



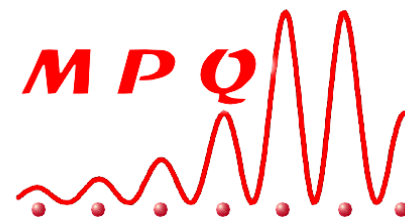
Potentiels interatomiques... jusqu'où aller dans le côté obscur ?

Céline Varvenne¹ et Hakim Amara^{2,3}

¹CINaM, CNRS-AMU université, Marseille, France

²LEM, ONERA-CNRS, Châtillon, France

³MPQ, CNRS-Université de Paris, Paris, France



Plan

I) Introduction : les nanoparticules

II) Les outils

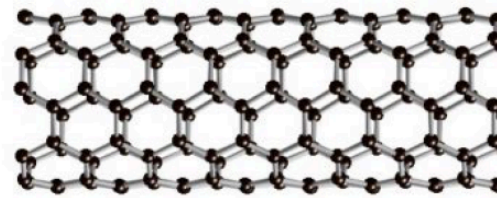
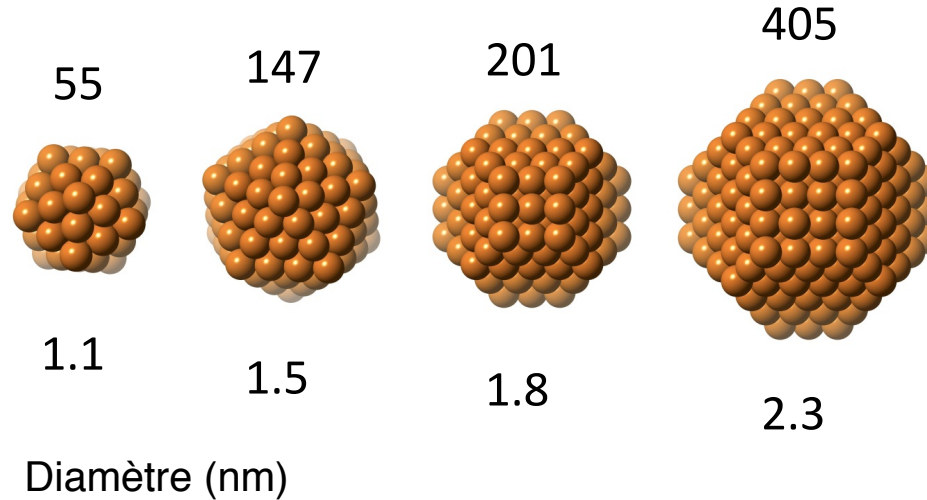
III) Exercices

- 1) Comment modéliser les problèmes physiques présentés en Introduction
- 2) Amas lacunaires dans Zr hcp
- 3) Croissance de structures carbonées à partir d'un catalyseur métallique

Le nanomonde

• De nouveaux objets

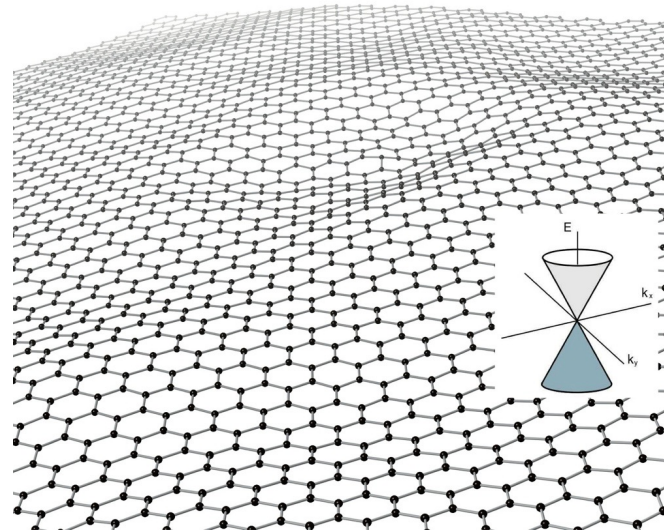
- 0D : nanoparticule
- 1D : nanotube
- 2D : graphène



Diamètre : 0.6 - 20 nm
longueur : qq mm

• Des propriétés originales et inattendues

- électronique
- thermodynamique
- mécanique
- magnétique
- optique
- ...



Une ou quelques épaisseurs atomiques



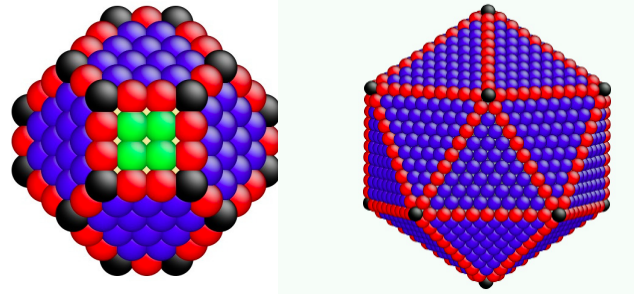
Applications originales et inattendues

Les nanoparticules

- A toute petite taille (nm), certaines propriétés des matériaux sont différentes

Agrégat isolé :

- Rapport surface/volume augmente lorsque taille diminue
- Pression de Laplace ($\sim \gamma / R$) devient significative : cœur sous pression
 γ : tension de surface; R : rayon
- Présence de facettes, arêtes, coins



