



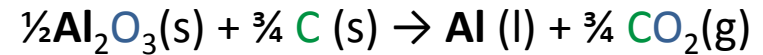
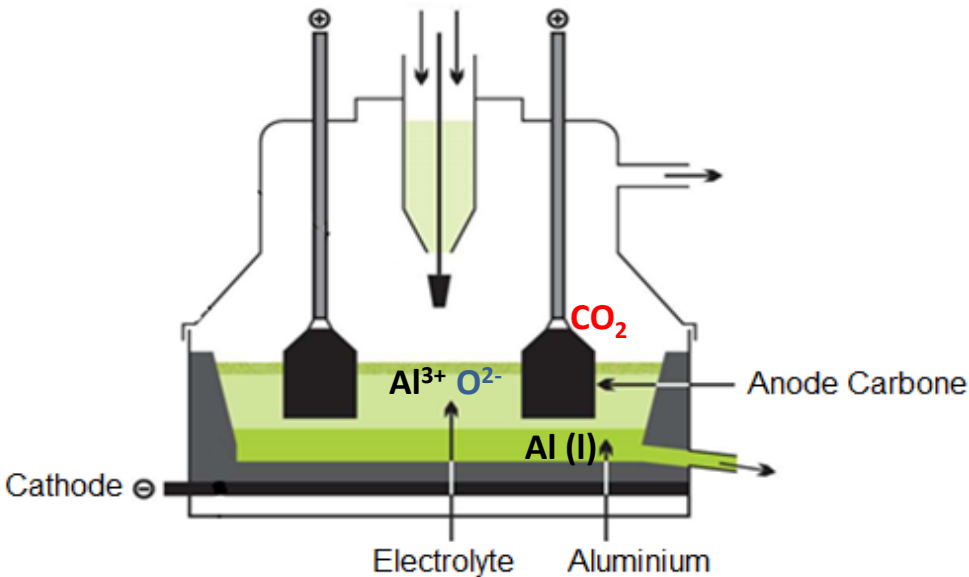
Calculs des déplacements chimiques RMN dans un bain de cryolite fondu en combinant simulation de dynamique moléculaire classique et calculs DFT

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Electrolyse de l'Aluminium

Procédé Hall-Héroult (1886)

Al_2O_3
Alumine



$T \approx 965\text{ }^\circ\text{C}$

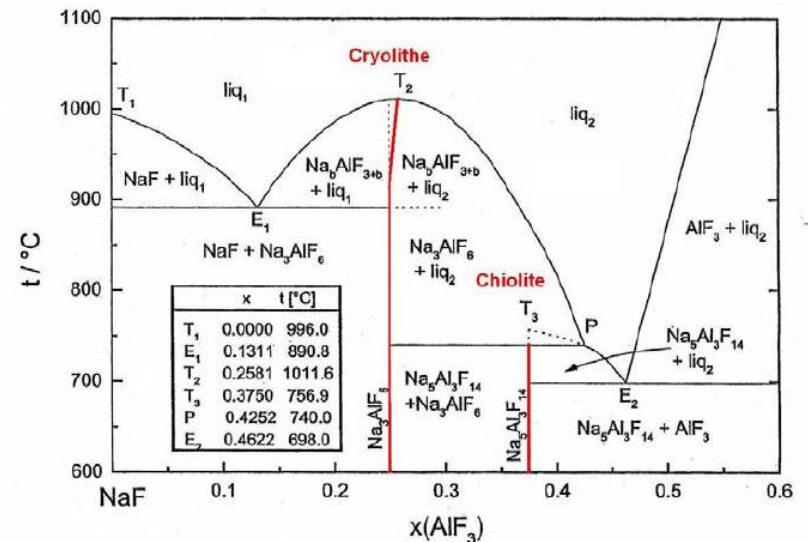
Bain cryolitique:

Cryolithe fondue (Na_3AlF_6)

Al_2O_3 dissoute

Additifs LiF , AlF_3 , CaF_2

Diagramme de phase



Quelles **espèces** dans le bain?

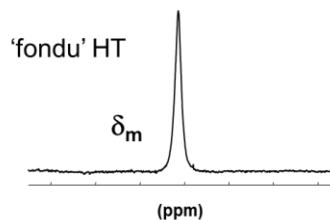
Influence de la température/composition?

Données **thermodynamiques** ?

Structure et propriétés du bain ?

Spéciation dans le bain électrolytique

Démarche...



$$\delta_m(N) = \sum_i X_{A_i}^N \cdot \delta^N(A_i)$$

$$X_{A_i}^N = \frac{\text{Nombre de N contenus dans } A_i}{\text{Nombre total de N}}$$

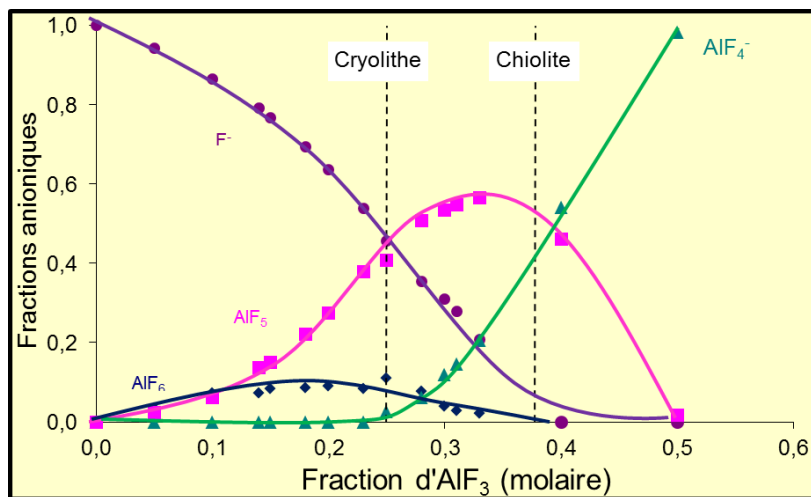
Fractions atomiques \rightarrow Fractions anioniques

RMN in situ à haute température [1]

^{27}Al , ^{23}Na , ^{19}F , ^{17}O

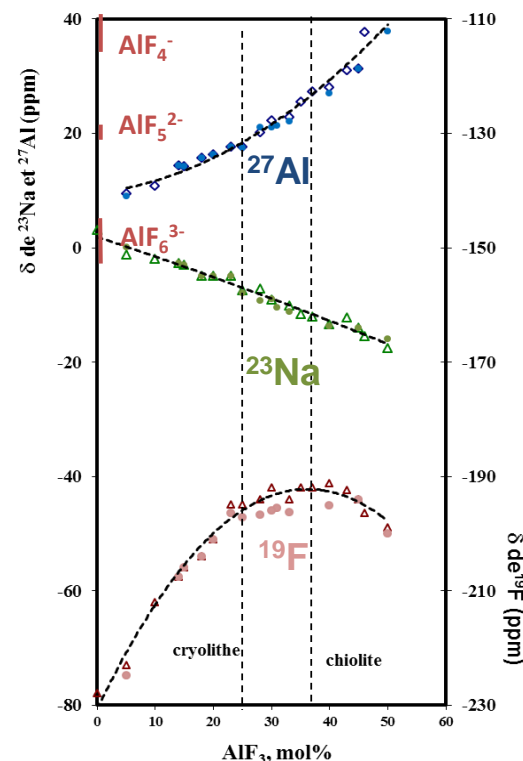
Déplacements chimiques RMN

960 - 1050 °C



Evolution du déplacement chimique

NaF-AlF_3 T liquidus + 20°C

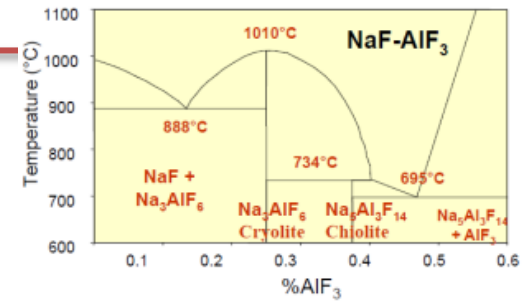
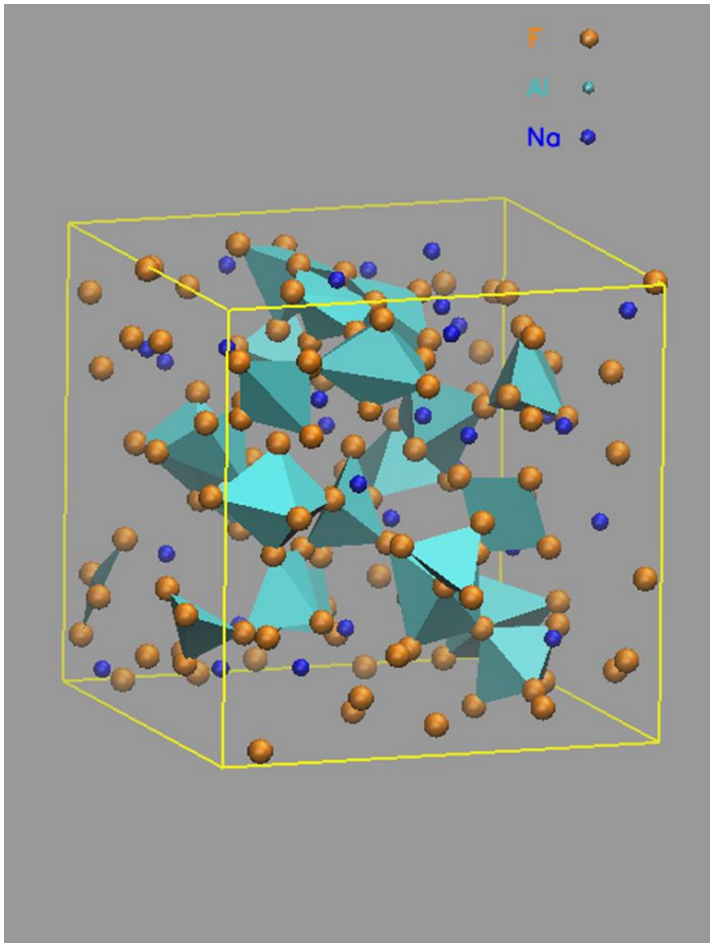


¹ V.Lacassagne et al. J. Phys. Chem. B 2002
I. Nuta Inorg. Chem. 2011

² Madden et al. Chem. Soc. Rev.1996

Dynamique Moléculaire

NaF-AlF₃ (50%-50% mol) 1030 °C



Simulation du liquide selon la composition/Température

Trajectoire atomique de chaque ion selon x, y, z d'une durée de 1 - 5 ns

Déduction des espèces anioniques présentes dans le bain

Grandeurs thermodynamiques (viscosité, conductivité électrique, densité)

Spéciation dans le bain électrolytique

Démarche...

