = \kappa^2\varphi\left(\vec{r}\right)$

$$\kappa = \frac{2IF^2}{\varepsilon_2 RT}$$

3. Boundaries $\lim_{r\to\infty}\varphi_2\left(\vec{r}\right) = 0$

at 1-2 boundary

$$\begin{cases} \varphi_1\left(\vec{r}\right) = \varphi_2\left(\vec{r}\right) & \varphi \text{ = continuous} \\ \varepsilon_1\nabla_n\varphi_1\left(\vec{r}\right) = \varepsilon_2\nabla_n\varphi_2\left(\vec{r}\right) & \nabla_n \text{ = continuous} \end{cases}$$

4. Solution φ_1 depends on: shape boundary,
ε_2 , ionic strength I, *temperature* T,
ε_1 , positions of q_i ,
method to solve equations

Momentary or instantaneous reaction field (RF)

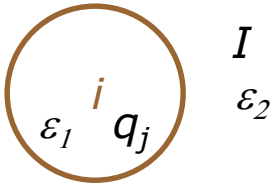
*Tironi et al., J. Chem. Phys. 102 (**1995**) 5451-5459*

Spherical cavity: = *cut-off sphere (radius R_C) around atom i*

Inside: charges q_j at $\vec{r}_j$

ε_1 = 1 non-polarisable model

≠ 1 polarisable model



Outside: ionic strength $I = \sum_{i=1}^{N_s} c_i z_i^2$

N_s species

c_i molar concentration

z_i charge number

ε_2 = dielectric permittivity

inverse Debye screening length: $\kappa^2 = \dfrac{2IF^2}{\varepsilon_0 \varepsilon_2 RT}$

R = gas constant

F = Faraday constant

ε_0 = vacuum permittivity

T = temperature

Derivation: *Tironi et al., J.Chem.Phys. 102 (**1998**) 5451*

Pair force:

$$\vec{f}_{ij}\left(r_{ij}\right) = \frac{q_i q_j}{4\pi\varepsilon_0\varepsilon_1}\left\{\frac{1}{r_{ij}^{\,3}} - \frac{1}{R_C^3}\frac{\left(2\varepsilon_2 - 2\varepsilon_1\right)\left(1+\kappa R_C\right) + \varepsilon_2\left(\kappa R_C\right)^2}{\left(2\varepsilon_2 + \varepsilon_1\right)\left(1+\kappa R_C\right) + \varepsilon_2\left(\kappa R_C\right)^2}\right\}\vec{r}_{ij}$$

$\vec{r}_{ij} = \vec{r}_i - \vec{r}_j$

Force on atom i:

$$\vec{f}_i = \underbrace{\sum_{j\neq i}^{N} \frac{q_i q_j}{4\pi\varepsilon_0\varepsilon_1}\frac{\vec{r}_{ij}}{r_{ij}^{\,3}}}_{\text{Coulomb}} + \underbrace{\frac{q_i}{4\pi\varepsilon_0\varepsilon_1}\frac{1}{R_C^3}\frac{\left(2\varepsilon_2 - 2\varepsilon_1\right)\left(1+\kappa R_C\right) + \varepsilon_2\left(\kappa R_C\right)^2}{\left(2\varepsilon_2 + \varepsilon_1\right)\left(1+\kappa R_C\right) + \varepsilon_2\left(\kappa R_C\right)^2}\sum_{j\neq i}^{N} q_j \vec{r}_{ji}}_{q_i\vec{E}_i \quad \text{reaction field}}$$

$\vec{M}_i$

Mean-field approximation

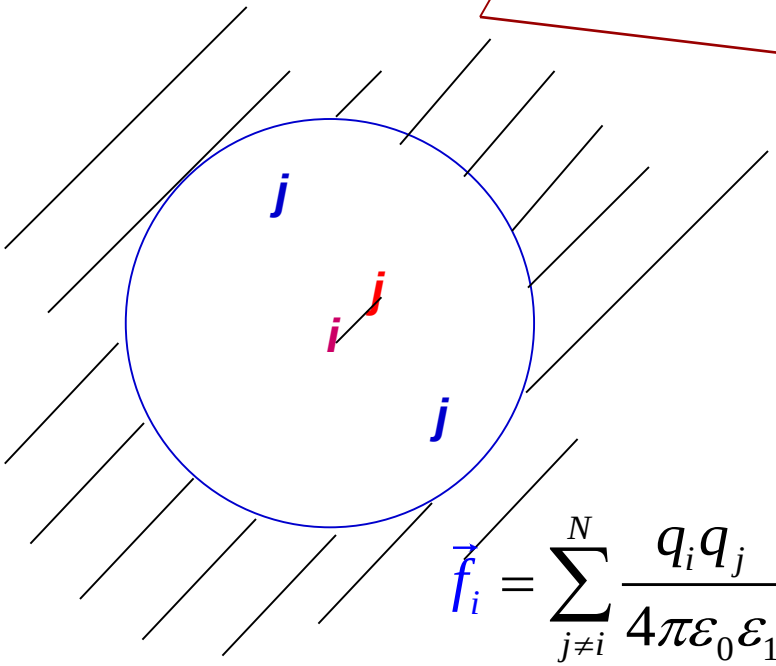
*Tironi et al., J. Chem. Phys. 102 (**1995**) 5451-5459*

Example: continuum dielectric outside a cut-off sphere

Each particle interacts

- explicitly with other particles within the cut-off sphere
- through a **mean field** originating from particles outside the cut-off sphere

reaction field



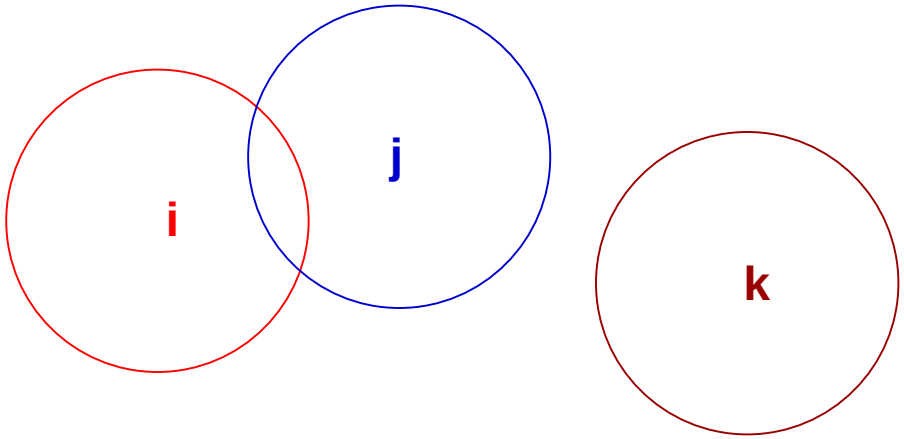
Note:

-The direct Coulomb term summation *excludes* nearest neighbour *excluded atoms*, because their interactions are in the *covalent terms*

- The reaction field term summation *does not exclude* nearest neighbour *excluded atoms*, because it depends on the *total dipole moment* M_i

$$\vec{f}_i = \underbrace{\sum_{j\neq i}^{N} \frac{q_i q_j}{4\pi\varepsilon_0\varepsilon_1} \frac{\vec{r}_{ij}}{r_{ij}^3}}_{\text{direct Coulomb (exclusions)}} + \underbrace{\frac{q_i}{4\pi\varepsilon_0\varepsilon_1} \frac{1}{R_C^3} \text{factor}\left(\varepsilon_0, \varepsilon_1, \kappa, R_C\right) \underbrace{\sum_{j\neq i}^{N} q_j \vec{r}_{ji}}_{\vec{M}_i}}_{q_i\vec{E}_i \text{ reaction field (no exclusions)}}$$

Note: inconsistency: parts of system are treated
as particles as well as continuum



Diffusion constants (10^{-9} m^2s^{-1})

		D(Na)	D(Cl)	D(water)
Cut-off plus reaction field	RF (R_c=0.9 nm)	1.6	2.2	4.7
	RF (R_c=1.5 nm)	1.5	2.3	4.0
Periodic sum	Ewald	1.3	2.1	3.6
Plain cut-off	VAC (R_c=0.9 nm)	1.3	1.3	5.3
	VAC (R_c=1.5 nm)	1.2	2.6	4.8

Long-range correlation → slower motion of water

Residence time (ps) of H_2O molecules in first hydration shells

	τ(Na)	τ(Cl)
RF (R_c=0.9 nm)	28	17
RF (R_c=1.5 nm)	33	13
Ewald	32	14
VAC (R_c=0.9 nm)	19	13
VAC (R_c=1.5 nm)	25	10

Long-range correlation → slower exchange H_2O

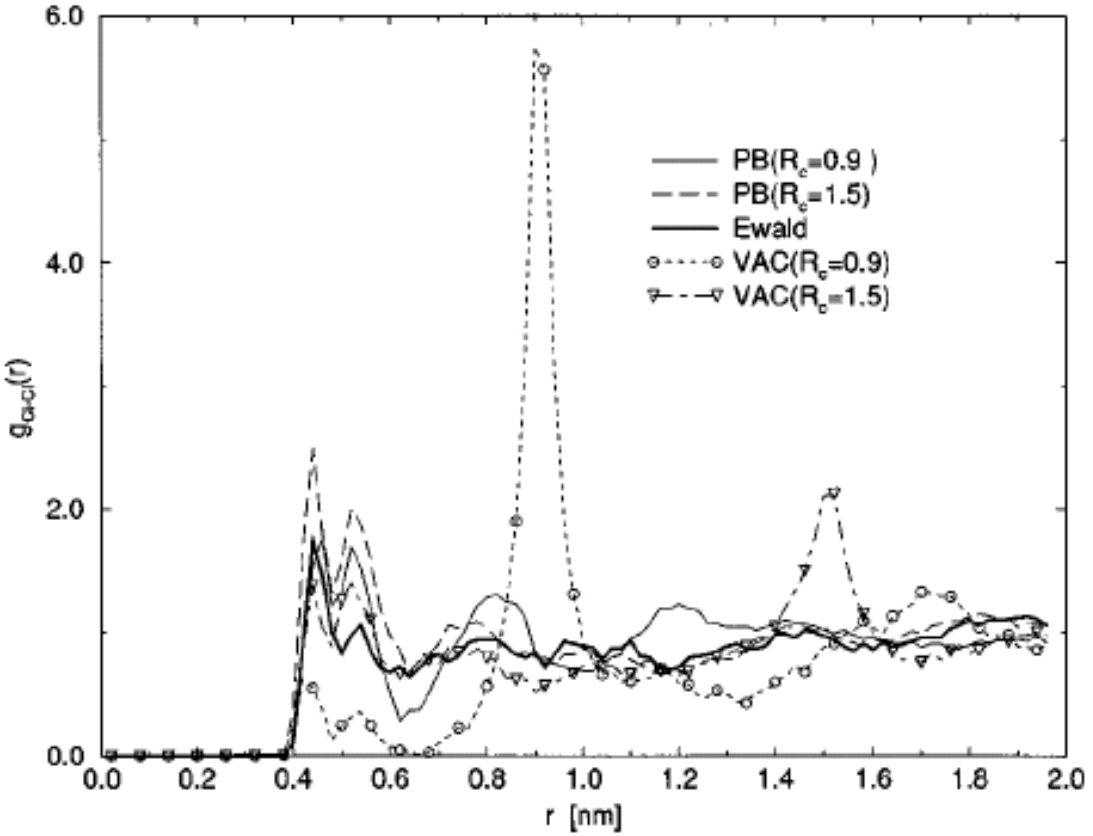
*Tironi et al., J. Chem. Phys. 102 (**1995**) 5451-5459*

MD simulation of 40 Na^+Cl^- in 2127 H_2O

Cubic periodic box: edge length = 4.05 nm

Dielectric permittivities $\varepsilon_1 = 1$, $\varepsilon_2 = 80$, Debye screening length $\kappa = 3.25$ nm^{-1}

Cl^- - Cl^- radial distribution function (≈ 200 ps)