- sommet
- arête
- facette (001)
- facette (111)

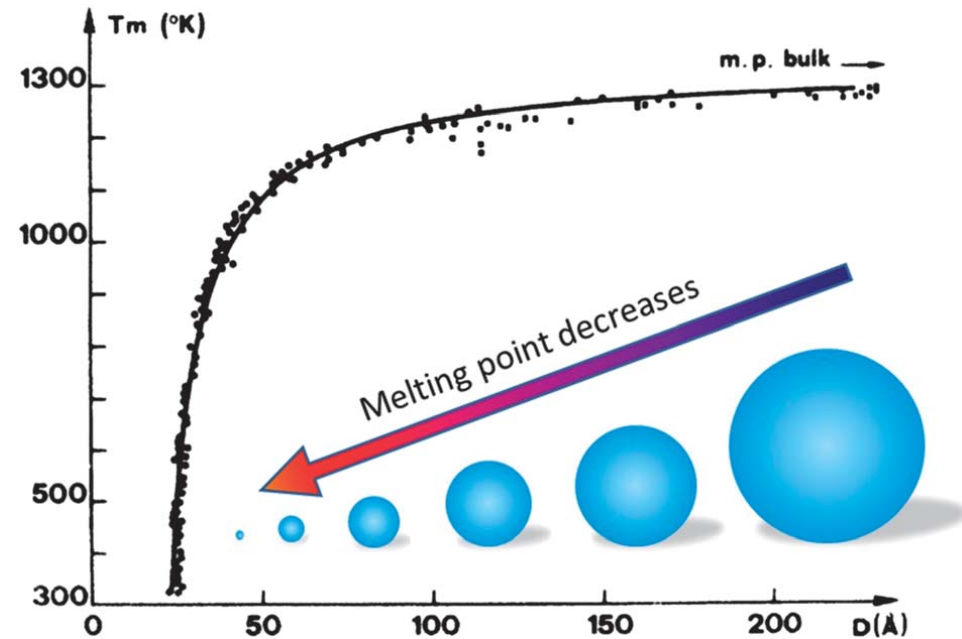
- Modification structure électronique (magnétisme, optique ... réactivité ...)

http://tel.archives-ouvertes.fr/docs/00/71/21/46/PDF/HDR_JCreuze_05052011.pdf

Open questions

Metallic nanoparticles

- melting temperature ?
- crystallographic structure ?
- phase transition ?
- Ostwald ripening ?
- environmental effect ?



Ph. Buffat and J.-P. Borel,
Phys. Rev. A **13**, 2287 (1976)



**Melting point decreases
with particle size**

Open questions

Metallic nanoparticles

- melting temperature ?
- **crystallographic structure** ?
- phase transition ?
- Ostwald ripening ?
- environmental effect ?