RMN in situ à haute température [1]

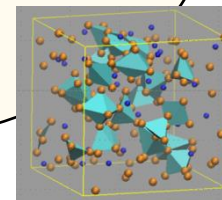
^{27}Al , ^{23}Na , ^{19}F , ^{17}O

Déplacements chimiques RMN



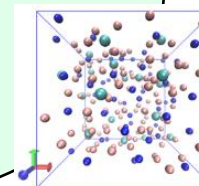
Dynamique Moléculaire

Simulation du liquide
Potentiel d'interaction
Code PIM [2]



Calculs DFT

Calcul des déplacements
chimiques
Code CASTEP [4]



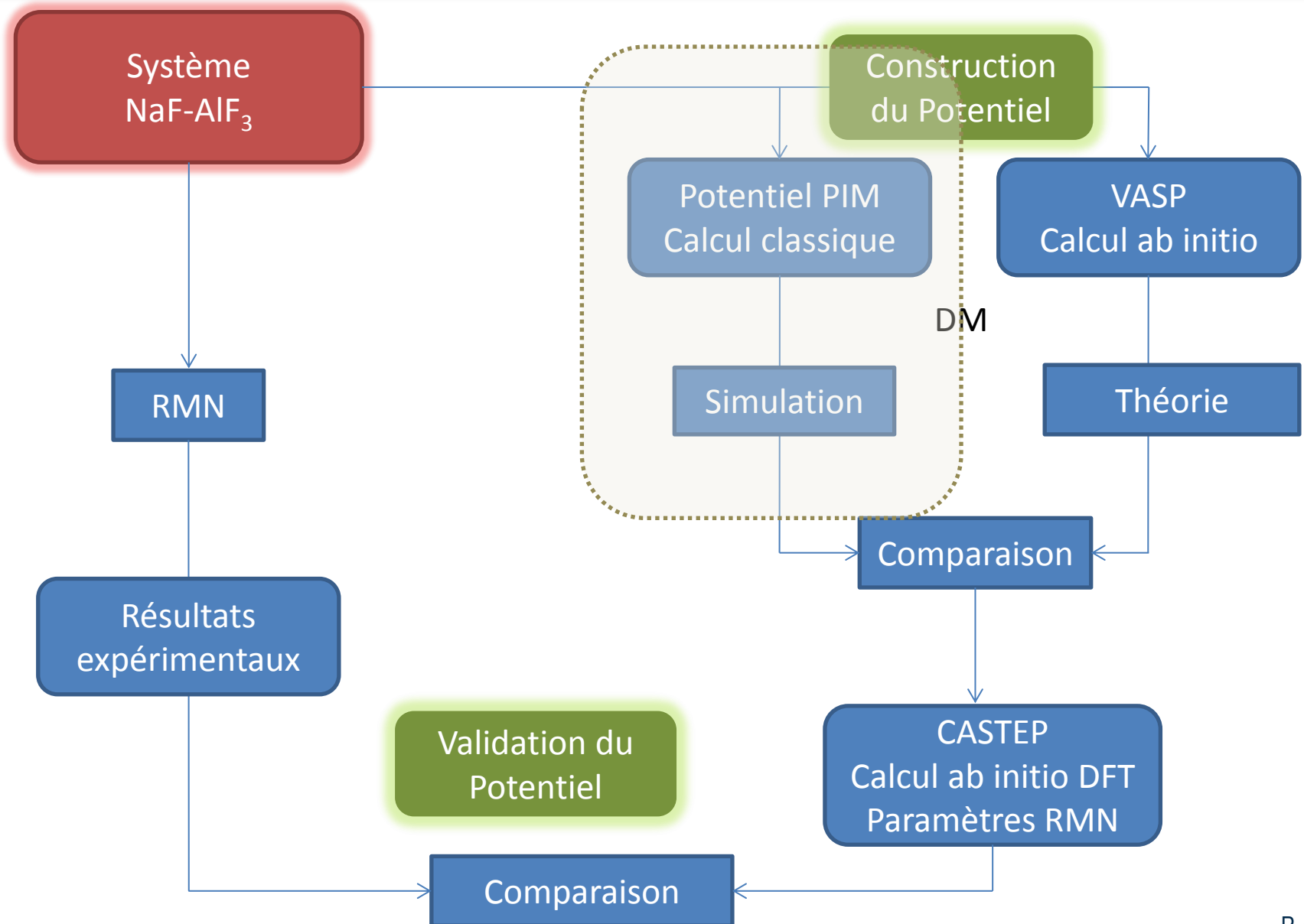
➤ Construction d'un potentiel d'interaction qui décrit le système NaF-AlF_3 de 0-50% AlF_3 à $\approx 1000^\circ\text{C}$

¹ V.Lacassagne et al. J. Phys. Chem. B 2002
I. Nuta Inorg. Chem. 2011

² Madden et al. Chem. Soc. Rev.1996

³ S. J. Clark et al. Zeit. Krist.2005

Démarche de la simulation



Démarche de la simulation

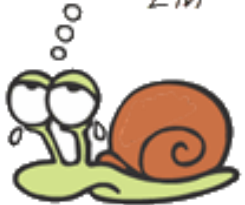
	Dynamique Classique PIM	Dynamique abinitio DFT
Particule élémentaire	Atome / Ion	Electron
Paramétrage / Approximations	<ul style="list-style-type: none"> Potentiels d'interaction atomiques (par paires) Ajusté pour reproduire les forces entres atomes pour une série de systèmes connus -> spécifique d'un type de système	<ul style="list-style-type: none"> Fonctionnelles (GGA, LDA) Pseudopotentiels (par atome) -> Caractère Universel
Nombre typique d'atomes	$\approx 10^3 - 10^6$	$\approx 500 - 1000$
Durée de la dynamique	$< 10^{-8} - 10^{-7} \text{ s}$	$< 10^{-12} - 10^{-11} \text{ s}$
Propriétés	<ul style="list-style-type: none"> Structure hors équilibre Structure Dynamique (longue): Conductivité ionique Viscosité Diffusion Vibration (IR) ... 	<ul style="list-style-type: none"> Structure d'équilibre Dynamique (très rapide) Chemin réactionnel Propriétés électroniques: Conductivité électronique Réponse RMN ...

Dynamique moléculaire

Hypothèse: le mouvement des particules considérées obéit aux lois de la mécanique classique

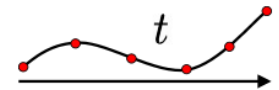
- Les forces entre particules (loi de Newton $\sum \vec{F} = m\vec{a}$) permettent de déterminer l'évolution des vitesses → positions des atomes à un instant t

$$x_j = x_i + v dt + \frac{F}{2m} dt^2$$



$$F = -\frac{dV}{dr} ; V = \text{Potentiel d'interaction}$$

Champ de Forces ?!



NaF-AlF₃: sel fondus

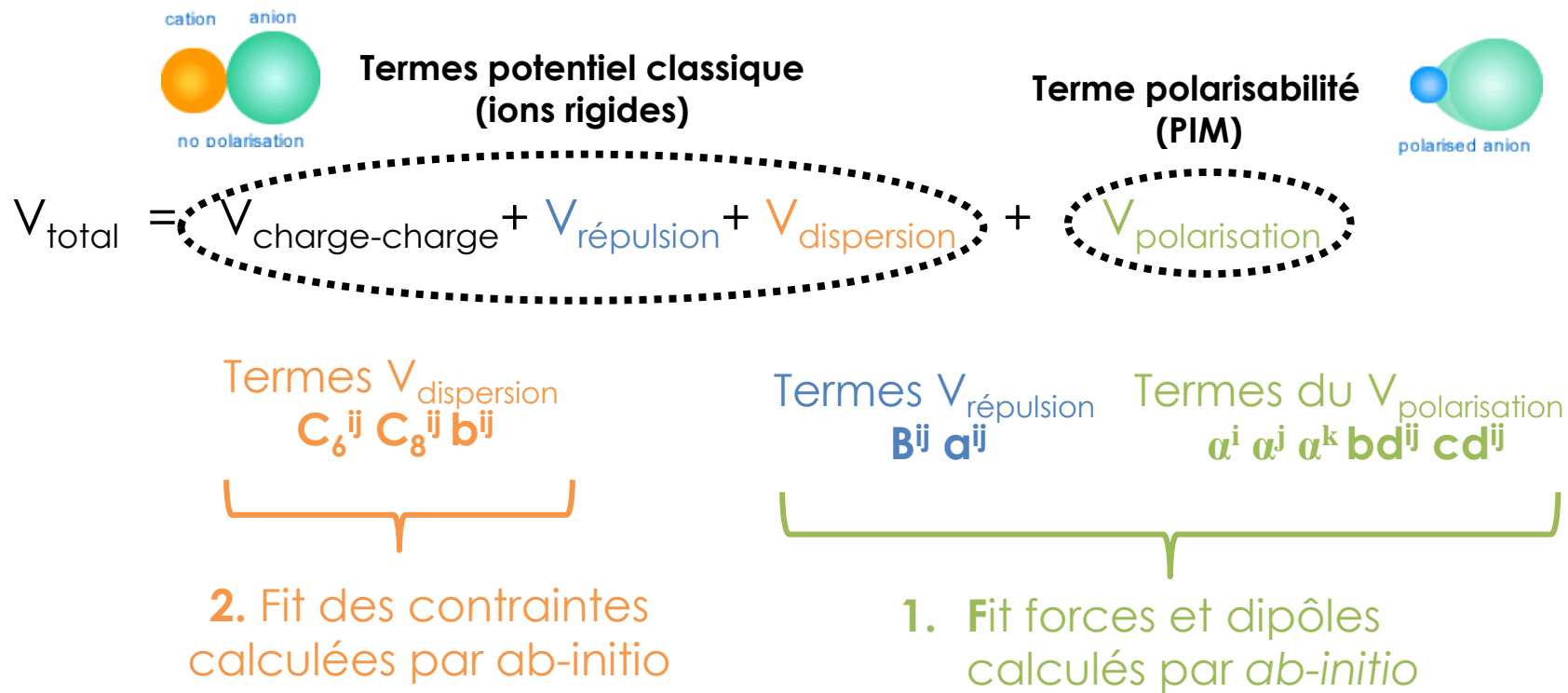


liquides ioniques à HT



Ions polarisables

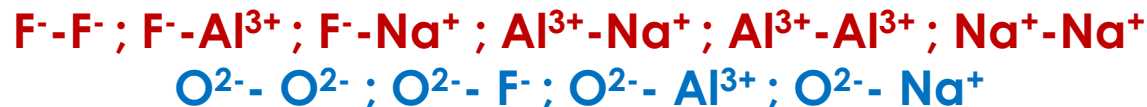
Potentiel PIM: Polarizable Ion Model ^[1]



Modèle de paires atomiques:

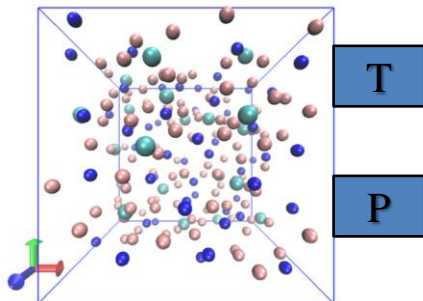
NaF-AlF₃: 3 espèces (F, Al, Na) → 6 paires

NaF-AlF₃-Al₂O₃: 4 espèces (F, Al, Na, O) → 10 paires



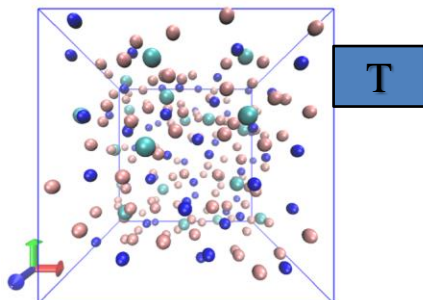
Dynamique Moléculaire Classique

Ensemble NPT



$L (\text{Å}) = \text{libre}$

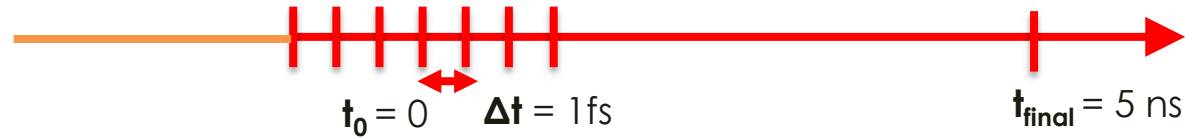
Ensemble NVT



$L (\text{Å}) = \text{fixé}$

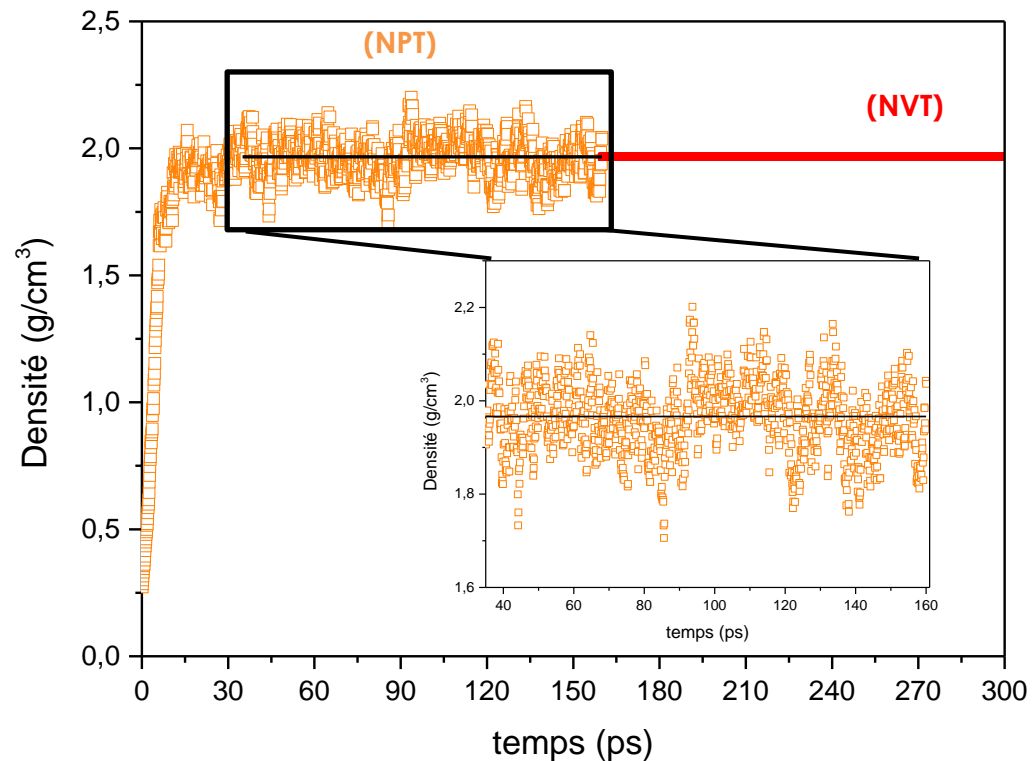
Phase équilibrage
(NPT)

