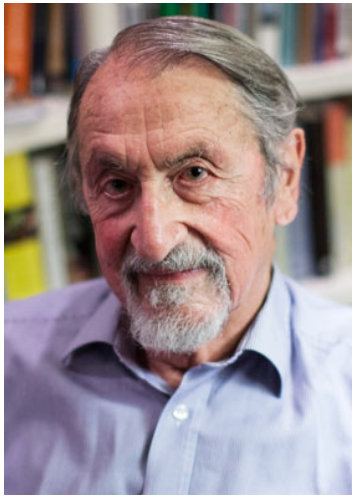
Molecular dynamics simulations of molten salts for MSFR

C. Simon

INP Orsay – EVOL – november 2013

UPMC SORBONNE UNIVERSITÉS

Nobel prize for Molecular Dynamics



M. Karplus

M. Levitt

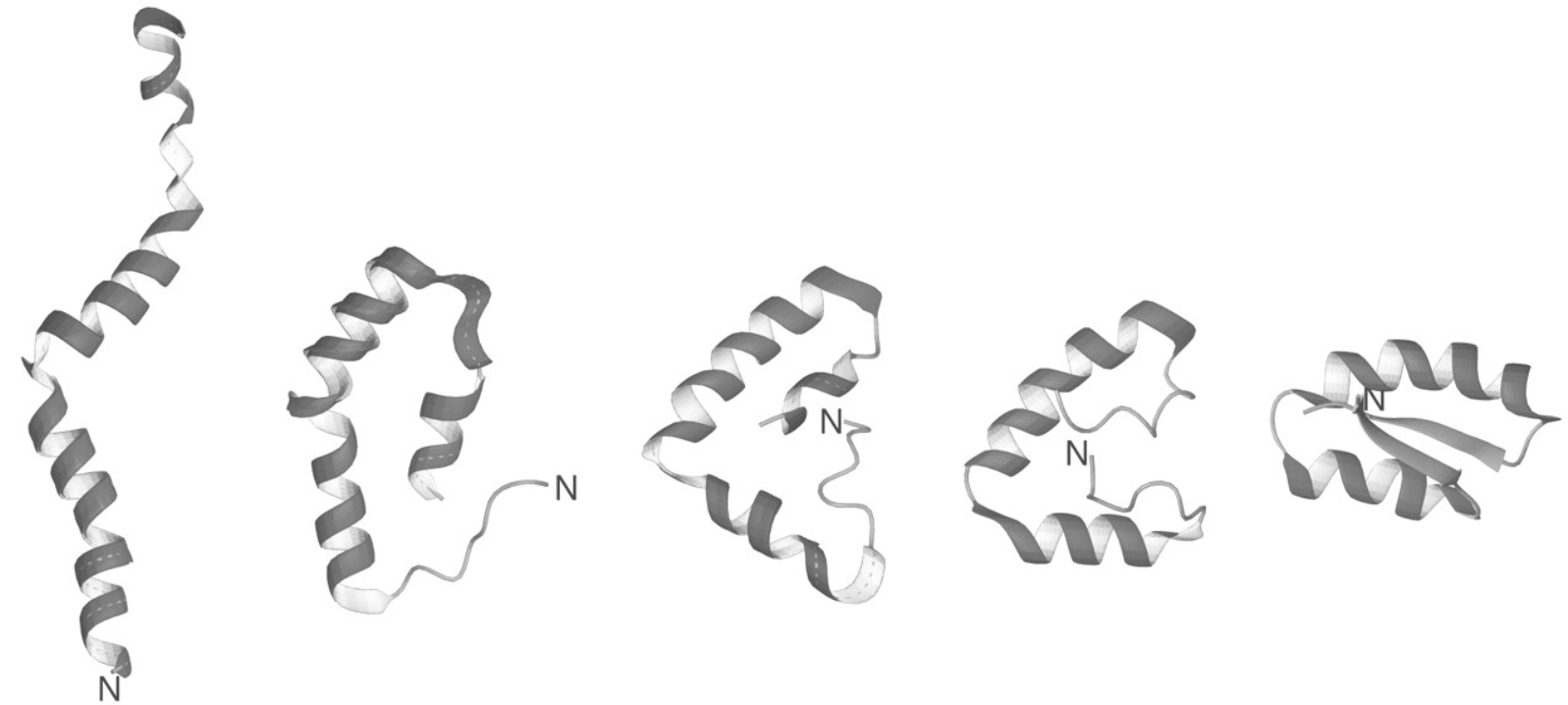
A. Warshel

Prize motivation:
"for the development of multiscale models for complex chemical systems"

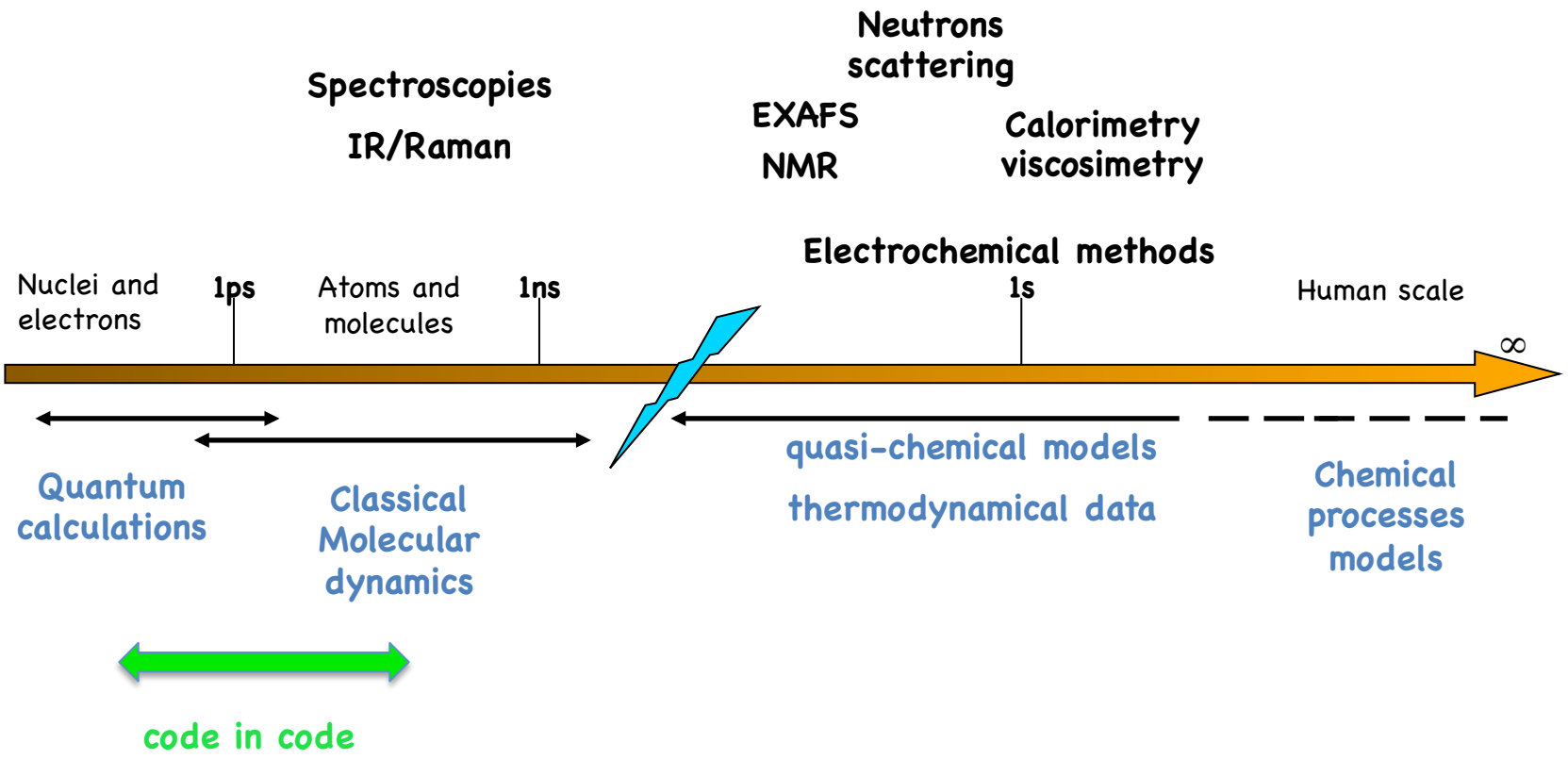
Application to biological systems

Prize motivation:

"for the development of multiscale models for complex chemical systems"



What are multiscale models ?



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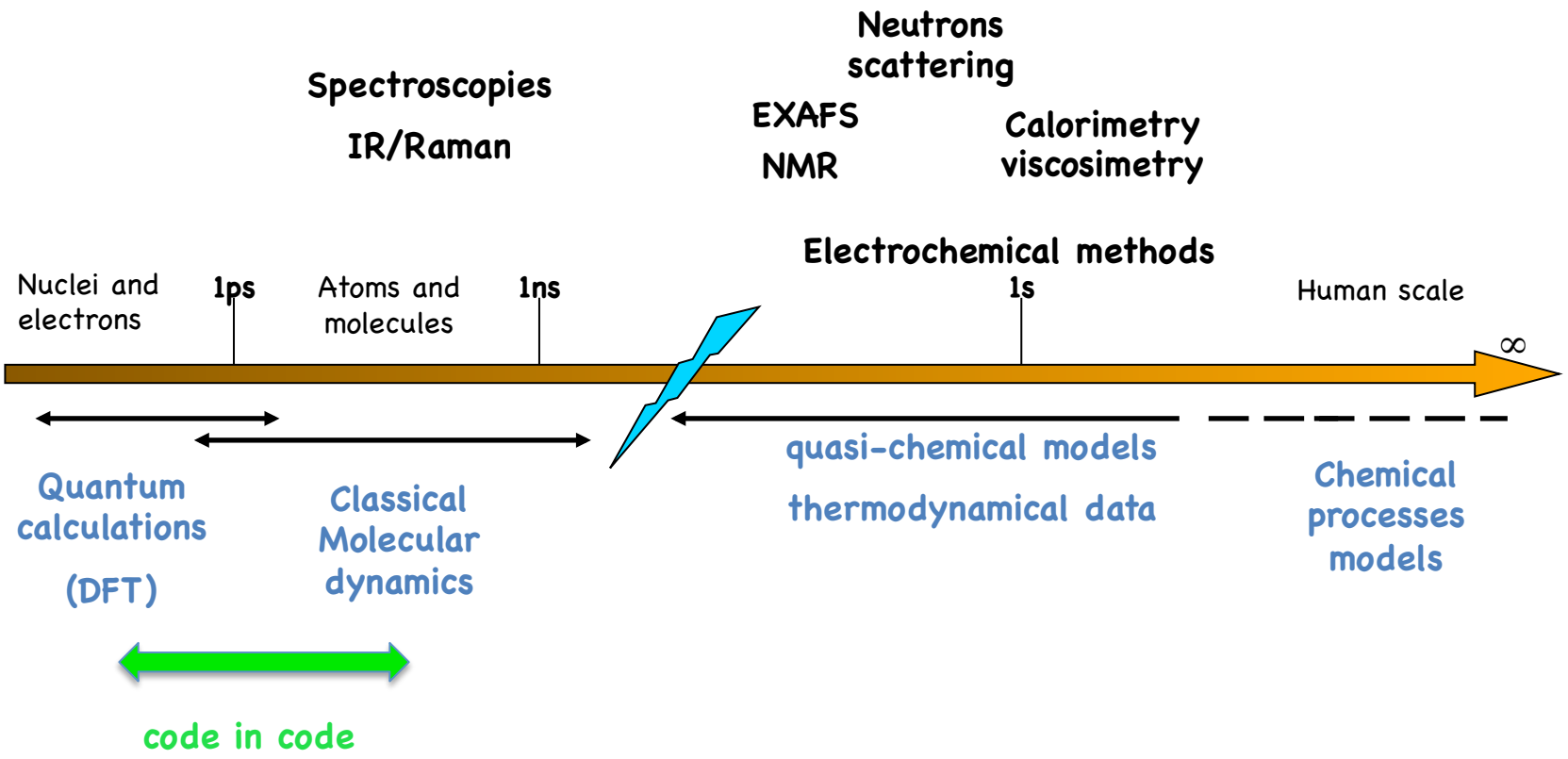
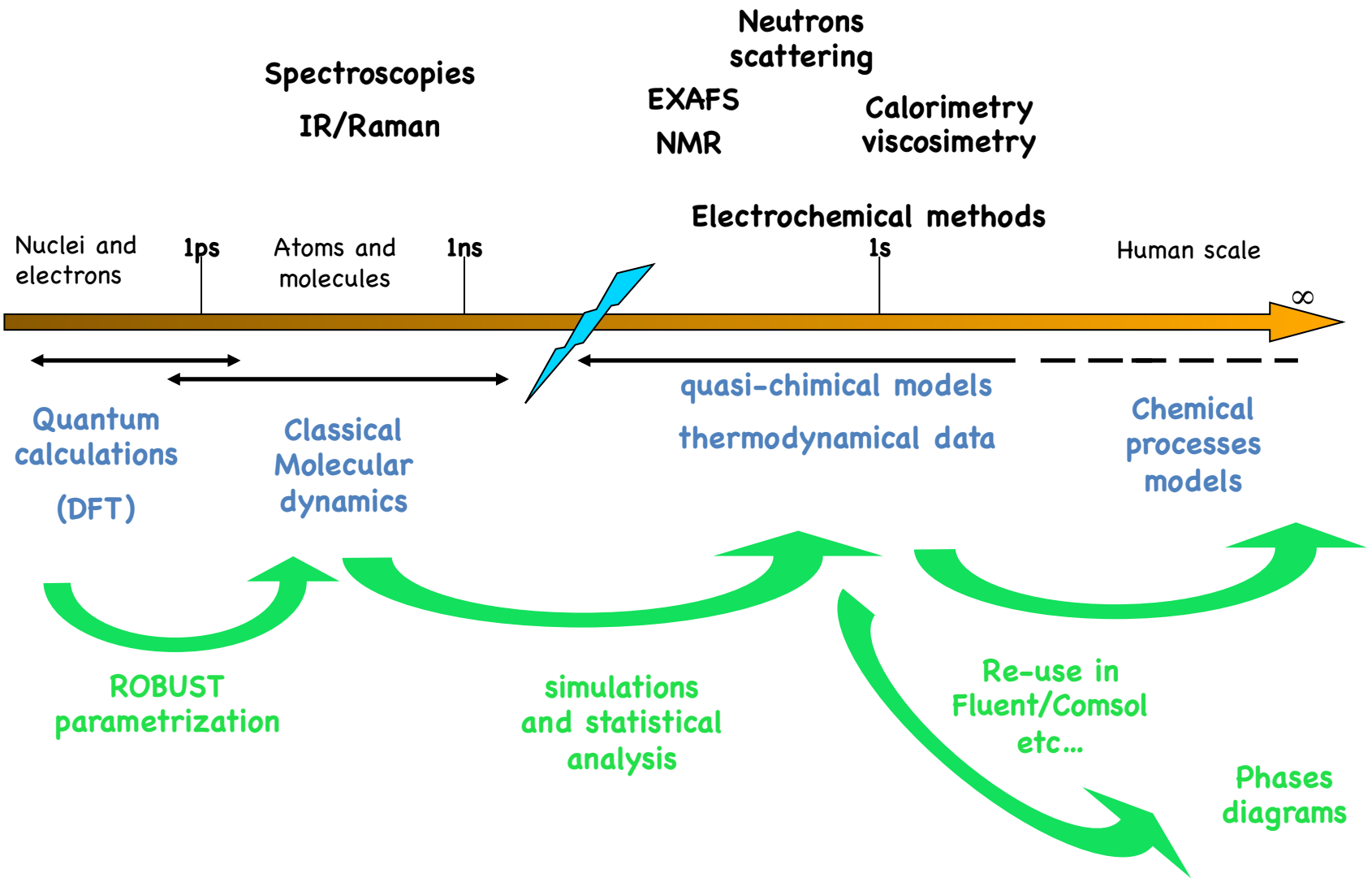
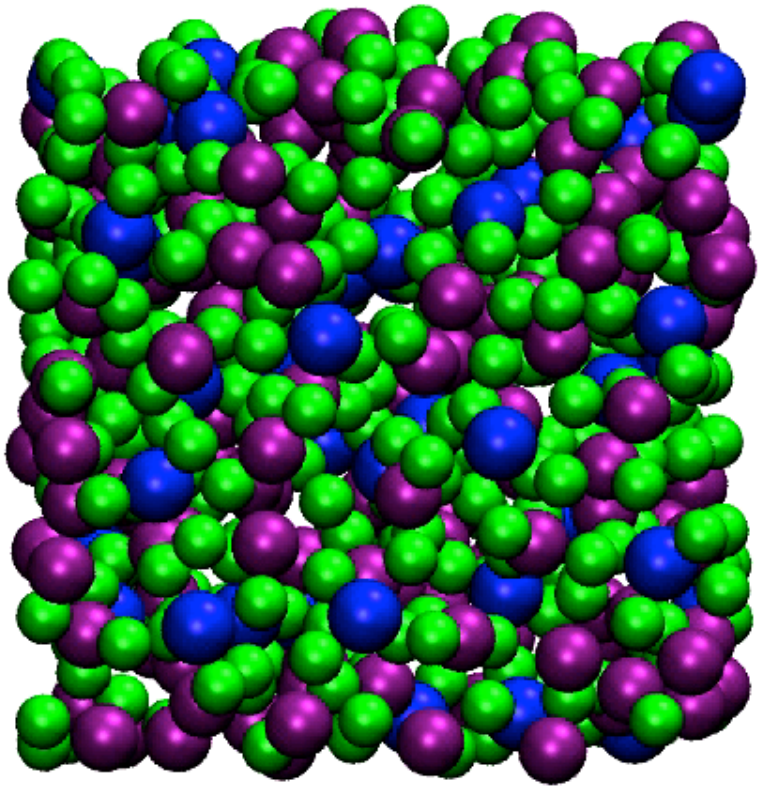


What are multiscale models ? Alternative approach



Molten salt simulation example



$LiF-ThF_4$

973 K - 1 ns

550 ions

How Molecular Dynamics works

Newtonian formulation :

$$f_i = -\frac{\partial V(q_i)}{\partial q_i} = \dot{p}_i = m_i \frac{\mathrm{d}^2 q_i}{\mathrm{d}t^2}$$

Idea to solve: limited development and iterative integration

Order 7 : Runge-Kutta

$$q_i(t+\delta t) = 2q_i(t) - q_i(t-\delta t) + \frac{f_i(t)}{m_i}\delta t^2$$

Used since the 60's, rigorously demonstrated > 1990 (Tuckerman and Martyna)

How it works

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~~Order 7 : Runge-Kutta~~ ~~Order 4-5 : Gear~~

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~~Order 7 : Runge-Kutta~~ ~~Order 4-5 : Gear~~ Order 2 : Verlet

$$q_i(t+\delta t) = 2q_i(t) - q_i(t-\delta t) + \frac{f_i(t)}{m_i}\delta t^2$$

Used since the 60's, rigorously demonstrated > 1990 (Tuckerman and Martyna)

How it works

- The model is fully described by $V(q_i)$
  either in terms of potential
  either in terms of force field (deriving from potential)

- Verlet algorithm yields trajectories of atoms and molecules

- From trajectories, statistical physics yield ***all*** properties

Fixed charges models

Coulomb potential: $$V = \frac{z_i z_j e^2}{4\pi\epsilon_0 r_{ij}}$$

Pauli repulsion: $$V = B_{ij} \mathrm{e}^{-a_{ij} r_{ij}}$$

Dispersion: $$V = -\left[\frac{C_6^{ij}}{r_{ij}^6} + \frac{C_{12}^{ij}}{r_{ij}^{12}}\right]$$

M. Tosi & F. Fumi *J. Phys. Chem. Solids*, **1964**, *25*, 45
F. Lantelme & P. Turq. *J. Chem. Phys.*, **1982**,*77*, 3177

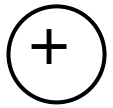
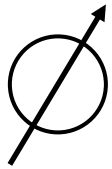
Fixed charges models (2)

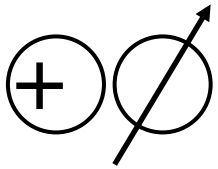
Origins of parameters a, B, C_6,C_8 :
Empirically fitted to reproduce experimental data

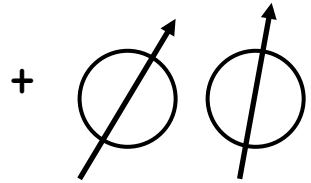
This class of models is « fragile » :

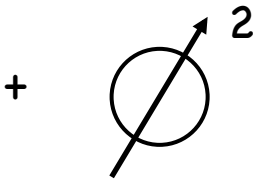
- Pair potentials: no collective effects.
- Non-transferable arameters
- Limited validity ranges (temperature, composition, pressure)
- Impossible to describe mixtures
- Reliable for some properties and disastrous for others...

