# Modelling Activities on Silver/Oxide Interfaces with AGC and Li-Ion Batteries with Solvay

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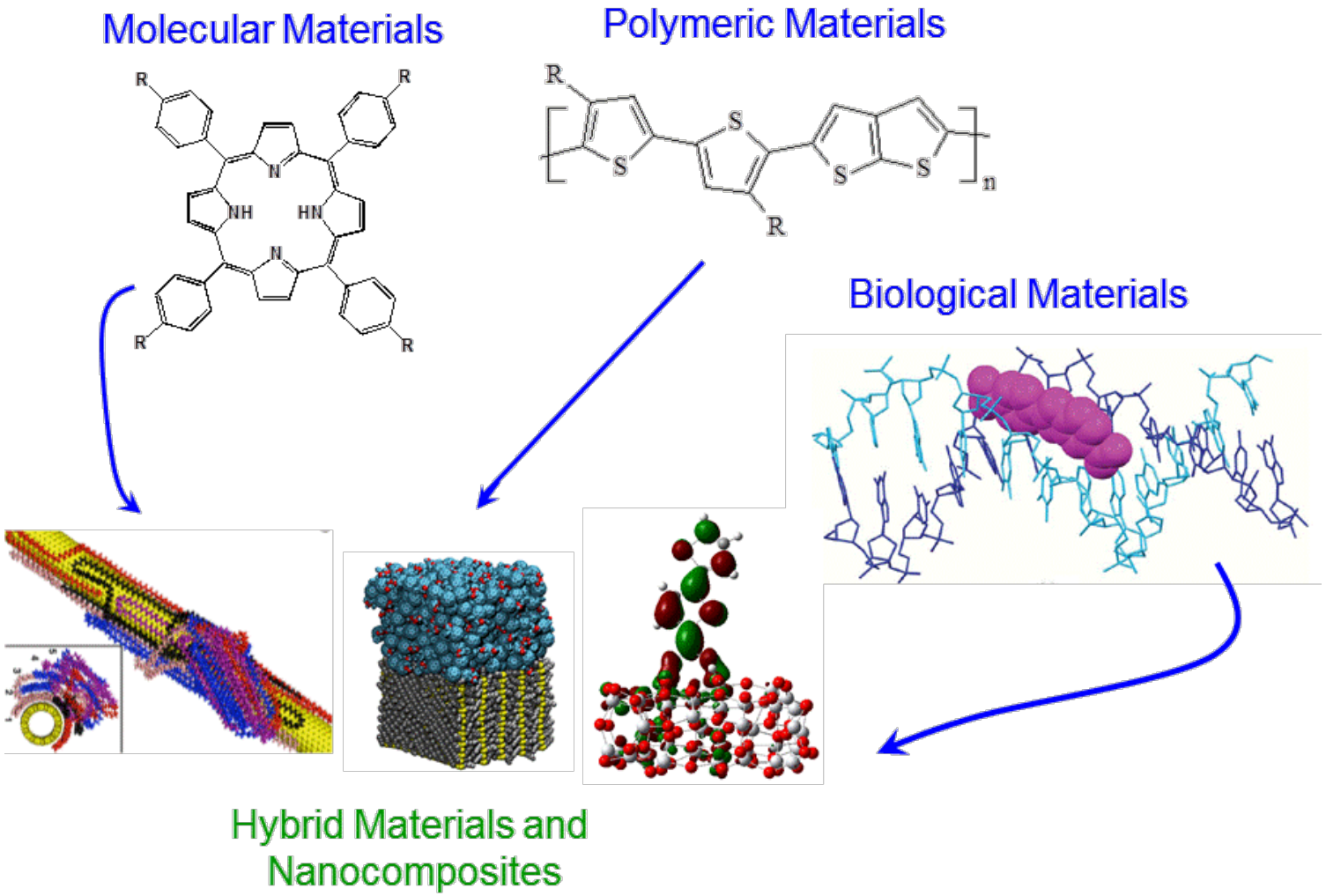
UMONS

# Group Presentation

Structural and Electronic Properties of Materials for Energy Applications



# Group Presentation

## Structure – Property Relationships

Optical properties: light absorption and emission

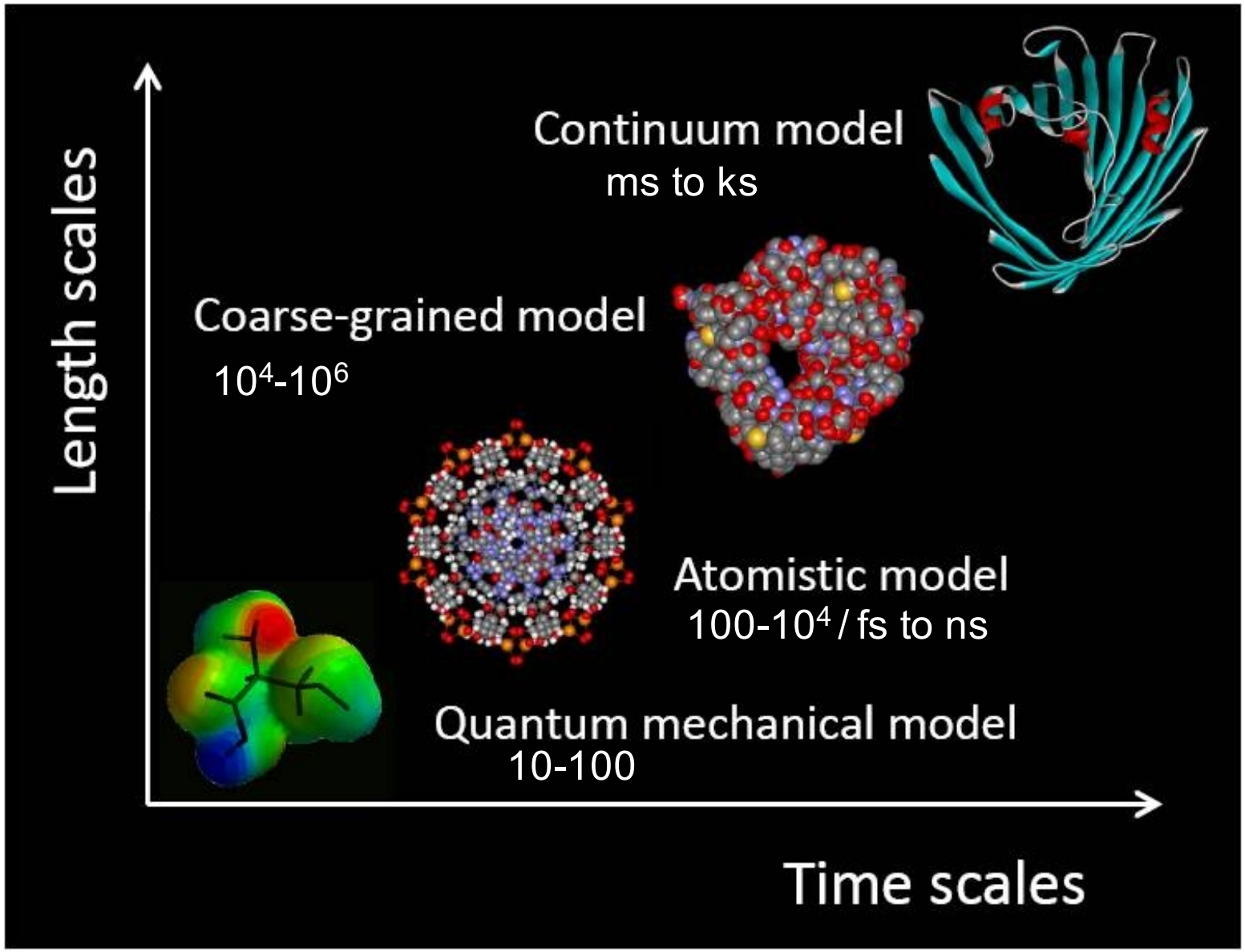
Electrical properties: generation and transport of charges (electrons / ions)