Cut-off radius R_C = 0.9 nm

R_C = 1.5 nm

Cut-off distortion in vacuo disappears when using a reaction field

(VAC) **(PB-RF)**

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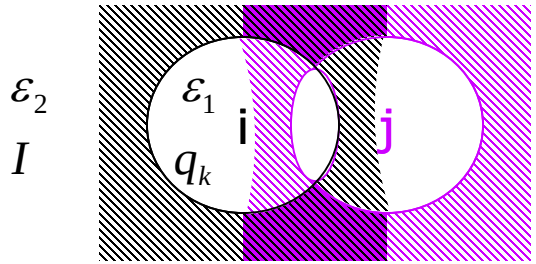

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⟹ Connected via fluctuation-dissipation theorem

Better physical model

Expensive (spatial correlation)

Delayed plus stochastic reaction field

*Tironi et al., J. Chem. Phys. 106 (**1997**) 6068-6075*

1. Momentary/instantaneous reaction field

$$\vec{E}_i = \frac{1}{4\pi\varepsilon_0\varepsilon_1}\frac{1}{R_c^3}\frac{(2\varepsilon_2 - 2\varepsilon_1)(1+\kappa R_c) + \varepsilon_2(\kappa R_c)^2}{(2\varepsilon_2 + \varepsilon_1)(1+\kappa R_c) + \varepsilon_2(\kappa R_c)^2}\vec{M}_i$$

water = 0.981

2. Delayed reaction field (κ=0 for simplicity) $\varepsilon_2(\omega)$

$$\vec{E}_i(t) = \underbrace{\frac{1}{4\pi\varepsilon_0\varepsilon_1}\frac{1}{R_c^3}}_{\gamma}\underbrace{\frac{2\varepsilon_2(\infty) - 2\varepsilon_1}{2\varepsilon_2(\infty) + \varepsilon_1}}_{\delta}\left\{\vec{M}_i(t) + \alpha\int_0^\infty e^{-\beta t'}\vec{M}_i(t-t')dt'\right\}$$

instantaneous part

delayed part

water = 0.741

α= 0.536 ps^{-1} β^{-1}= 0.60 ps

Delayed plus stochastic reaction field

*Tironi et al., J. Chem. Phys. 106 (**1997**) 6068-6075*

3. Missing term: reaction-field fluctuations (stochastic)

$$\vec{E}_i(t) = \gamma\delta\left\{\vec{M}_i(t) + \alpha\int_0^\infty e^{-\beta t'}\vec{M}_i(t-t')dt'\right\} + \vec{E}_i^{\,st}(t)$$

energy conserved — dissipation — noise

related

Fluctuation-dissipation theorem:

$$\left\langle \vec{E}^{st}(0)\cdot\vec{E}^{st}(t)\right\rangle = \gamma\delta\alpha\beta^{-1}3k_BTe^{-\beta t}$$

4. Generalized Langevin equation

$$m_i d\vec{v}_i(t)/dt = \vec{f}_i(t) - m_i\int_0^\infty \gamma_i(t')\vec{v}_i(t-t')dt' + \vec{f}_i^{\,st}(t)$$

$$\left\langle \vec{f}_i^{\,st}(0)\cdot\vec{f}_i^{\,st}(t)\right\rangle = m_i 3k_BT\gamma_i(t) \longrightarrow$$ techniques to sample $\vec{f}_i^{\,st}(t)$

5. Correlation in space:

also exponential (neighbour atoms)

MD simulation of 512 H_2O molecules

Cubic box: edge length = 2.486 nm
SPC/E water ≈ 900 psec

$\varepsilon_2(static) = 80$
$\varepsilon_2(\infty) = 5.3$
$R_C = 0.9\ nm$

	Instantaneous		**Delayed + stochastic**
Property	Ewald	Reaction field	Reaction field
Diffusion coefficient D ($10^{-9}m^2s^{-1}$)	2.3	3.0	3.0
Rotational correlation times: τ_1 (psec) τ_2 (psec)	4.6 1.7	3.8 1.4	4.0 1.4
Dipole moment fluctuation: $<M^2>$ (e^2nm^2)	5.1	3.0	2.8
Debye relaxation time: τ_D (psec)	11.1	5.4	4.8

Small differences between *instantaneous* and *delayed* reaction field

*Tironi et al., J. Chem. Phys. 106 (**1997**) 6068-6075*

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   1. Conducting boundary method: CBM

Methods to evaluate long-range electrostatic forces:

particle/particle **periodic**

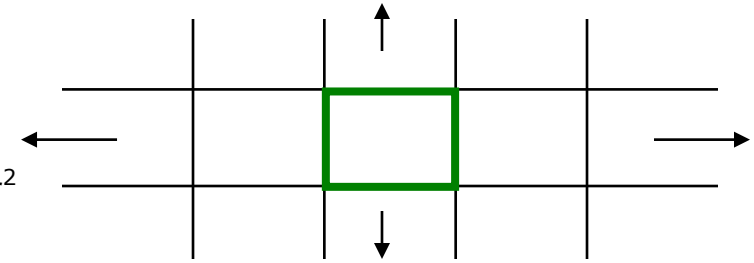
Lattice sum

1. Ewald sum

Effort: $\sim N^2$ (fixed R_C or α)

Gaussian charge shape: $\gamma(r) = \frac{\alpha^2}{\pi^{3/2}} e^{-\alpha^2 r^2}$

↳ Analytical solution Poisson



2. Particle-particle-particle-mesh: P³M

Hockney, Eastwood (1981)

Effort: $\sim N \log N$ FFT

$\sim N$ iterative Poisson solver

Speed-up for 17000 atoms ≈ factor 100 compared to Ewald

*Luty et al., Mol. Sim. 14 (**1994**) 11*

3. Particle-mesh-Ewald:

Darden et al. (1993)

Is P³M without optimised influence function (to reduce discretisation errors)

Originally 20 times less accurate than P³M

*Luty et al., J. Chem. Phys. 103 (**1995**) 3014*

4. Fast multipole method:

Speed break-even point with respect to Ewald estimated:

30 000 atoms Petersen et al. (1994)

100 000 atoms Esselink (1995)

P³M seems most efficient

Treatment of long-range forces (1)

*Luty et al., Mol. Sim. 14 (**1994**) 11-20, J. Chem. Phys. 103 (**1995**) 3014-3021*

Particle-particle methods

- Ewald sum
- PPPM (particle-particle/particle-mesh) method

Idea:

Poisson for infinite set of charges q_i

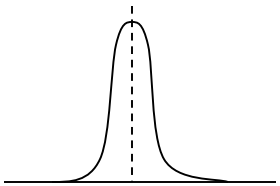
$$-\varepsilon_0 \vec{\nabla}^2 \phi(\vec{r}) = \sum_{\vec{n}} \sum_{i=1}^{N} q_i \left[\delta\left(\vec{r} - \left(\vec{r}_i + \vec{n}\right)\right) - \gamma\left(\vec{r} - \left(\vec{r}_i + \vec{n}\right)\right) + \gamma\left(\vec{r} - \left(\vec{r}_i + \vec{n}\right)\right) \right]$$

$\downarrow$

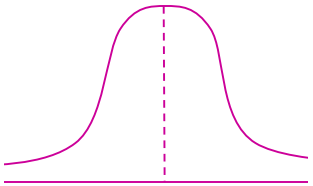
$\phi_s(\vec{r}) =$ short range $\longleftrightarrow$ zero net charge

$+$

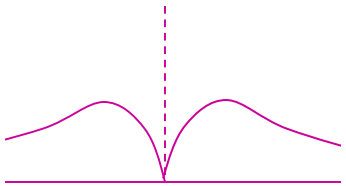
$\phi_l(\vec{r}) =$ long range $\longleftrightarrow$ smeared charge distribution



$\delta(\vec{r})$



$$\gamma(\vec{r}) = \frac{\alpha^2}{\pi^{3/2}} e^{-\alpha^2 r^2}$$



$$\gamma(\vec{r}) = \frac{5r}{\pi a^4}\left[1 - \frac{r}{a}\right] \qquad r < a$$

$$= 0 \qquad r > a$$

Treatment of long-range forces (2)

*Luty et al., Mol. Sim. 14 (**1994**) 11-20, J. Chem. Phys. 103 (**1995**) 3014-3021*

Ewald:

Short range (particle-particle): $\varphi_s(r_{ij}) = \frac{1}{4\pi\varepsilon_0}\left[\frac{1}{r_{ij}} - \frac{erf(\alpha r_{ij})}{r_{ij}}\right]$

= potential at $\vec{r}_i$ due to j

Long range: $\phi_l(\vec{r}) = \frac{1}{\varepsilon_0 V}\sum_{\vec{k}\neq 0}\frac{e^{-k^2/4\alpha^2}}{k^2}\sum_{i=1}^{N} q_i e^{+i\vec{k}\cdot(\vec{r}-\vec{r}_i)}$ $\sim N^2$

PPPM:

Short: $\varphi_s(r_{ij}) = \frac{1}{4\pi\varepsilon_0}\left[\frac{1}{r_{ij}} - \frac{5}{3a} + \frac{5r_{ij}^{\,3}}{3a^4} - \frac{r_{ij}^{\,4}}{a^5}\right]$ $r_{ij} < a$

$= 0$ $r_{ij} > a$

Long:

1. Assign q_i to grid: $\rho(\vec{r})$
2. FFT ⟶ $\hat{\rho}(\vec{k})$ ~NlogN
3. Solve Poisson: $\hat{\phi}_l(\vec{k}) = \hat{\rho}(\vec{k})\frac{\hat{\gamma}(\vec{k})}{\varepsilon_0 k^2}$
4. FFT ⟶ $\phi_l(\vec{r})$ at grid ⟶ interpolate ~NlogN

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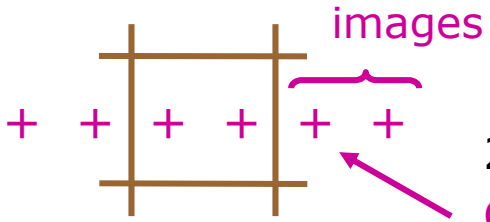
Example of failure of full periodic boundary conditions (1)

1. Full periodic

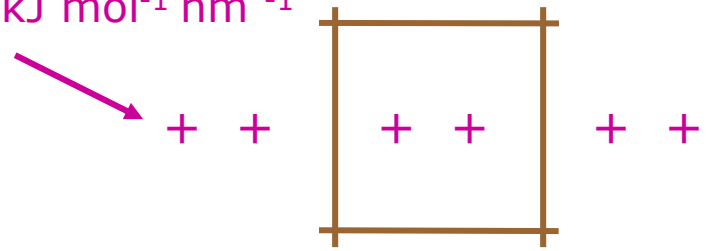


2 charges at half box-length distance (1.25nm)

Coulomb force between charges = 0

Boxsize effect: For box 1.5 times larger

the Coulomb force = 70 kJ mol^{-1} nm $^{-1}$



2. Infinite vacuum

+ + Coulomb force = 89 kJ mol^{-1} nm $^{-1}$

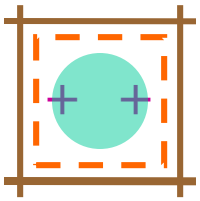
3. In water (ε = 80)

+ + Coulomb force = 1 kJ mol^{-1} nm $^{-1}$

Boxsize effect is small

Example of failure of full periodic boundary conditions (2)

4. In low dielectric (*sphere*, ε = 1) solvated by water



compare: - full periodic ⌗
- half periodic with conducting boundary
δ = distance between conducting and periodic boundary

Boundary condition	Boxsize nm	δ nm	Force on atom 1 kJ mol^{-1} nm $^{-1}$	Force on atom 2	Average force
- fully periodic	2.486	-	-262	268	265
	3.729	-	-306	302	304
- half periodic conducting	2.486	-0.1	-316	312	314
	3.724	-0.1	-313	311	312

15% change

Fully periodic gives boxsize dependent result

Half periodic with conducting boundary condition gives boxsize ***in***dependent result

Literature on periodicity artefacts of infinite lattice sum techniques

To evaluate long-range electrostatic forces:

- Ewald
- Particle-particle-particle-mesh (P^3M)
- Particle-mesh-Ewald (PME)

Luty, van Gunsteren,	*J. Phys. Chem.* 100 (1996) 2581
Hünenberger, McCammon,	*Biophys. Chem.* 78 (1999) 69
	J. Phys. Chem. 110 (1999) 1856
...	*Disc. Faraday Soc.*, ... (1978)
...	