Polarization description

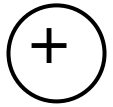
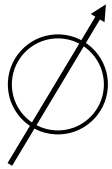
charge q^i  charge q^i *and* dipole μ^i 

$V_{\text{polarisation}} =$ 





Polarization description

charge q^i  charge q^i *and* dipole μ^i 

$$V_{\text{polarisation}} = \sum_{ij} \left(q^i \mu^j_\alpha g^{ij}_D(r^{ij}) - q^j \mu^i_\alpha g^{ij}_D(r^{ij}) \right) T^\alpha_{ij}$$

$$- \mu^i_\alpha \mu^j_\beta T^{\alpha\beta}_{ij}$$

$$+ \sum_i \frac{1}{2\alpha^i} |\mu^i|^2$$

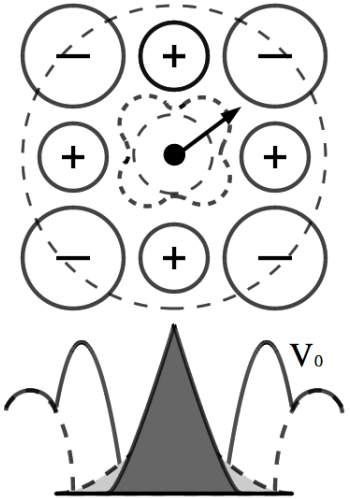
$$T^\alpha_{ij} = \nabla_\alpha \frac{1}{r^{ij}} \qquad T^{\alpha\beta}_{ij} = \nabla_\alpha \nabla_\beta \frac{1}{r^{ij}} \qquad \alpha, \beta \equiv x, y, z$$

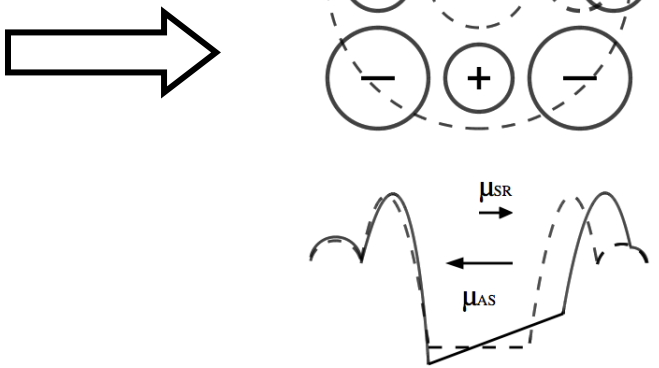
α^i : polarisability dipole $\mu^i = \alpha^i E$ field

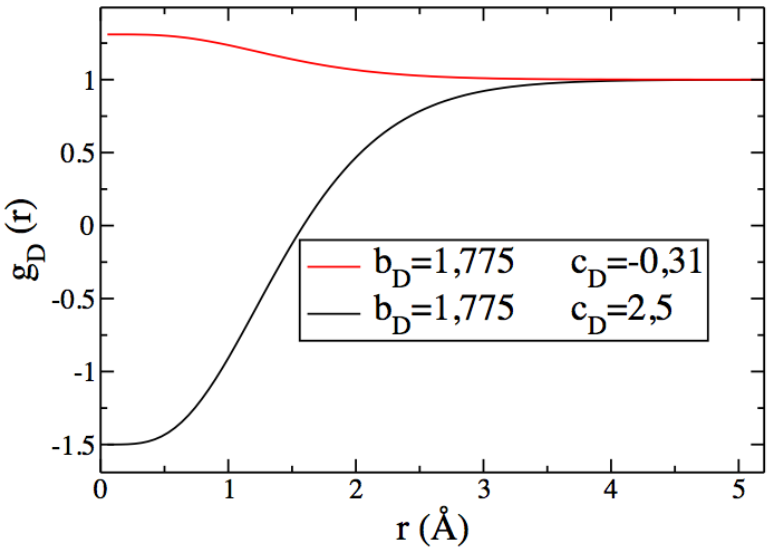
P. A. Madden & M. Wilson, *Chem. Soc. Rev.* **1996**, *25*, 339.

Polarization description (2)

Electronic density confinement (in condensed phase)







anion : $c_D > 0$
cation : $c_D < 0$

$$g_D(r) = 1 - c_D \mathrm{e}^{-b_D \times r} \sum_{k=0}^{4} \frac{(b_D \times r)^k}{k!}$$

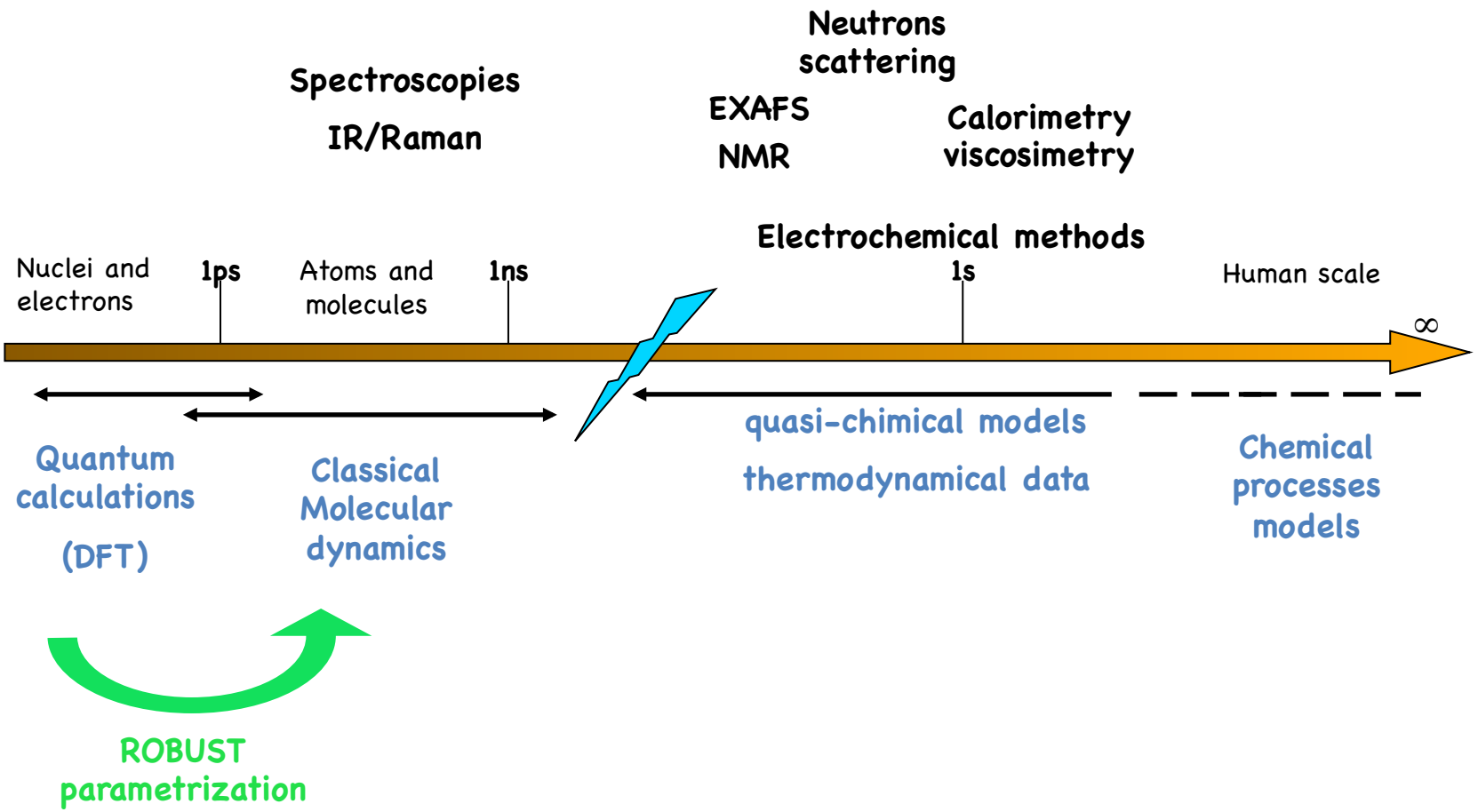
Polarization description (3)

Origins of parameters a, B, C_6,C_8, a, b, c :

Empirically fitted to reproduce experimental data

More tolerant models, but still non-transferable
Too much empirical parameters !

How to parametrize ?



How to use quantum mechanics ?

We need to compute dipoles, and therefore charges.

Many tools are available :
- Mulliken charges
- Davidson charges
- ELF
- RESP
- etc...

Often difficult to interpret
Often non-consistent

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Walter Kohn
(Nobel prize 1998)

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Often non-consistent

For condensed phase, DFT is the main method
Wannier localization is the best method

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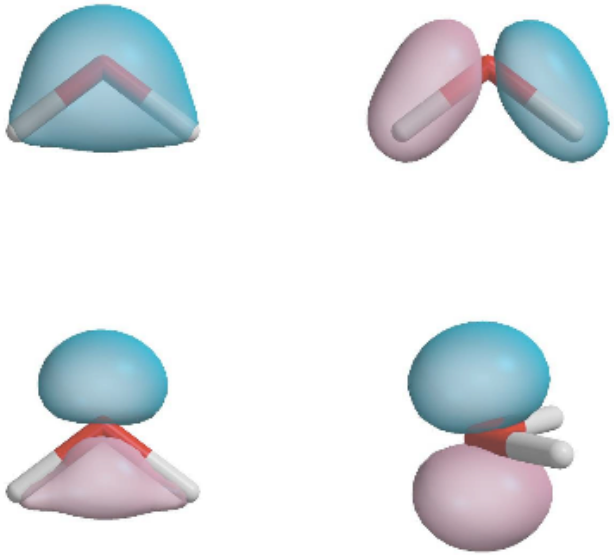
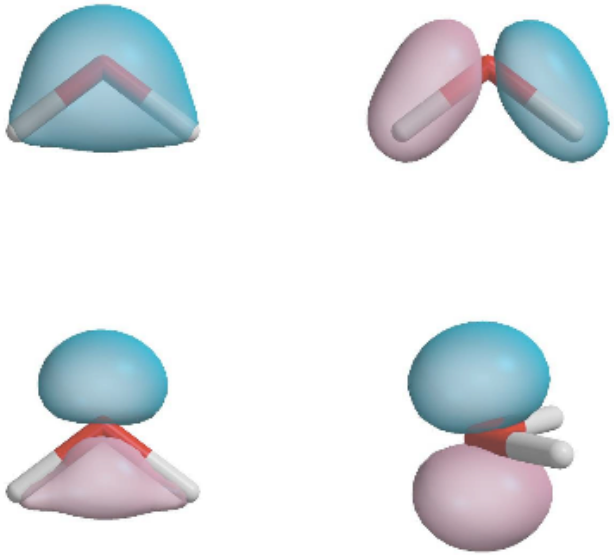
Wannier orbitals

Kohn-Sham canonical orbitals

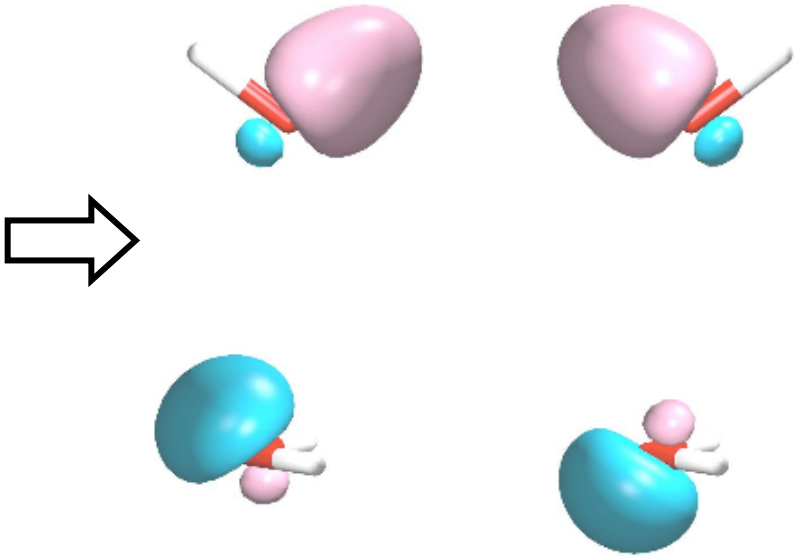


Wannier orbitals

Kohn-Sham canonical orbitals



Localized Wannier orbitals



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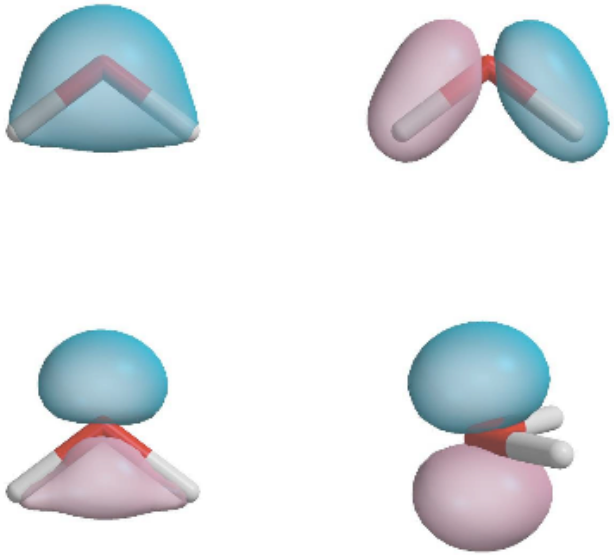

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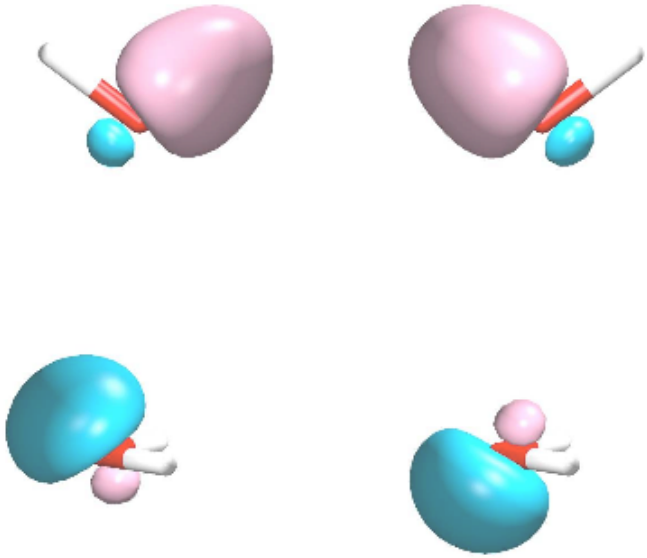
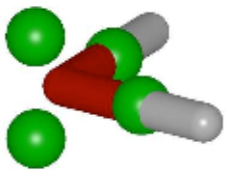


One criteria : minimize the spread

$$S = \sum_{k=1}^{N_{states}} \left[\langle w_k | r^2 | w_k \rangle - \langle w_k | \vec{r} | w_k \rangle^2 \right]$$

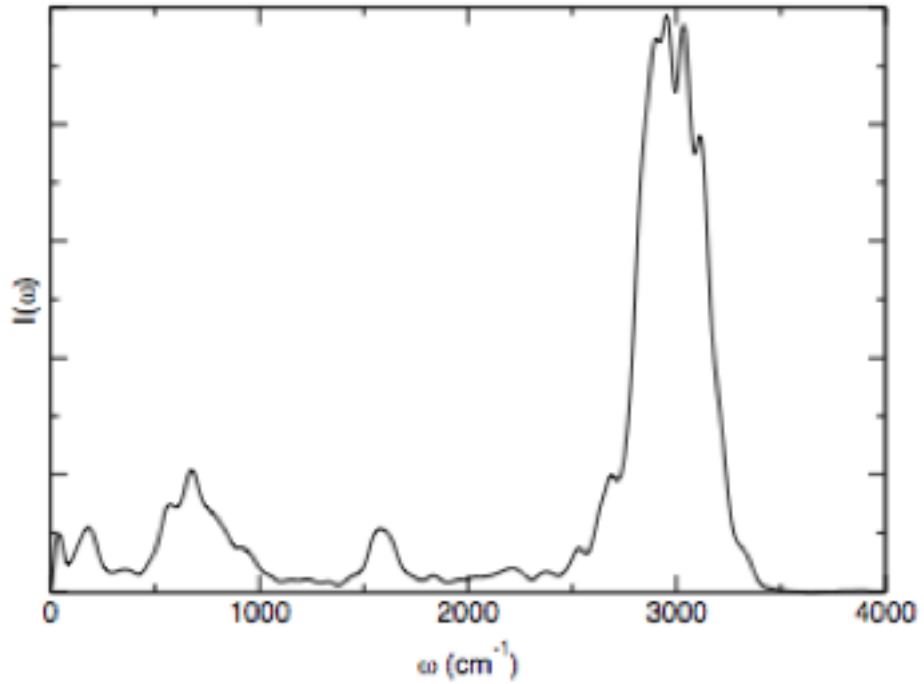
Wannier centers :



charges:
q_H=+1 q_O=+6
q_{WC}=-2

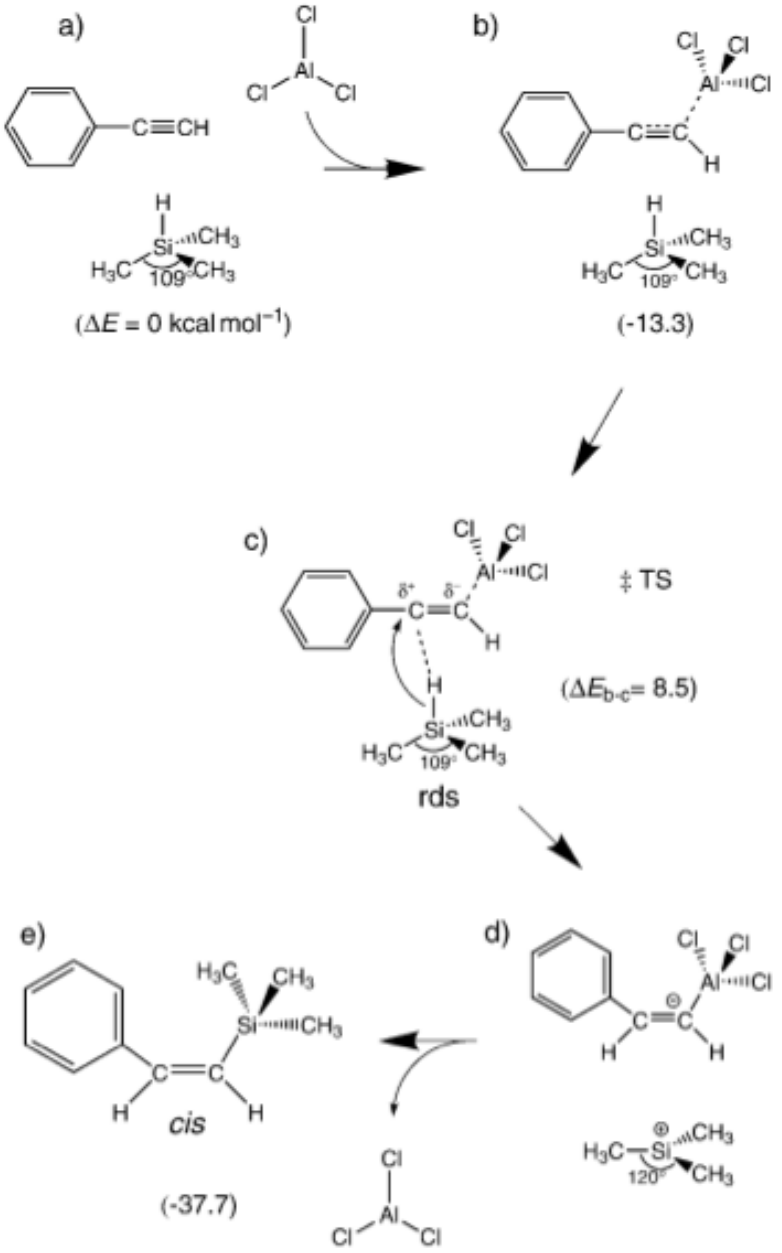
Wannier centers have physical meaning

Water infrared spectrum

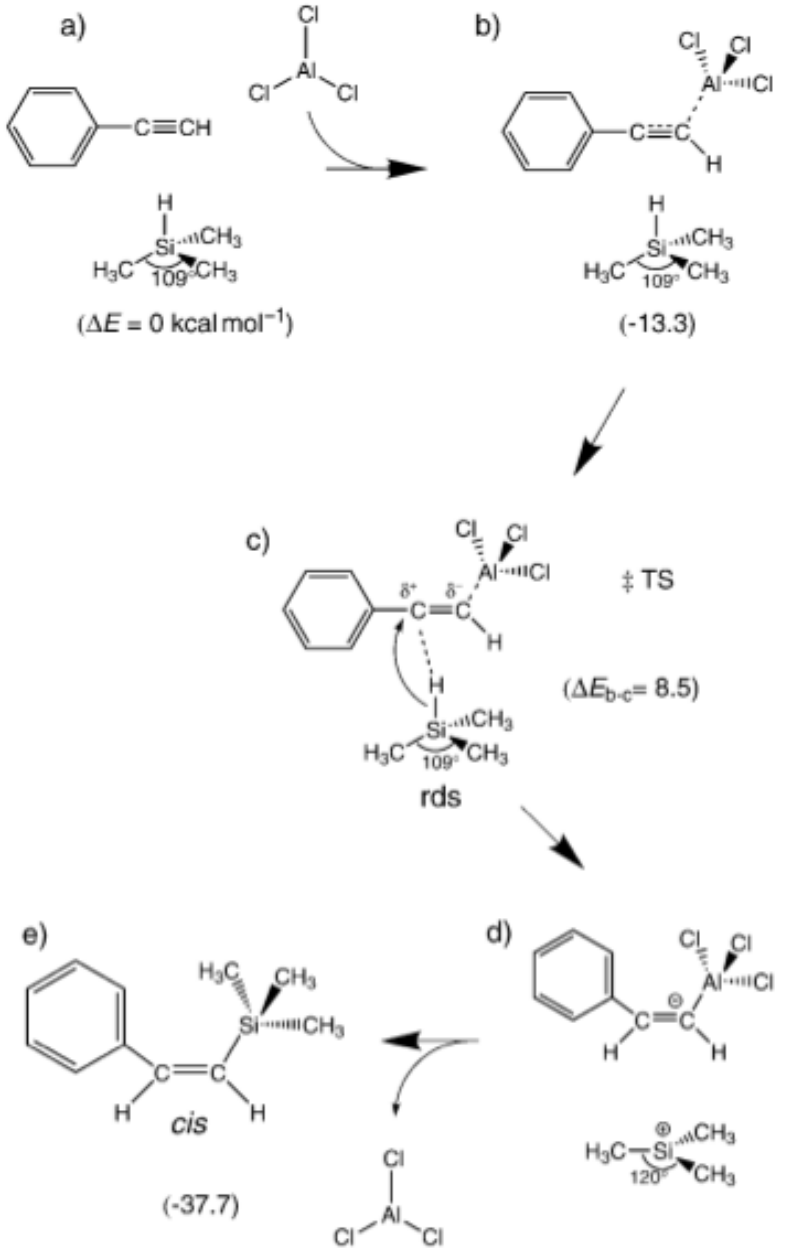


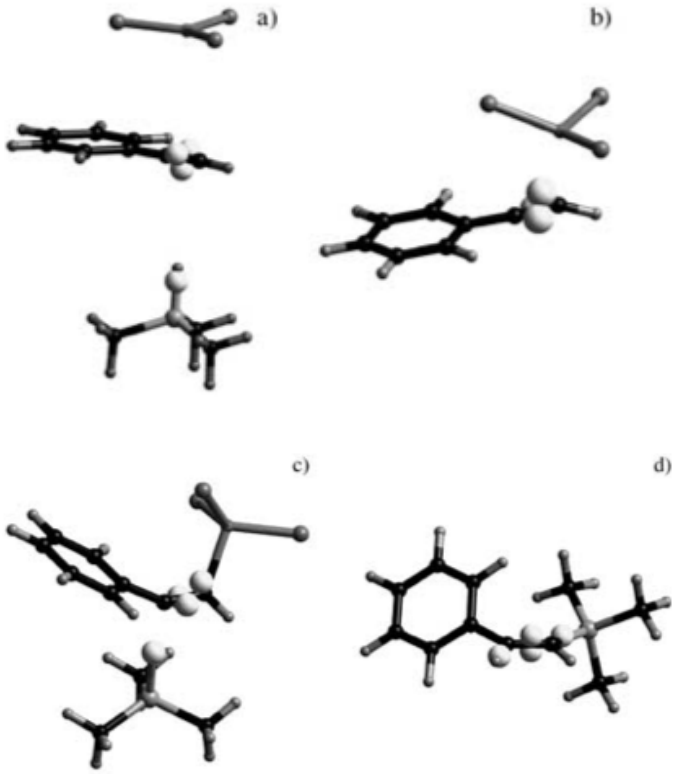
$$I(\omega) = \frac{\beta\omega^2}{2}\int_{-\infty}^{\infty} e^{i\omega t}\langle M(0)M(t)\rangle_0 \mathrm{d}t$$