**Different sizes /
morphologies**

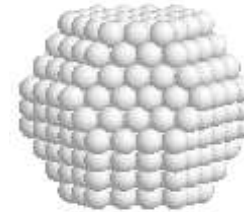
Wulff



38



201



405

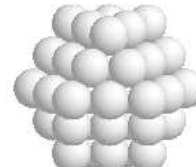


807

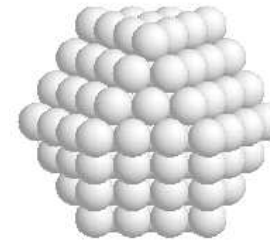
cuboctaèdre



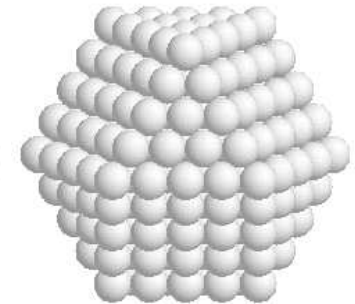
13



55



147

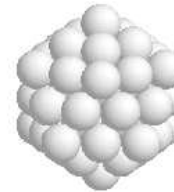


309

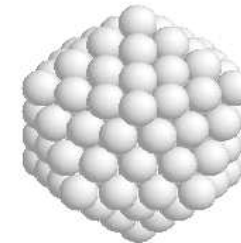
icosaèdre



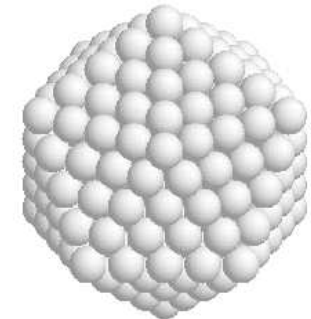
13



55



147



309

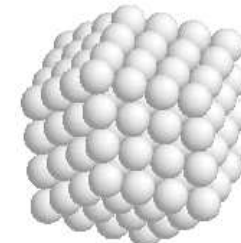
dodécaèdre



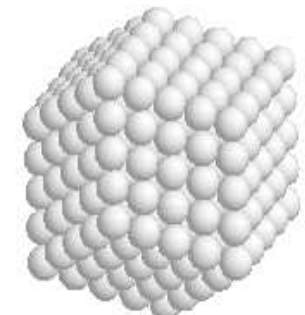
15



65



175



369

Open questions

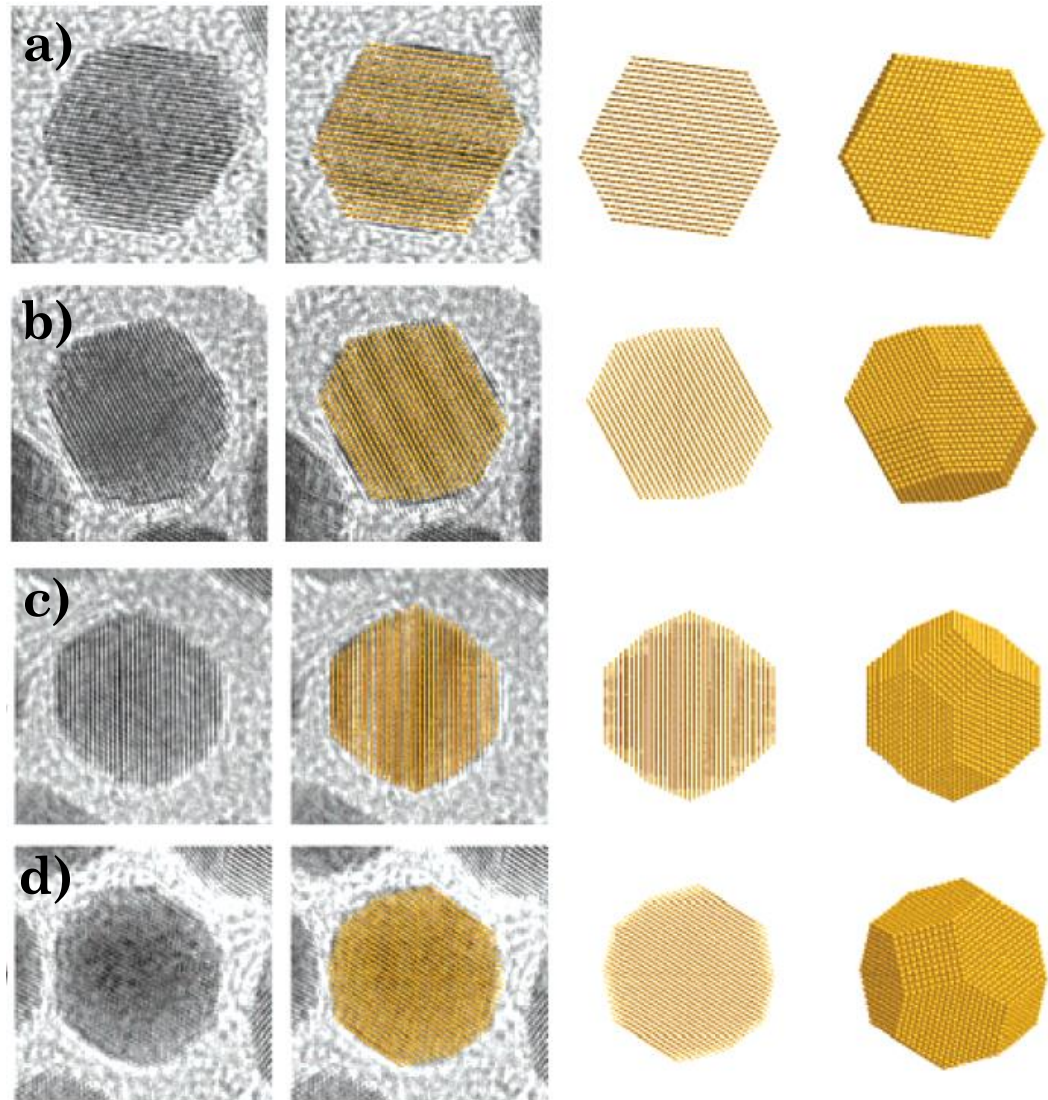
Metallic nanoparticles

- melting temperature ?
- **crystallographic structure ?**
- phase transition ?
- Ostwald ripening ?
- environmental effect ?



**Different sizes /
morphologies**

Au NPs with different morphologies ...



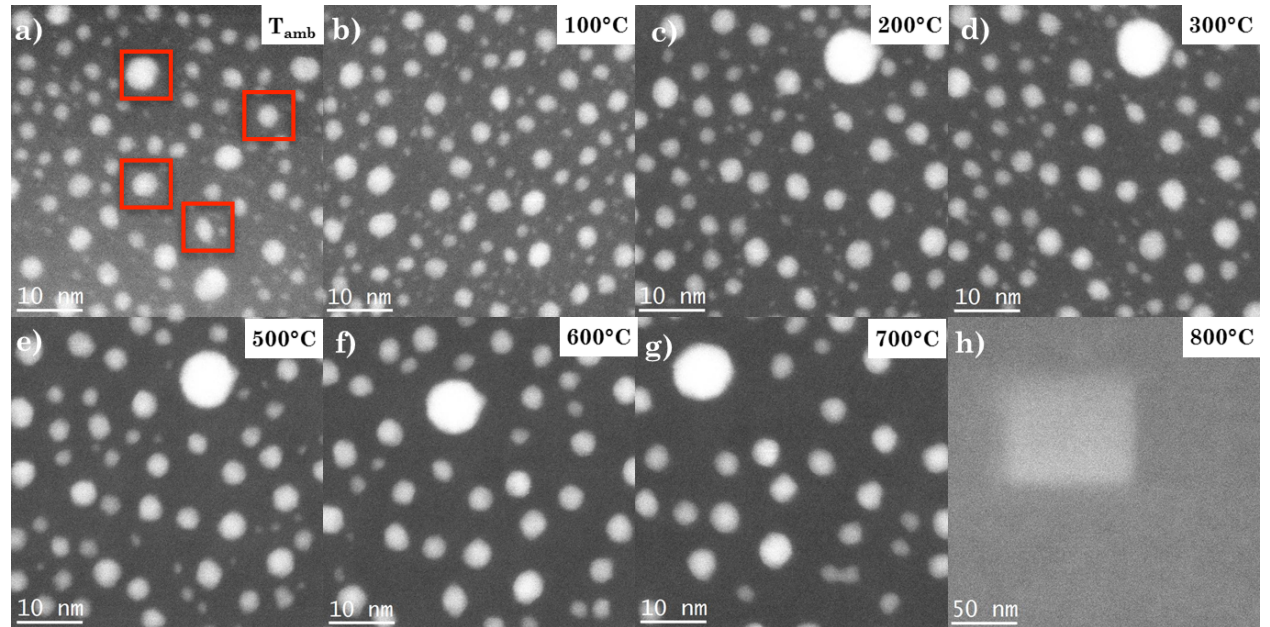
Thèse A. Chmielewski / MPQ - Université de Paris (2018)