Structural properties: packing, supramolecular structures

Mechanical properties: Deformation at the nanoscale

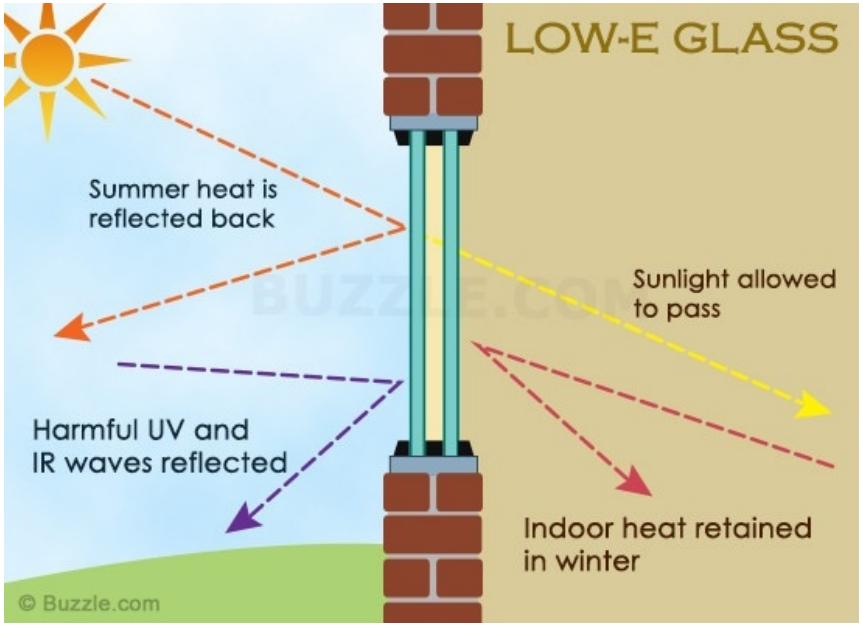
Interfacial properties: Adhesion

# Multiscale Modelling




http://www.cse.sc.edu/~heyden/Multi-ScaleModelling.html

# Low-E Glasses




- Multilayered structures
- Ag / oxide interfaces

↓

Key parameter

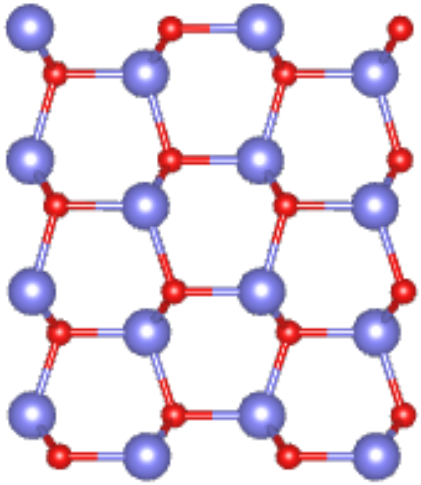
Work of adhesion

# Which Oxides ?

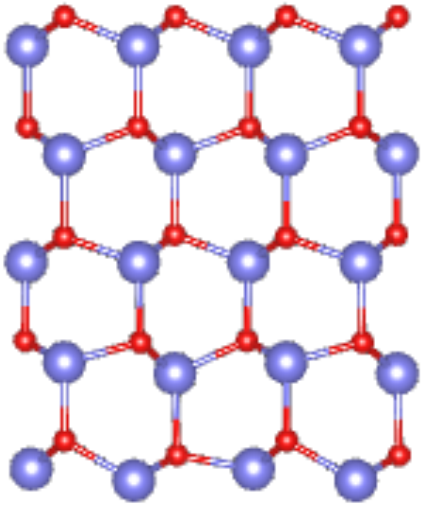
$ZnO$, $TiO_2$, $SnO_2$, $ZrO_2$

- Stable surfaces
- Polar versus non polar surfaces
- Surface termination

Non polar

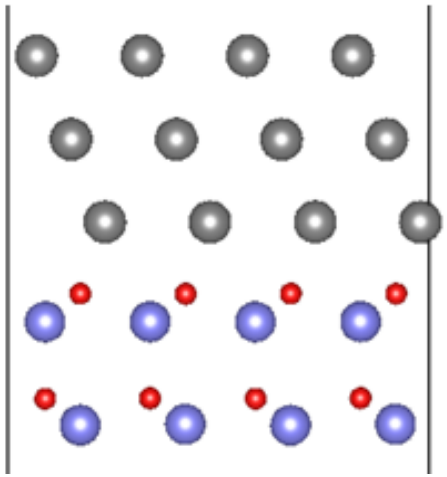


Polar



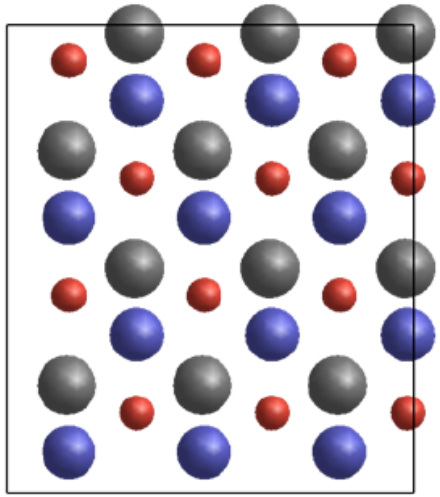
# Modelling : The Slab Approach

Side View



Unit cell

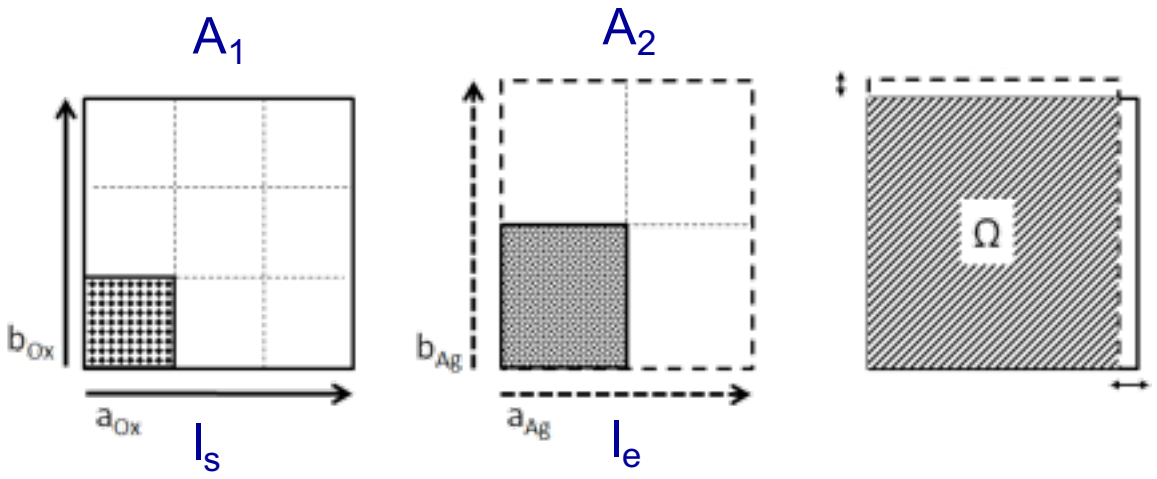
Top view



Zn 0 Ag

Density Functional Theory (DFT)

# Lattice Commensurability




Lattice misfit (M > 0)

$$M = 1 - \frac{2\Omega}{A_1 + A_2}$$

Lattice mismatch strain

$$f = \frac{l_s - l_e}{l_e}$$

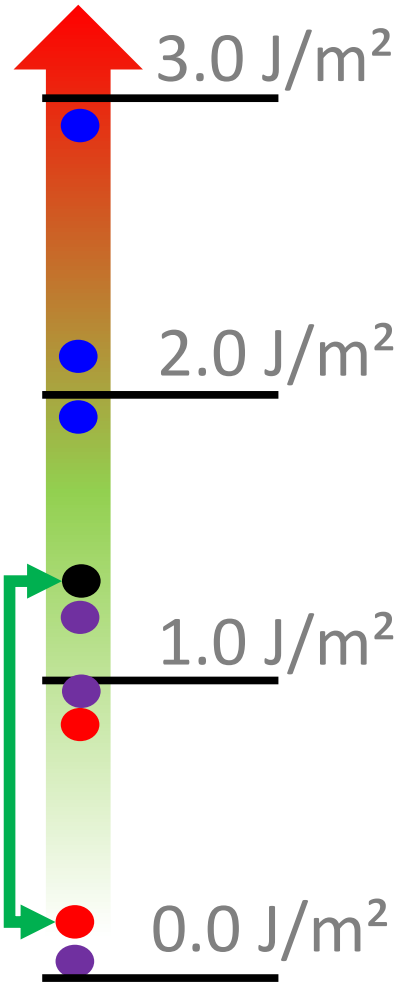
f > 0 : tensile stress

f < 0 : compressive stress

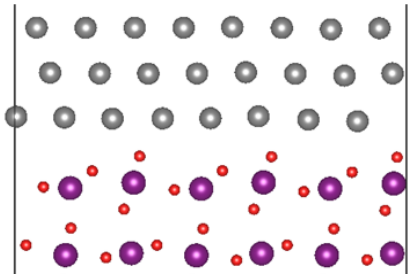
| | Interfaces | M (%) | $f_a$ (%) | $f_b$ (%) |
|---|---|---|---|---|
| | (1) ZnO(10-10) \|\| Ag(111) | 7.0 | 3.2 | 11.6 |
| P | (2) ZnO(0001)[12] \|\| Ag(111) | 11.0 | 11.7 | 11.7 |
| P | (3) ZnO(0001)[16] \|\| Ag(111) | 3.3 | -3.3 | -3.3 |
| P | (4) $TiO_2$(101) \|\| Ag(111) | 2.0 | -2.7 | 1.2 |
| P | (5) $TiO_2$(101):N \|\| Ag(111) | 2.0 | -2.7 | 1.2 |
| P | (6) $SnO_2$ (110) \|\| Ag(111) | 4.7 | 9.6 | -0.3 |
| | (7) $SnO_2$ (100) \|\| Ag(111) | 6.9 | 8.5 | -6.0 |
| | (8) $ZrO_2$ (111) \|\| Ag(111) | 6.5 | 6.7 | 6.7 |
| P | (9) $ZrO_2$ (110) \|\| Ag(111) | 2.5 | 4.5 | 0.6 |