Wannier centers have <u>chemical</u> meaning



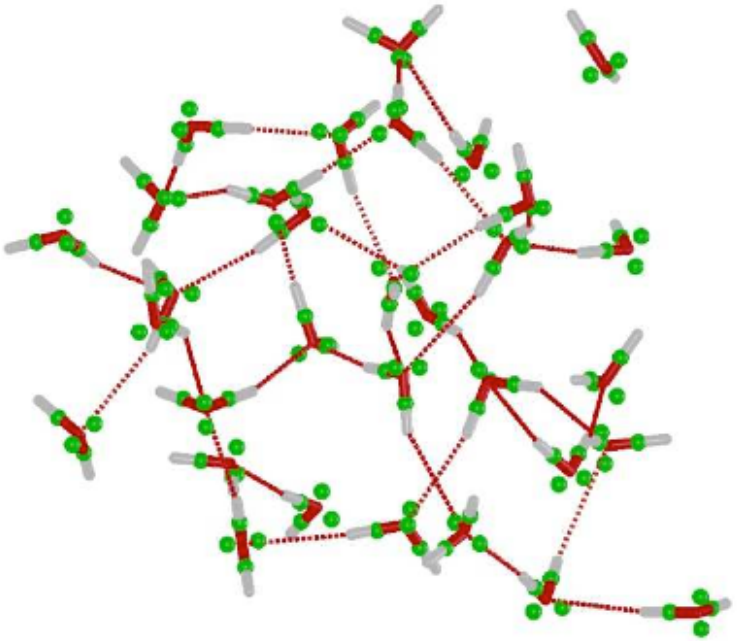
Wannier centers have chemical meaning





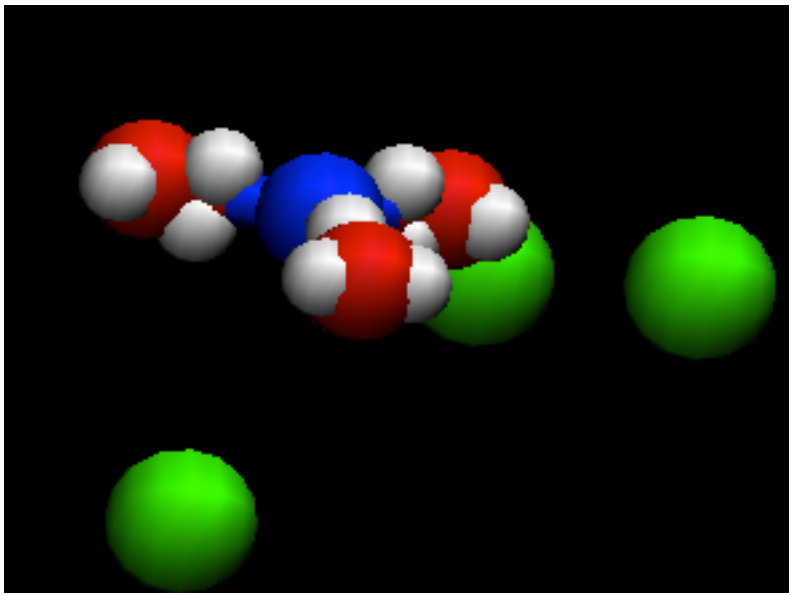
Zipoli et al., *ChemPhysChem*, **2005**,*6*,1772

Wannier have limitations...



H-bonding

Conjugaison

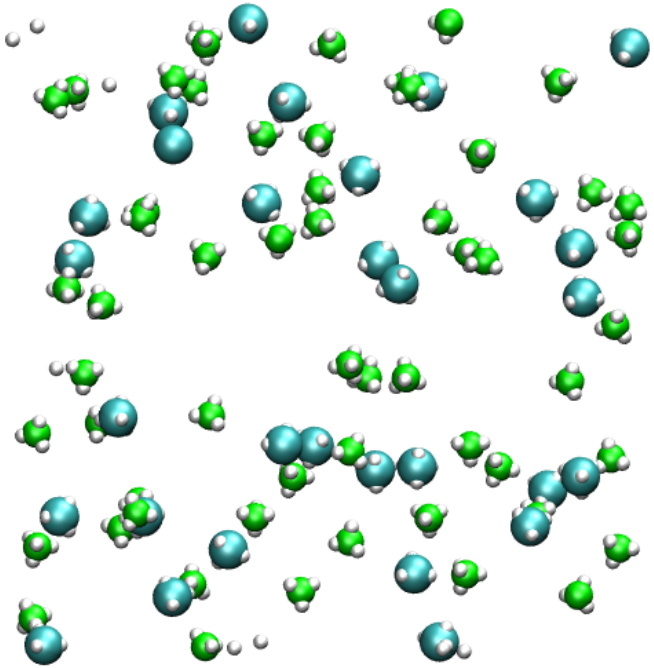


Use of Wannier centers to build models

DFT calculation for the condensed phase ⇒ Forces acting on ions

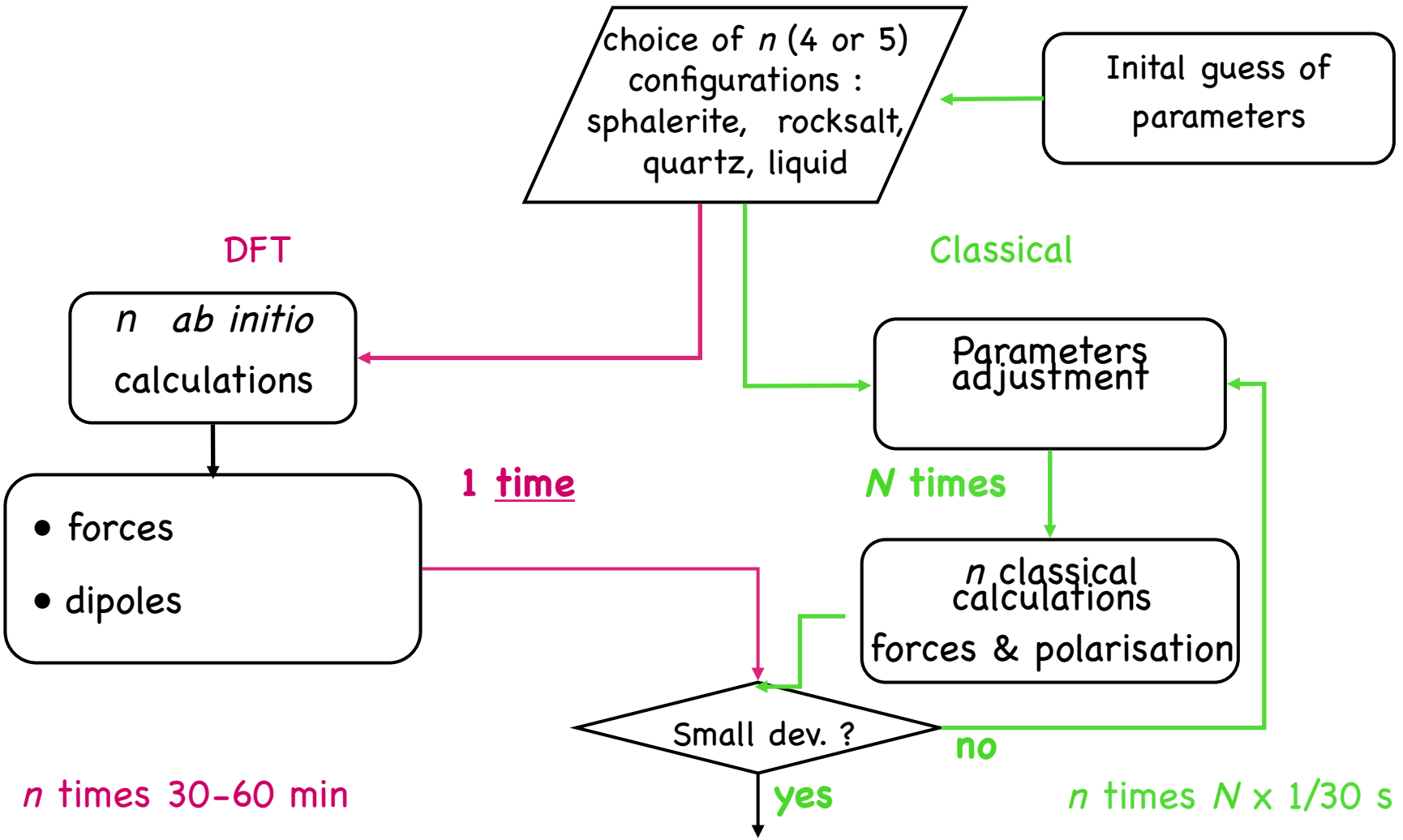
⇓

Wannier centers

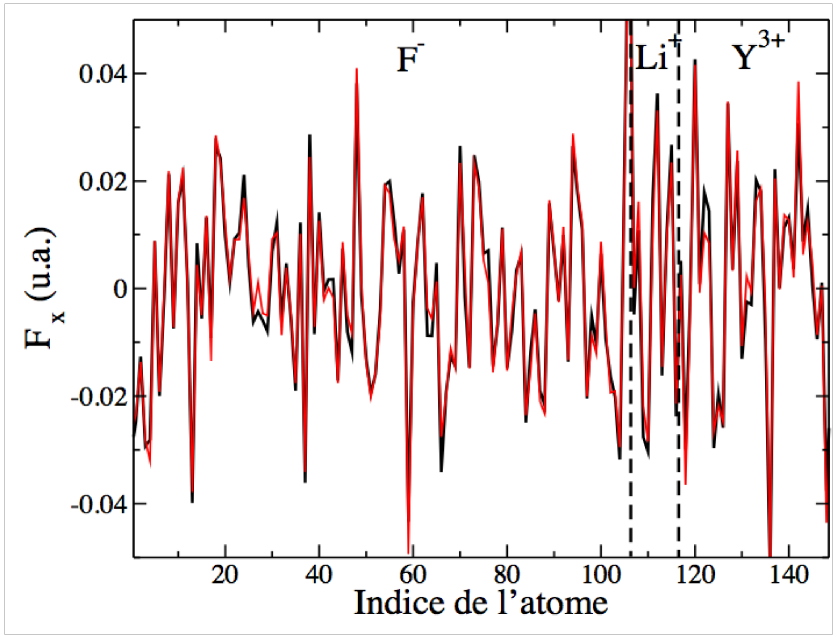


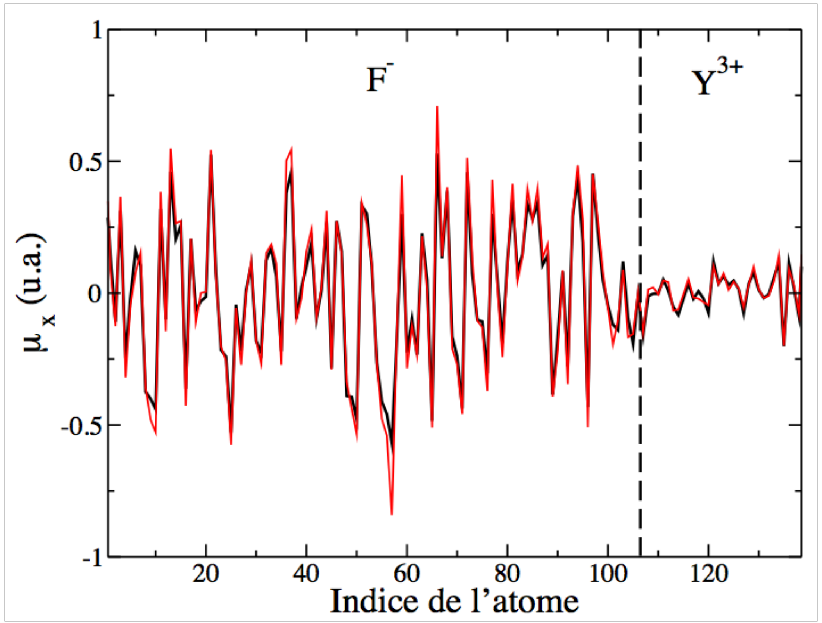
⇒ Ions dipoles

Algorithm


choice of n (4 or 5) configurations : sphalerite, rocksalt, quartz, liquid
Inital guess of parameters
DFT
Classical
n ab initio calculations
Parameters adjustment
1 time
N times
forces
dipoles
n classical calculations forces & polarisation
Small dev. ?
no
yes
n times 30-60 min
n times N x 1/30 s

Results





c_P = 5,6 % and c_F = 6,8 %

Parameters fitted on DFT :

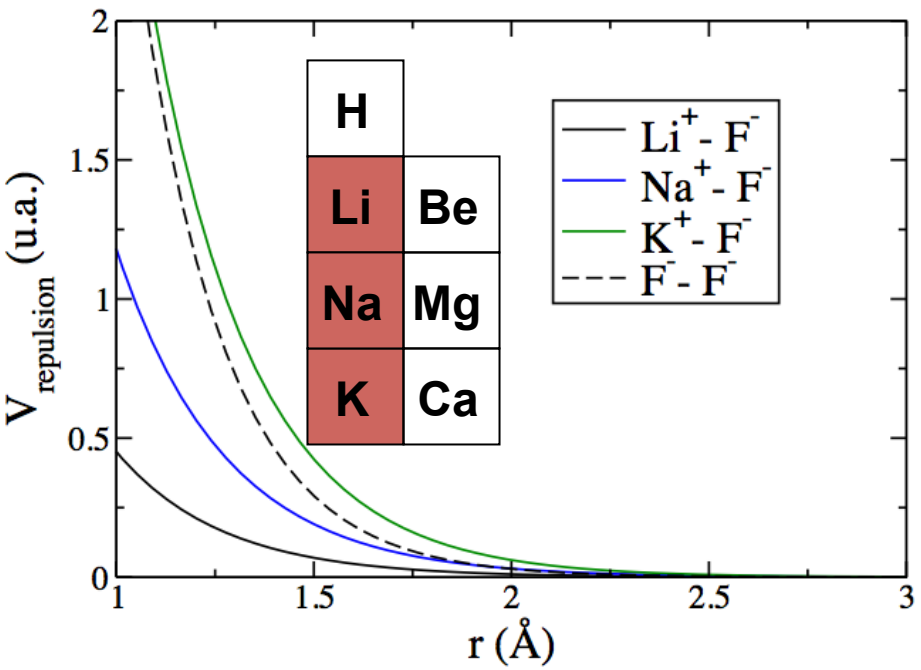
B, a, α, b, c.

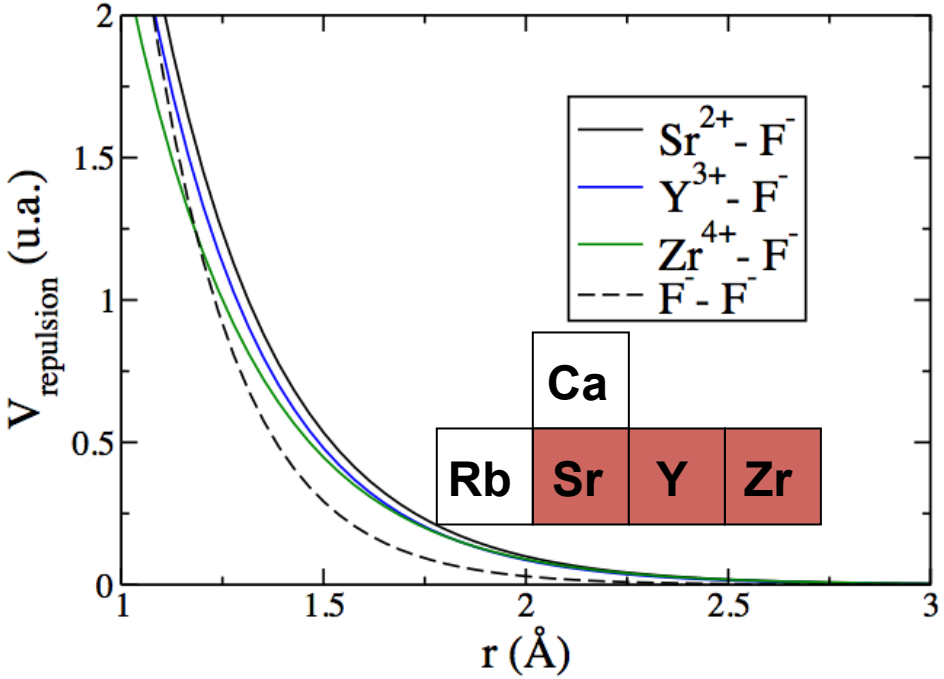
Still C_6 , C_8 empirical

Non-sensitive to choices
- pseudo-potentials
- fonctional (PBE, BLYP...)

Transferable models

Meaningful parameters



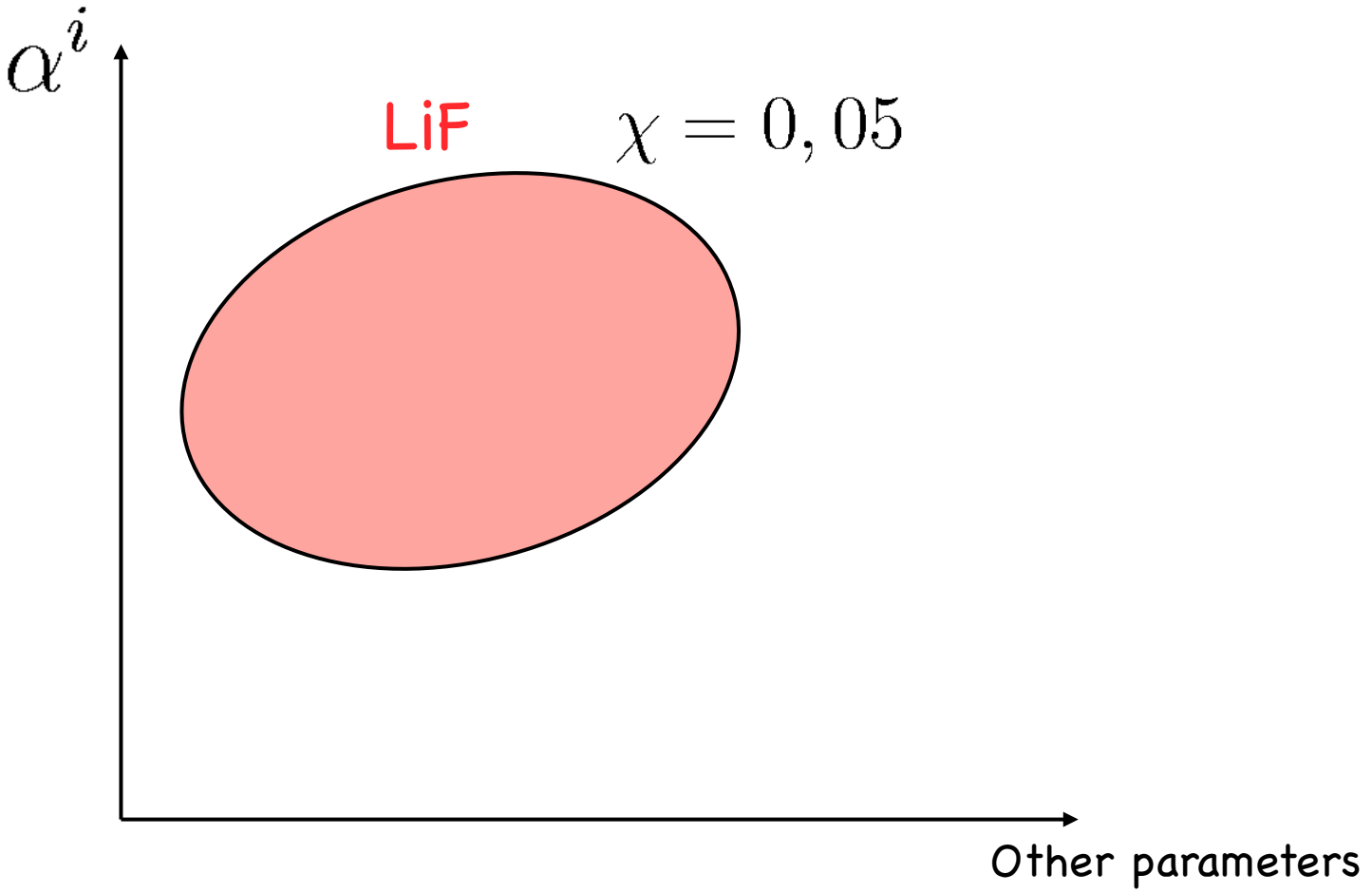


In the column, cation radius increases with Z

In the period, cation radius is almost constant

Transferable potentials : all the mixtures use the same parmeters

Can we fit a global model ?