Open questions

Au NPs : temperature effect

Metallic nanoparticles

- melting temperature ?
- crystallographic structure ?
- **phase transition ?**
- Ostwald ripening ?
- environmental effect ?



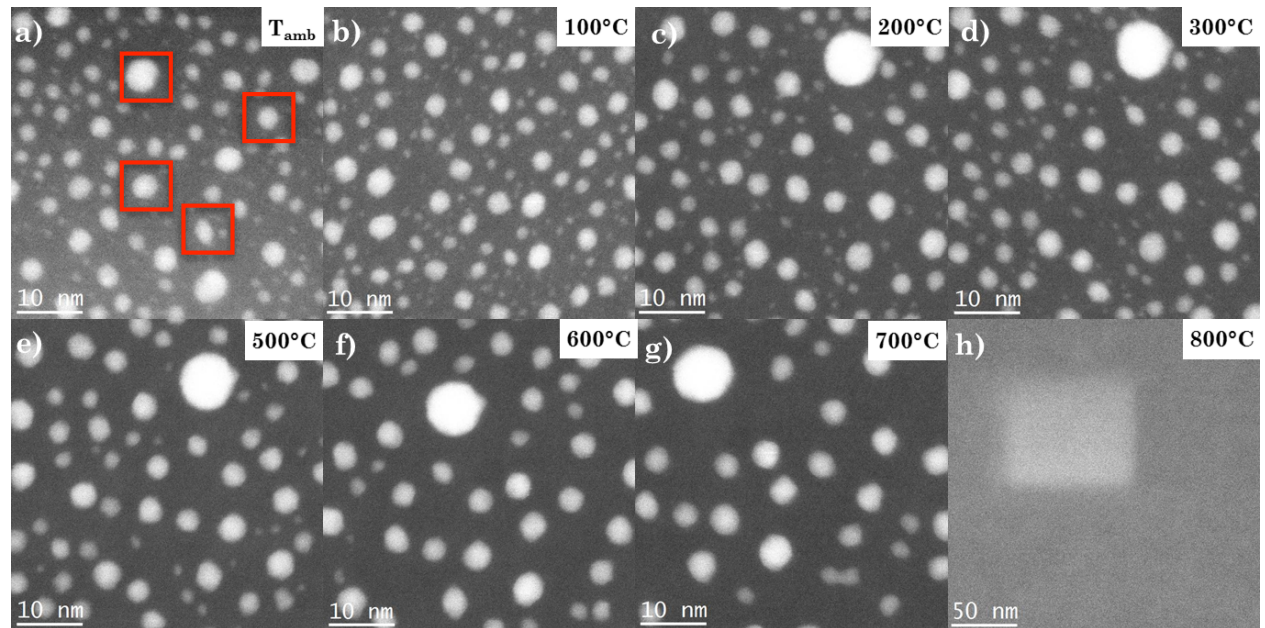
- at low T : any kind of shape with many facets
- increasing T : truncated octahedrons (thermodynamic equilibrium)