Phase production
(NVT)



$$d(\text{at}/\text{Å}^3) = \frac{N_{\text{atomes}}}{L^3}$$

N : nombre d'atomes
V : volume
P : pression
T : température



Dynamique moléculaire Classique

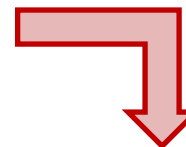
Caractéristiques des fichiers d'entrée

runtime.inpt : Conditions du calcul

potential.inpt : Paramètres du potentiel

restart.dat : Positions des atomes

Trajectoire de 1ns pour
200 atomes avec
13 coeurs ~ 3h



Runtime.inpt

```
160000      Number of steps in the run.
1305        Translational temperature.
1           Number of ionic molecular units.
3           Number of ionic species.
120,20,60   Number of species of type 1.
-1.0,3.0,1.0 Permanent charge on ions.
18.9984,26.97,22.997 Atomic masses
.true,..false,..true.    Polarizable ?
.false,..false,..false.  Deformable ?
41.342      Timestep (a.u.).
dippim      Type of run (rim,dippim,quadpim)
epp         Type of run 2 (epp,cim,aim)
.false.     AIM effects on anion-anion interactions?
.true.     Like-like multipole damping?
.false.     Isolated cluster?
.false.     Environmental effects on PIM?
.false.     Environmental effects on AIM?
.true.     Conjugate gradient minimisation? (PIM)
1.0d-08     Conjugate gradient minimisation? (AIM)
1.0d-08     Restart?
.false.     Set up velocities?
.true.     Velocity rescale prior to main run ?
.false.     Random displacement of ions.
.true.     Move ions?
.false.     Do a dynamical matrix calculation?
.false.     Relax input structure?
100         Number of steps inbetween periodic output (energies).
100         Number of steps inbetween periodic output (velocities etc).
100         Number of steps inbetween periodic output (frictions etc).
100         Number of steps inbetween periodic output (pressure etc).
50          Number of steps inbetween rdf call in main loop.
1           Number of ions to monitor.
1           Ion number to monitor. (1)
5.60d0     eta = <x>/boxlen.
19.2d0     rcut (au).
1.0d-7     convergence parameter
0.1d0     convergence factor.
19.2d0     rcut (au) short range.
.true.     Nose-Hoover thermostat? (if true then enter a relaxation time)
20000     Periodic rescale of temperature?
.false.     Isotropic barostat?
20000     Anisotropic barostat?
1.0d-8     Orthorhombic cell?
.false.     Orthorhombic cell?
```

Caractéristiques des fichiers de sortie

positions.out : Trajectoire atomique x, y, z

xxyzzstress.out : Tenseur des contraintes

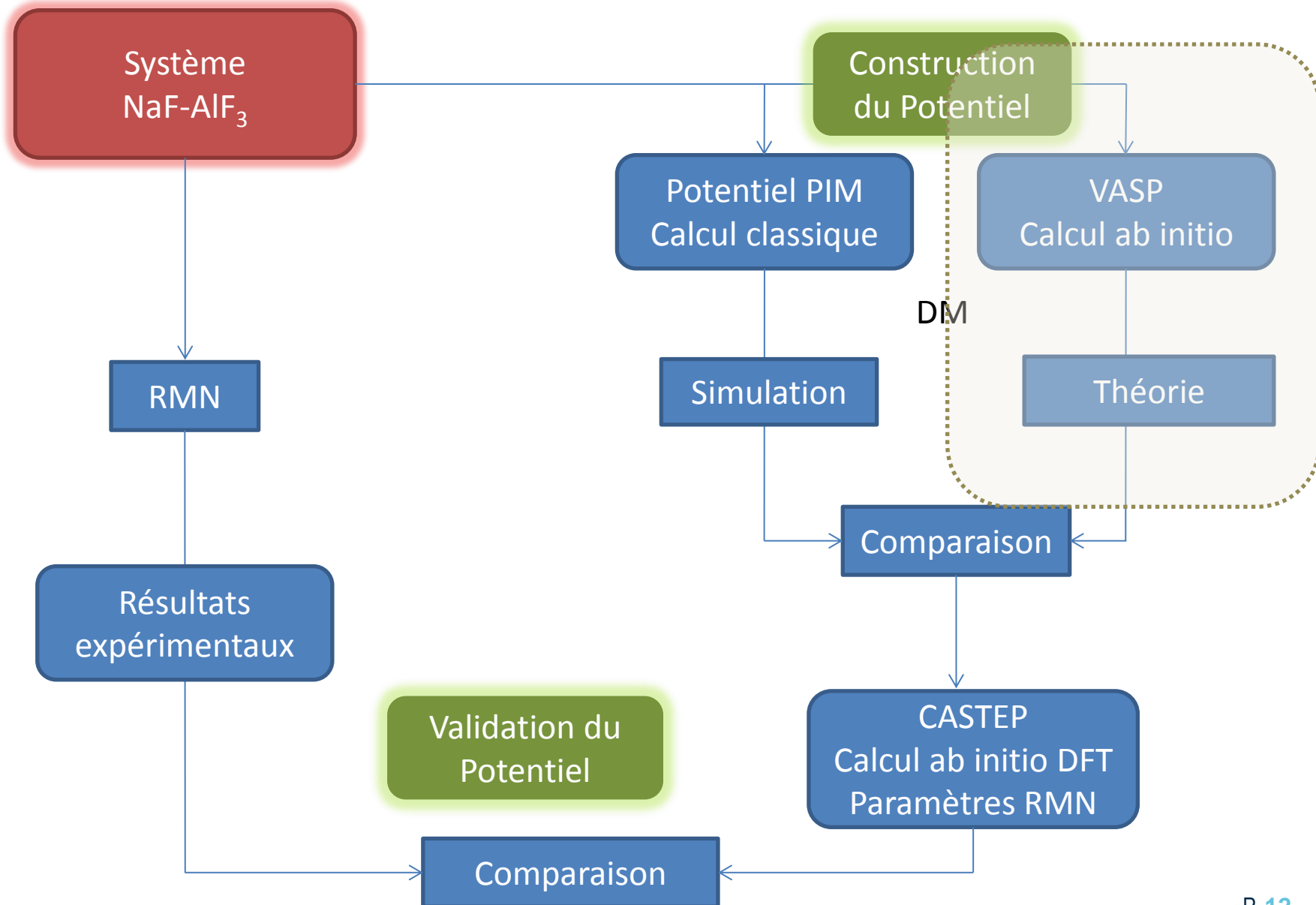
xyxzyzstress.out :

rdfij.out : fonction distribution radiale ij

Fort.48 : Forces

Fort.45 : Dipôles

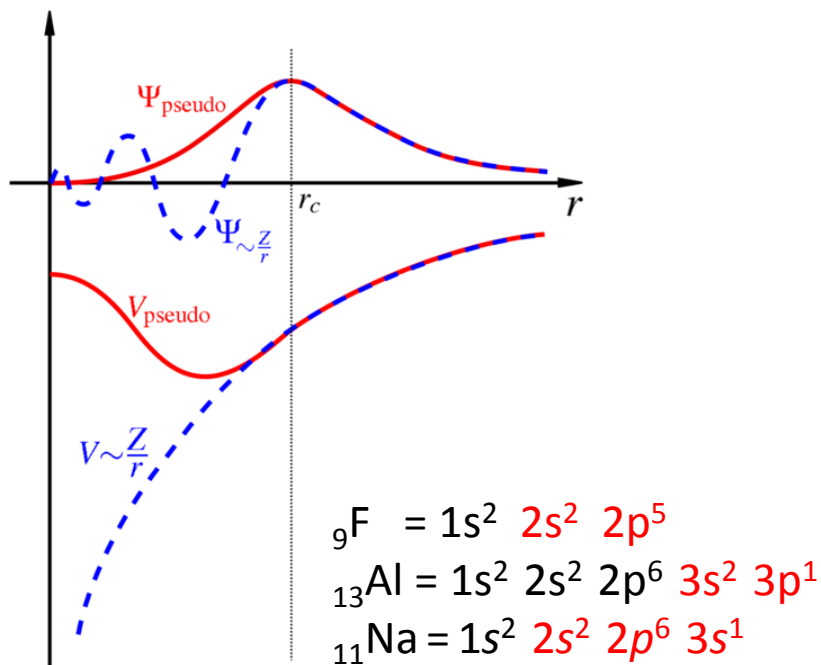
Démarche de la simulation



Calcul ab initio – DFT

VASP 5.3 : Vienna Ab initio Simulation Package

- Logiciel qui utilise DFT pour résoudre le problème quantique pour les matériaux



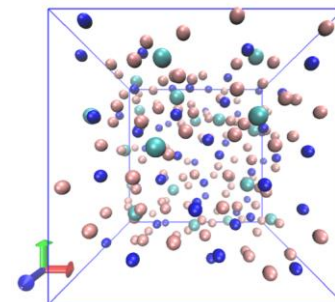
Pour la cryolite 1440 électrons
Durée de la DM: 200 fs

	Dynamique abinitio DFT
Particule élémentaire	Electron
Paramétrage / Approximations	<ul style="list-style-type: none"> Fonctionnelles (GGA, LDA) Pseudopotentiels (par atome) -> Caractère Universel
Nombre typique d'atomes	≈ 500 - 1000
Durée de la dynamique	< 10^{-12} - 10^{-11} s
Propriétés	<ul style="list-style-type: none"> Structure d'équilibre Dynamique (très rapide) Chemin réactionnel Propriétés électroniques: Conductivité électronique Réponse RMN ...

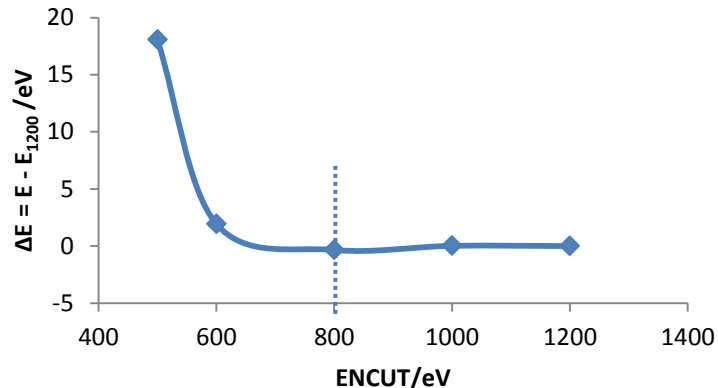
Stratégie – calcul ab initio VASP

Etape préliminaire création de boîtes :

nombre d'atomes en fonction de la composition du système
≈ 200 atomes (1400 – 1800 électrons)



I. Ajustement de Energie cut-off (ENMAX)

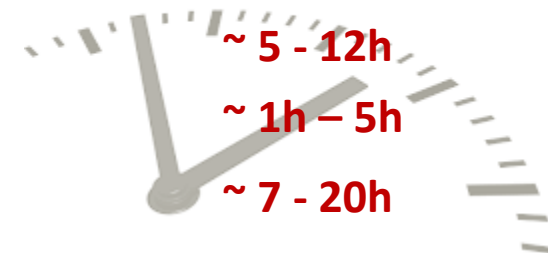


II. Equilibration DM → calcul rapide – 200 fs

III. Single point Forces

IV. Single point Dipôle

} calcul précis sur 1 pas de temps



Calcul ab initio – DFT

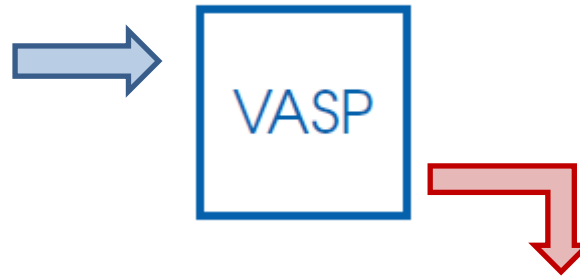
VASP 5.3 : Vienna Ab initio Simulation Package