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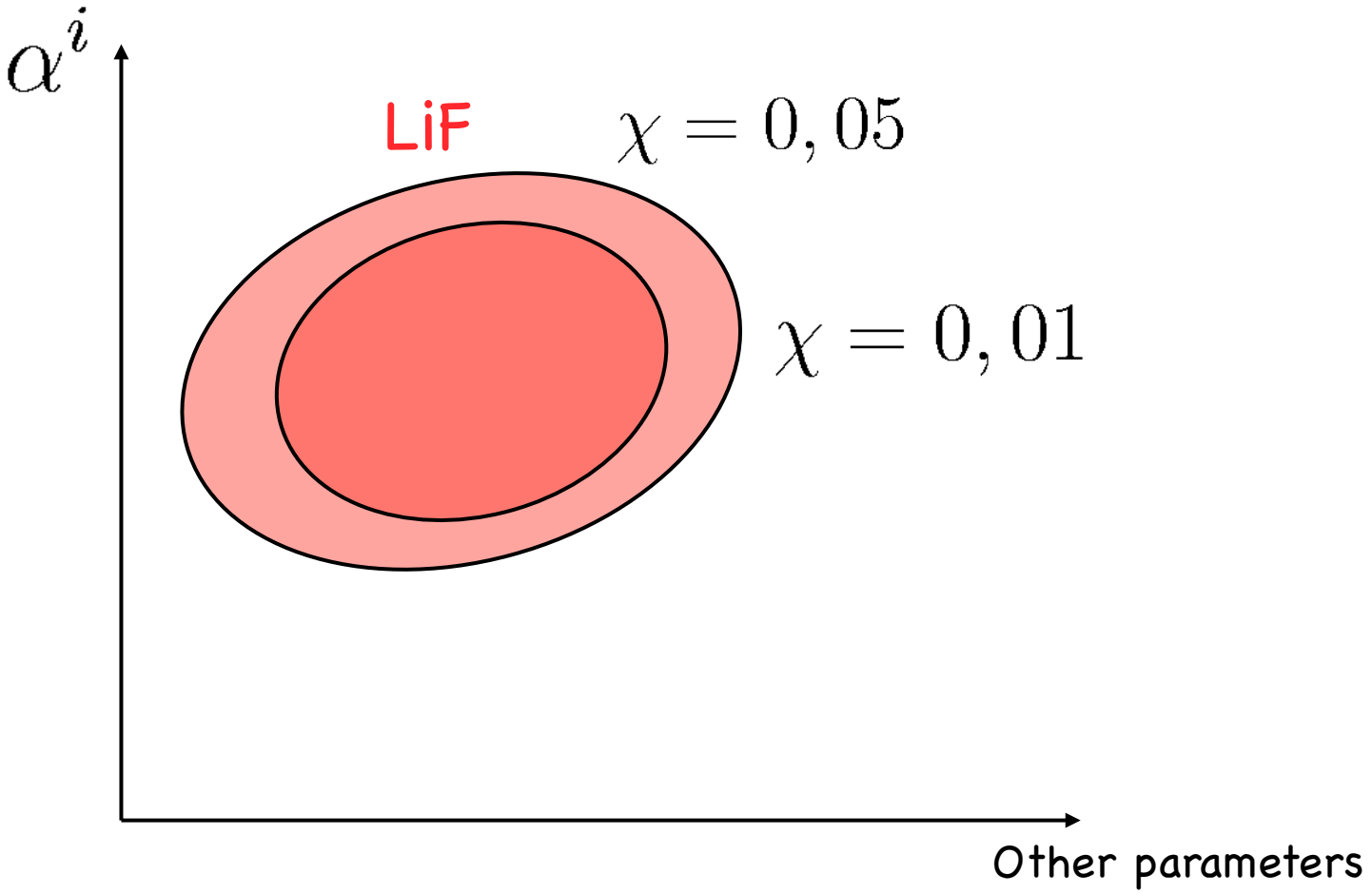

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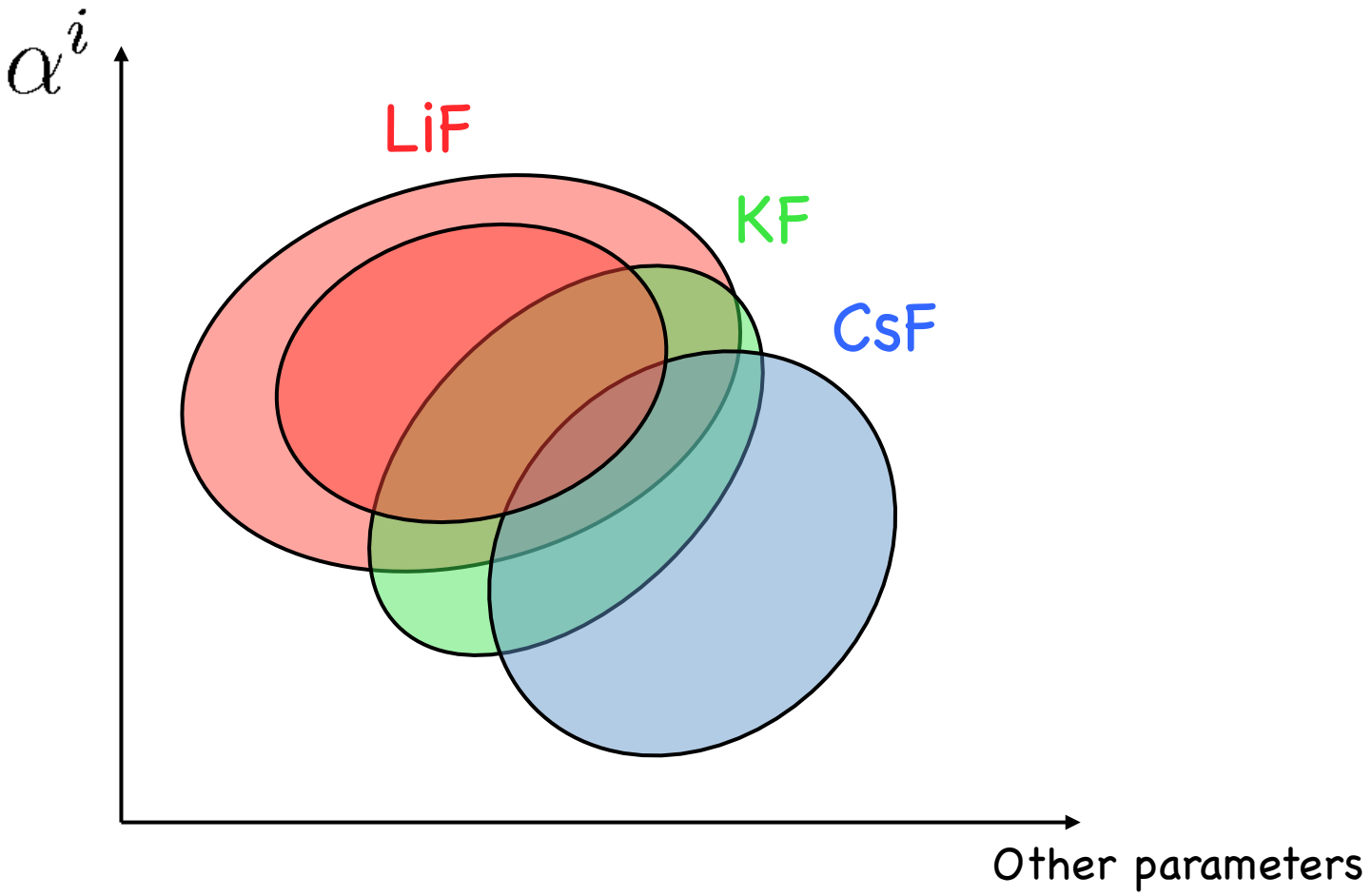


Fitted models (and validated !)

Fluorides (non-empirical)

Li^+, Na^+, K^+, Cs^+,

Be^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, (Sn^{2+}, Pb^{2+})

Y^{3+}, Al^{3+}, La^{3+}

Zr^{4+}, Th^{4+}, (U^{4+})

Chlorides (semi-empirical, non-empirical in progress)

Li^+, Na^+, K^+, ...

Sc^{3+}, Y^{3+}, La^{3+}, Tb^{3+}, U^{3+}

Oxydes (semi-empirical, non-empirical)

Ca^{2+}, Mg^{2+}, Sr^{2+}, Ba^{2+}

Al^{3+}

Si^{4+}

Simple applications examples

Thermodynamical properties
Structure
IR-Raman
Transport properties
(diffusion, electrical conductivity, viscosity)

Thermodynamics

Obviously….

Thermodynamics

Obviously...

$$U = \langle V \rangle$$

Thermodynamics

Obviously...

$$U = \langle V \rangle$$

Thermodynamical properties U, C_v , H, C_p

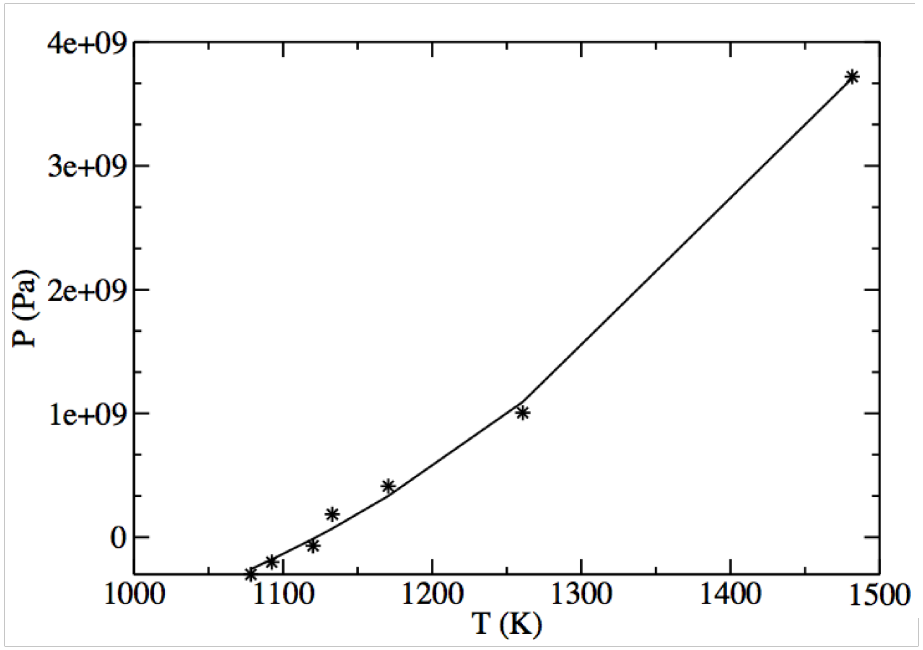
Thermodynamics

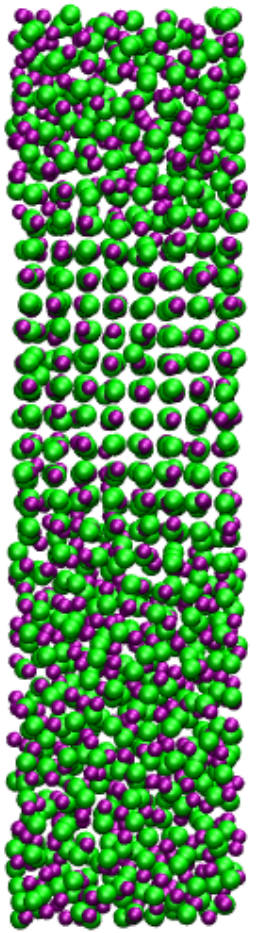
Thermodynamical properties U, C_v , H, C_p
(we even have access to the contributions of various interactions)

Phase changes :

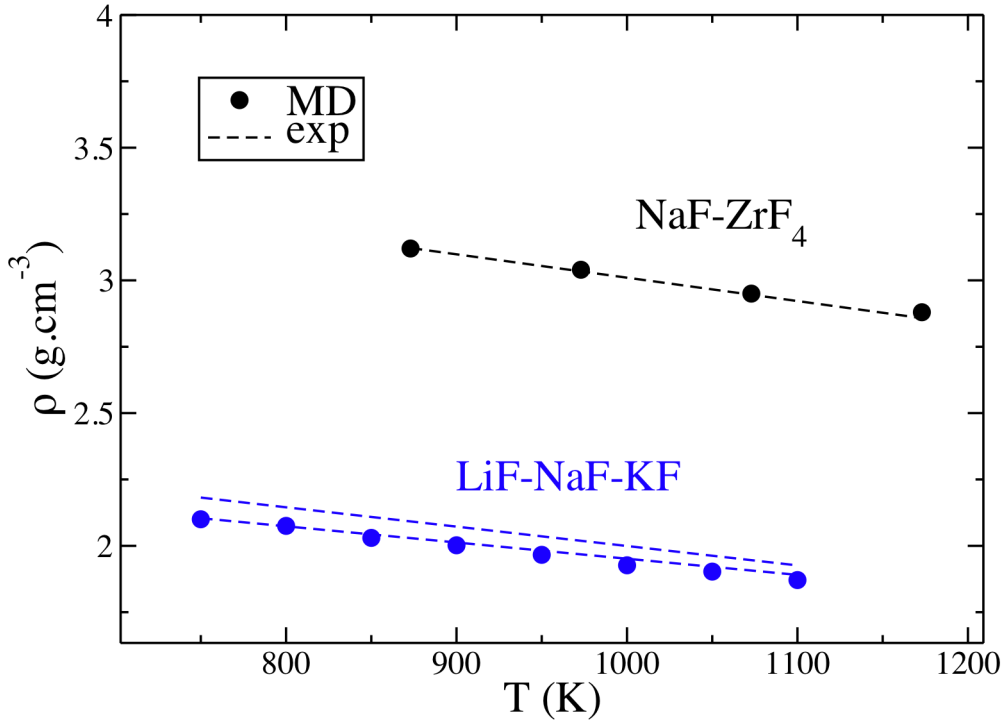
LiF : T_{exp}= 1121±2K

T_{calc}= 1122±1K





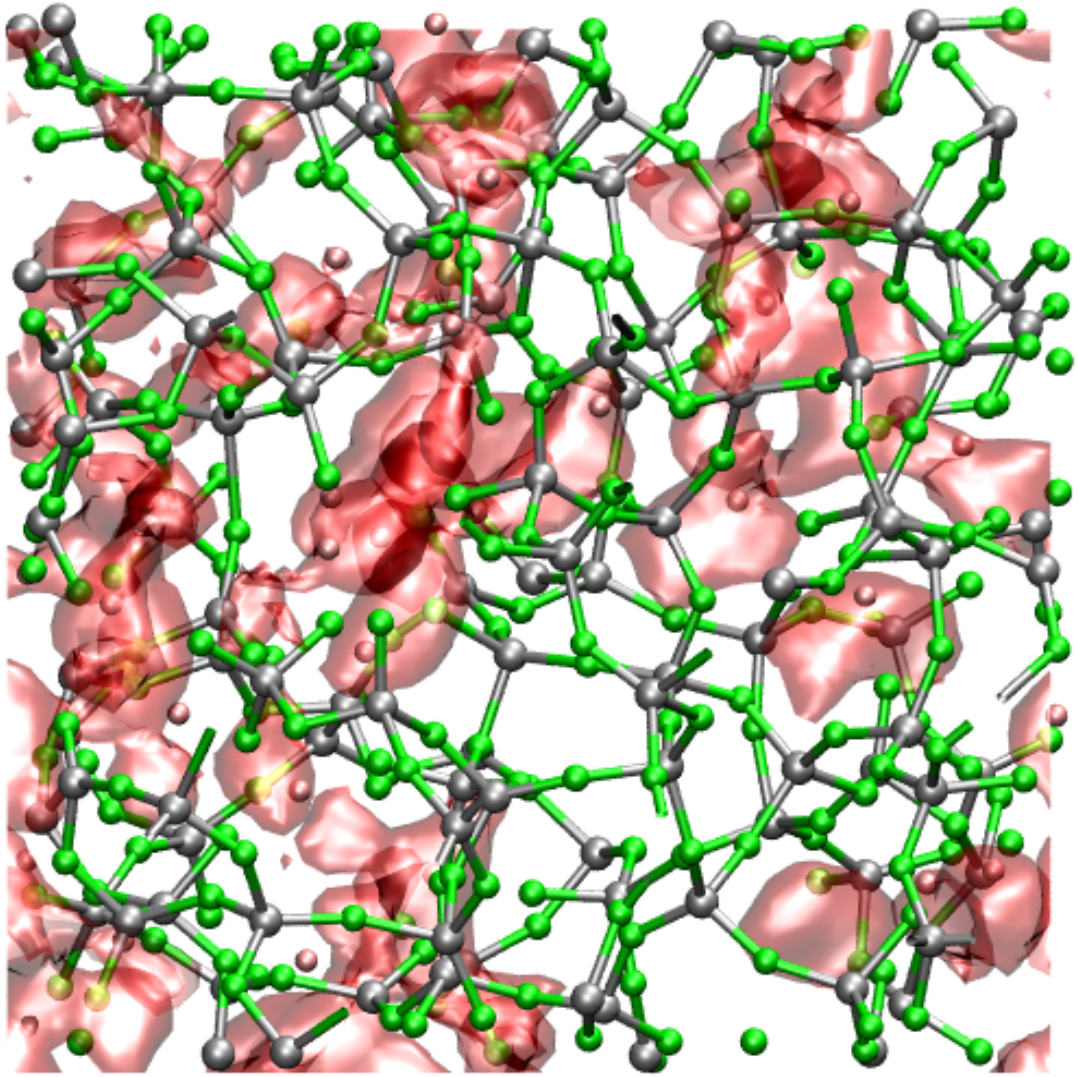
Density-compressibility



Structure

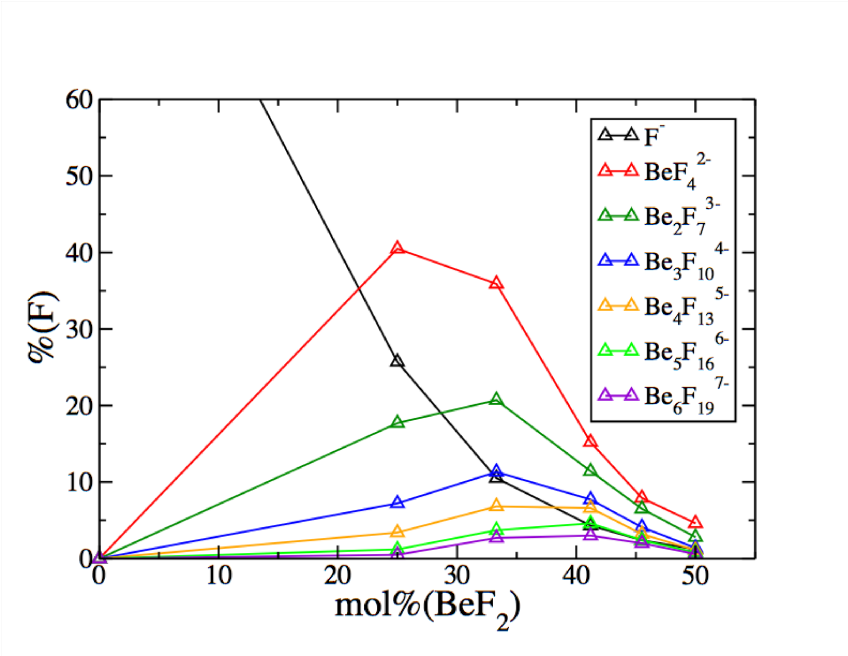
$LiF-BeF_2$ 20:80
at 800 K

Zones with high Li^+ density =
Zones for cooperative diffusion of Li^+



Speciation

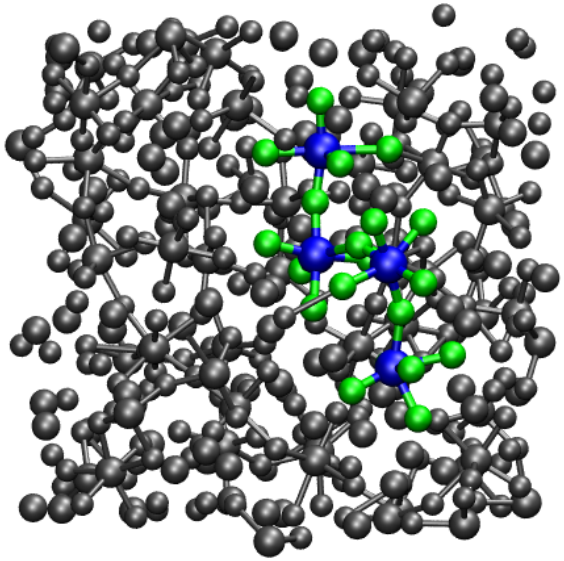
$LiF-BeF_2$
Mixtures at 1200 K

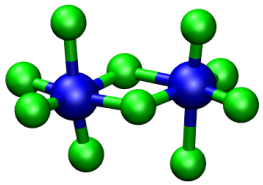


Proportions for species
-> injection in CALPHAD

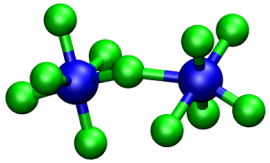
Speciation (2)