Artificial periodicity:

- **reduces** magnitude free energy of ionic solvation
- **induces** attractive force between ions of like charges, repulsive force between ions of opposite charges
- **size of artefact** is related to :
  1. size of ε^{-1}
  2. ratio: $\frac{\textit{solute size}}{\textit{box size}}$
  3. overall charge of solute

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Methods to evaluate long-range electrostatic forces:
particle/particle non-periodic

Idea:

Short range: *periodic*

Long-range: *non-periodic*

1. Conducting boundary method

Fixed conducting boundary

P^3M algorithm

Effort ~NlogN

~N

No periodicity artefacts

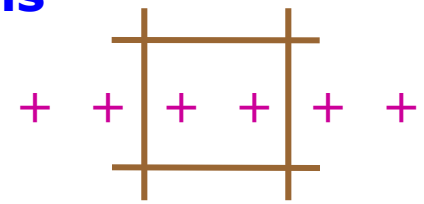
Electrostatic interactions using the particle-particle-particle-mesh method with non-periodic long-range interactions (1)

*Luty et al., J. Phys. Chem. 100 (**1996**) 2581-2587*

1. Full periodic boundary conditions

Short range: vdWaals, Coulomb } periodic

Long range: Coulomb periodic



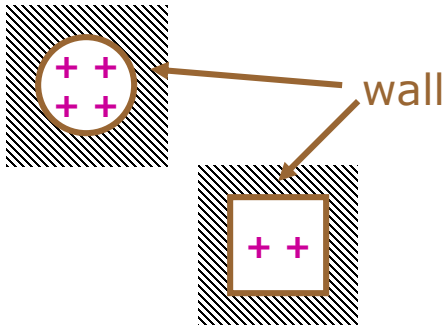
Force between charges at half boxlength is zero

Artefacts from periodicity → long range order → mainly due to long range force

2. Continuum methods

Short range: vdWaals, Coulomb } particle/continuum

Long range: Coulomb particle/continuum



Artefacts, severe distortion of properties near the wall → mainly due to wrong short range forces

Electrostatic interactions using the particle-particle-particle-mesh method with non-periodic long-range interactions (2)

*Luty et al., J. Phys. Chem. 100 (**1996**) 2581-2587*

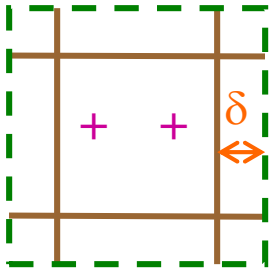
3. Half periodic, conducting boundary

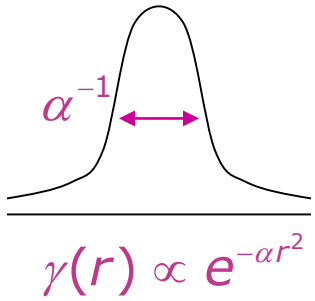
Short range: vdWaals, Coulomb } periodic box

Long range: Coulomb — continuum (conducting) box (fixed)

↓

use smoothened charge (PPPM)





$\delta = 1/2$ (edge conducting box – edge periodic box)

Test: compare to full periodic properties near wall

Comparison of different boundary conditions

512 SPC water molecules

δ = ½ (edge fixed conducting box – edge periodic box)

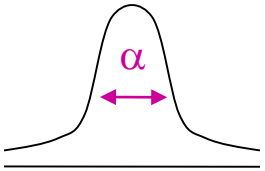
α = width^{-1} of Gaussian shielding charge

R_c = short-range cut-off radius

D = diffusion constant

τ_x = dipole rotational correlation times

ΔQ = heat removed from the system by the temperature bath



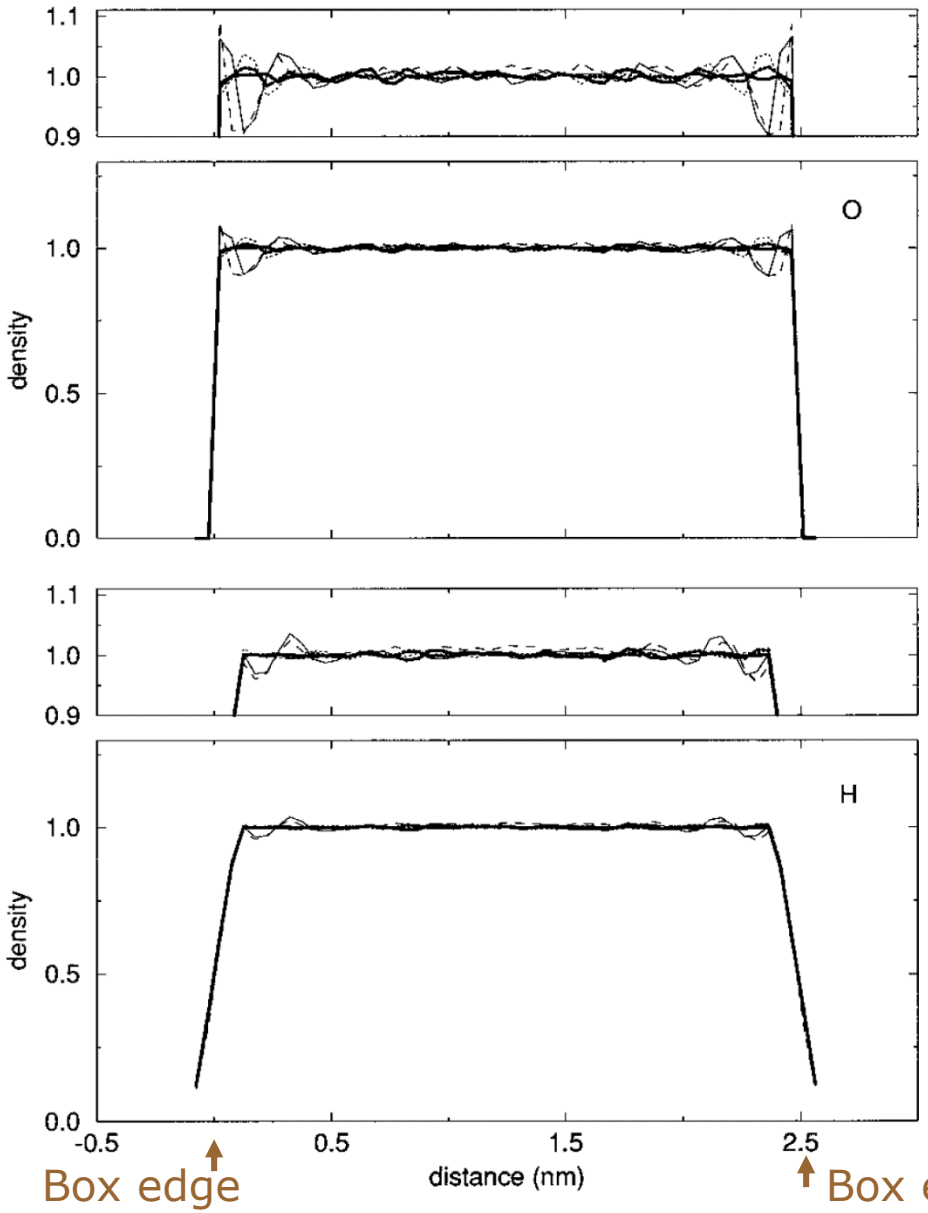
Boundary condition	δ nm	α nm^{-1}	R_c nm	D 10^{-9} m^2/s	τ_1 ps	τ_2 ps	ΔQ kJmol^{-1}step^{-1}
- Fully periodic	-	4.0	0.8	3.9	2.9	1.07	$<10^{-6}$
- Conducting half-periodic	0.0	4.0	0.8	4.4	2.7	0.98	0.42
	0.1	4.0	0.8	5.2	2.5	0.90	1.76
	-0.1	4.0	0.8	4.2	2.8	0.99	0.05
	-0.1	3.2	0.9	4.2	3.0	1.04	0.02