Caractéristiques des fichiers d'entrée

INCAR : Type de calcul et paramètres du calcul

POSCAR : Positions initiales des atomes

POTCAR : Pseudo-potentiels utilisés



POTCAR

Pseudo potentiel pour chaque ion

GGAPBE

Caractéristiques des fichiers de sortie

WAVECAR : Fonction d'onde

OUTCAR : Convergence électronique et géométrique

XDATCAR : Positions des atomes

Fort.98 : Forces

Fort.91 : Tenseur des contraintes

Fort.95 : Dipôles

```
PAW_PBE_F_08Apr2002
7.000000000000000 valence
parameters from POTCAR are:
URHFIL = F: s2p5
LEXCH = PE
EATOM = 659.6475 eV, 48.4827 Ry
énergie pseudo atome isolé
TITEL = PAW_PBE_F_08Apr2002
LULTRA = F use ultrasoft PP ?
IUNSCR = 1 unscreen: 0-lin 1-nonlin 2-no
RPACOR = 1.200 partial core radius
POMASS = 18.998; ZVAL = 7.000 mass and valenz
RCORE = 1.520 outmost cutoff radius
RWIGS = 1.500; RWIGS = 0.794 wigner-seitz radius (au A)
ENMAX = 400.000; ENMIN = 300.000 eV
LCOR = T correct aug charges
LPAW = T paw PP
EAUG = 613.614
RMAX = 1.555 core radius for proj-oper
RAUG = 1.300 factor for augmentation sphere
RDEP = 1.539 radius for radial grids
RDEPT = 1.299 core radius for aug-charge
```

Atomic configuration

VASP: Vienna Ab initio Simulation Package

INCAR

```
SYSTEM = NaF-AlF3

!Start Parameters:
!!NWRITE = 2 (Medium-level output information)
NWRITE = 0 (Low-level output information for MD)
ISTART = 1 (Read existing wavefunction)
INIWAV = 1 (Random initial wavefunction)
!!CORELEVEL = 1 (Print corelevels in OUTCAR)
!!ICHARG = 11 (Non-selfconsistent: band structures)
!!NELECT = 352 (Number of electrons: charged cells)
!NBANDS = 816 (Increase no. bands)

!Parallel Options:
!LPLANE = .TRUE.
!NCORE = 12 number of cores per nodes (e.g. 4 or 8)
!NPAR = 12
!LSCALU = .FALSE.
!NSIM = 1

!Electronic Relaxation:
!PREC = Normal (Precision level)
PREC = Low (Precision level)
LREAL = Auto (Projection operators: automatic)
ROPT = 1E-04 1E-04 1E-04 1E-04
!ALGO = FAST (Elect. algorithm: 38/48)
ALGO = Very Fast (Elect. algorithm for MD)
!ALGO = ALL (IALGO=58: Metals/Insulators for HSE)
!ALGO = DAMPED (Dampen: IALGO=53: Metals/Insulators for HSE)
ENMAX = 400.00 eV (Plane-wave cutoff)
NELM = 80 (Max number of SCF steps)
!NELMIN = 4 (Min number of SCF steps)
EDIFF = 1E-04 (SCF convergence)
ISPIN = 1 (Closed shell)
!ISPIN = 2 (Spin polarized)
GGA = PE (PBE exchange-correlation)
ADDGRID = .TRUE. (Increase grid: helps GGA)
LASPH = .TRUE. (Non-spherical elements: f

!Ionic Relaxation:
EDIFFG = -0.030 (Ionic convergence eV/A)
NSW = 100 (Max ionic steps)
NBLOCK = 10 (Update XDATCAR/DOSCAR every X steps)
NBRION = 0 (Ions: 0-MD, 1-Quasi-New, 2-CG)
ISIF = 2 (Stress/Relaxation: 2-Ions 3-Shape/Ions/V 7-Vol)
ISYM = 0 (Symmetry: Use all, 0: f
!SYMPREC = 1E-05 (Symmetry: POSCAR precis
LCORR = F (Add non-SCF force corre
ISMEAR = 0 (Gaussian smearing, Met
ISMEAR = -1 (Fermi smearing)
!!ISMEAR = -5 (Tetra. methd. smearing)
SIGMA = 0.01 (Smearing in eV, Metals:

!Molecular Dynamics:
POTIM = 2.0 (Timestep fs)
MDALGO = 2 (NH thermostat, define SMASS)
!MDALGO = 3 (NPT dynamics Parrinello-Rahman)
!LANGEVIN_GAMMA = 75 55 45 75
!LANGEVIN_GAMMA_L = 12
PSTRESS = 0 (external pressure)
TEBEG = 1305 (Start temp K)
TEEND = 2000 (End temp K)
SMASS = 1 (T scaling every NBLOCK stps in NH NVT)
!!SMASS = 3 (Prod. MD run)
!PMASS = 400 (NPT ensemble)
MAXMIX = 40

!wannier90 interface
!LWANNIER90 = .TRUE.
!LWANNIER90_RUN = .TRUE.
!LWRITE_MMN_AMN = .TRUE.

!Start Parameters:
!!NWRITE = 2 (Medium-level output information)
NWRITE = 0 (Low-level output information for MD)
ISTART = 1 (Read existing wavefunction)
INIWAV = 1 (Random initial wavefunction)
!!CORELEVEL = 1 (Print corelevels in OUTCAR)
!!ICHARG = 11 (Non-selfconsistent: band structures)
!!NELECT = 352
!NBANDS = 816

!Miscellaneous:
LORBIT = 11 (PAW radii for projected DOS)
!!LORBIT = 1 (Supply radii for projected DOS)
!RWIGS = 1.5 1.5 (Radii for each atomic species)
!!LOPTICS = .TRUE. (Output OPTIC file)
!NEDOS = 1000 (Increase DOSCAR points)
!!LVTOT = .TRUE. (Electrostatic potential)
!!LELF = .TRUE. (Localization function)
!VDW = 11

!Electronic Relaxation:
!PREC = Normal (Precision level)
PREC = Low (Precision level)
LREAL = Auto (Projection operators: automatic)
ROPT = 1E-04 1E-04 1E-04 1E-04
!ALGO = FAST (Elect. algorithm: 38/48)
ALGO = Very Fast (Elect. algorithm for MD)
!ALGO = ALL (IALGO=58: Metals/Insulators for HSE)
!ALGO = DAMPED (Dampen: IALGO=53: Metals/Insulators for HSE)
ENMAX = 400.00 eV (Plane-wave cutoff)
NELM = 80 (Max number of SCF steps)
!NELMIN = 4 (Min number of SCF steps)
EDIFF = 1E-04 (SCF convergence)

!Molecular Dynamics:
POTIM = 2.0 (Timestep fs)
MDALGO = 2 (NH thermostat, define SMASS)
!MDALGO = 3 (NPT dynamics Parrinello-Rahman)
!LANGEVIN_GAMMA = 75 55 45 75
!LANGEVIN_GAMMA_L = 12
PSTRESS = 0 (external pressure)
TEBEG = 1305 (Start temp K)
TEEND = 2000 (End temp K)
SMASS = 1 (T scaling every NBLOCK stps in NH NVT)
!!SMASS = 3 (Prod. MD run)
!PMASS = 400 (NPT ensemble)
MAXMIX = 40
```

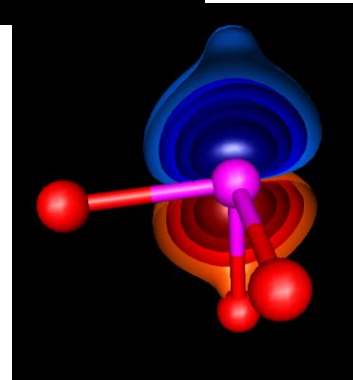
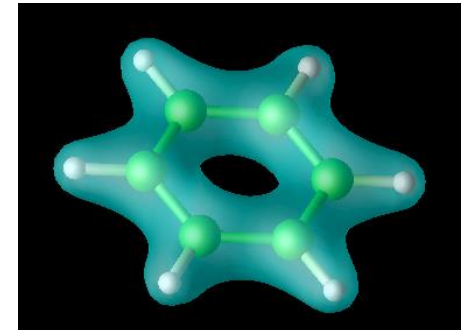

Obtention des Forces, Dipôles et Contraintes

Single Point

Forces et Contraintes

- Relaxation électronique précision normal (PREC)
- Convergence de la relaxation ionique plus petit (EDIFFG)

INCAR



```
!Electronic Relaxation:
PREC = Normal (Precision level)
!PREC = Low (Precision level)
LREAL = Auto (Projection operators: automatic)
ROPT = 1E-04 1E-04 1E-04 1E-04
ALGO = FAST (Elect. algorithm: 38/48)
!ALGO = Very Fast (Elect. algorithm for MD)
!ALGO = ALL (IALGO=58: Metals/Insulators for HSE)
!ALGO = DAMPED (Dampen: IALGO=53: Metals/Insulators for HSE)
ENMAX = 600.00 eV (Plane-wave cutoff)
NELM = 200 (Max number of SCF steps)
!NELMIN = 4 (Min number of SCF steps)
EDIFF = 1E-05 (SCF convergence)
ISPIN = 1 (Closed shell)
!ISPIN = 2 (Spin polarized)
GGA = PE (PBE exchange-correlation)
ADDGRID = .TRUE. (Increase grid: helps GGA convergence)
LASPH = .TRUE. (Non-spherical elements: PAW d/f convergence)

!Ionic Relaxation:
EDIFFG = -0.010 (Ionic convergence eV/A)
NSW = 0 (Max ionic steps)
NBLOCK = 10 (Update xDATCAR/POSCAR every X steps)
IBRION = 2 (Ions: 0-MD, 1-Quasi-New, 2-CG)
ISIF = 2 (Stress/Relaxation: 2-Ions, 3-Shape/Ions/V, 7-vol)
ISYM = 1 (Symmetry: Use all, 0: none)
!SYMPREC = 1E-05 (Symmetry: POSCAR precision)
LCORR = F (Add non-SCF force correction)
ISMEAR = 0 (Gaussian smearing, Metals:1, MP)
!SMEAR = -1 (Fermi smearing)
!!ISMEAR = -5 (Tetrah. methd.smearing, Metals:1, MP)
SIGMA = 0.01 (Smearing in eV, Metals:0.2)
```

Obtention des Forces, Dipôles et Contraintes

Single Point

Forces et Contraintes

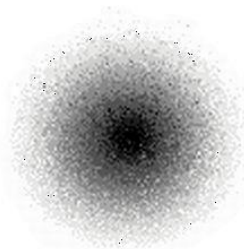
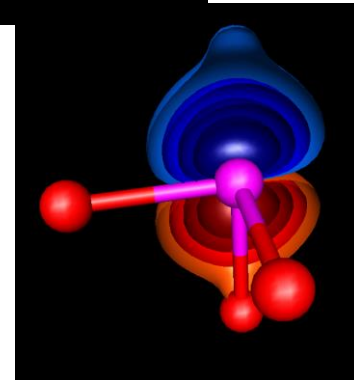
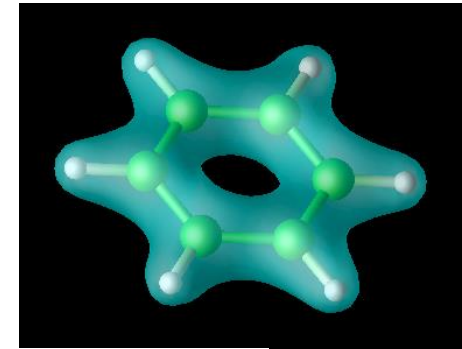
- Relaxation électronique précision normal (PREC)
- Convergence de la relaxation ionique plus petit (EDIFFG)

INCAR

Dipôles (Librairie Wannier)

- Localisation des charges dans la fonction d'onde
- Fonctions Wannier localisent les centres wannier (CW) qui représentent les électrons de la couche de valence
- Dipôle = barycentre entre CW et la position du noyau

Perl^[1]
Programming



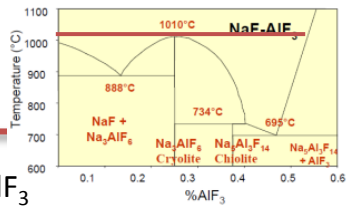
Electron



Noyau
atomique



Ajustement du Potentiel



$$V_{\text{total}} = V_{\text{charge-charge}} + V_{\text{dispersion}} + V_{\text{répulsion}} + V_{\text{polarisation}}$$

$$C_6^{ij} C_8^{ij} b^{ij} B^{ij} a^{ij} \alpha^i \alpha^j \alpha^k bd^{ij} cd^{ij}$$