$LiF-AlF_3$





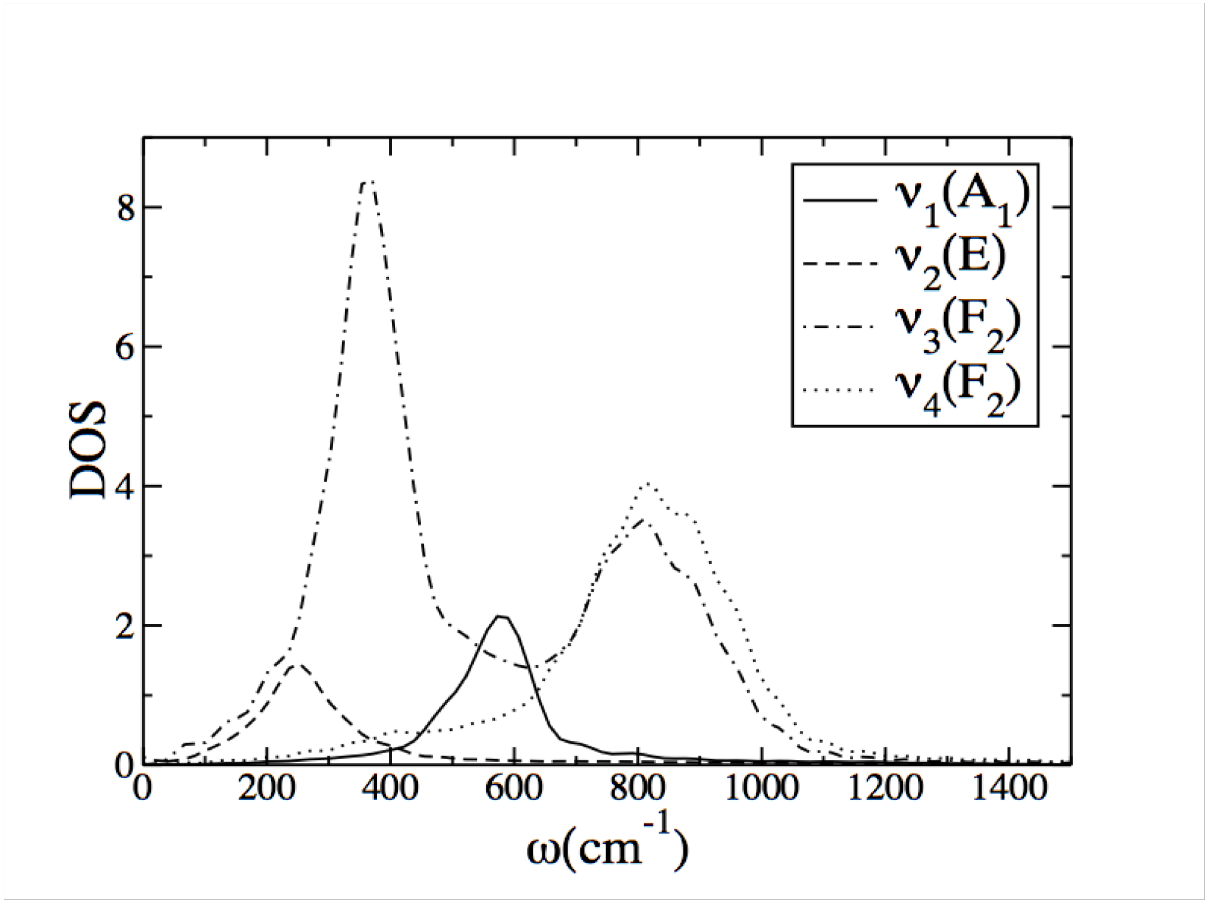
Edges: 5%



Corners: 5%

IR-Raman spectroscopy

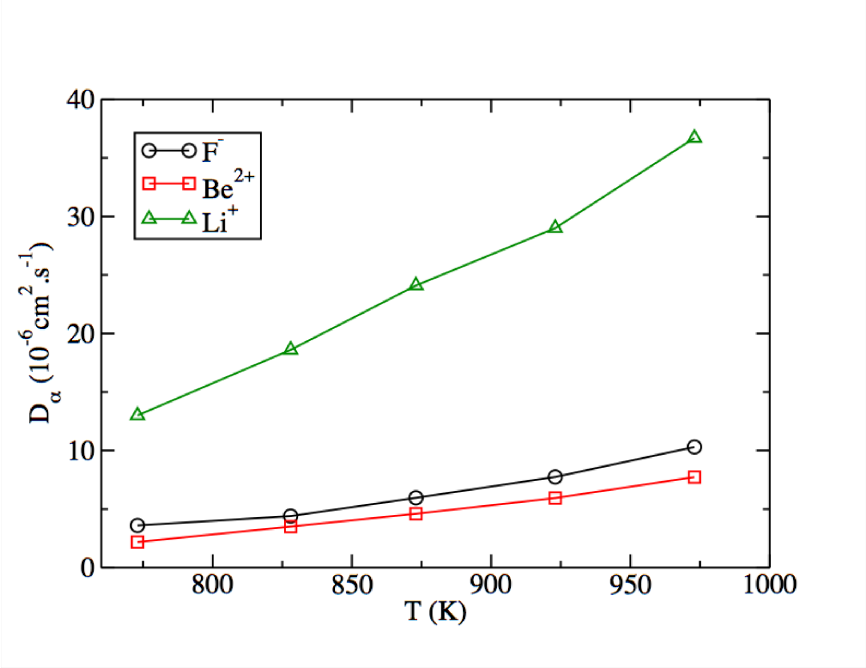
$LiF-BeF_2$



$$I(\omega) = \frac{\beta\omega^2}{2}\int_{-\infty}^{\infty} e^{i\omega t}\langle M(0)M(t)\rangle_0 \mathrm{d}t$$

Self-diffusion

$LiF-BeF_2$

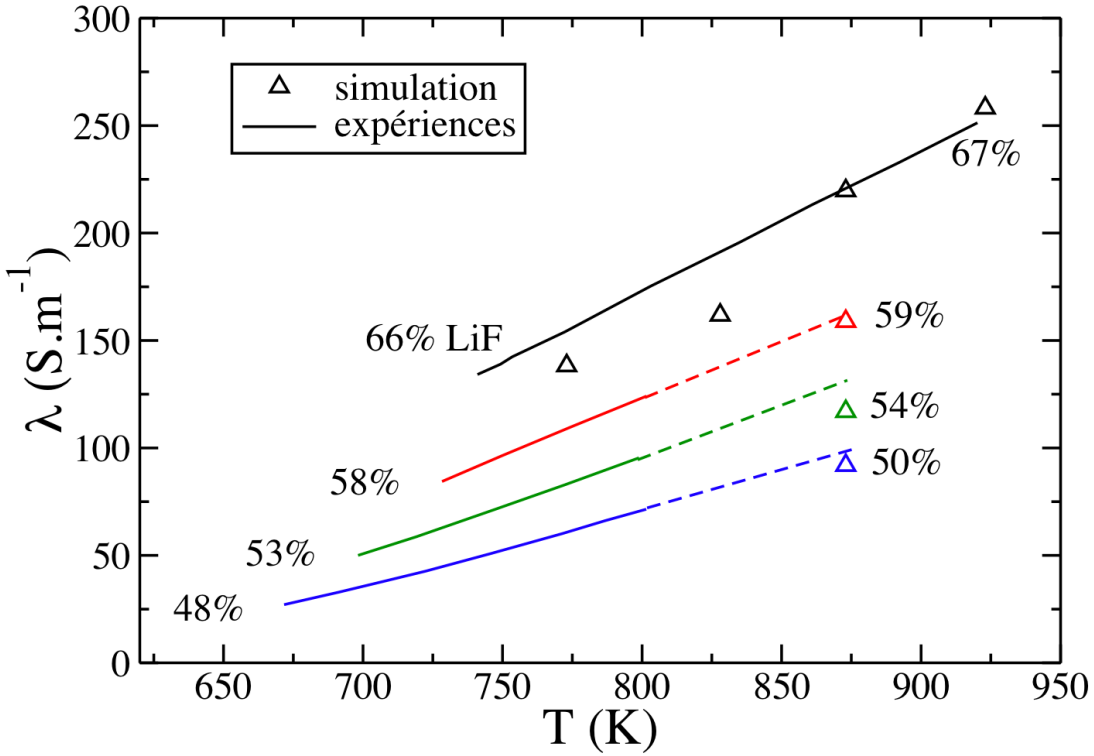


$$D = \lim_{t \to \infty} \frac{1}{3} \left\langle (r(t) - r(0))^2 \right\rangle$$

Electrical Conductivity

LiF-BeF_2

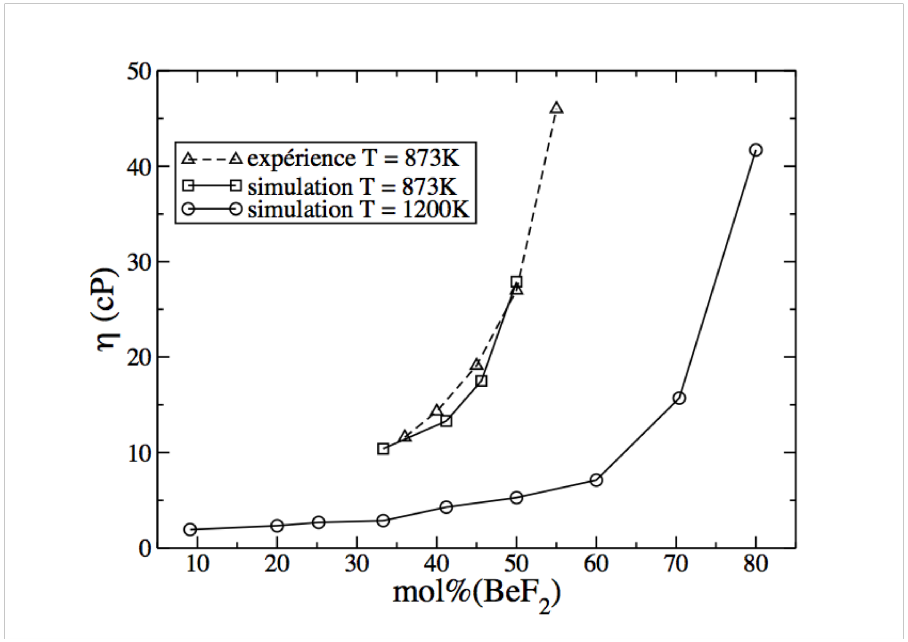
$$\lambda = \frac{\beta e^2}{3V} \int_0^\infty \langle j(t).j(0) \rangle \, \mathrm{d}t$$



Viscosity

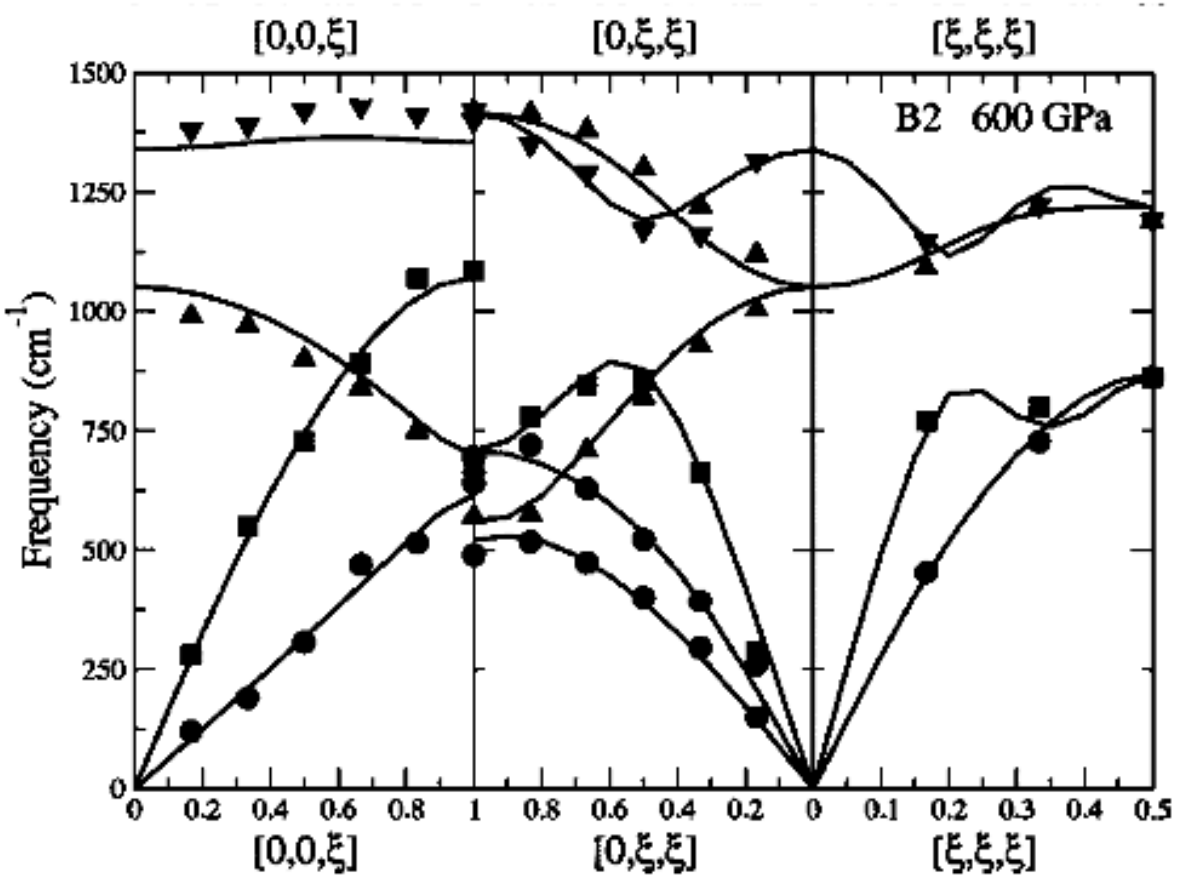
LiF-BeF_2

$$\eta = \frac{\beta}{V} \int_0^\infty \langle \sigma_{\alpha\beta}(t).\sigma_{\alpha\beta}(0) \rangle \, \mathrm{d}t$$

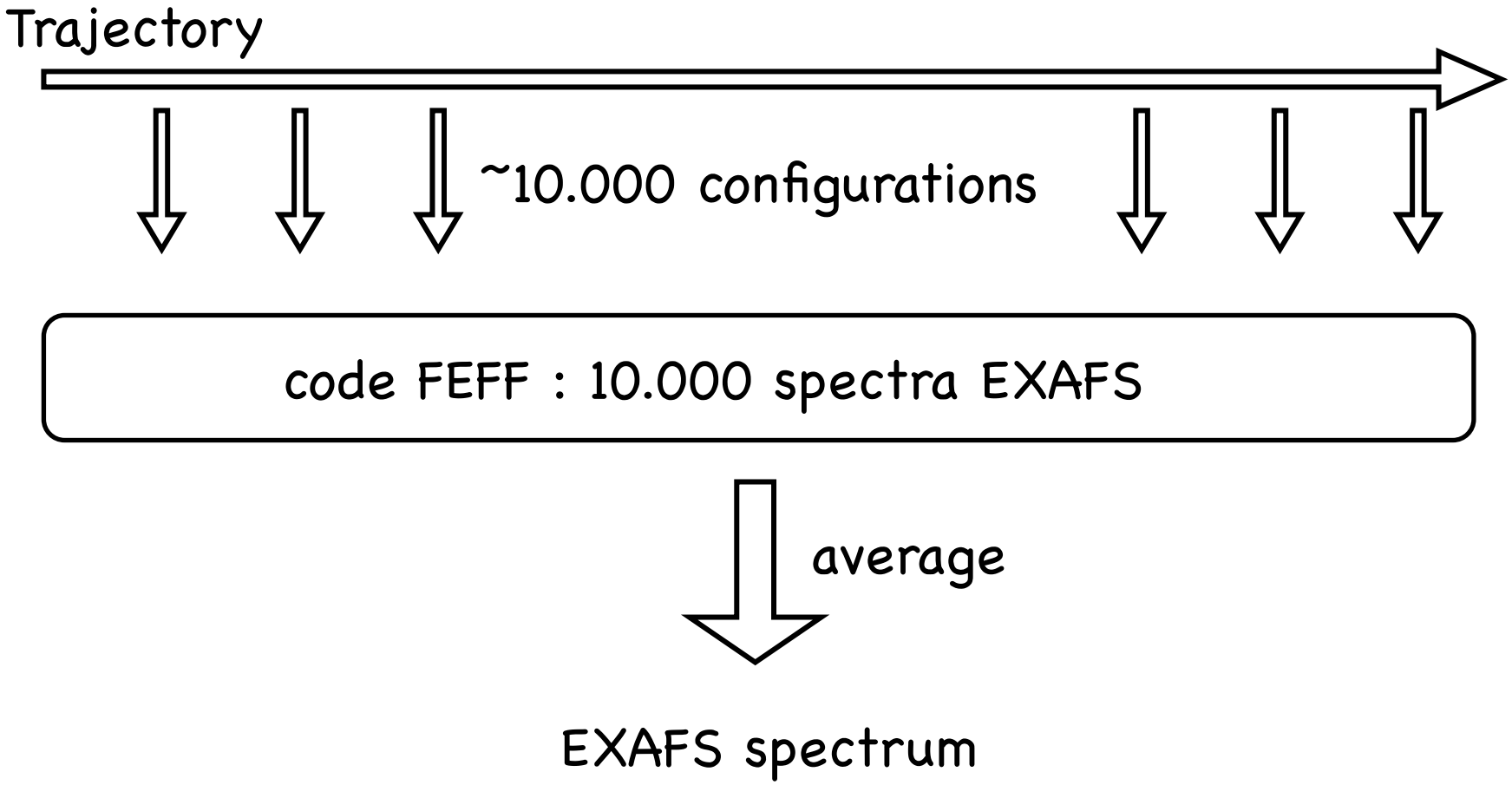


Phonons (solid)