Open questions

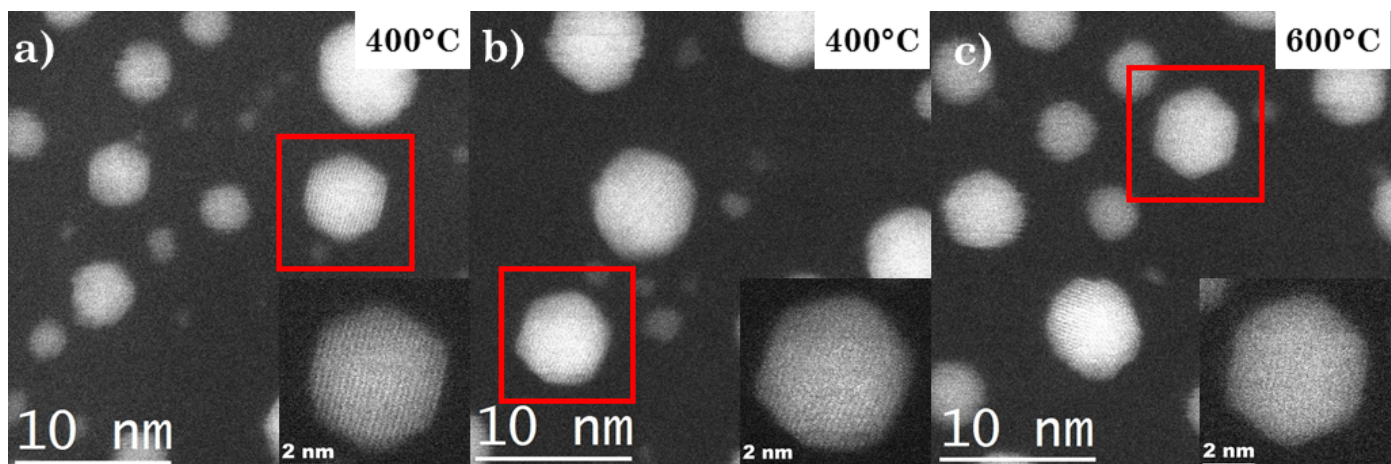
Au NPs : temperature effect

Metallic nanoparticles

- melting temperature ?
- crystallographic structure ?
- **phase transition ?**
- Ostwald ripening ?
- environmental effect ?



- III ➡
- at low T : any kind of shape with many facets
 - increasing T : truncated octahedrons (thermodynamic equilibrium)

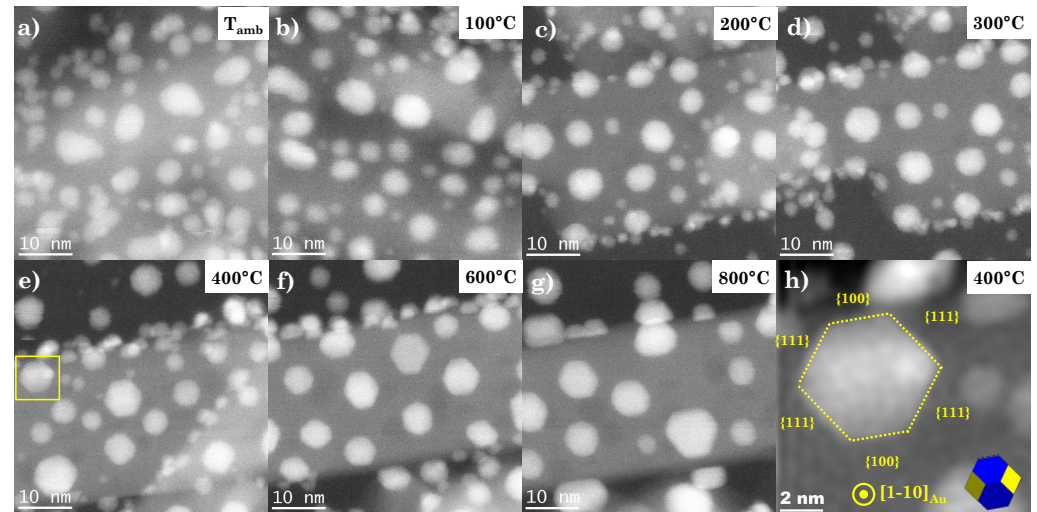


Open questions

Metallic nanoparticles

- melting temperature ?
- crystallographic structure ?
- phase transition ?
- Ostwald ripening ?
- **environmental effect ?**

Substrate : Au NPs on r-TiO₂ nanorods



Thèse A. Chmielewski / MPQ - Université de Paris (2018)

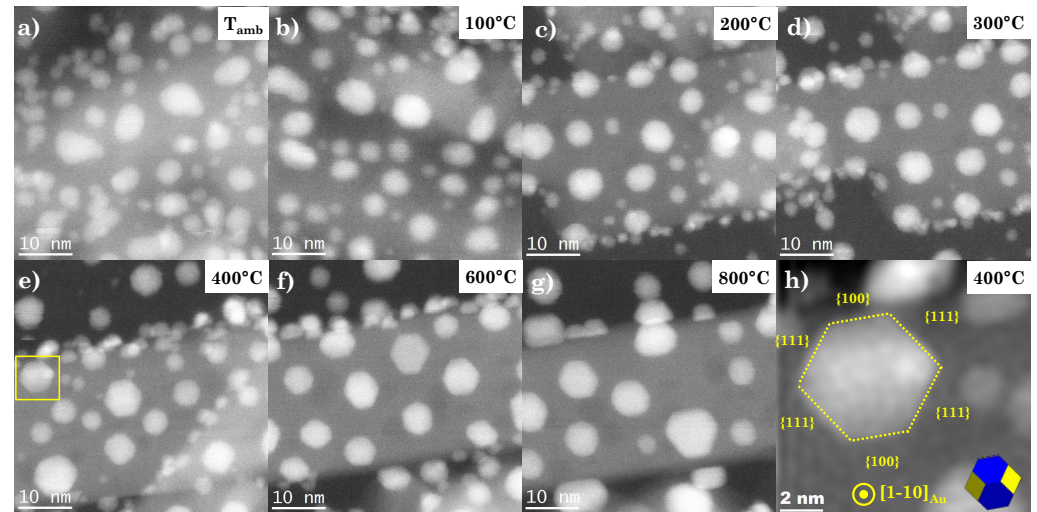
|||➡ **oriented and faceted NPs**

Open questions

Metallic nanoparticles

- melting temperature ?
- crystallographic structure ?
- phase transition ?
- Ostwald ripening ?
- **environmental effect ?**