VASP

PIM

Calcul Abinitio – DFT

Calcul Classique

Forces

Forces

Dipôles

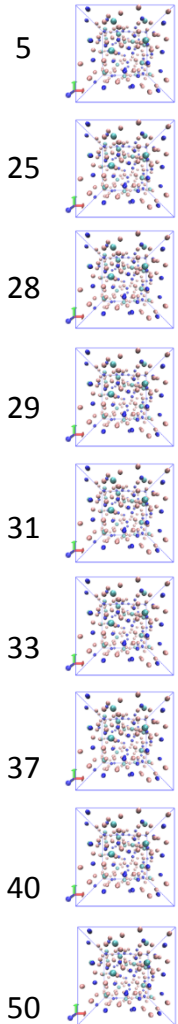
Dipôles

Contraintes

Contraintes

≡

$$C_6^{ij} C_8^{ij} b^{ij} B^{ij} a^{ij} \alpha^i \alpha^j \alpha^k bd^{ij} cd^{ij}$$



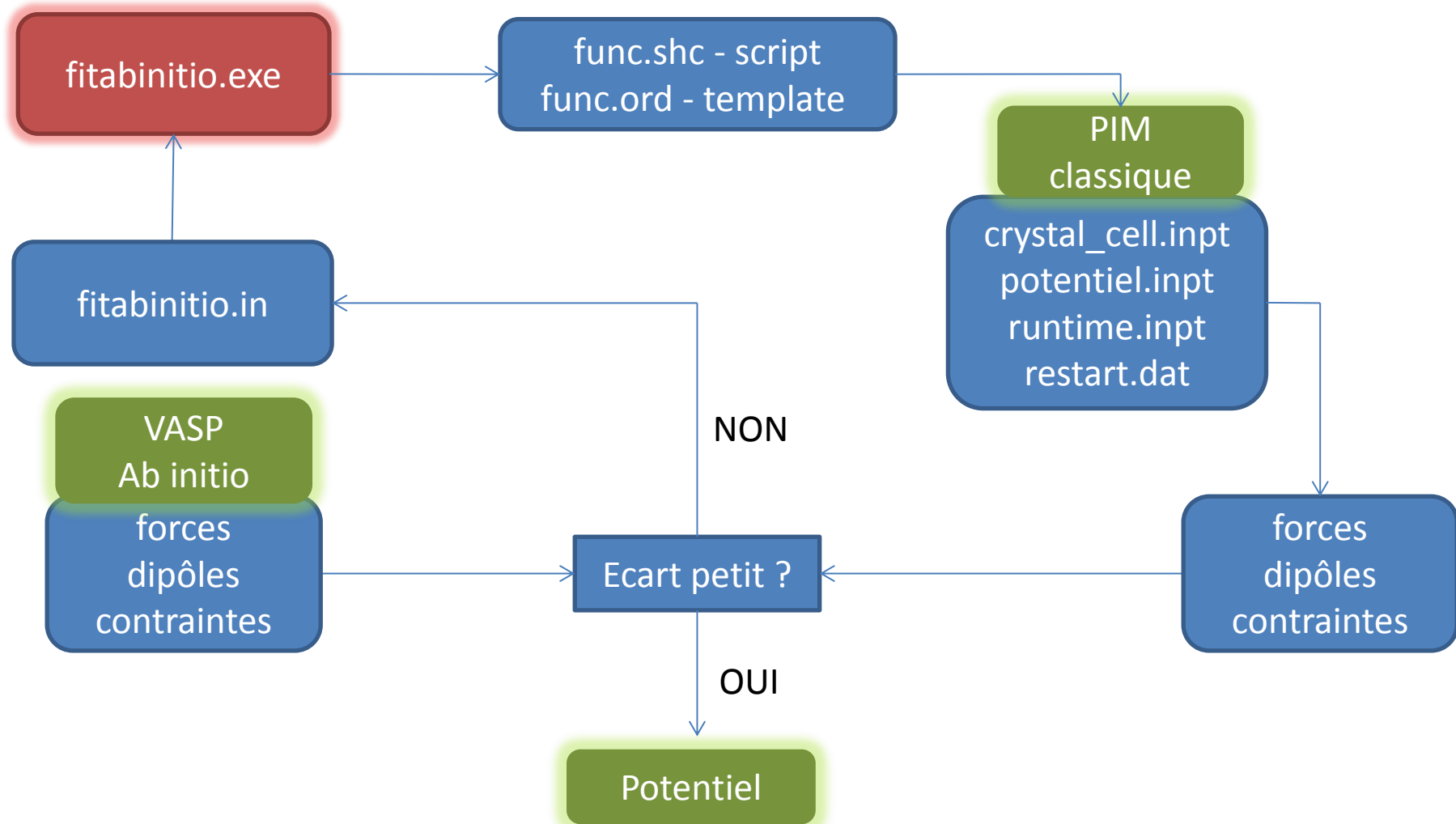
9 Boites ≈ 200atomes

1812 Forces 1812 Dipôles
9 Contraintes

Ajustement par « Force Matching »

Ajustement du Potentiel

Programme fit multi paramètres: fortran ^[1]



Paramétrage du Potentiel

NaF – AlF₃ -> 6 paires

fitabinitio.in

NaF – AlF₃ – Al₂O₃ -> 10 paires

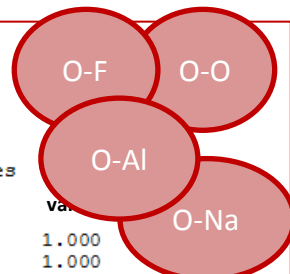
```
37 fit parameters
1606 dipoles all
0 quadrupoles
1812 forces all: somme Nionstot
9 sets of stress tensor all
1.0d0 scaling between multipoles and forces
```

	Paramètres	val°	pas fit	val-	val+
FF	1 A-1-1	2.440	.00	1.000	3.000
FF	2 B-1-1	282.3	.00	10.00	400.0
FF	3 C6FF	15.0	1.00	1.000	30.000
FF	4 C8FF	150.0	1.00	100.0	200.0
FAI	5 A-1-2	1.870	.00	0.010	3.000
FAI	6 B-1-2	39.85	.00	1.000	200.0
FAI	7 C6FAl	5.000	.10	1.000	60.000
FAI	8 C8FAl	150.0	1.00	100.0	400.0
FNa	9 A-1-3	1.974	.00	0.010	6.500
FNa	10 B-1-3	52.83	.00	1.000	200.0
FNa	11 C6FNa	13.25	1.00	0.010	60.00
FNa	12 C8FNa	88.15	1.00	50.00	400.0
FNa	13 A-2-2	5.000	.00	0.010	6.500
FNa	14 B-2-2	1.000	.00	0.010	200.0
FNa	15 C6AlAl	5.000	.10	1.001	60.00
FNa	16 C8AlAl	150.0	1.00	100.0	400.0
FNa	17 A-2-3	5.000	.00	0.010	6.50
FNa	18 B-2-3	1.000	.00	0.010	200.0
FNa	19 C6AlNa	5.000	.10	1.001	60.00
FNa	20 C8AlNa	150.0	1.00	100.0	400.0
FNa	21 A-3-3	5.000	.00	0.010	6.5
FNa	22 B-3-3	1.000	.00	0.010	200.0
FNa	23 C6NaNa	11.70	1.00	0.010	60.00
FNa	24 C8NaNa	51.80	1.00	10.00	400.0
FNa	25 ALPH1	7.885	.00	06.00	12.00
FNa	26 ALPH3	0.991	.00	0.010	12.00
FF	27 BD-1-1	2.730	.10	0.010	10.00
FAI	28 CD-1-1	4.693	.10	0.001	5.000
FAI	29 BD-1-2	2.009	.10	0.010	5.000
FNa	30 CD-1-2	1.762	.10	0.010	5.000
FNa	31 BD-1-3	1.971	.10	0.010	5.000
FNa	32 CD-1-3	2.386	.10	0.010	5.000
FNa	33 CD-3-1	4.175	.10	0.010	10.00
FNa	34 BD-3-2	10.00	.10	1.000	20.00
FNa	35 CD-3-2	0.001	.10	0.000	5.000
FNa	36 BD-3-3	10.00	.10	0.000	30.00
FNa	37 CD-3-3	0.001	.10	0.000	10.00

+ 28

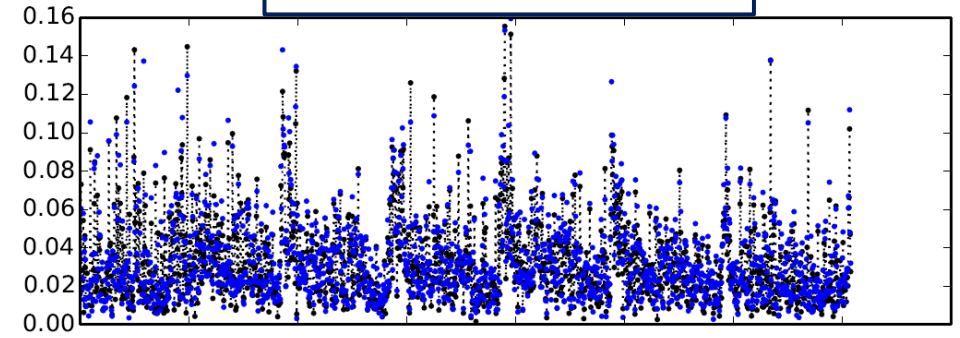
```
65 fit parameters
7 dipoles all
0 quadrupoles
1264 forces all: somme Nionstot
7 sets of stress tensor all
1.0d0 scaling between multipoles and forces
```

	Paramètres	val°	pas fit	val-	val+
	1 A-1-1	2.406	.00	1.000	
	2 B-1-1	290.4	.00	1.000	
	3 C600	44.00	.00	1.000	100.0
	4 C800	853.0	.00	600.0	1000
	5 A-1-2	2.495	.10	1.000	200.0
	6 B-1-2	278.4	1.00	100.0	400.0
	7 C6OF	28.20	1.00	1.000	60.00
	8 C8OF	391.7	1.00	100.0	500.0
	9 A-1-3	1.808	.10	0.010	9.500
	10 B-1-3	63.09	1.00	1.000	120.0
	11 C6OAl	2.000	1.00	0.010	10.00
	12 C8OAl	25.00	1.00	1.000	50.00
	13 A-1-4	2.166	.00	0.010	9.500
	14 B-1-4	221.5	.00	50.00	350.0
	15 C6ONa	2.000	1.00	0.010	10.00
	16 C8ONa	25.00	1.00	1.000	50.00
	...				
	41 ALPH1	10.74	.00	05.00	15.00
	...				
	44 BD-1-1	2.513	.10	0.010	10.00
	45 CD-1-1	2.227	.10	0.001	5.000
	46 BD-1-2	2.298	.10	0.010	5.000
	47 CD-1-2	2.821	.10	0.010	5.000
	48 BD-1-3	1.908	.10	0.010	5.000
	49 CD-1-3	1.627	.10	0.010	5.000
	50 BD-1-4	1.964	.10	0.010	5.000
	51 CD-1-4	3.493	.10	0.010	5.000
	52 BD-2-1	5.000	.10	0.010	5.000
	53 CD-2-1	0.000	.10	0.010	5.000
	60 CD-4-1	0.066	.10	0.010	5.000