MgO

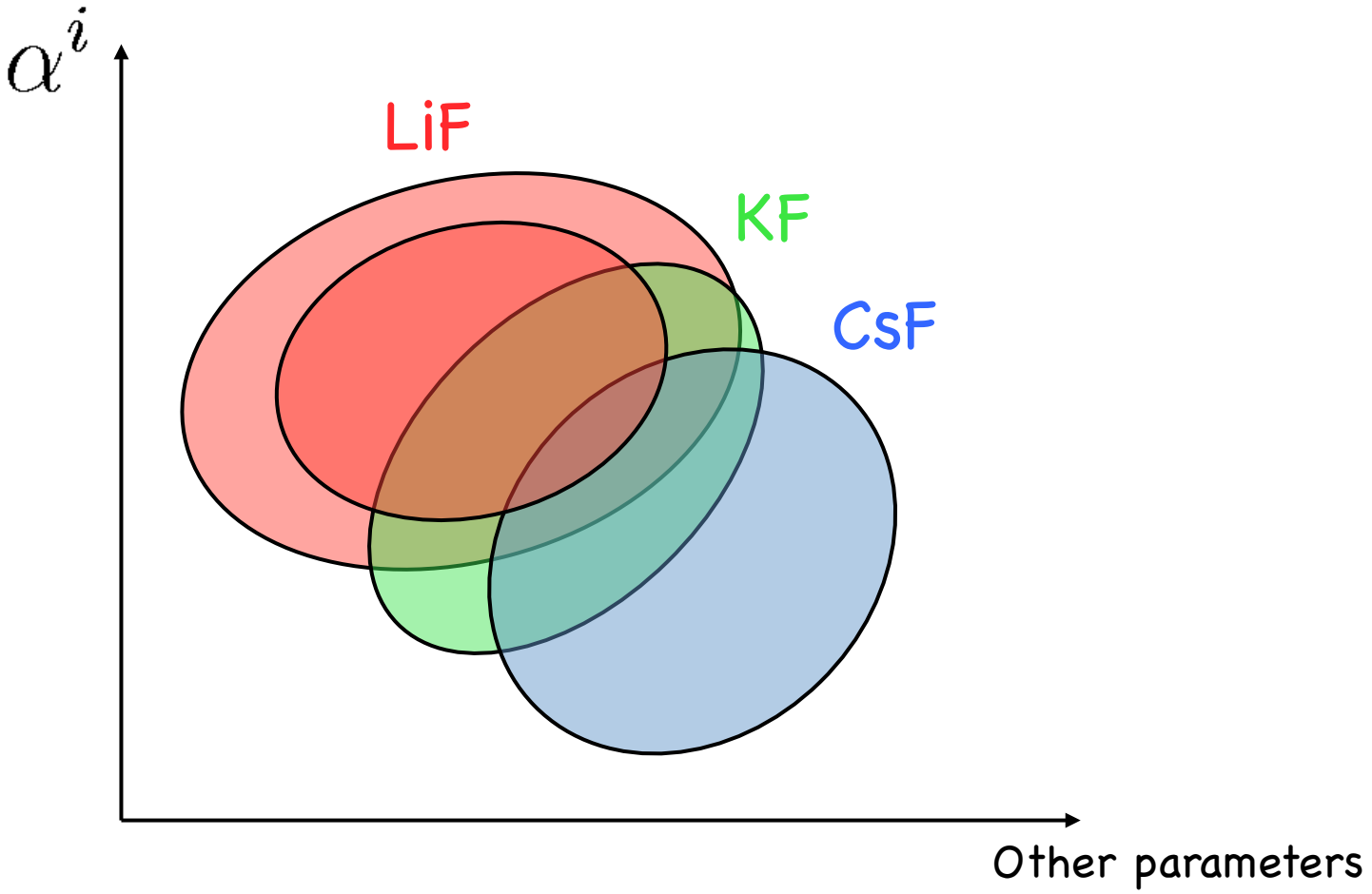


Testing structure description: EXAFS



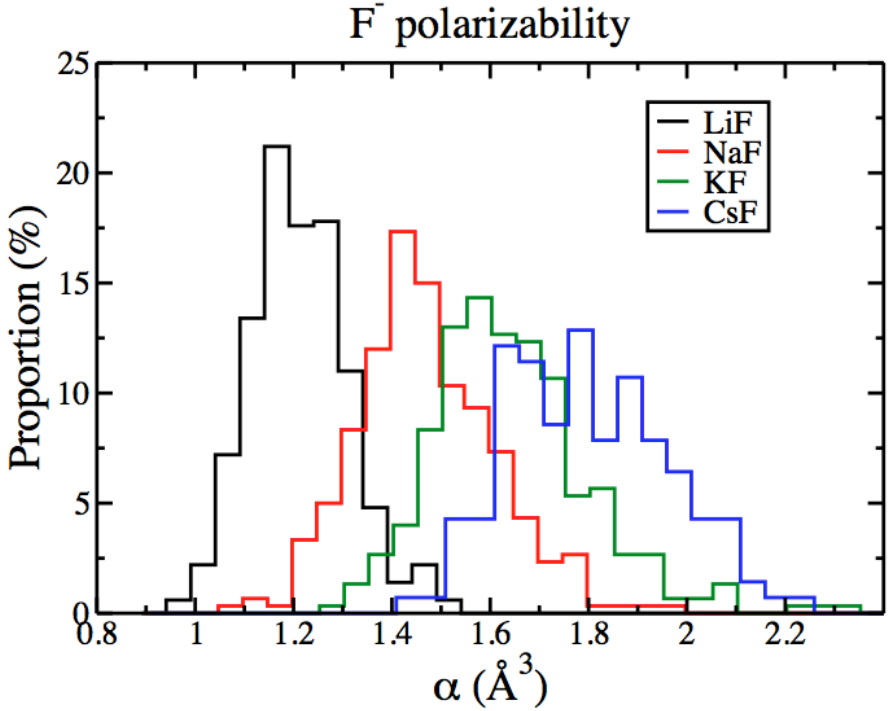
... next talk

Can we build a global model ? (2)



Can we build a global model ? (2)

Invert $\mu^i = \alpha^i E$



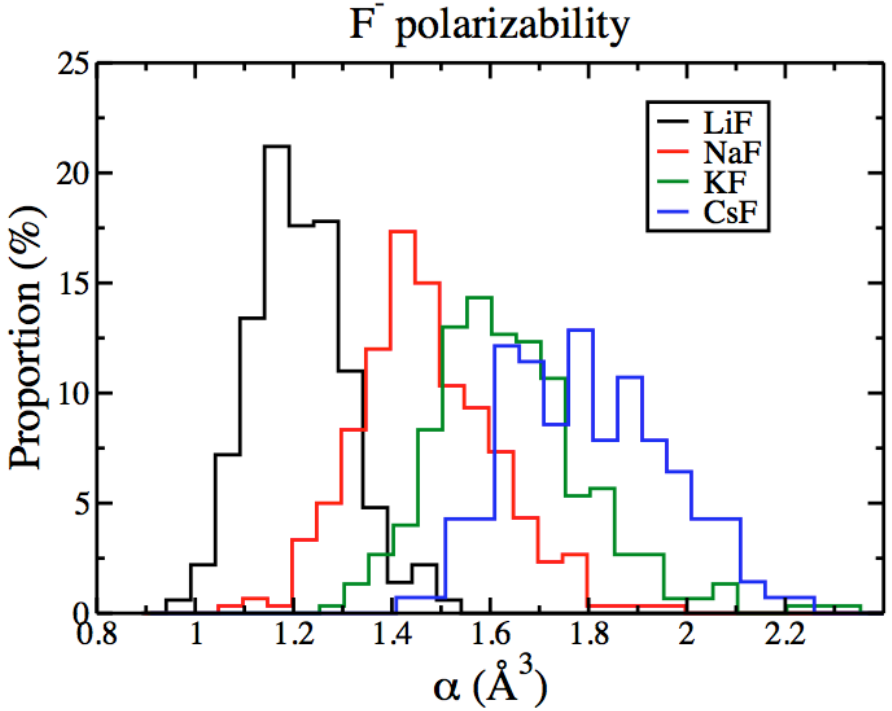
Paramètres ajusté d'après la DFT: *B, a, b, c*

Paramètre *dérivé* de la DFT: α

Paramètres ajusté sur des données expérimentales : C_6,C_8

Derive α

Invert $$\mu^i = \alpha^i E$$



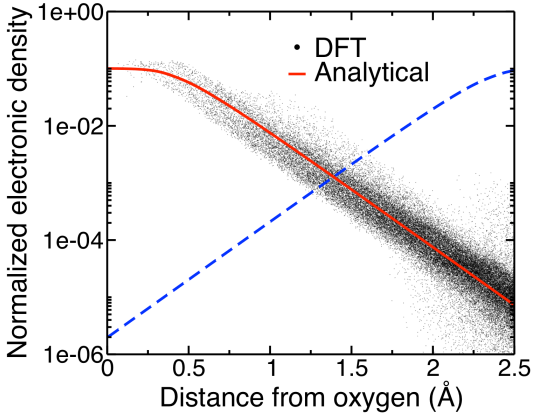
Parameters fitted on DFT: *B, a, b, c*

Parameter *derived from* DFT: α

Parameters fitted on experimental data : C_6,C_8

Derive C_6 and C_8 from Wannier centers

$$C_6^{kl} = \frac{3}{32\pi^{3/2}} \int_{|\mathbf{r}|\leq r_c} \mathrm{d}\mathbf{r} \int_{|\mathbf{r}'|\leq r'_c} \mathrm{d}\mathbf{r}' \frac{\sqrt{\rho_k(\mathbf{r})\rho_l(\mathbf{r}')}}{\sqrt{\rho_k(\mathbf{r})} + \sqrt{\rho_l(\mathbf{r}')}}$$



$$\rho_k(\mathbf{r}) = 2 \times \frac{\kappa_k^3}{8\pi} e^{-\kappa_k|\mathbf{r}-\mathbf{r}_k|}$$

$$\kappa_k = \frac{2\sqrt{3}}{S_k}$$

$$C_6^{IJ} = \sum_{k\in I, l\in J} C_6^{kl}$$

$$C_8^{IJ} = \sum_{k\in I, l\in J} 5(d_k^2 + d_l^2) C_6^{kl}$$

B. Rotenberg, et al. *Phys. Rev. Lett.* **2010**,*104*, 138301

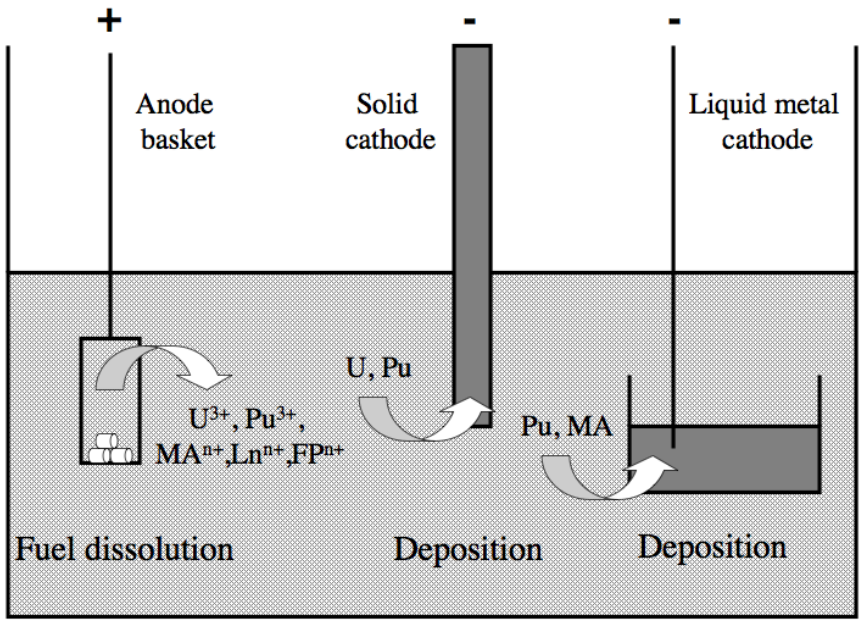
Parameters *derived* from DFT: a, C_6 et C_8, B, a

Parameters fitted on DFT: *b, c*

More applications : toward electrochemistry and separations

Activity coefficients for separation

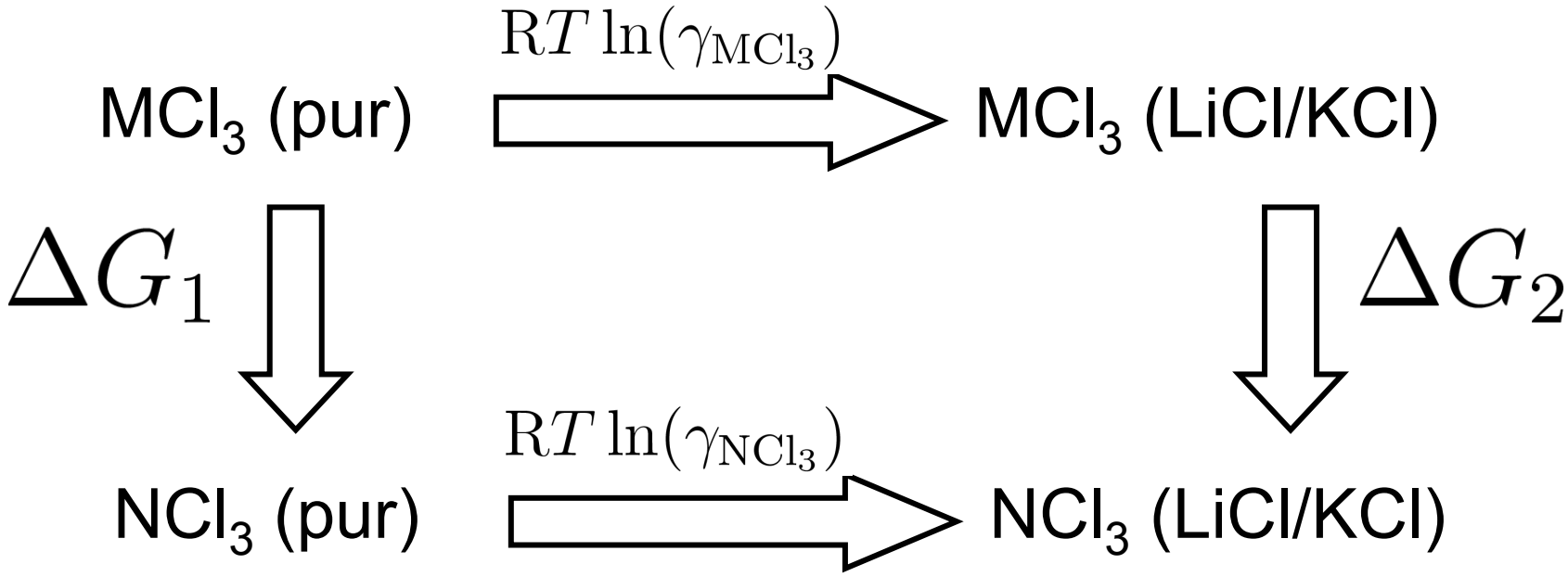
Eutectic mixture LiCl-KCl



Apparent standard potential is related to activity coefficients:

$$E'^{0}_{\mathrm{M}^{n+}/\mathrm{M}(0)} = E^{0}_{\mathrm{M}^{n+}/\mathrm{M}(0)} + \frac{\mathrm{R}T}{n\mathrm{F}} \ln\left(\frac{\gamma_{\mathrm{M}^{n+}}}{\gamma_{\mathrm{M}(0)}}\right)$$

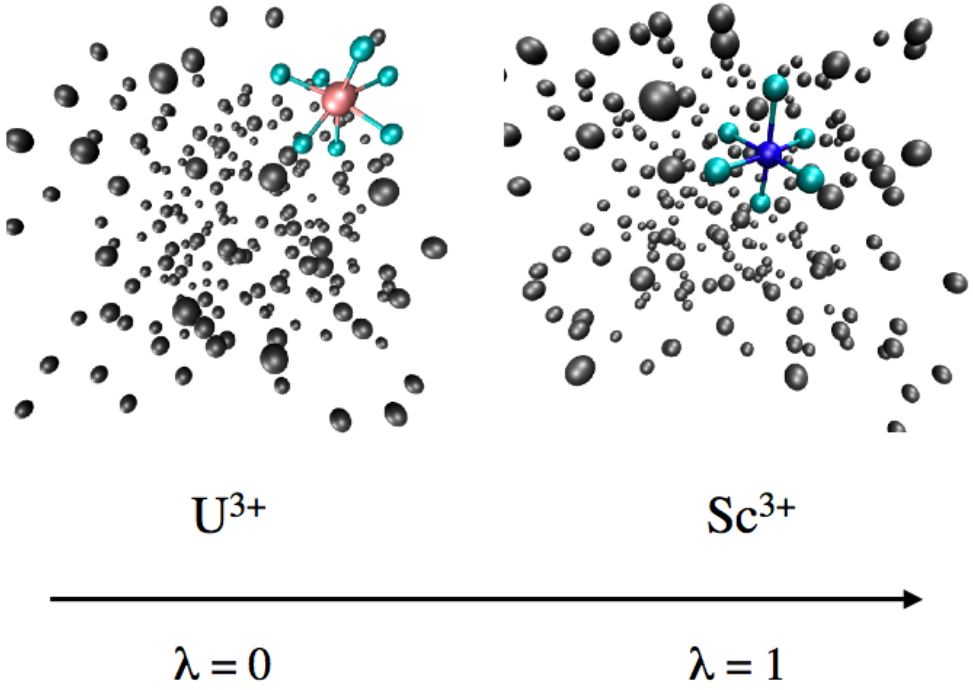
Thermodynamical cycle



$$\Delta G_2 - \Delta G_1 = \mathrm{R}T\ln(\frac{\gamma_{\mathrm{MCl_3}}}{\gamma_{\mathrm{NCl_3}}})$$

"Virtual" transmutation

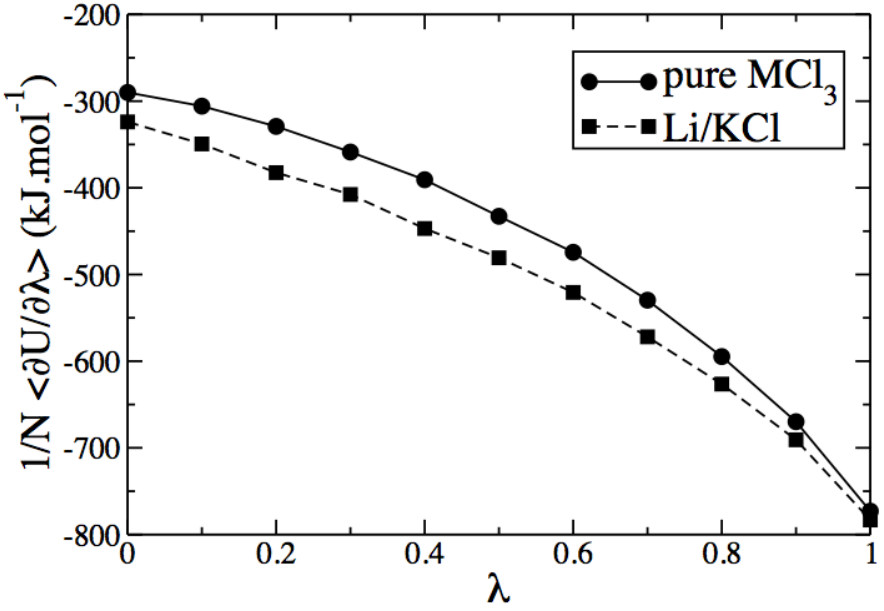
$$V(\lambda) = (1-\lambda)V_{\mathrm{MCl_3/LiKCl}} + \lambda V_{\mathrm{NCl_3/LiKCl}}$$



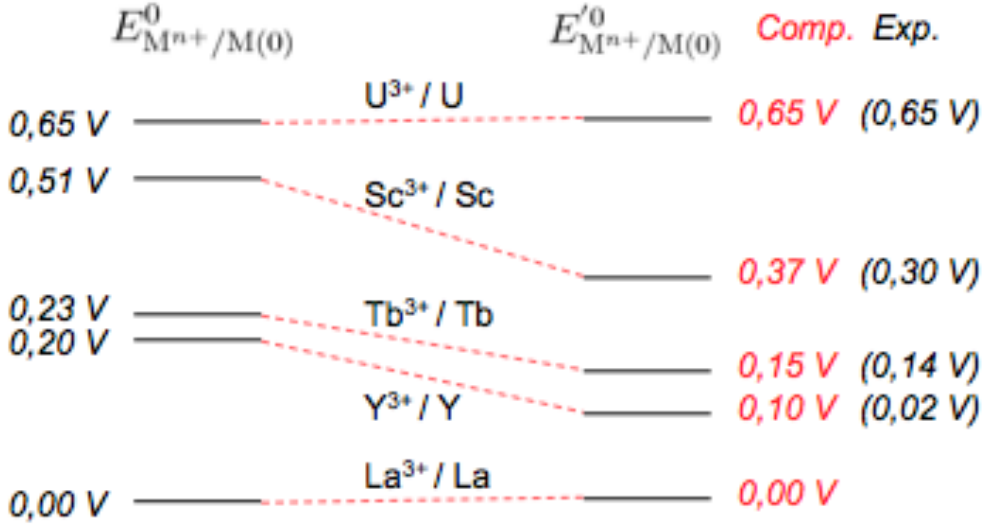
« transmutation »
d' U^{3+} en Sc^{3+}

J. G. Kirkwood, J. Chem. Phys., **1935,** *3*, 300.

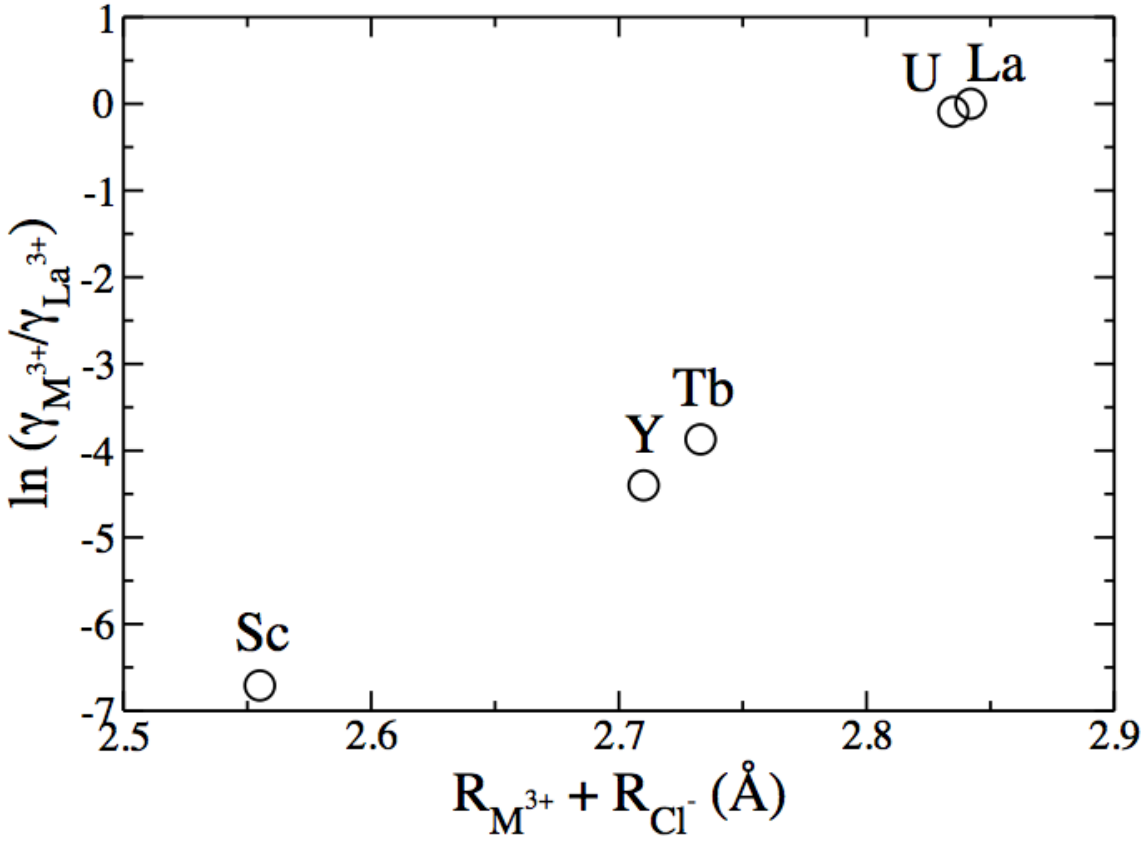
Results



$$\Delta G_i = \int_0^1 \langle \frac{\partial V(\lambda)}{\partial \lambda} \rangle_\lambda \mathrm{d}\lambda$$