# Work of Adhesion

$$W_{ad} = \frac{[E_{Ag} + E_{Ox}] - E_{Ag/Ox}}{A}$$




$SnO_2$ rough



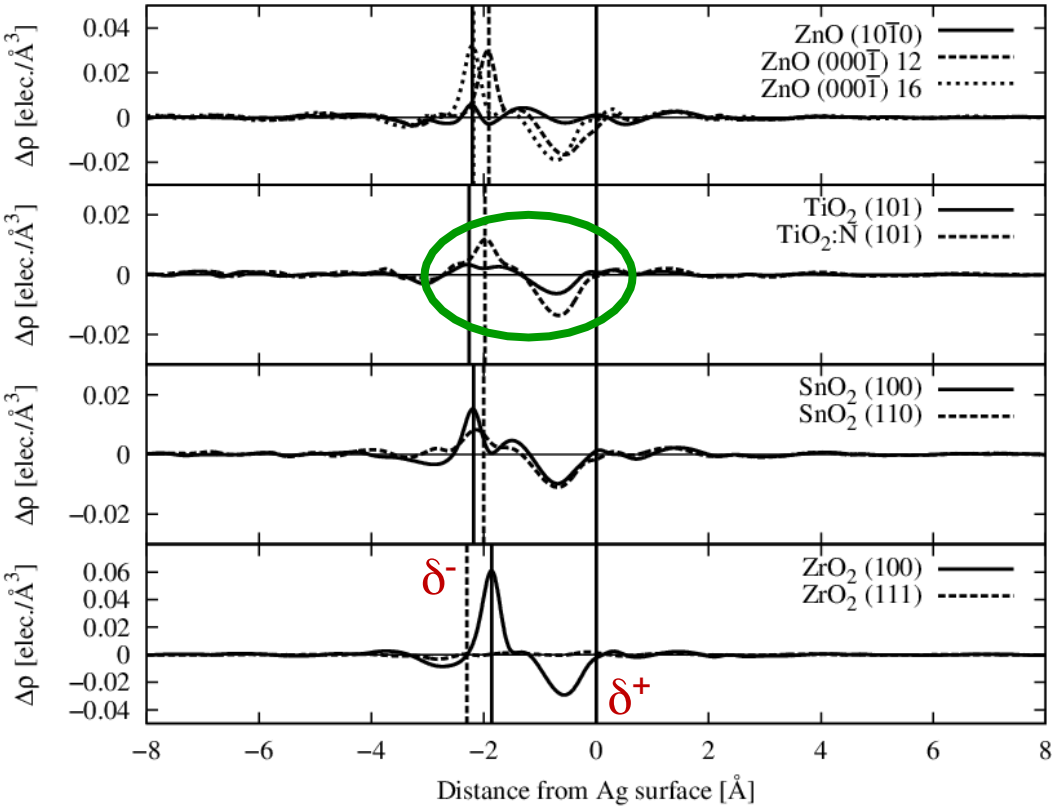
| Interface | Nature of the oxide | Wsep [J/m²] |
|---|---|---|
| (1) ZnO(10-10)/Ag(111) | Non polar | 0.959 |
| (2) ZnO(000-1)/Ag(111)-12 | Polar | 2.086 |
| (3) ZnO(000-1)/Ag(111)-16 | Polar | 1.956 |
| (4) TiO2(101)/Ag(111) | « Rough » | 0.159 |
| (5) TiO2(101):N/Ag(111) | Doped | 1.364 |
| (6) SnO2(110)/Ag(111) | « Rough » | 0.862 |
| (7) SnO2(100)/Ag(111) | Non polar | 1.201 |
| (8) ZrO2(111)/Ag(111) | Non polar | 0.060 |
| (9) ZrO2(100)/Ag(111) | Polar | 2.876 |

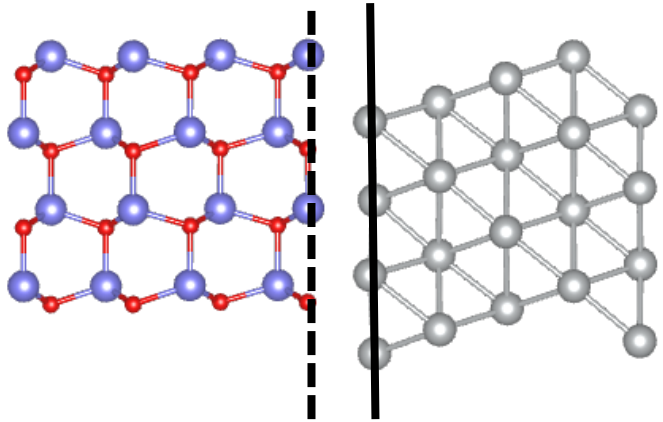
Doping ratio ~ 5% : oxygens substituted by nitrogens

# Interfacial Charge Transfer

Charge reorganization

$$\Delta\rho = \rho_{int} - \left(\rho_{Ag} + \rho_{M-Ox}\right)$$



Variation in the amplitude of the charge transfer

# Interfacial Charge Transfer

| Interface | Nature of the oxide | Wsep [J/m²] | qAg |
|---|---|---|---|
| (1) ZnO(10-10)/Ag(111) | Non polar | 0.959 | 0.022 |
| (2) ZnO(000-1)/Ag(111)-12 | Polar | 2.086 | 0.239 |
| (3) ZnO(000-1)/Ag(111)-16 | Polar | 1.956 | 0.145 |
| (4) $TiO_2$(101)/Ag(111) | « Rough » | 0.159 | 0.053 |
| (5) $TiO_2$(101):N/Ag(111) | Doped | 1.364 | 0.126 |
| (6) $SnO_2$(110)/Ag(111) | « Rough » | 0.862 | 0.117 |
| (7) $SnO_2$(100)/Ag(111) | Non polar | 1.201 | 0.077 |
| (8) $ZrO_2$(111)/Ag(111) | Non polar | 0.060 | -0.044 |
| (9) $ZrO_2$(100)/Ag(111) | Polar | 2.876 | 0.299 |

- Large charge transfer for the polar surfaces
- N doping increases the charge transfer
- Small charge transfer for ZnO (10-10)
- Anticorrelation for $SnO_2$

# Bonding Character

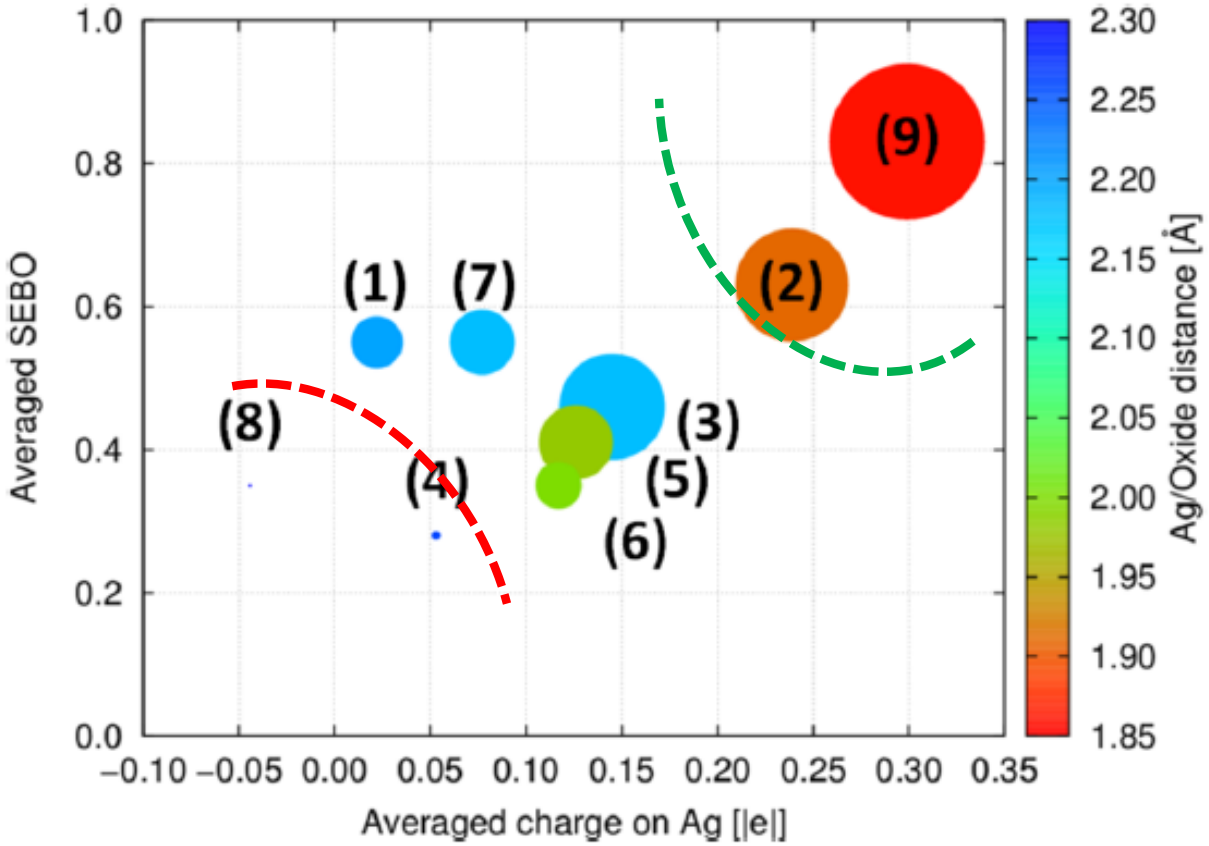
Effective bond order

$$\langle EBO \rangle = \frac{1}{N} \sum_{1st\ layer} EBO(Ag-O) + EBO(Ag-M)$$

| Interface | SEBO |
|---|---|
| (1) ZnO(10-10)/Ag(111) | 0.55 |
| (2) ZnO(000-1)/Ag(111)-12 | 0.63 |
| (3) ZnO(000-1)/Ag(111)-16 | 0.46 |
| (4) $TiO_2$(101)/Ag(111) | 0.28 |
| (5) $TiO_2$(101):N/Ag(111) | 0.41 |
| (6) $SnO_2$(110)/Ag(111) | 0.35 |
| (7) $SnO_2$(100)/Ag(111) | 0.55 |
| (8) $ZrO_2$(111)/Ag(111) | 0.35 |
| (9) $ZrO_2$(100)/Ag(111) | 0.83 |

Strong variations from 0.28 to 0.80 !