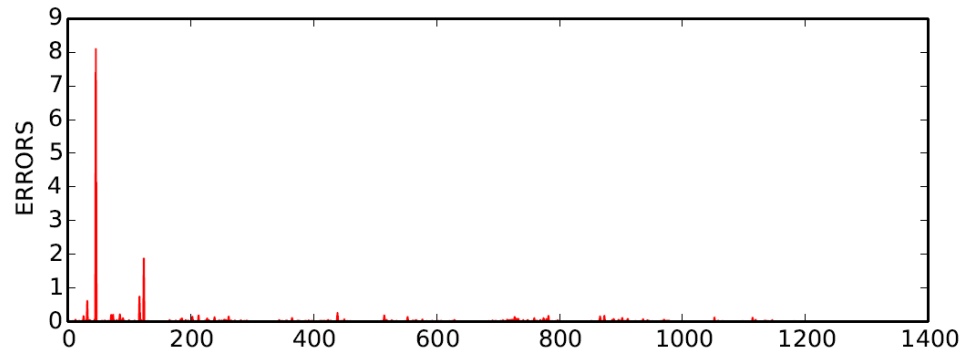
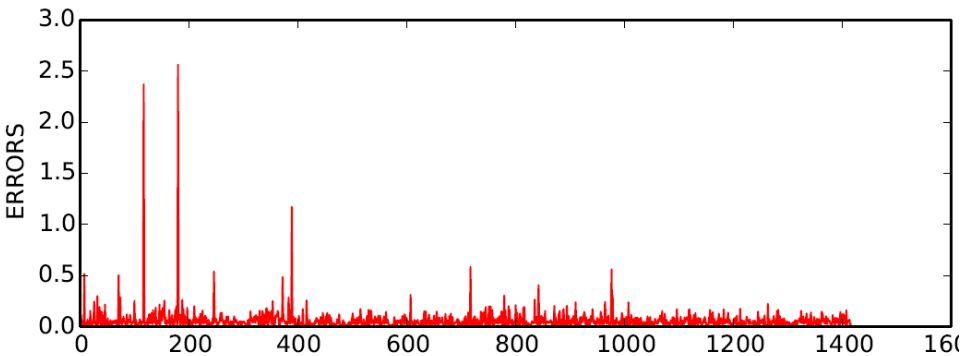
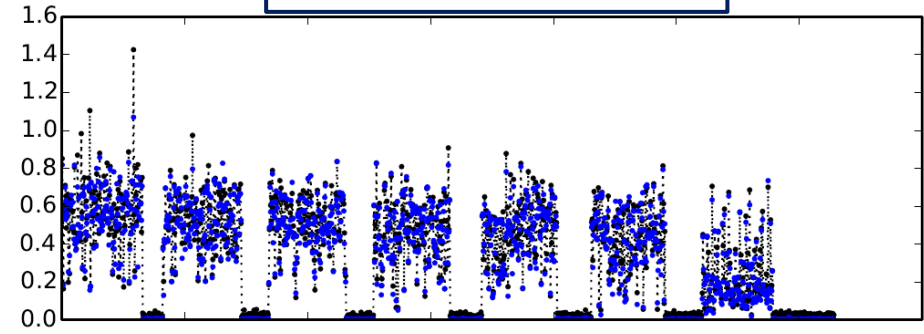


Qualité de l'ajustement NaF- AlF_3

Forces



Dipôles



$$X_{Total}^2 = \alpha X_{Forces}^2 + \beta X_{Dipoles}^2 + \gamma X_{Contraintes}^2$$

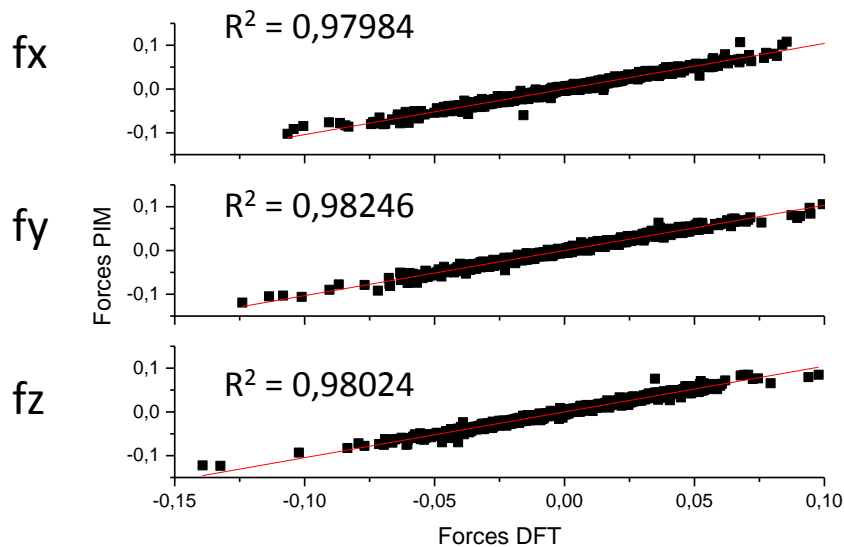
$$X_i^2 = \frac{1}{N} \sum_i \frac{[x_i^{PIM} - x_i^{ai}]^2}{[x_i^{ai}]^2}, \quad x = \text{Forces, Dipôles ou Contraintes}$$



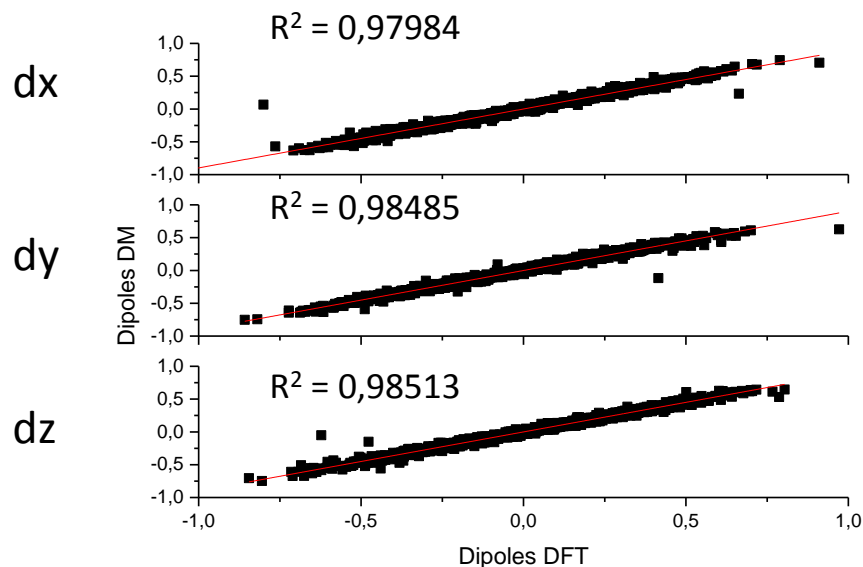
On cherche le jeu de paramètres minimisant l' écart quadratique moyen des forces, des dipôles et des contraintes (<5%)