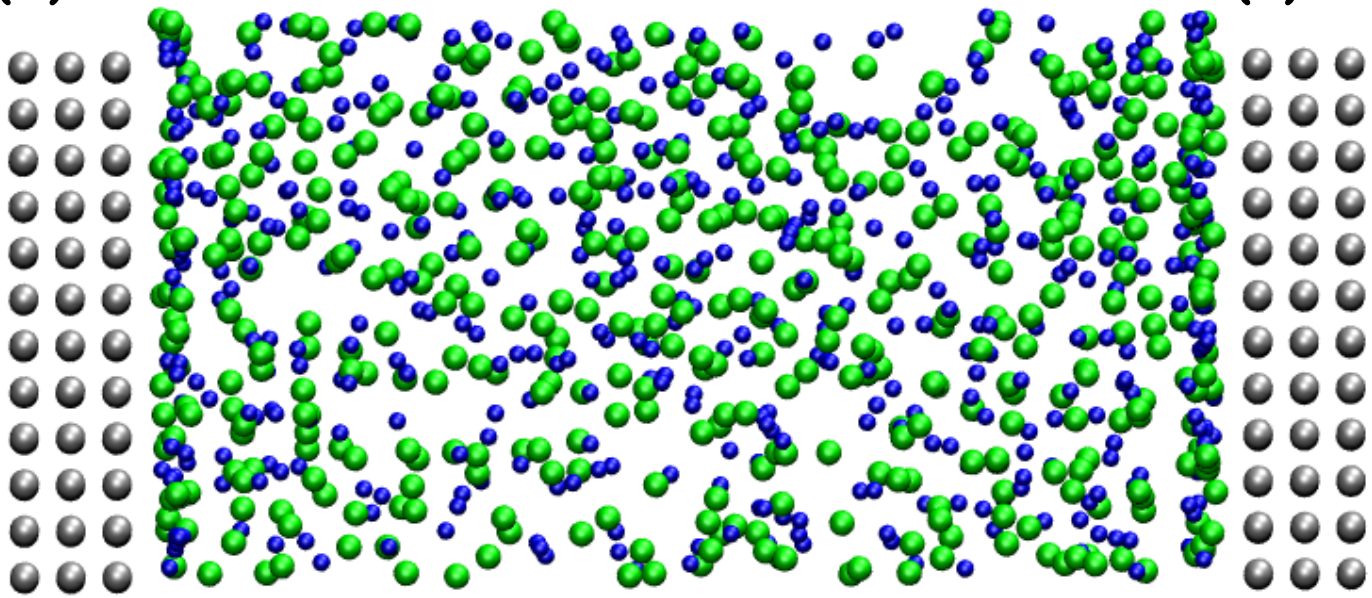
Correlation radius-activity coefficient



Explicit electrochemical cell

Anode (+)

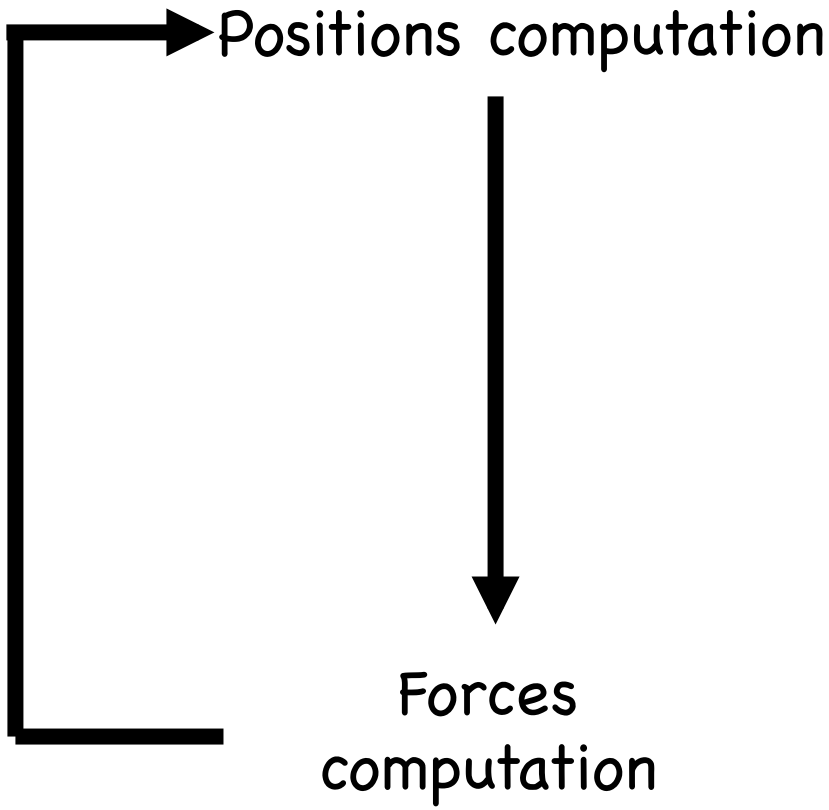
(-) Cathode



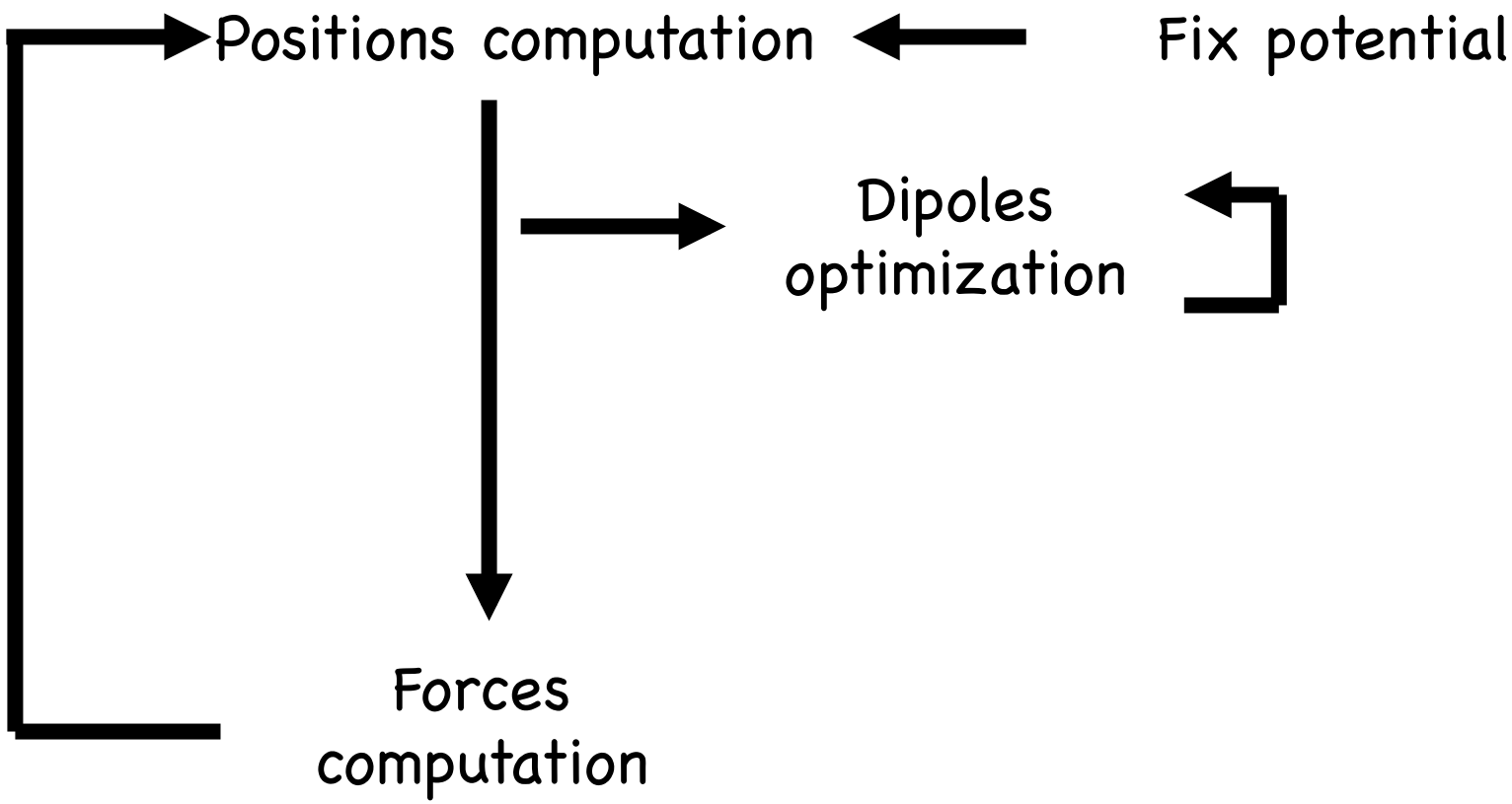
LiCl (1000 ions) + Al (432 atoms, CC [100])

Constant potential simulation

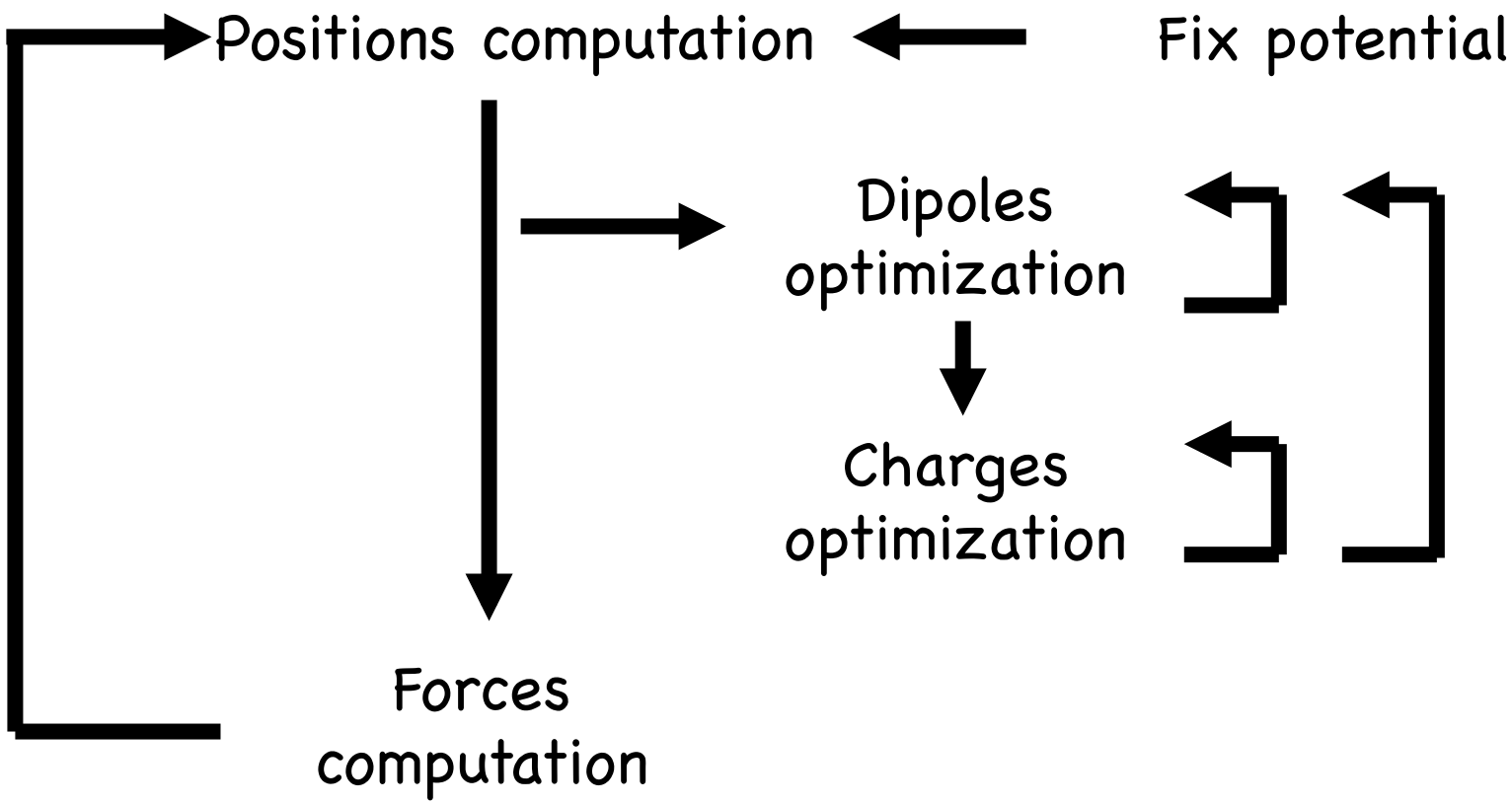
Modified MD algorithm



Modified MD algorithm



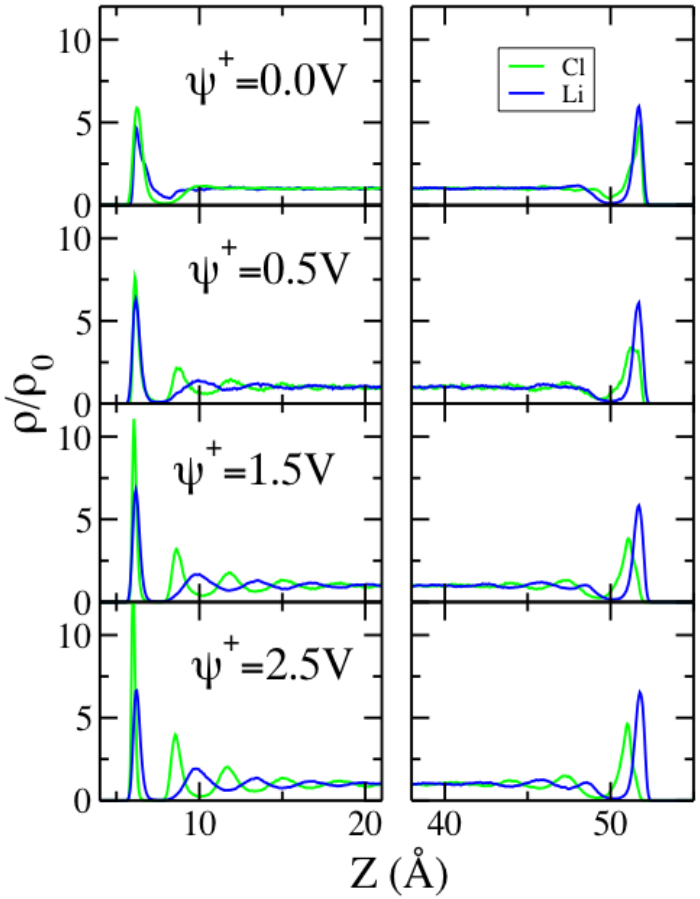
Modified MD algorithm



Surface (100)

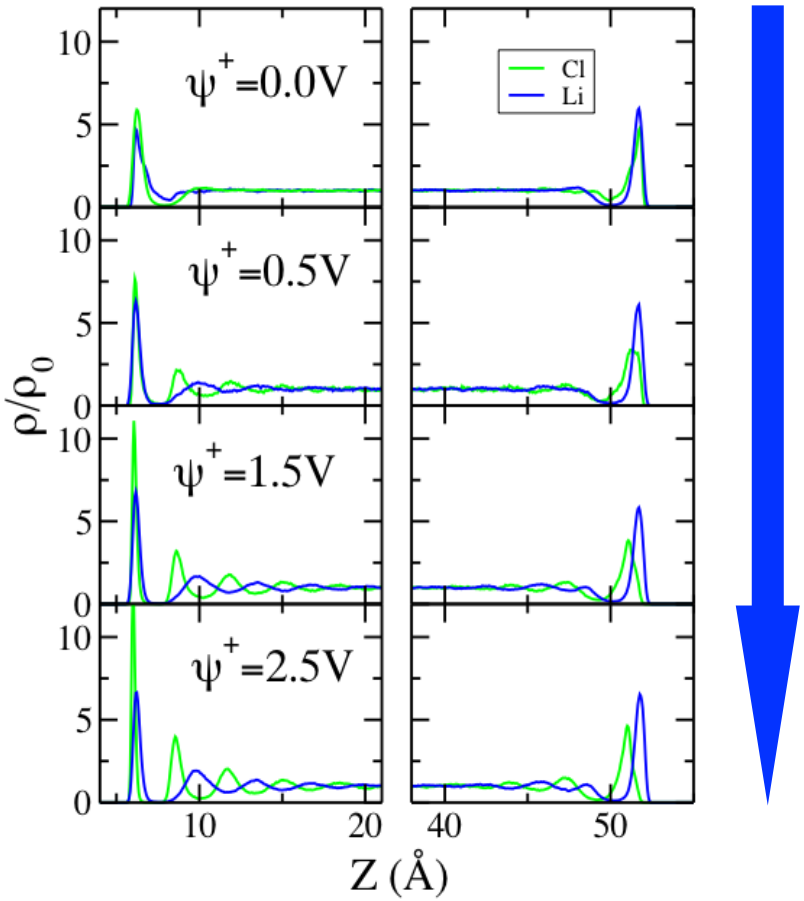
Anode (+)

(-) Cathode



Surface (100)

Anode (+)



(-) Cathode

Adsorption peaks moves

Li^+ stays, Cl^- goes further

Positive charge raising

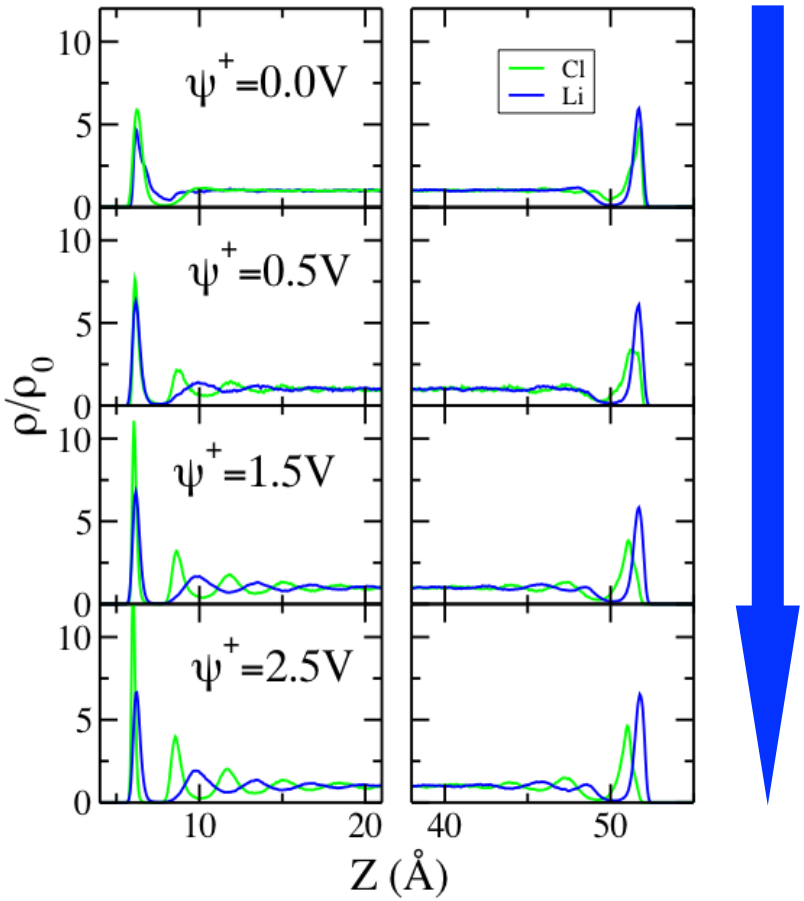
Surface (100)

Anode (+)