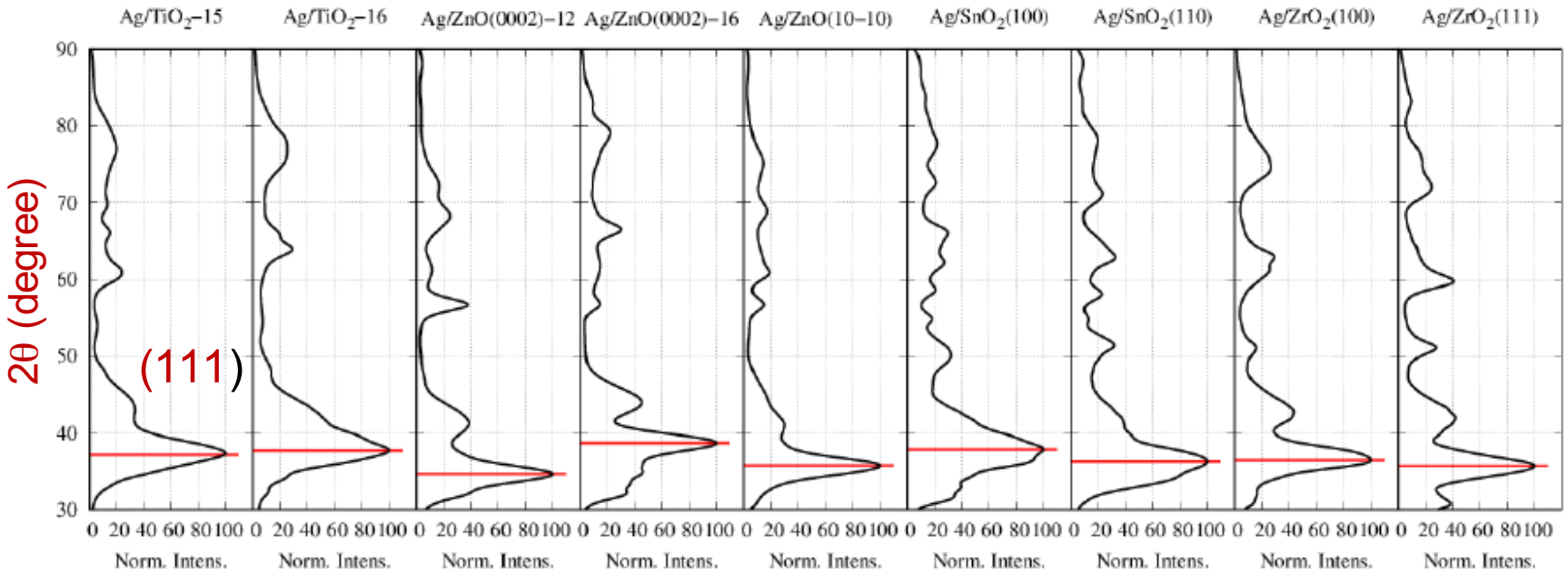
# Two-Dimensional Plot

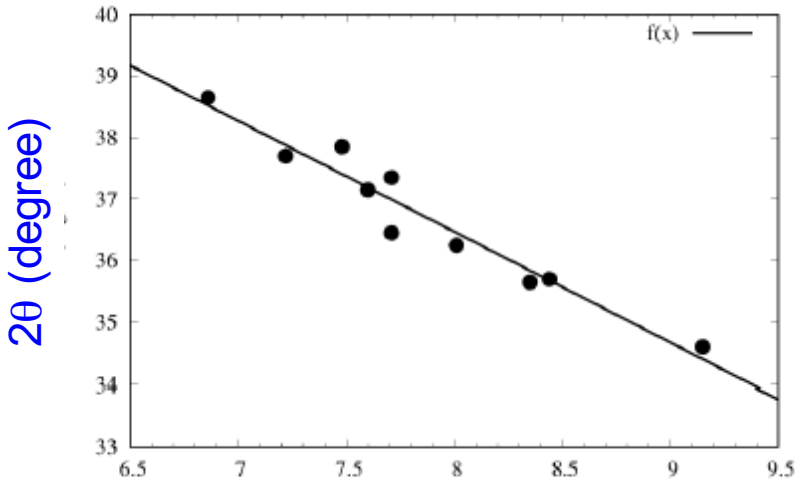



| Interface |
|---|
| (1) ZnO(10-10)/Ag(111) |
| (2) ZnO(000-1)/Ag(111)-12 |
| (3) ZnO(000-1)/Ag(111)-16 |
| (4) $TiO_2$(101)/Ag(111) |
| (5) $TiO_2$(101):N/Ag(111) |
| (6) $SnO_2$(110)/Ag(111) |
| (7) $SnO_2$(100)/Ag(111) |
| (8) $ZrO_2$(111)/Ag(111) |
| (9) $ZrO_2$(100)/Ag(111) |

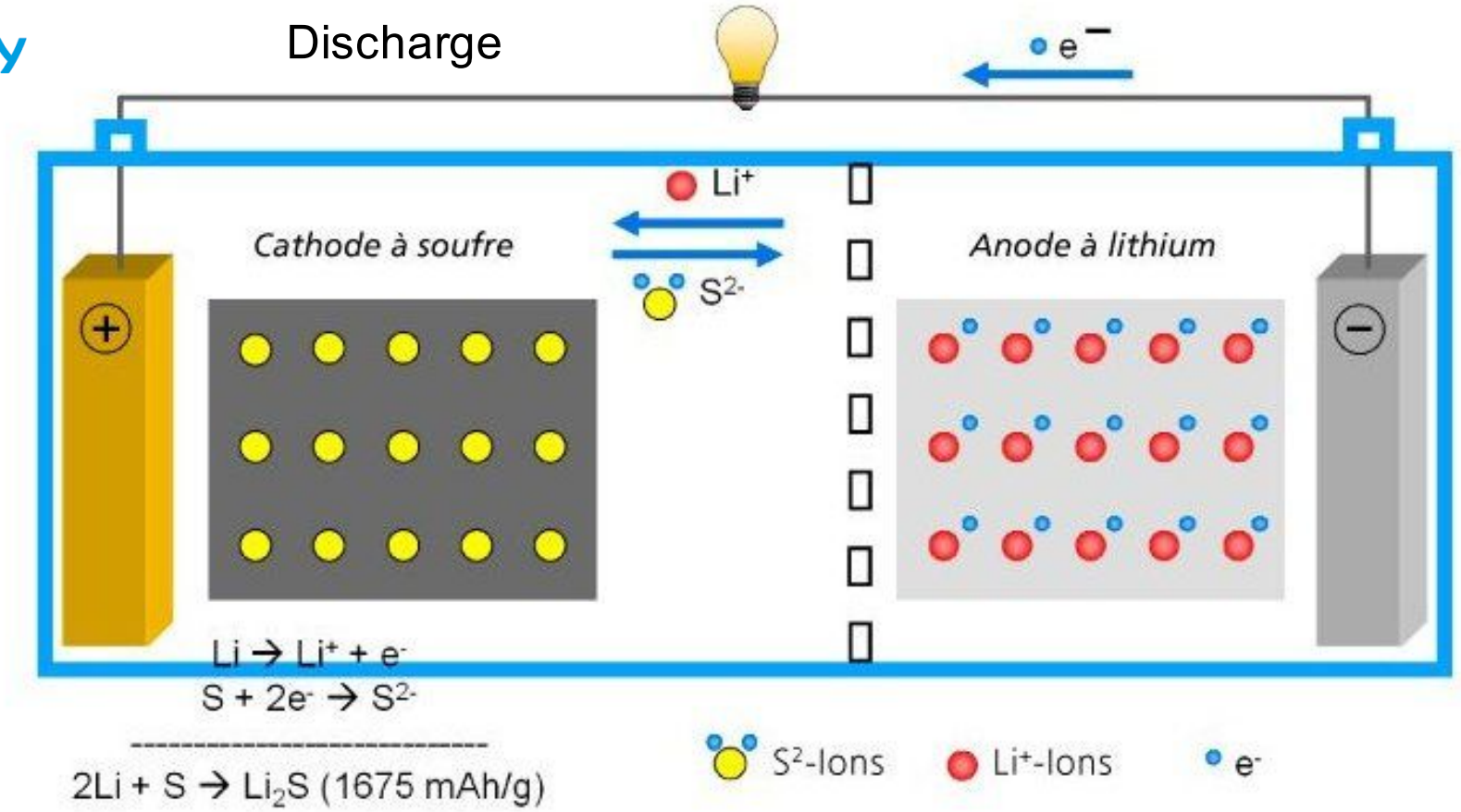
*D. Cornil et al., ACS Applied Materials & Interfaces 9, 18346-18354 (2017)*

# X-Ray Diffraction Spectra



# Lithium – Sulfur Batteries




Drawbacks : - Solubilisation of PS (destructuration of the cathode)

- Diffusion of PS → Chemical corrosion of the Li electrode

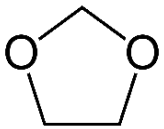
- Precipitation of $Li_2S$ → Passivation of the electrodes

# Lithium Ion Diffusion

Hopping – Structure Diffusion Mechanism

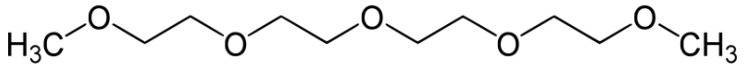
Vehicular mechanism

Solvents



Dioxolane (DOL)

TEGDME

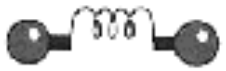


# Force Field Calculations

- Systems described as balls connected by sticks

- No absolute values

$$V = \sum \frac{1}{2}k(r - r_0)^2 + \sum \frac{1}{2}k_\theta(\theta - \theta_0)^2$$