Qualité de l'ajustement NaF-AlF₃

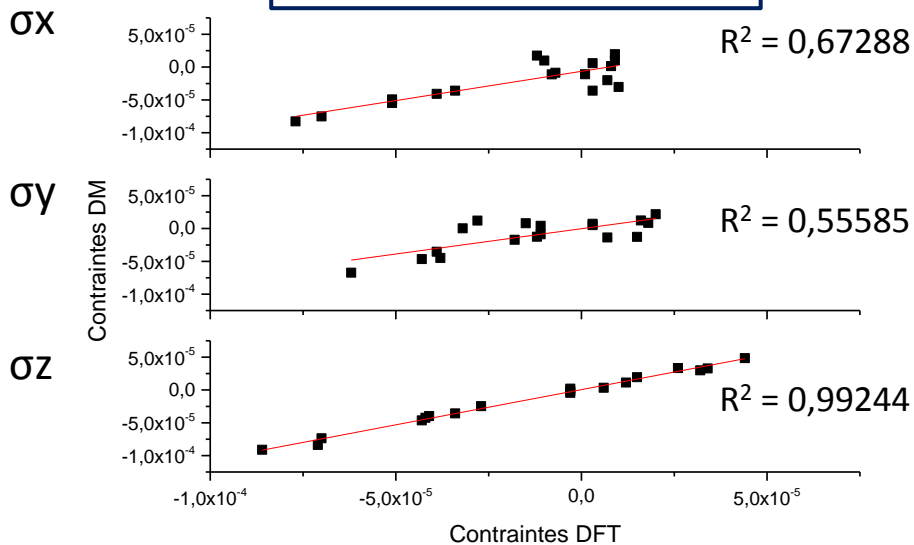
Forces



Dipôles



Contraintes



9 Boites \approx 200atomes

1812 Forces 1812 Dipôles

9 Contraintes

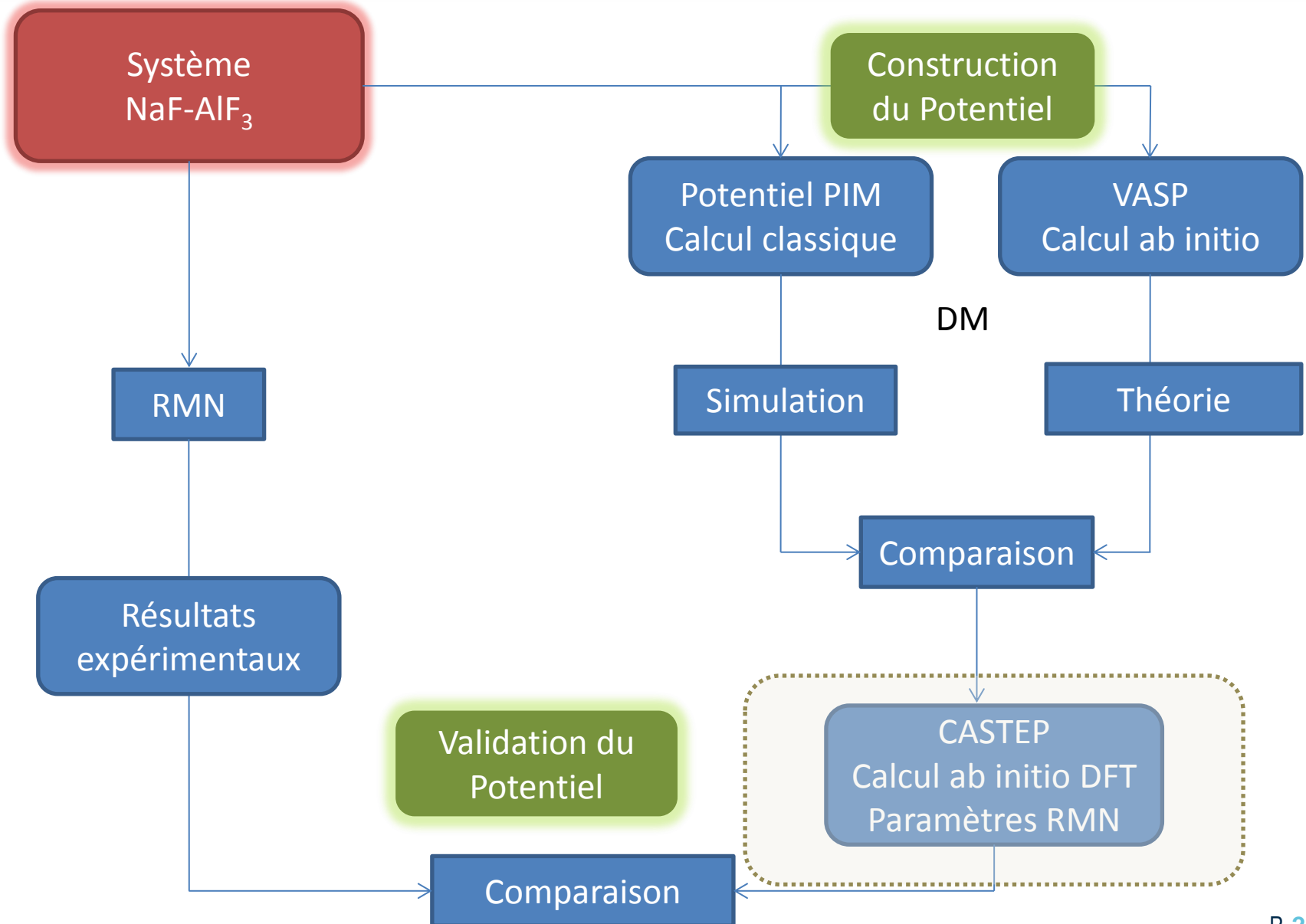
$$X_F^2 = 0,044$$

$$X_D^2 = 0,046$$

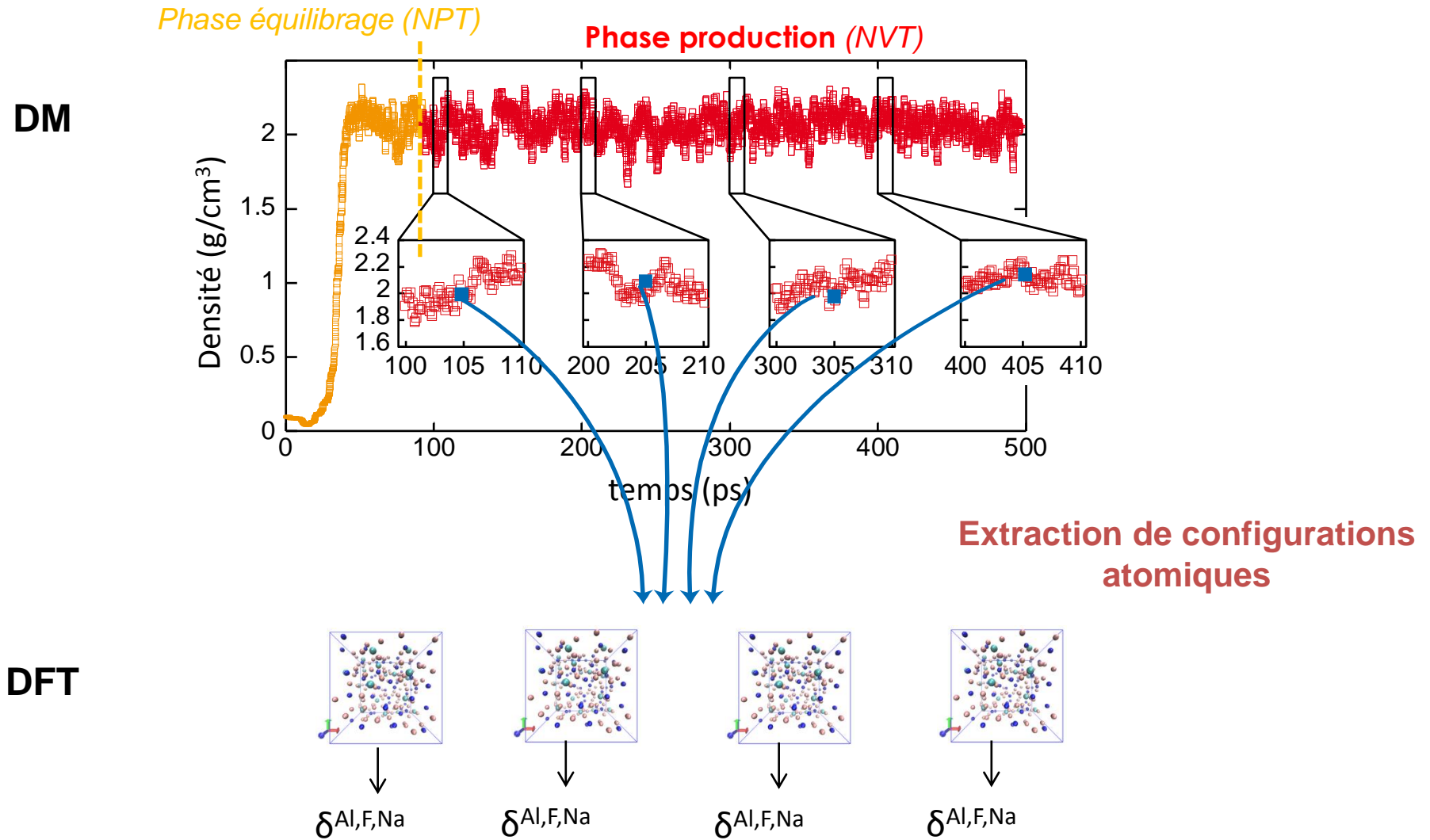
$$X_C^2 = 0,24$$

$$X_T^2 = 0,054$$

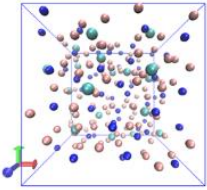
Démarche de la simulation



Calculs DFT des paramètres RMN - CASTEP



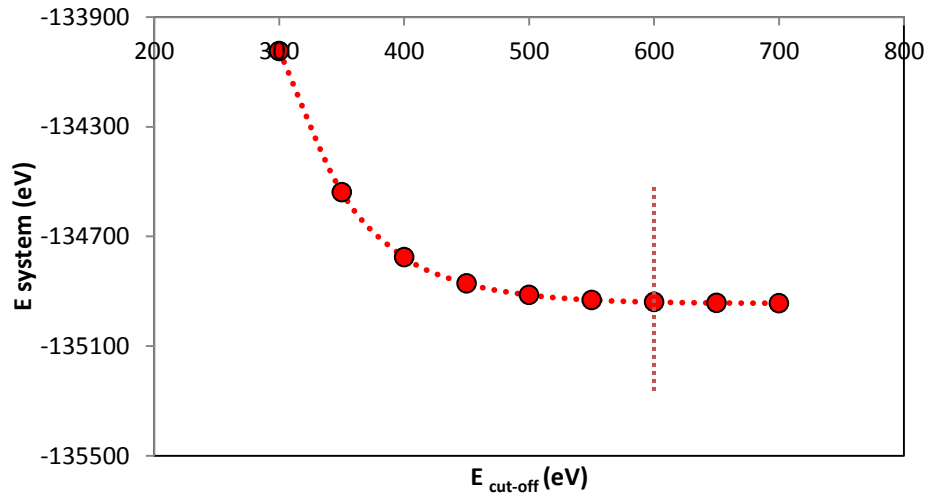
Calculs DFT des paramètres RMN - CASTEP



 MATERIALS
STUDIO



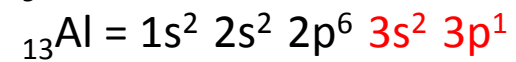
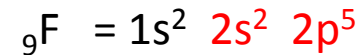
Fichiers d'entrée pour CASTEP



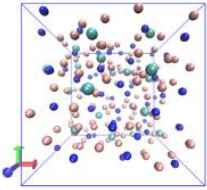
Paramètres

Fonctionnel	GGA/PBE
E cutt off	600 eV
k-point spacing	0.05 Å ⁻¹
Grille point k	1 x 1 x 1
Pseudo potentiel	On the fly

Sans optimisation de la structure



Calculs DFT des paramètres RMN - CASTEP



 MATERIALS
STUDIO



200 atomes (1400 – 1800 électrons)
14h en 20 cœurs pour un instantané
1 composition \approx 140h

Caractéristiques des fichiers d'entrée

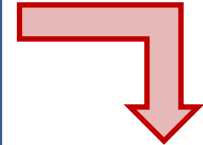
file.cell: Positions des atomes

file.param : Paramètres calculs (Ecut off, potentiel, ...)

file.xsd : Configuration atomique



CASTEP



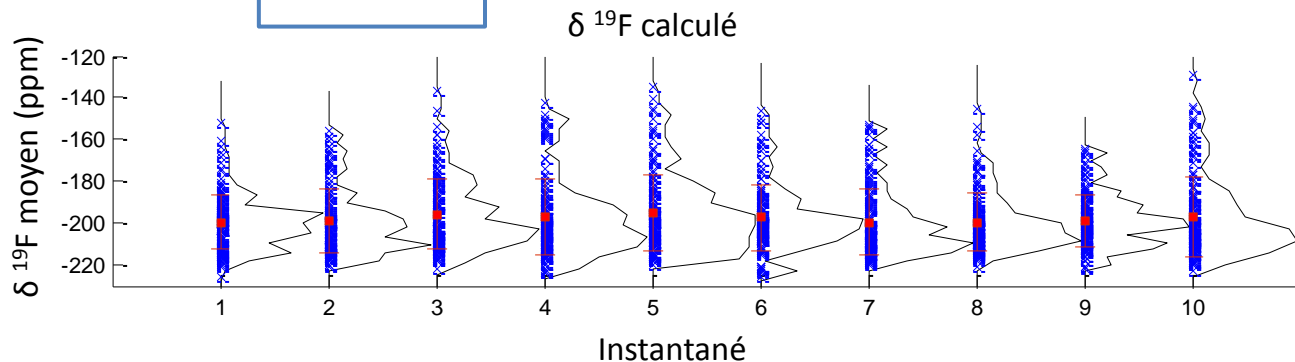
Caractéristiques des fichiers de sortie

file.castep

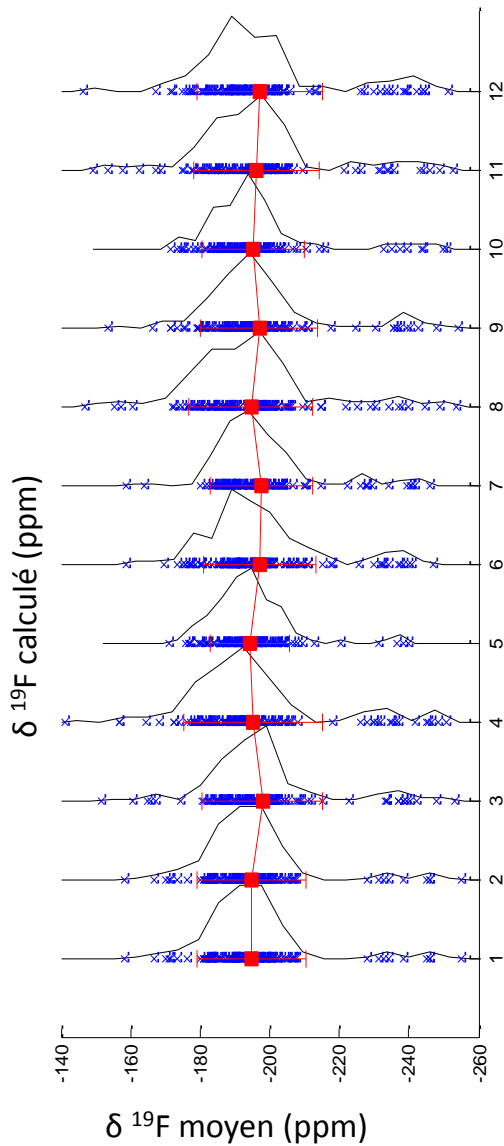
file_NMR.castep



$$\delta = \frac{\sigma_{ref} - \sigma}{1 - \sigma_{ref}} 10^6$$



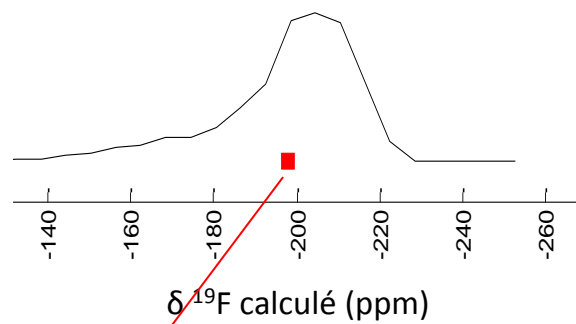
Calculs des paramètres RMN - CASTEP



Hypothèse d'ergodicité

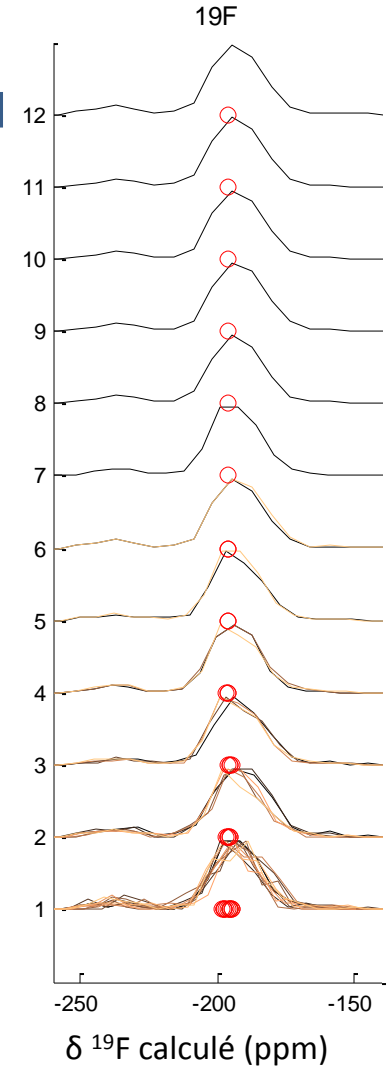


Moyenne de plusieurs instantanés



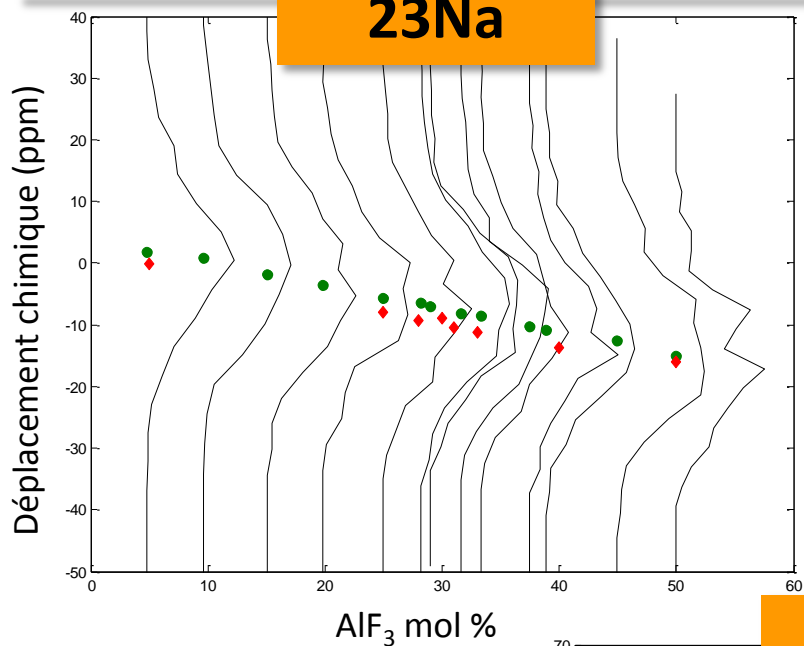
$\delta^{19}\text{F}$ moyen de tous les atomes ^{19}F
dans tous les instantanés