Adsorption peak increases

more Cl^- than Li^+

Negative charge raising



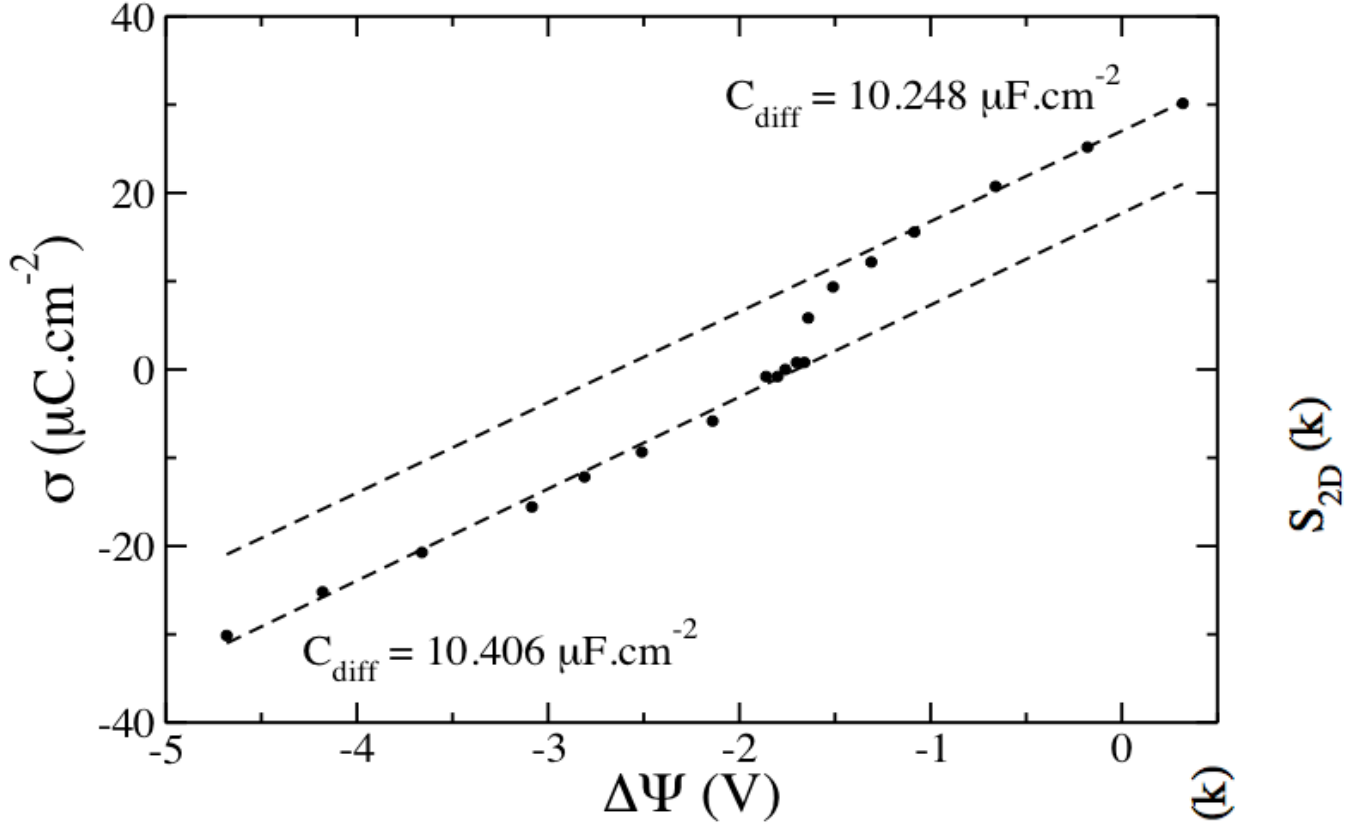
(-) Cathode

Adsorption peaks moves

Li^+ stays, Cl^- goes further

Positive charge raising

Electrodes polarization

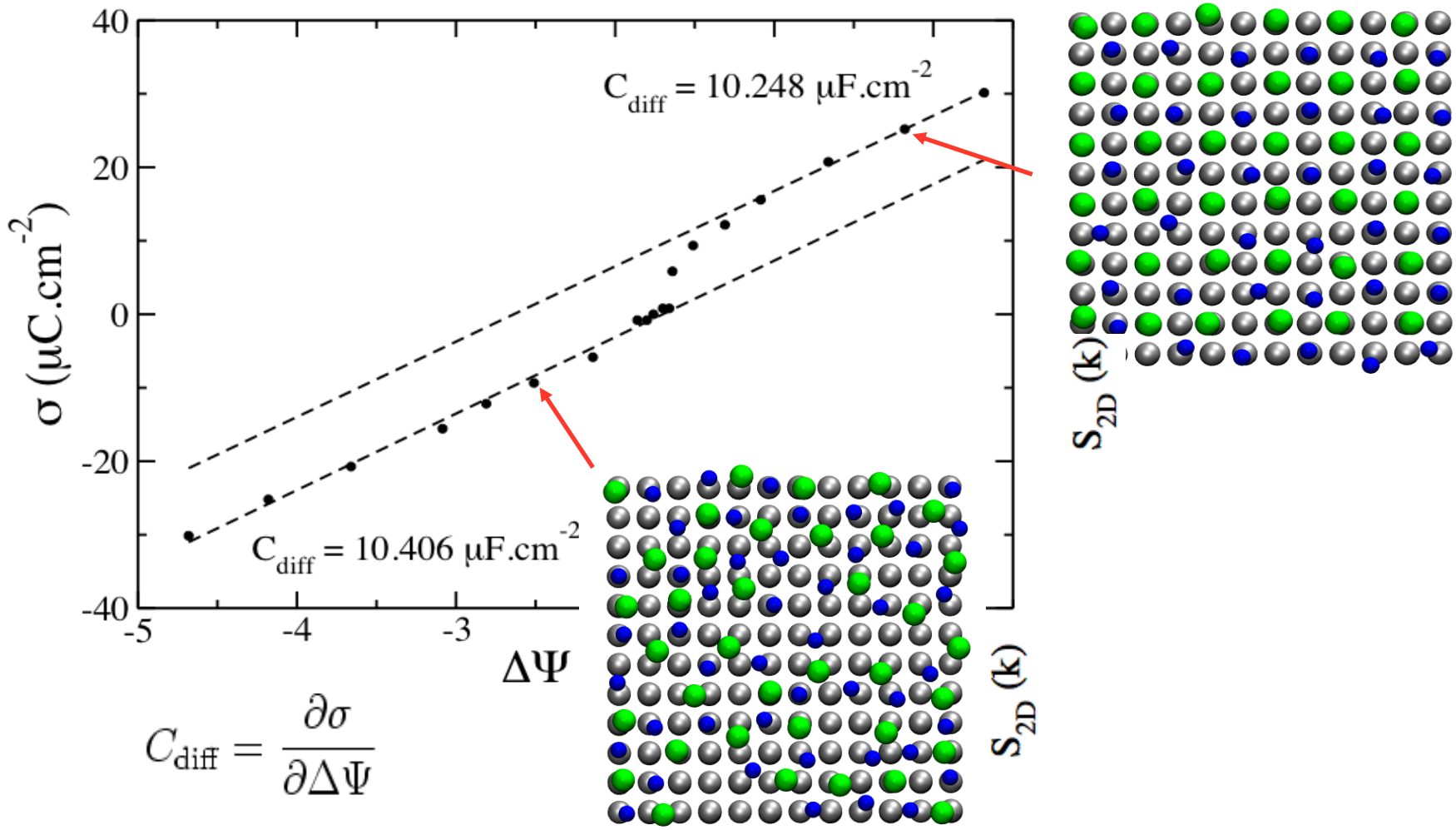


$$C_{\text{diff}} = \frac{\partial \sigma}{\partial \Delta \Psi}$$

S_{2D} (k)

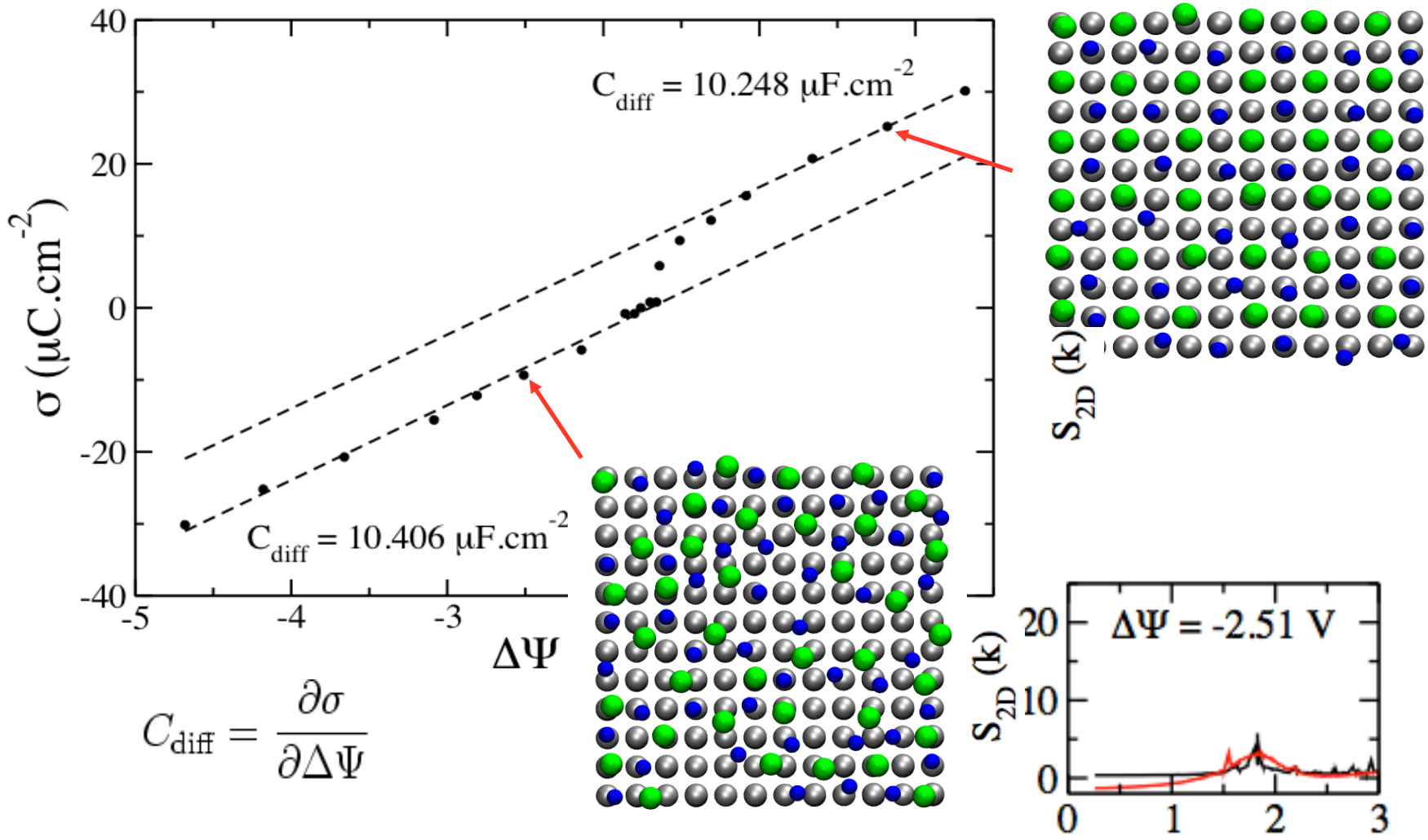
S_{2D} (k)

Electrodes polarization



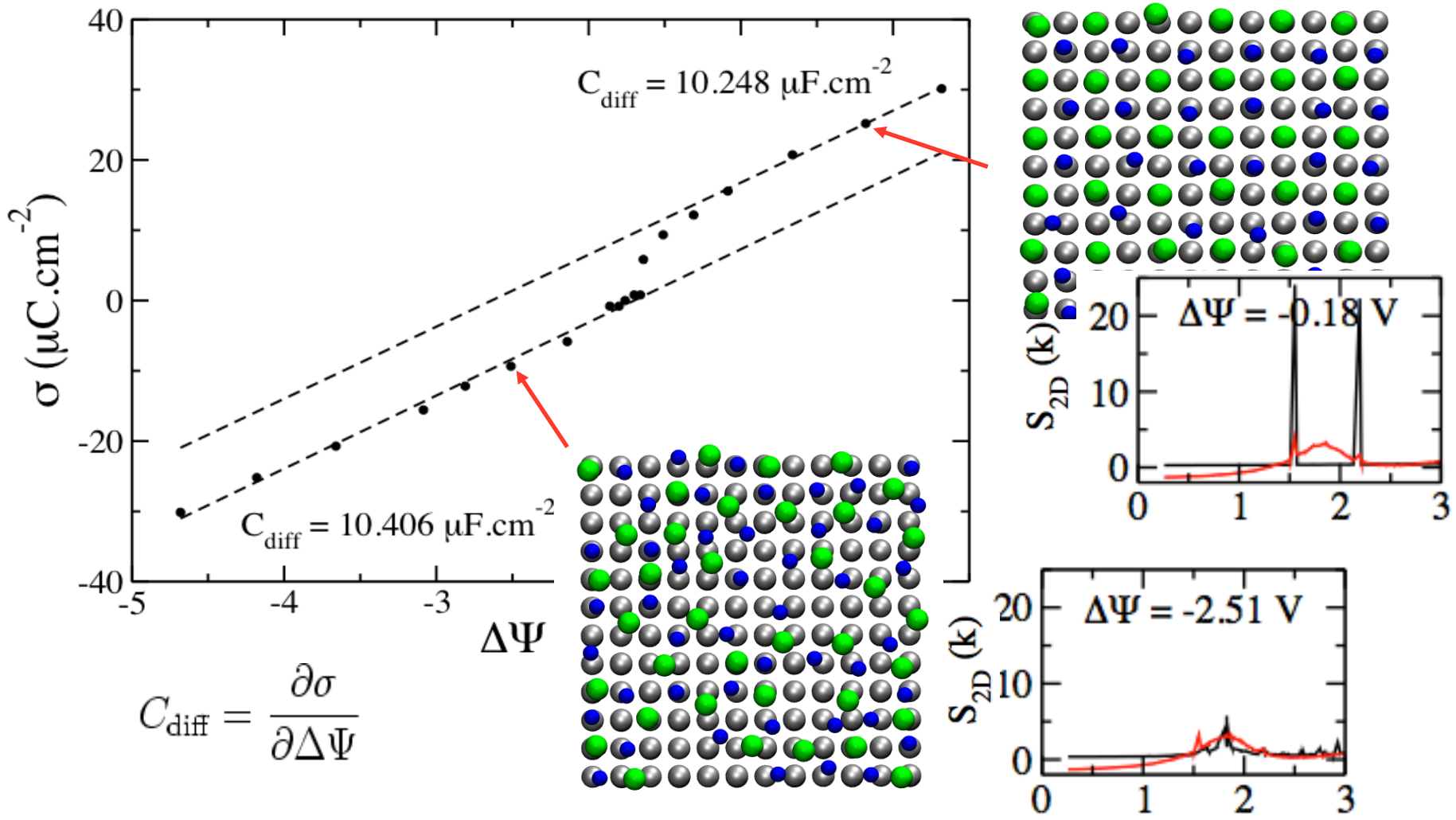
$$C_{\text{diff}} = \frac{\partial \sigma}{\partial \Delta \Psi}$$

Electrodes polarization



$$C_{\text{diff}} = \frac{\partial \sigma}{\partial \Delta \Psi}$$

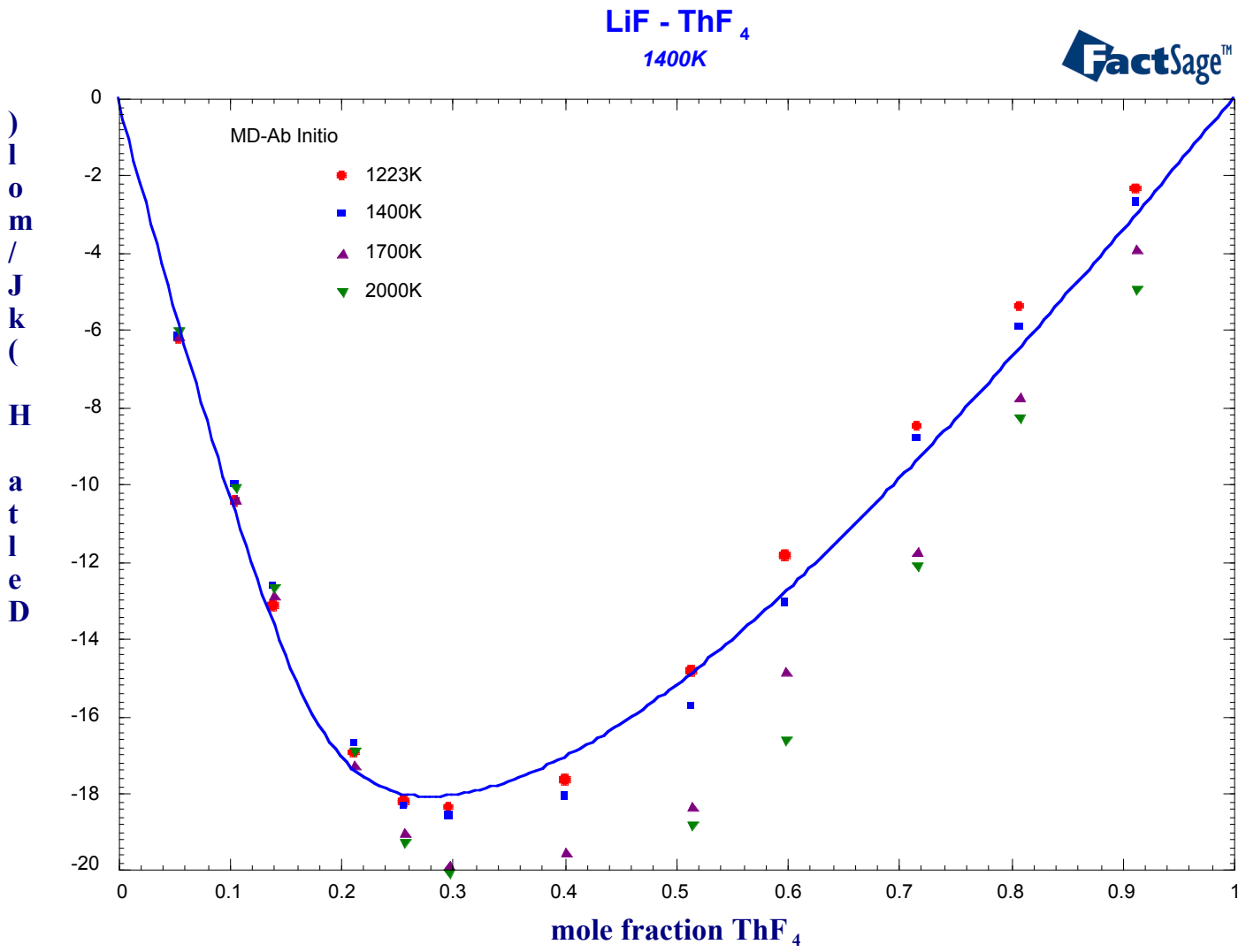
Electrodes polarization



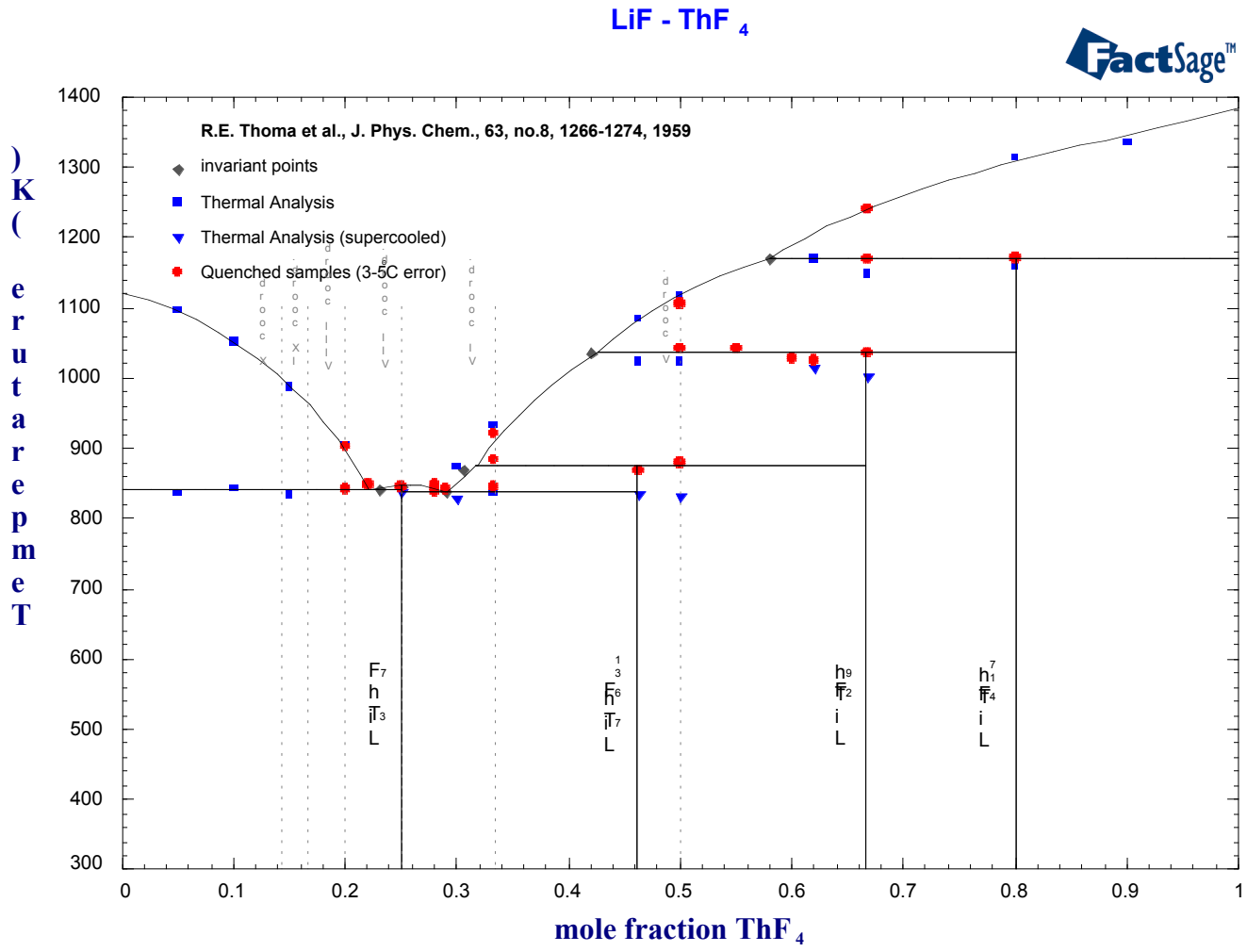
$$C_{\text{diff}} = \frac{\partial \sigma}{\partial \Delta \Psi}$$

More applications : toward thermodynamical models

Enthalpy of mixing



Binary phase diagram



Ternary phase diagram