Stretching

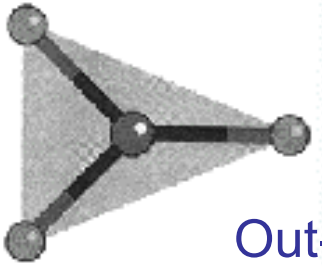
Bending

Fourier series

$+\sum$

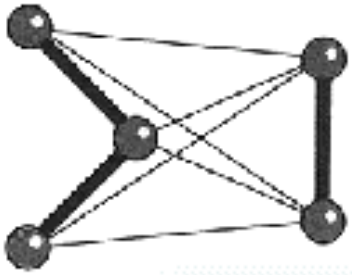
Torsions

$+\sum$



Out-of-plane

$+\sum$



Lennard – Jones potential

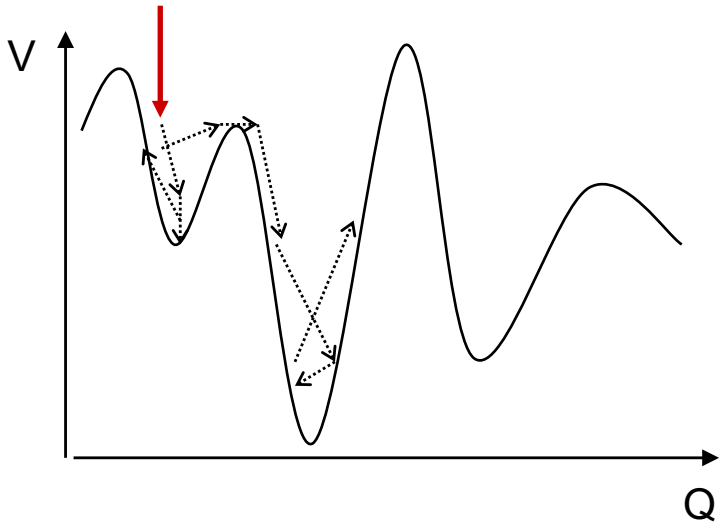
$$\sum_i \sum_j \left( \frac{A_{ij}}{r^{12}} - \frac{B_{ij}}{r^6} \right)$$


H-bonds

Non bonded interactions
(van der Waals, Coulombic)

$$\sum_i \sum_j \frac{1}{4\pi\varepsilon_0} \frac{Q_i Q_j}{r_{ij}}$$

# Molecular Dynamics




Lagrange equations $\frac{d}{dt}\frac{\partial L}{\partial \dot{r}} - \frac{\partial L}{\partial r} = 0$

L = Lagrangian = K - V

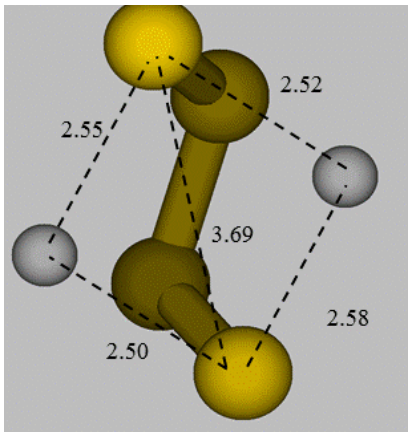
$K = \sum_i \frac{1}{2} m_i v_i^2 = \frac{3}{2} N\, k\, T$

No analytical solutions → Time discretization (time step ~ fs)

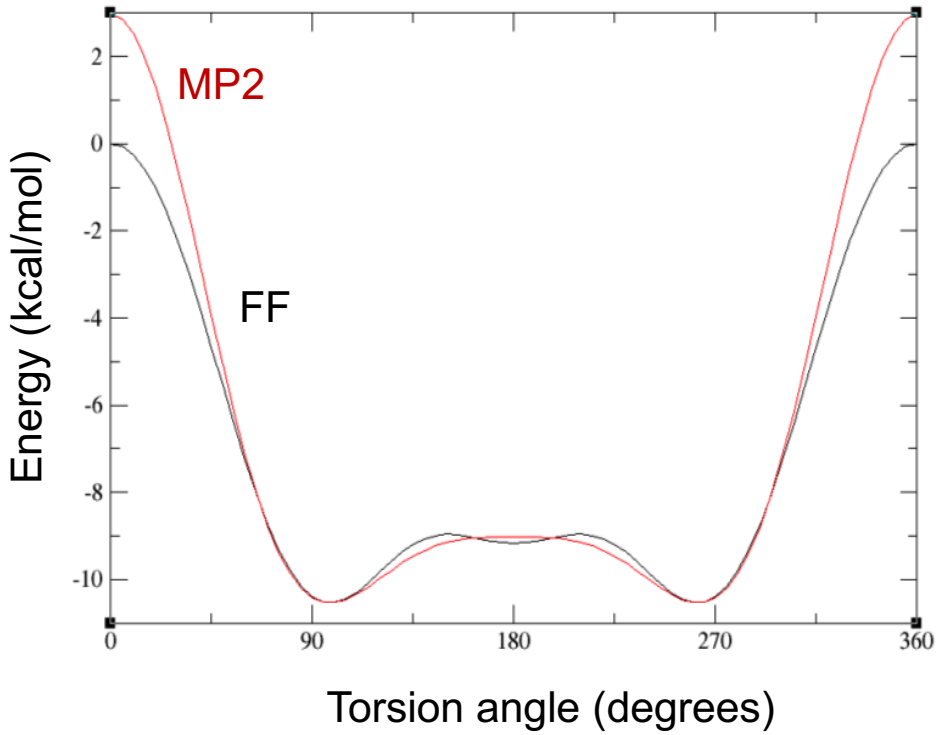
$$\begin{array}{ccccc} R_i & & R_t & & R_t \\ V_i & \rightarrow & V_t & \rightarrow & V_t \\ t = 0 & & t = \Delta t & & t = 2\Delta t \end{array}$$

→ Trajectory

# Reparameterization : Torsional Terms




- Equilibrium values and force constants estimated from MP2 calculations



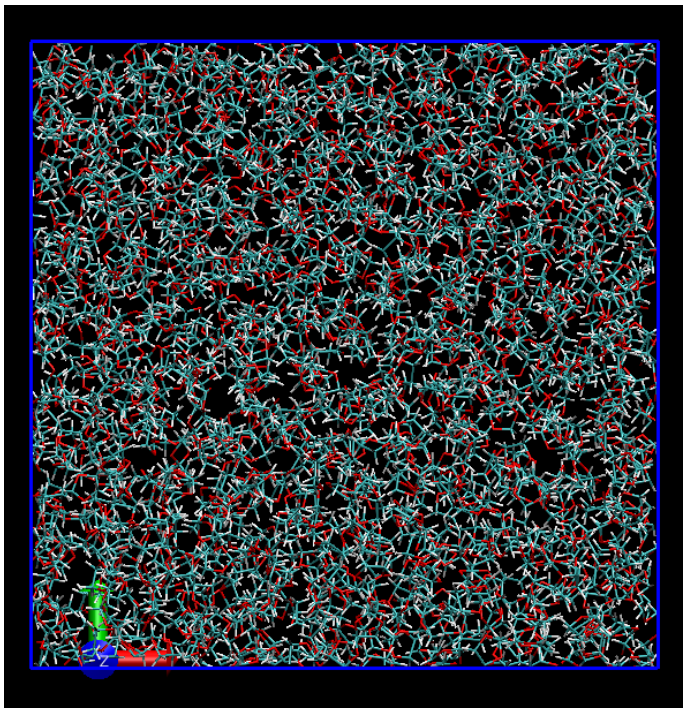

Coulomb term

$$\sum_i \sum_j \frac{1}{4\pi\varepsilon_0} \frac{Q_i Q_j}{\varepsilon_{\text{eff}} r_{ij}}$$

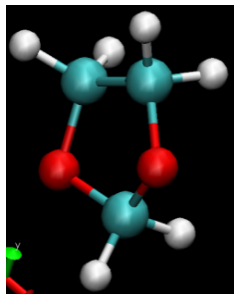
- Static atomic charges from MP2 calculations
- Electronic polarization effects: $\varepsilon_{\text{eff}}$