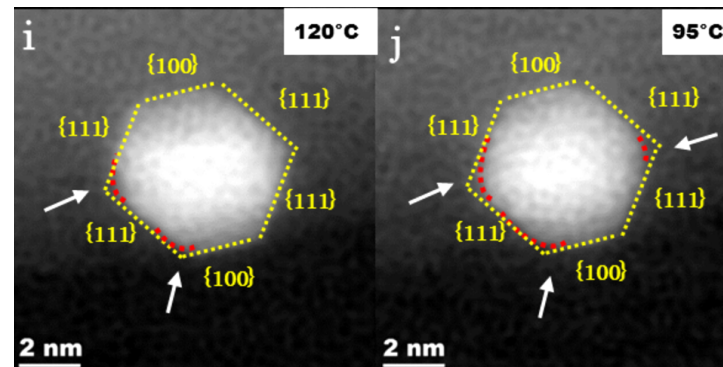
Substrate : Au NPs on r-TiO₂ nanorods



Thèse A. Chmielewski / MPQ - Université de Paris (2018)

oriented and faceted NPs

Gas : Au NPs on r-TiO₂ under O₂



A. Chmielewski et al., ACS Nano **13**, 2024 (2018)

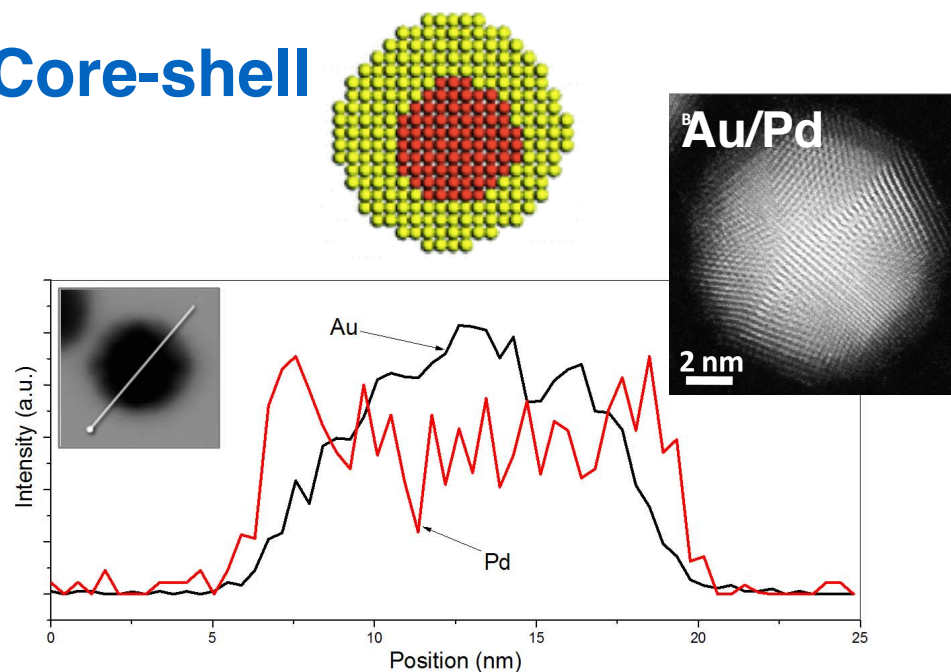
adsorption on reactive sites

Open questions

Bimetallic nanoparticles

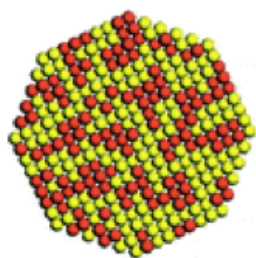
- melting temperature ?
- crystallographic structure ?
- phase transition ?
- Ostwald ripening ?
- environmental effect ?
- **chemical ordering** ?
- optical properties ?

Core-shell

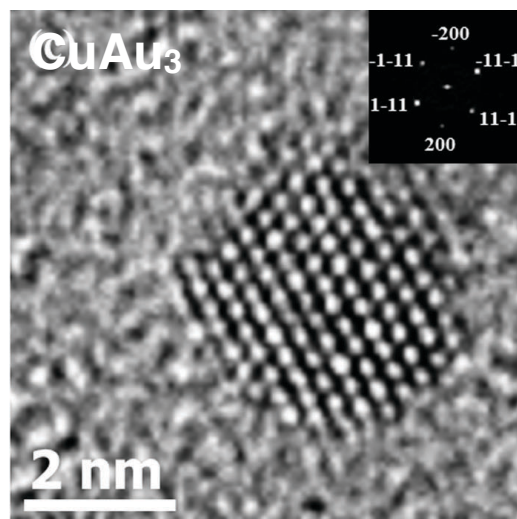


Y. Feng *et al.*, Sci. Adv. **3**, e1700580 (2017)

Alloy



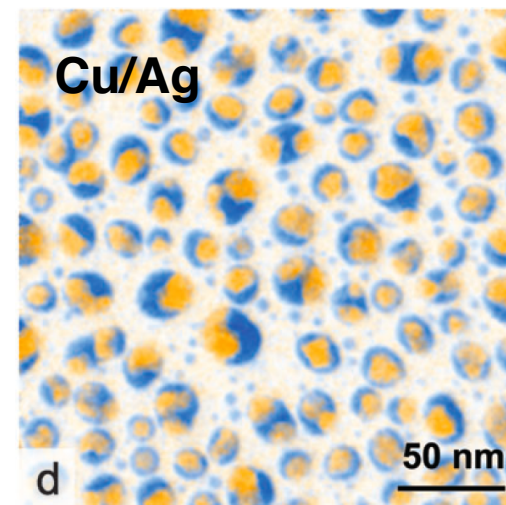
H. Prunier *et al.*,
Phys. Chem. Chem. Phys.
17, 28339 (2015)