Half periodic with conducting boundary yields: - correct properties
- little heating

when δ = -0.1 nm

*Luty et al., J. Phys. Chem. 100 (**1996**) 2581-2587*

Distribution of H_2O molecules over the 25*25*25 Å^3 box



conducting

δ = ½ (edge fixed box – edge periodic box)

Target

Fully periodic BC = thick solid

Short range periodic BC

Long range conducting BC

δ = 0.0 : thin solid

δ = +0.1: dashed

δ = -0.1 : thin dotted

δ = -0.1 + smoother charge: thick dotted

Good results

O = Oxygen

H = Hydrogen

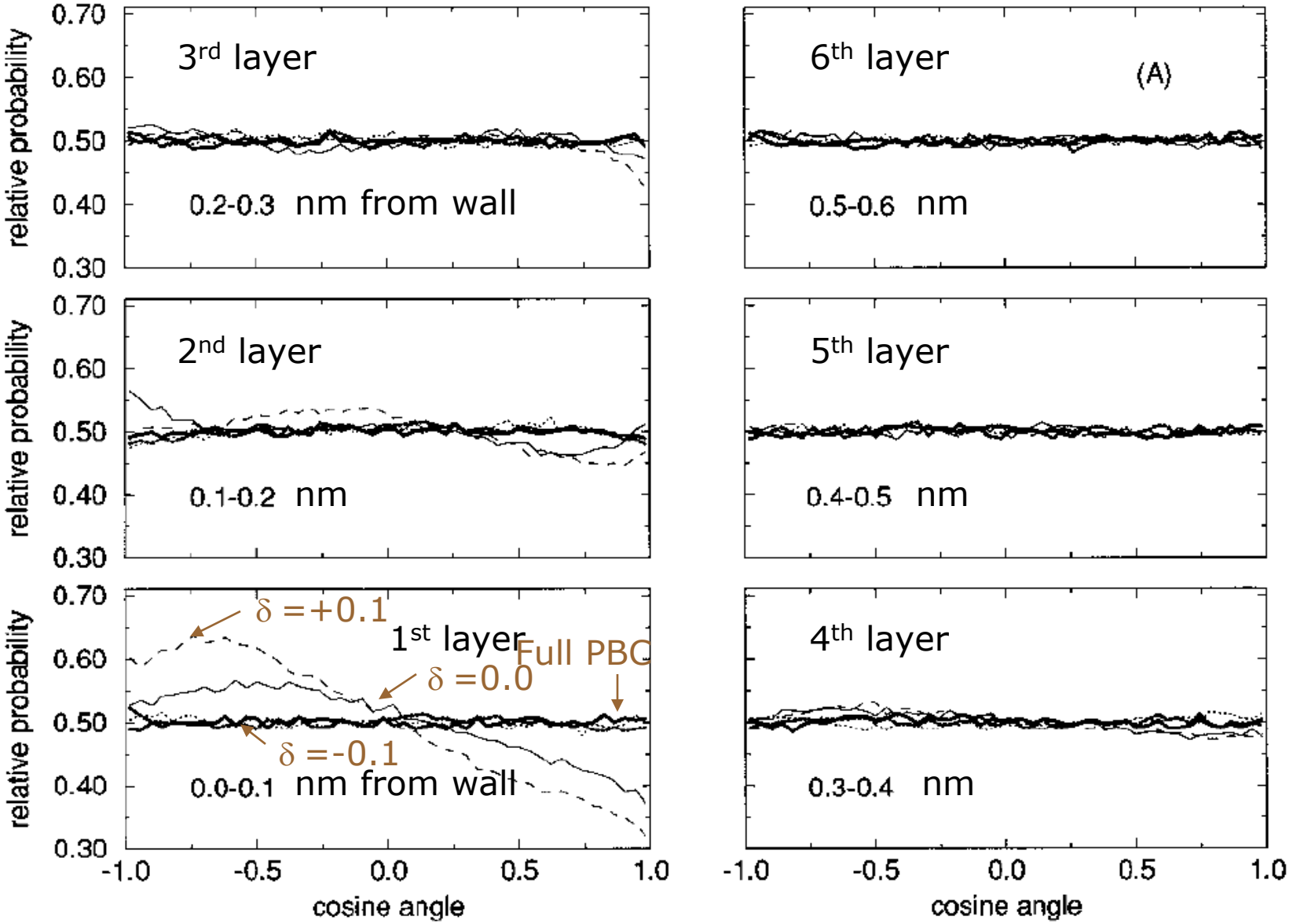
Luty et al.,
*J. Phys. Chem. 100 (**1996**) 2581-2587*