# Dioxolane

NPT, RT, 20 ns



1000 dioxolane molecules



## Hildebrand parameter

$$\delta = \underbrace{[(\Delta H_v - RT)/V_m]}^{1/2}$$

Cohesive Energy Density

$$\Delta H_v = \left\langle E_{cell} - \sum_{i=1}^{n} E_i \right\rangle_p$$

Enthalpy of vaporization

FF : $\delta$ = 17.42 $MPa^{1/2}$

Exp : $\delta$ = 22.07 / 21.8 $MPa^{1/2}$

## Density

| $\rho$ (MD, g/cm$^3$) | $\rho$ (exp, g/cm$^3$) |
|---|---|
| 0.97 | 1.06 |

$\delta\rho$ = 8%

## Diffusion constant – Einstein relation

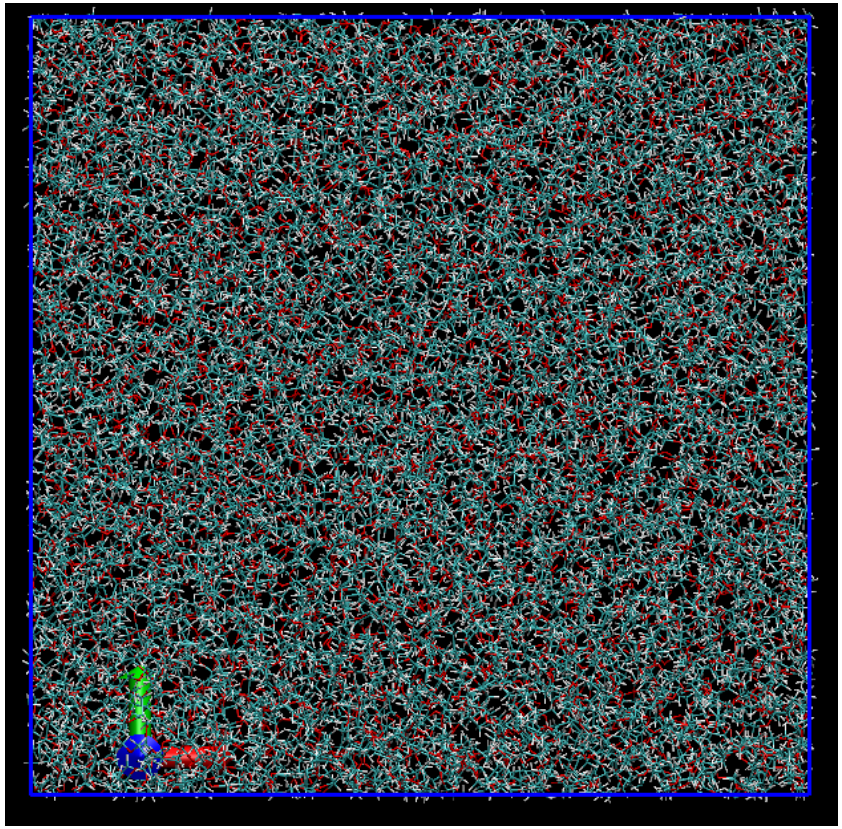
$$D = \lim_{t\to\infty} \frac{< R^2(t) >}{6\,t}$$