Janus



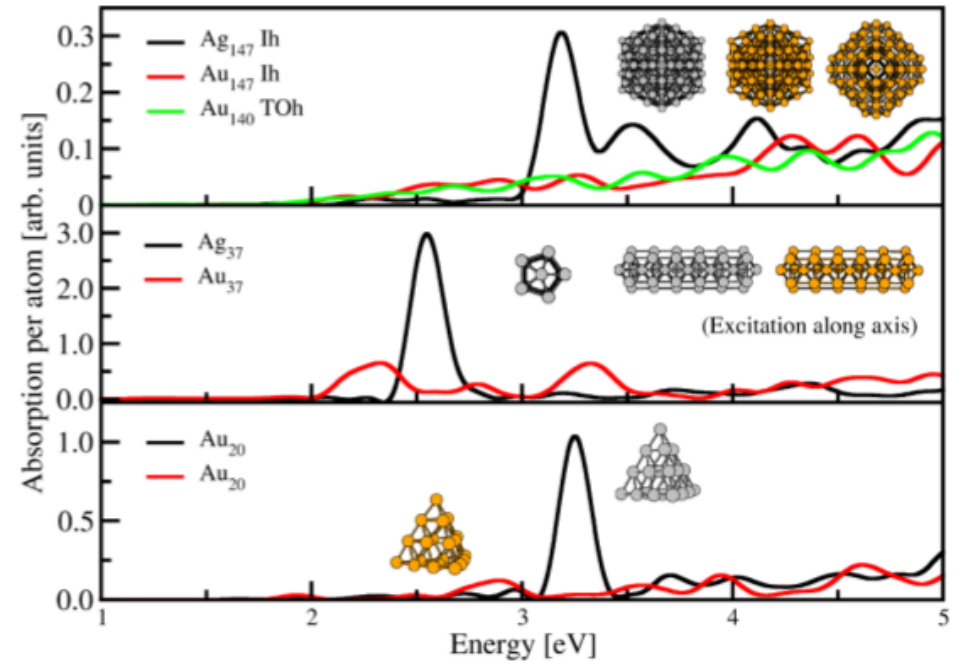
C. Langlois *et al.*,
Faraday Discuss.
138, 375 (2008)



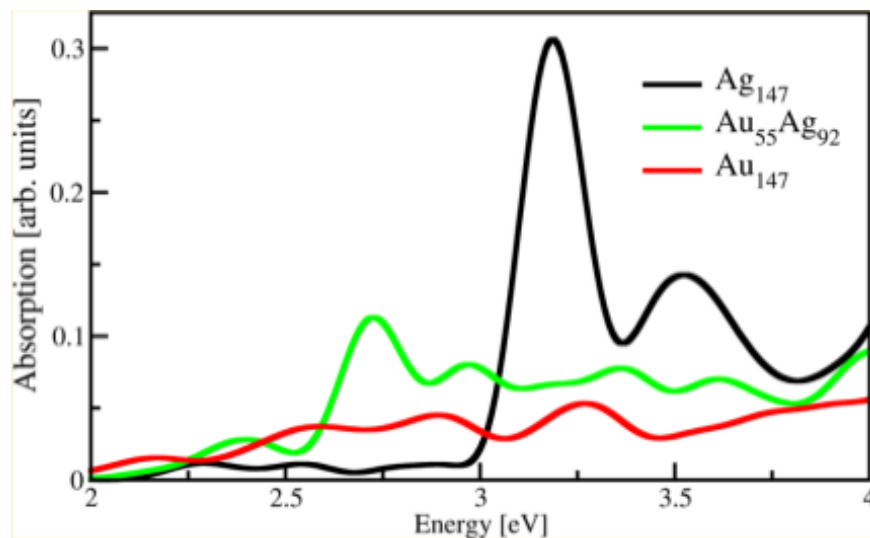
Open questions

Bimetallic nanoparticles

- melting temperature ?
- crystallographic structure ?
- phase transition ?
- Ostwald ripening ?
- environmental effect ?
- chemical ordering ?
- **optical properties ?**



X. Lopez-Lozano *et al.*, J. Phys. Chem. C 117, **2013**



Nanoparticules Ag vs Au

- même a_0 , chimie, ...
- propriétés optiques différentes !
- effet d'alliage ?