Distribution of $\cos(\vec{\mu}_{H_2O} \square \overrightarrow{vector\ orthogonal\ to\ wall})$

↳ pointing outwards

δ = ½ (edge fixed box – edge periodic box) in nm

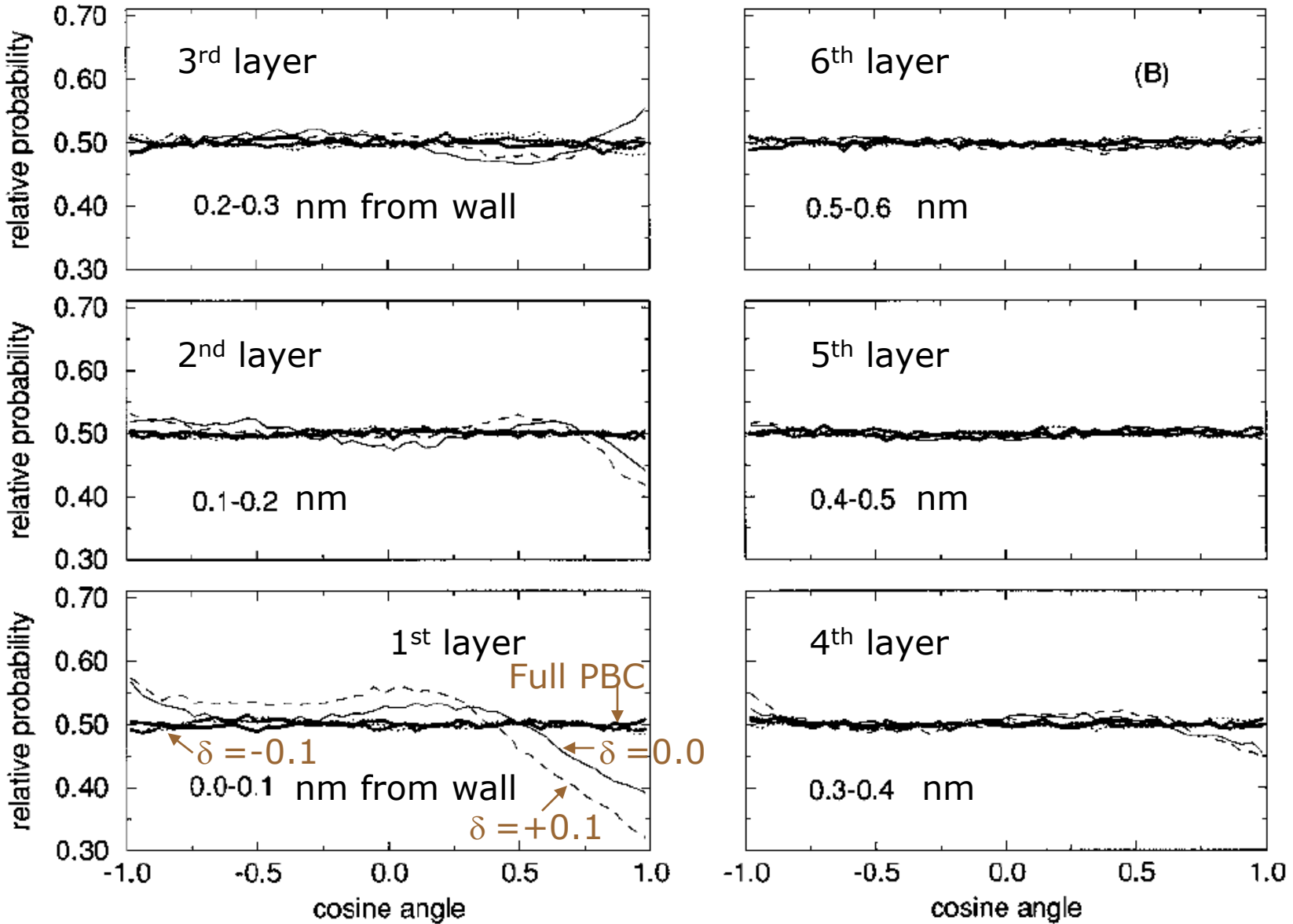
↳ conducting



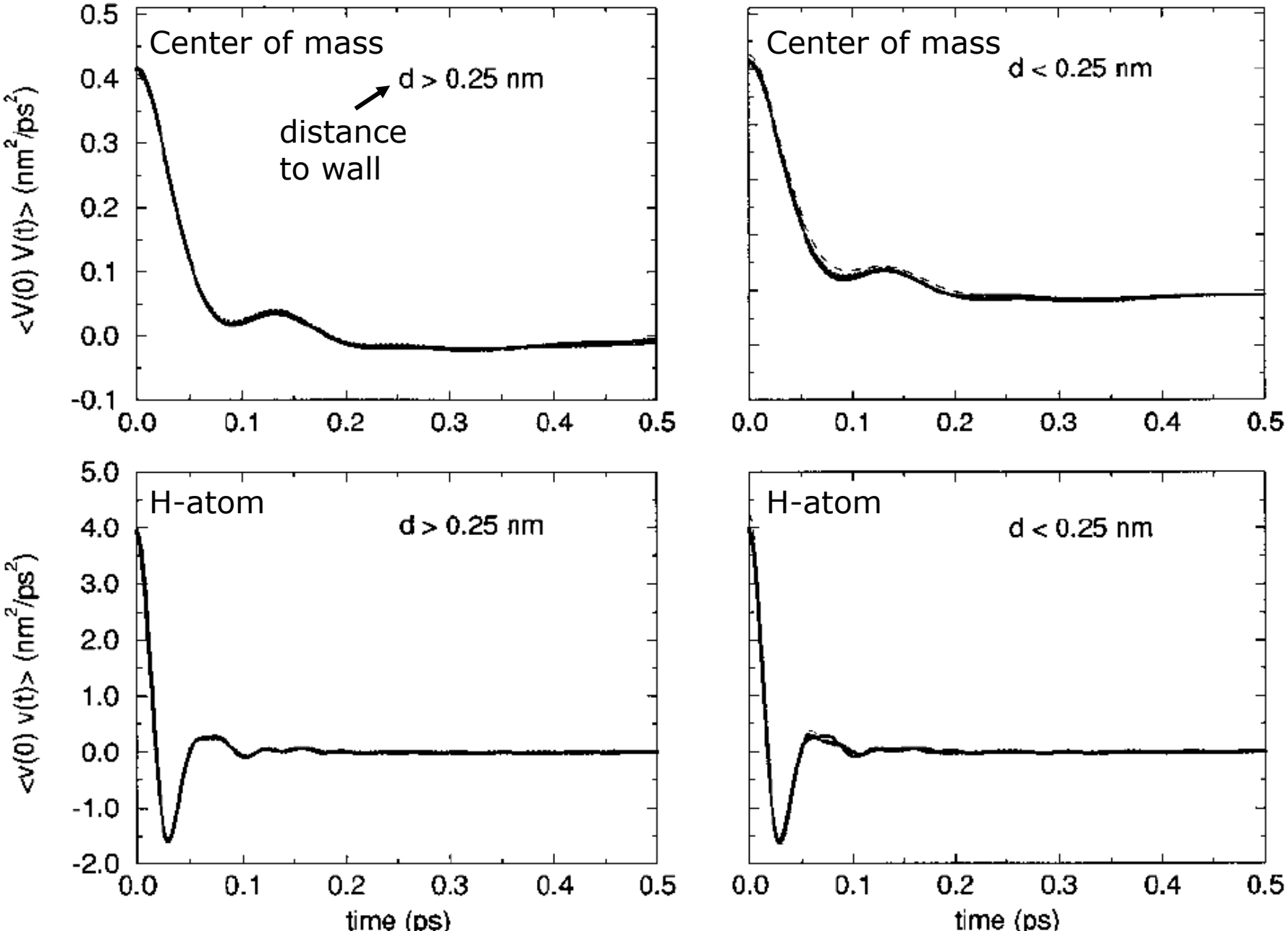
Distribution of $\cos(\overrightarrow{O-H} \square \overrightarrow{vector}\ orthogonal\ to\ wall)$