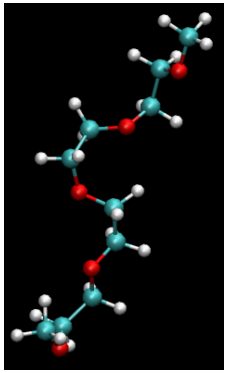
FF : D = 33.1 $10^{-10}$ $m^2/s$

Exp : D = 23.5 $10^{-10}$ $m^2/s$

# TEGDME

NPT, RT, 80 ns





Size = 7.20 * 7.20 * 7.20 $nm^3$

980 TEGDME molecules

## Density

| $\rho$ (MD, $g/cm^3$) | $\rho$ (exp, $g/cm^3$) |
|---|---|
| 0.978 | 1.009 |

$\delta\rho$ = 3%

## Diffusion constant

FF : D = 1.5 $10^{-10}$ $m^2/s$

Exp : D = 3.25 $10^{-10}$ $m^2/s$

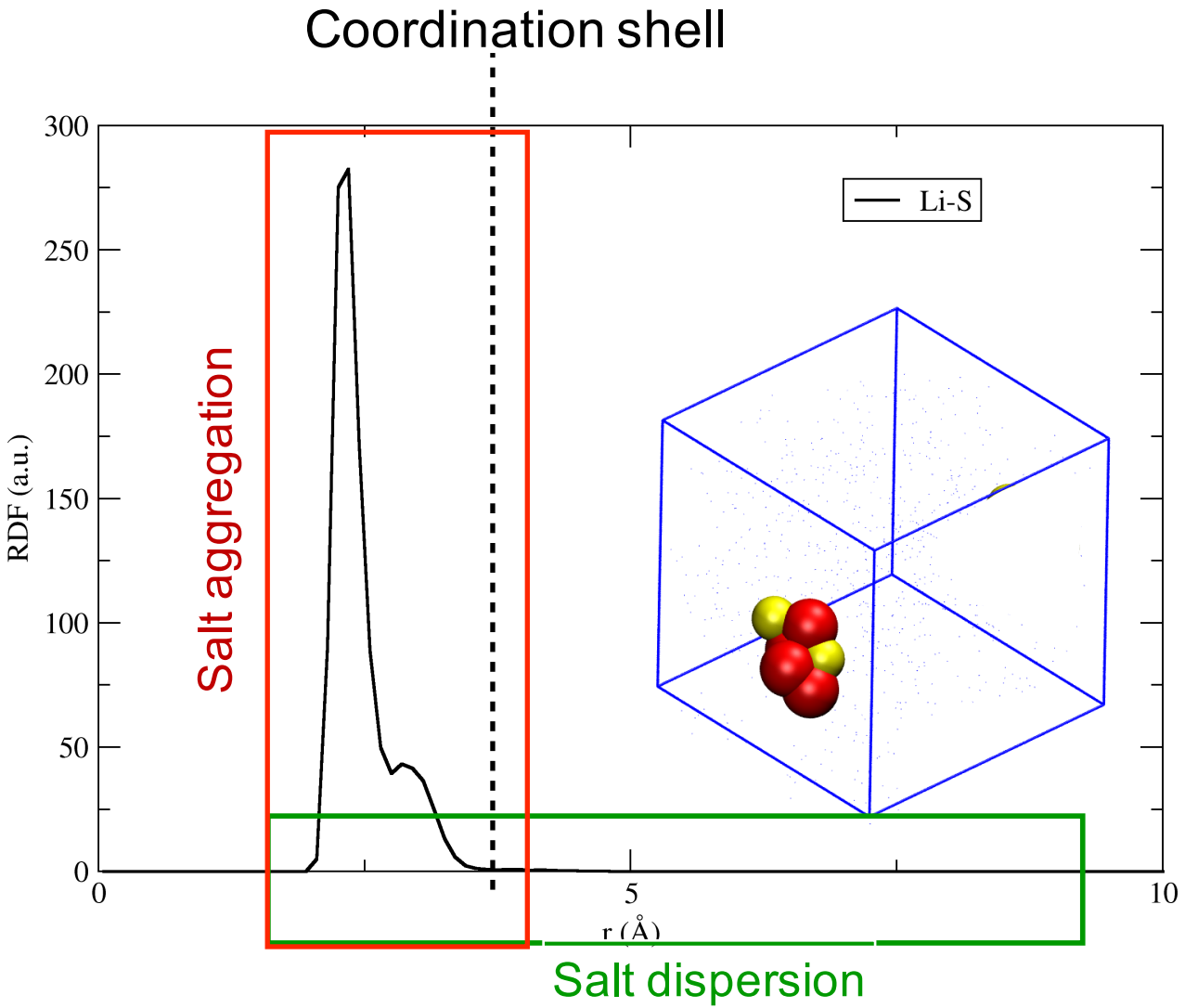
$D_{TEDGME} < D_{dioxolane}$

Coiling of the TEDGME molecules

Full length : 14.1 Å

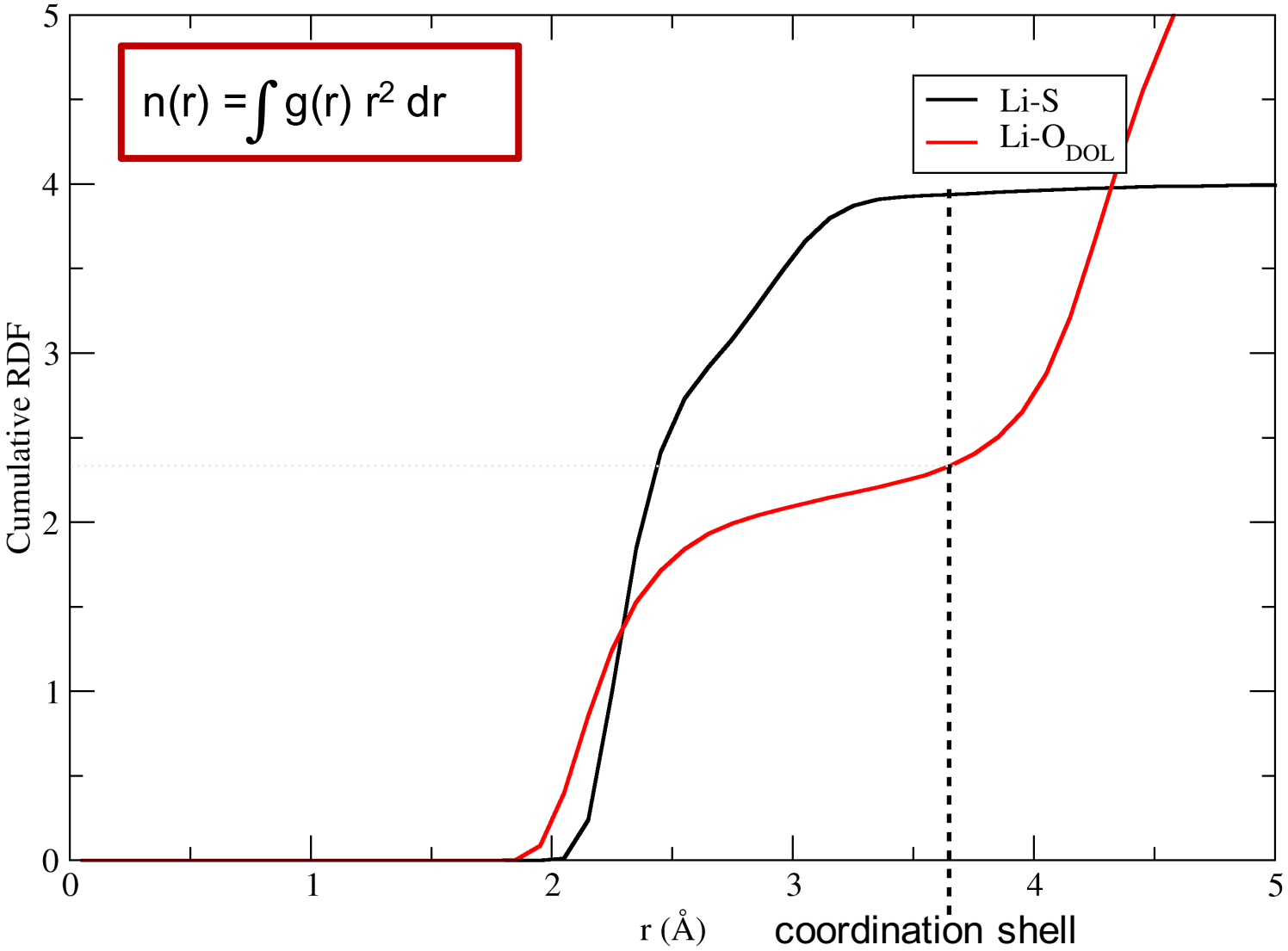
Average length : 11.2 Å

# $Li_2S4$ in Dioxolane




First coordination shell : 3.75 Å

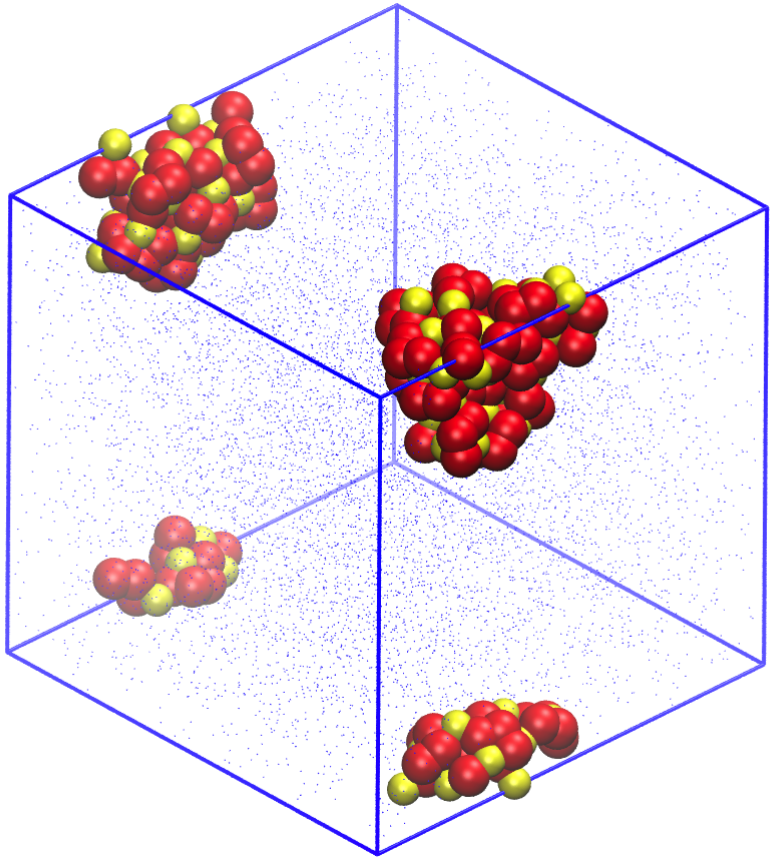
# $Li_2S4$ in Dioxolane



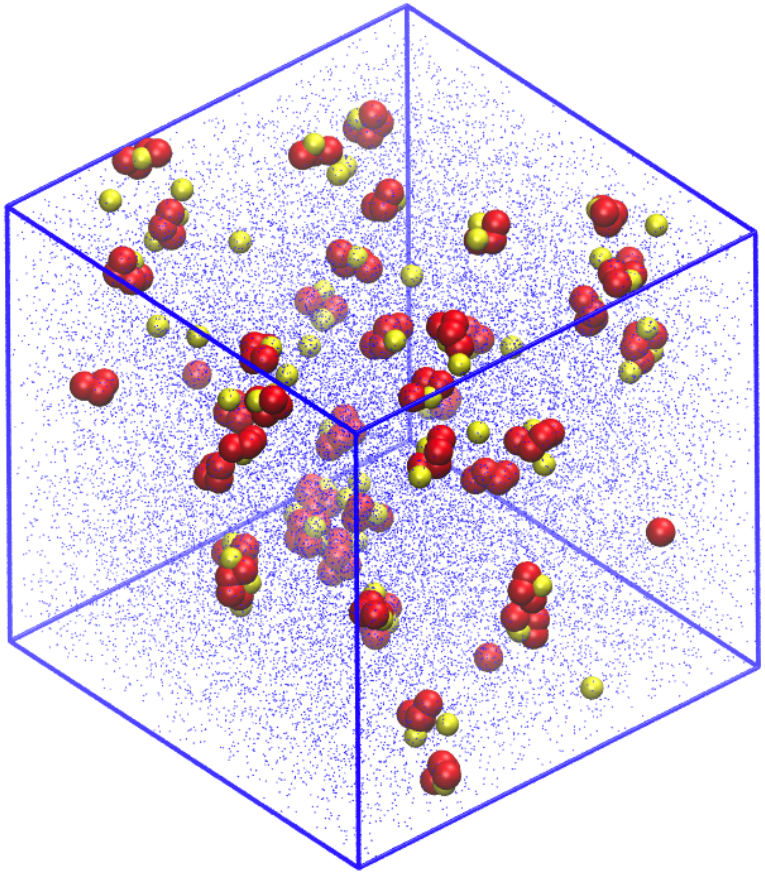

First coordination shell : 0.9 Li, 4 S, 2.4 $O_{dol}$

# $Li_2S4$ in Dioxolane versus TEGDME

**DOL**

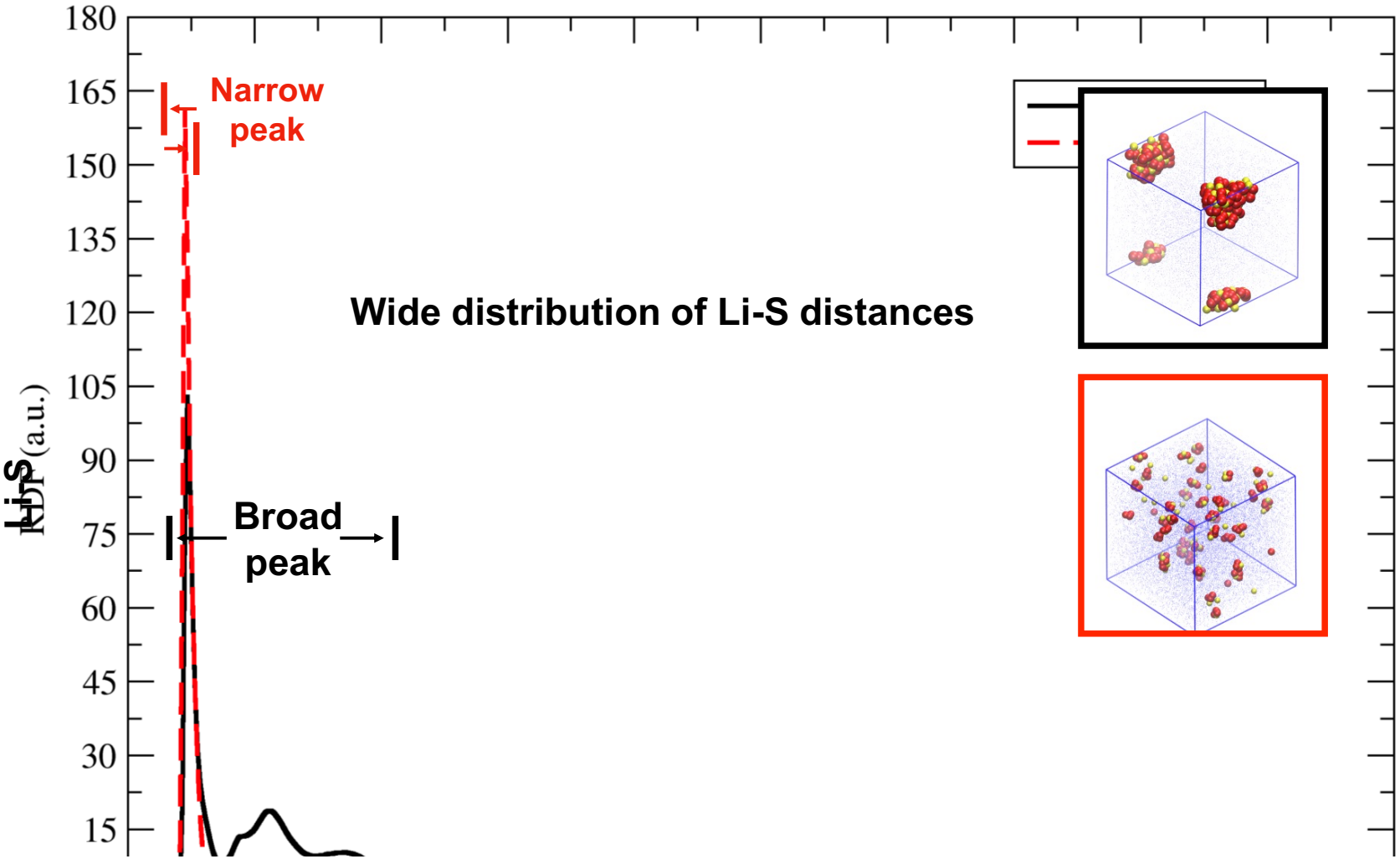


**TEGDME**

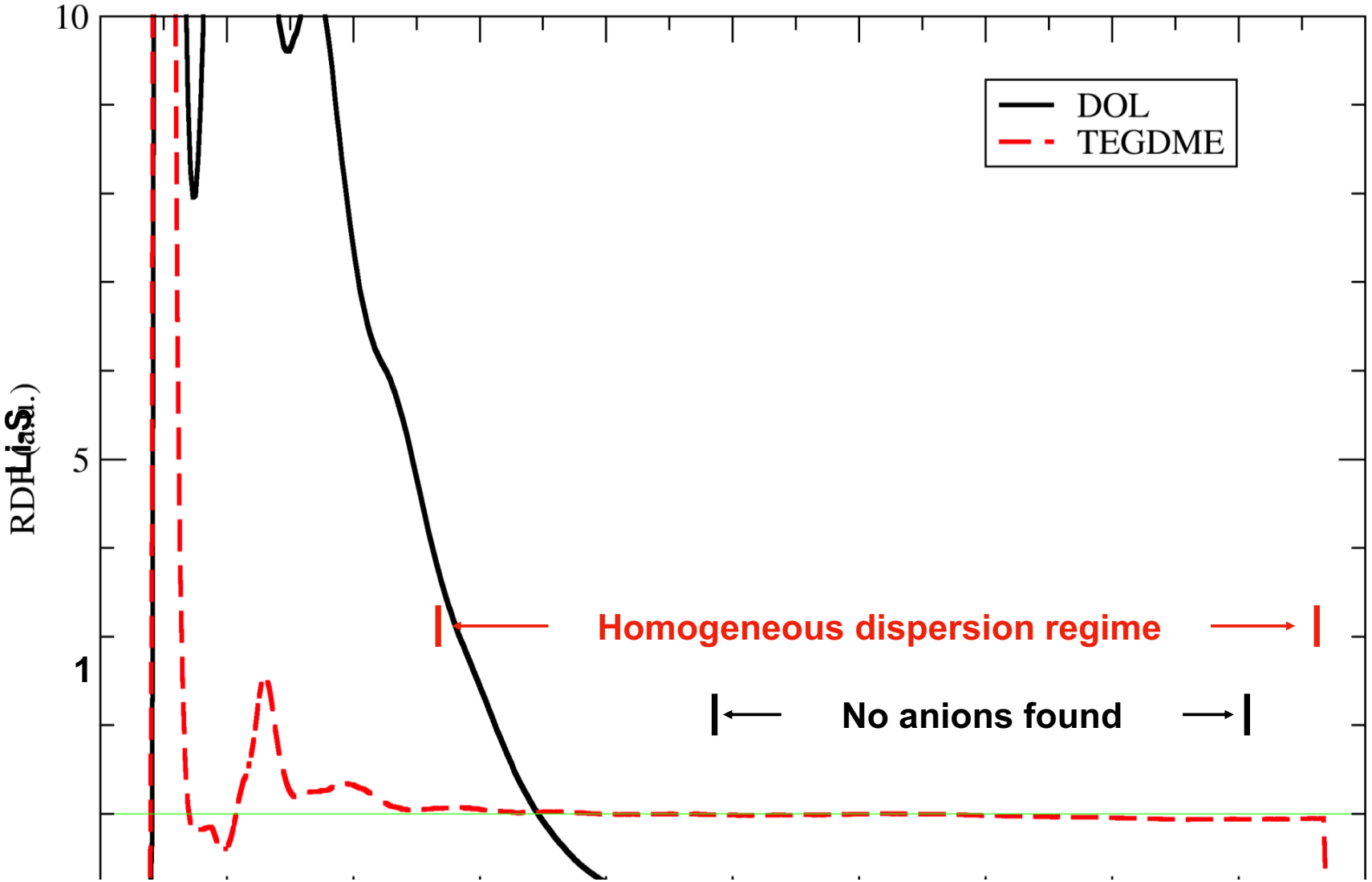