- x $\delta^{19}\text{F}$ individuel
- $\delta^{19}\text{F}$ moyen
- Distribution $\delta^{19}\text{F}$

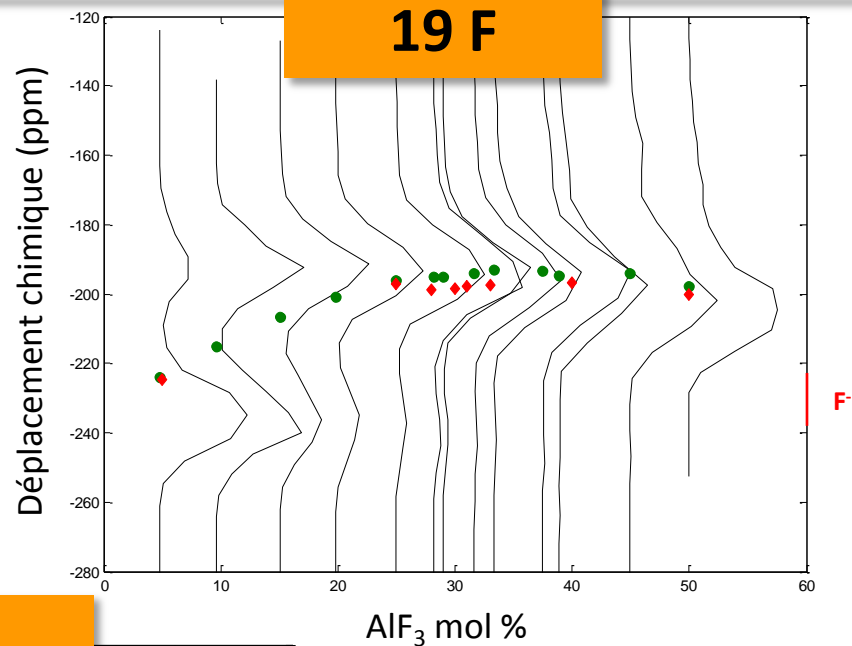


Comparaison des Déplacements chimiques RMN (calculé et expérimentaux)

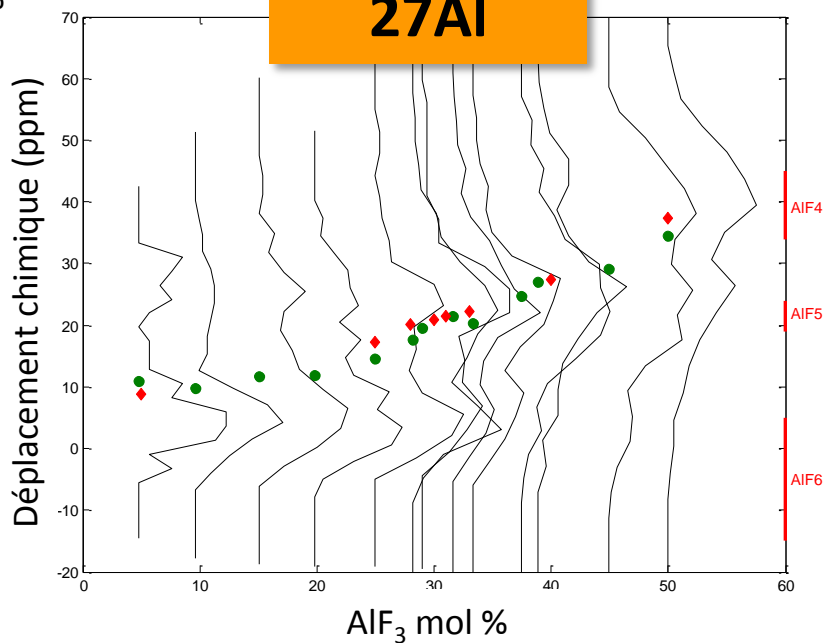
23Na



19F



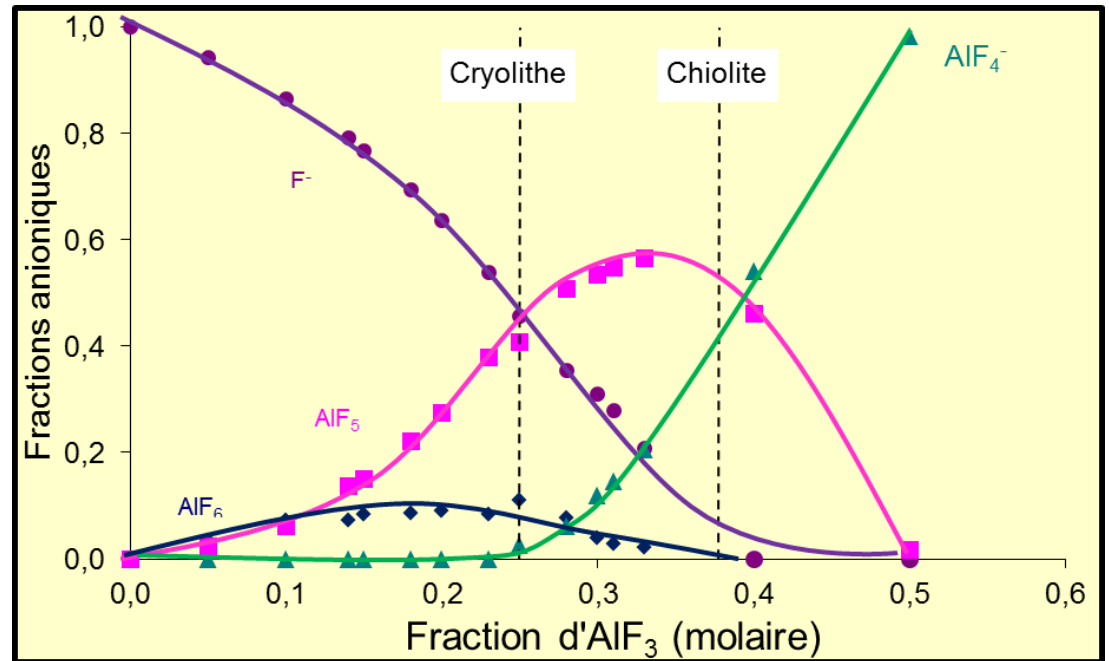
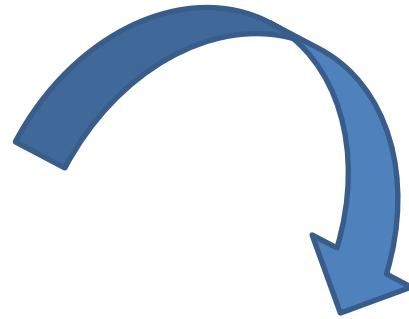
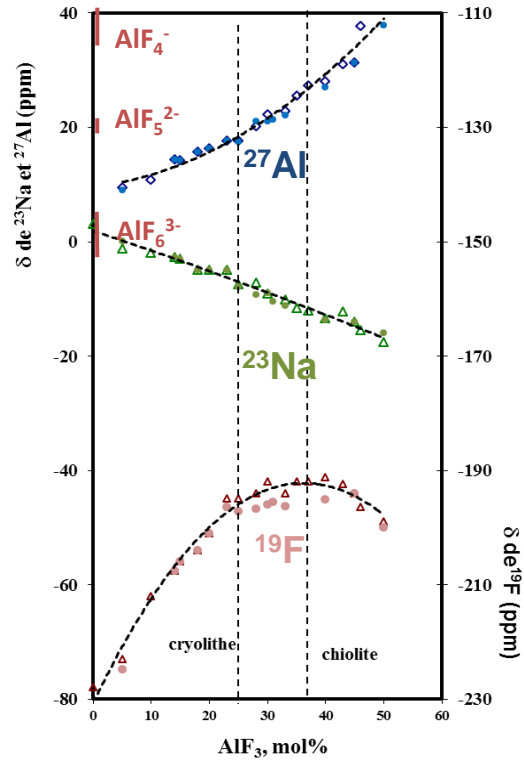
27Al



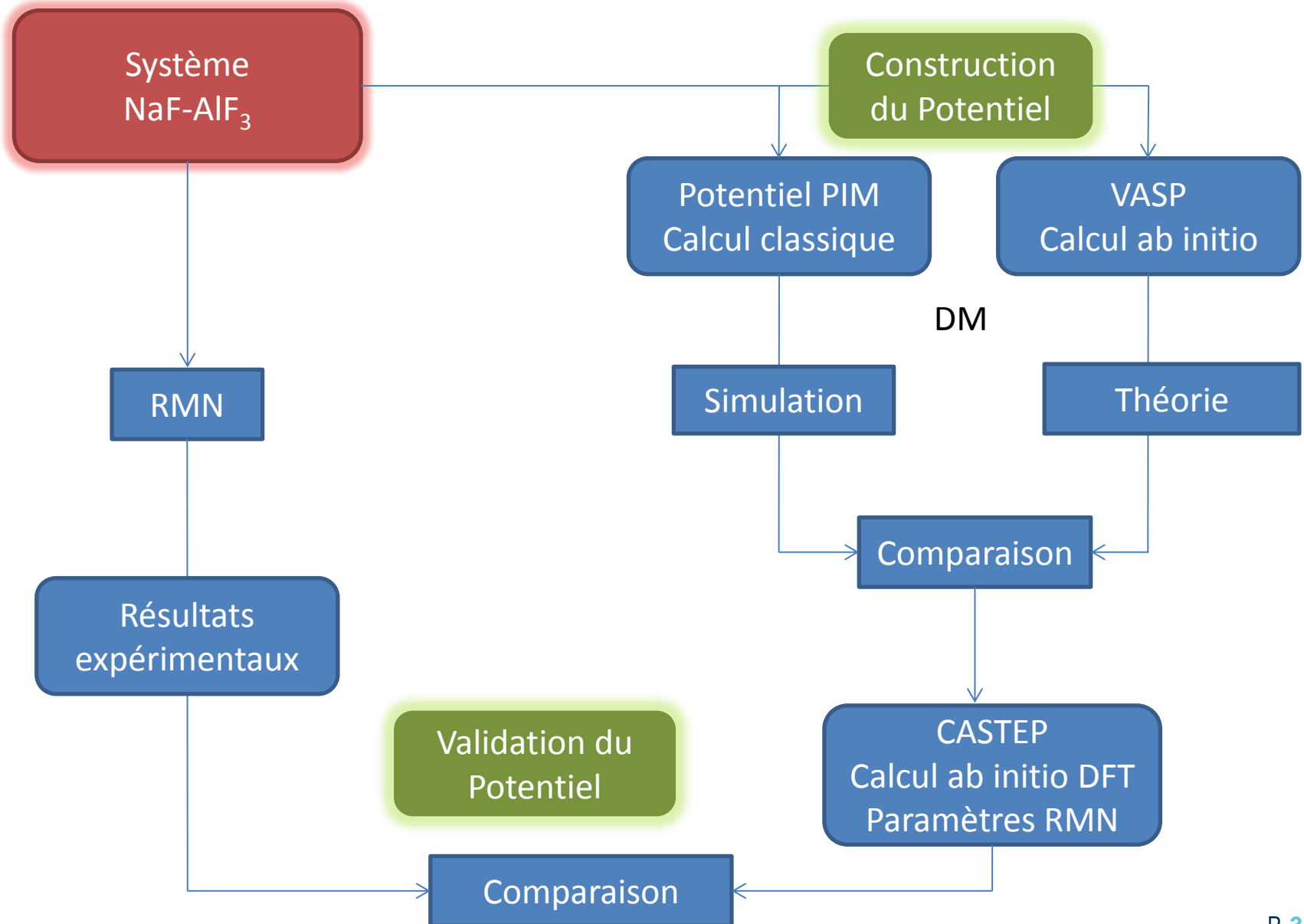
Déplacements chimiques

- Calculs DM+DFT
- ◆ Mesures RMN

Comparaison des Déplacements chimiques RMN (calculé et expérimentaux)



Démarche de la simulation



Remerciements



**Catherine
BESSADA**



**Didier
ZANGHI**



**Mathieu
SALANNE**



**Mario
BURBANO**



**Vincent
SAROU-KANIAN**



**Sylvian
CADARS**