↳ pointing outwards

δ = ½ (edge fixed box – edge periodic box) in nm



Velocity autocorrelation function



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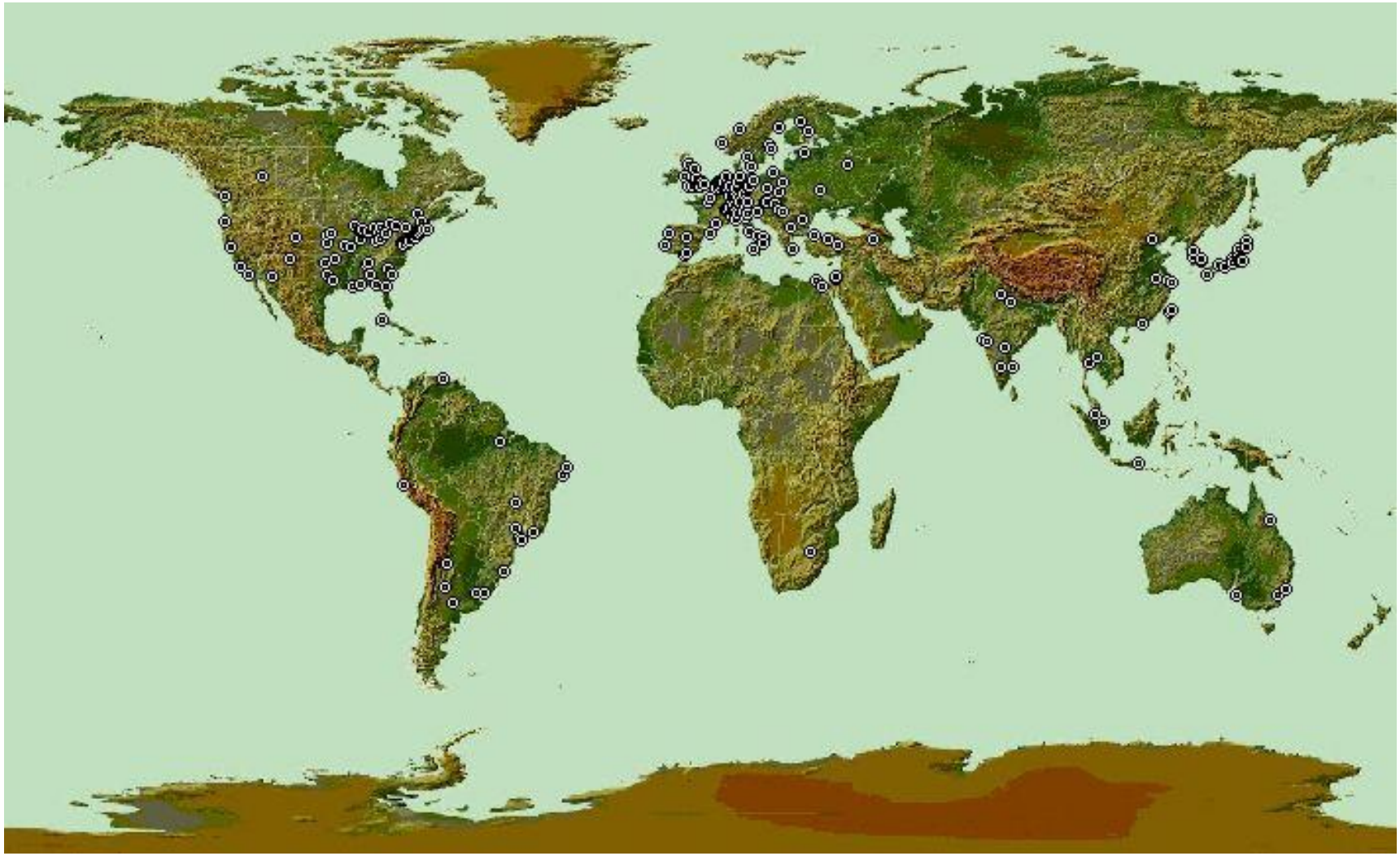
Spatial distribution of licences
GROMOS biomolecular simulation software



GROMOS = Groningen Molecular Simulation + GROMOS Force Field

Generally available: http://www.gromos.net