Ratio salt / solvent = 1 /20

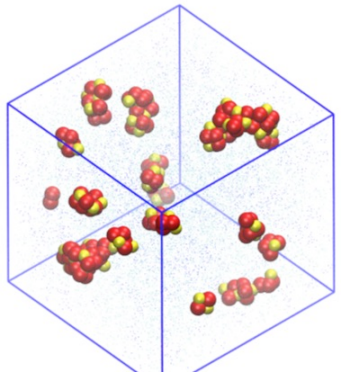
# $Li_2S4$ in Dioxolane versus TEGDME

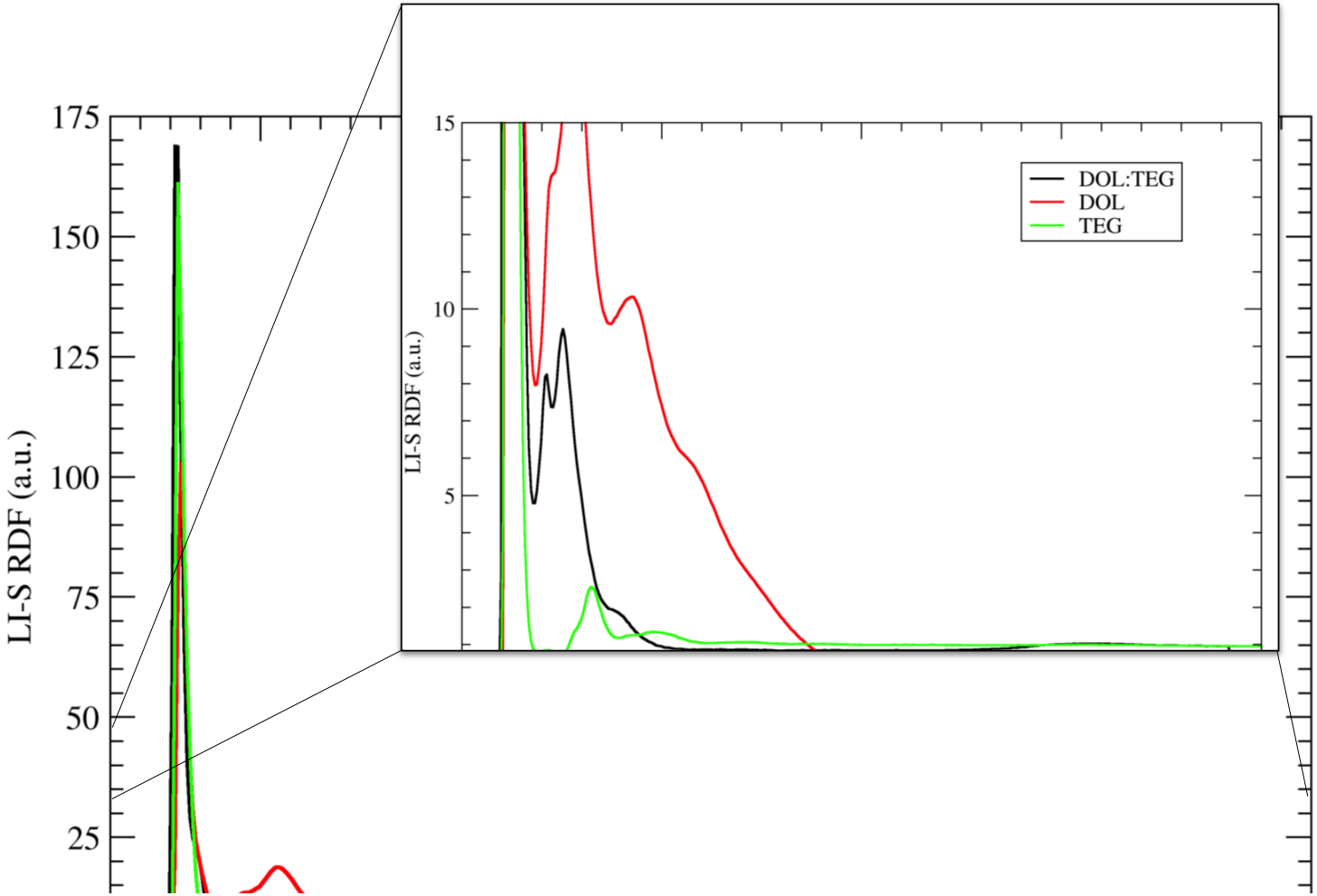


# $Li_2S4$ in Dioxolane versus TEGDME



# $Li_2S4$ in Dioxolane AND TEGDME





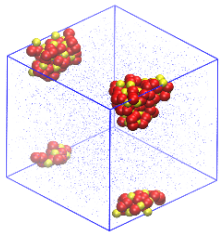

Intermediate behavior in mixed solvents

# Transport Mechanism

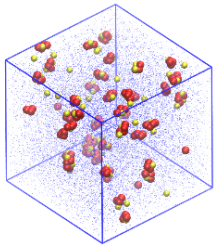
$$\alpha = \frac{\lambda}{\lambda_{uncorr}} = \lim_{t\to\infty} \alpha(t) = \lim_{t\to\infty} \frac{\lambda^{app}(t)}{\lambda^{app}_{uncorr}(t)}$$

$\alpha = 0$ Vehicular mechanism

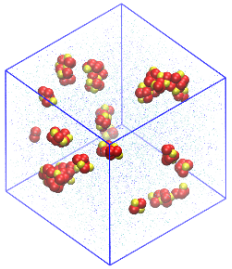
$\alpha = 1$ Hopping mechanism



$Li_2S_4$ in DOL



$Li_2S_4$ in TEGDME



$Li_2S_4$ in DOL / TEGDME

| Diffusion $Li^+$ ($*10^{-10}$ $m^2/s$) | Diffusion $A^-$ ($*10^{-10}$ $m^2/s$) | α | Dominant Mechanism |
|---|---|---|---|
| 3 | 3 | 0.49 | Mixed |
| 0.5 | 0.5 | 0.61 | Hopping |
| 0.4 | 0.4 | 0.53 | Mixed |

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