Plan

I) Introduction : les nanoparticules

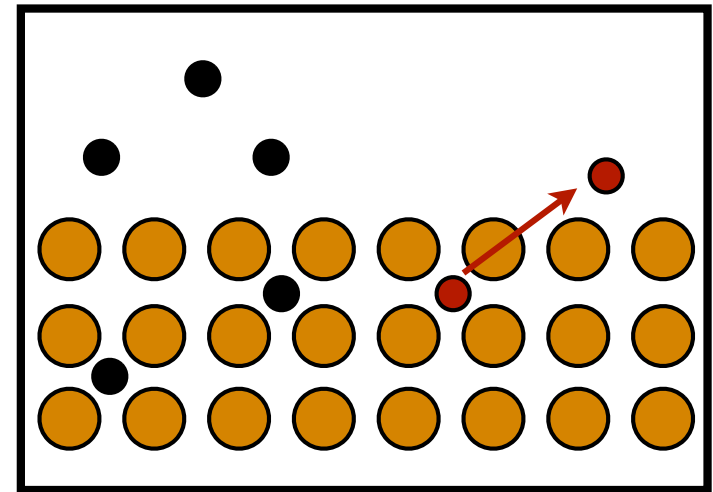
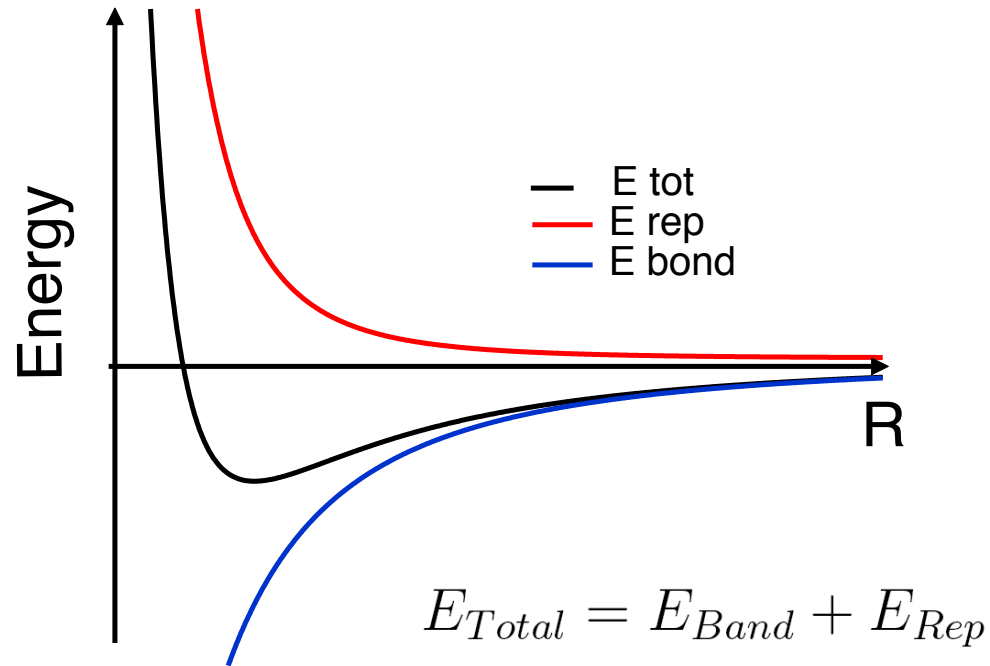
II) Les outils

III) Exercices

- 1) Comment modéliser les problèmes physiques présentés en Introduction
- 2) Amas lacunaires dans Zr hcp
- 3) Croissance de structures carbonées à partir d'un catalyseur métallique

Computer simulation studies

Energetic model



$$E_{Band} \quad ? \quad E_{band} = \int_{-\infty}^{E_f} E n(E) dE$$

$$E_{Rep} \quad ?$$

- Structural relaxation
 - Molecular Dynamics
 - Monte Carlo simulations

Tight-binding Hamiltonian

To sum up the lecture of F. Ducastelle ...

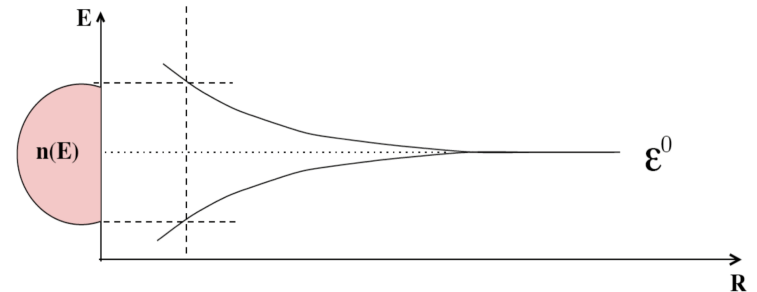
- Define the basis set : s, p_x, p_y, p_z

$$d_{xy}, d_{yz}, d_{zx}, d_{x^2-y^2}, d_{3z^2-r^2}$$

...

- Diagonalization of the tight-binding Hamiltonian

$$(H) = \begin{pmatrix} \epsilon_n & \beta_{nm} & \dots & \dots \\ \beta_{mn} & \epsilon_n & \beta_{nm} & \dots \\ \dots & \beta_{mn} & \epsilon_n & \beta_{nm} \\ \dots & \dots & \beta_{mn} & \epsilon_n \end{pmatrix} \Rightarrow n(E)$$



$$E_{band} = \int_{-\infty}^{E_f} E n(E) dE$$



$$ss\sigma(r) = ss\sigma_0 \exp\left[-q\left(\frac{r_{ij}}{r_{eq}} - 1\right)\right]$$

$$sp\sigma(r) = sp\sigma_0 \exp\left[-q\left(\frac{r_{ij}}{r_{eq}} - 1\right)\right]$$

Tight-binding Hamiltonian

To sum up the lecture of F. Ducastelle ...

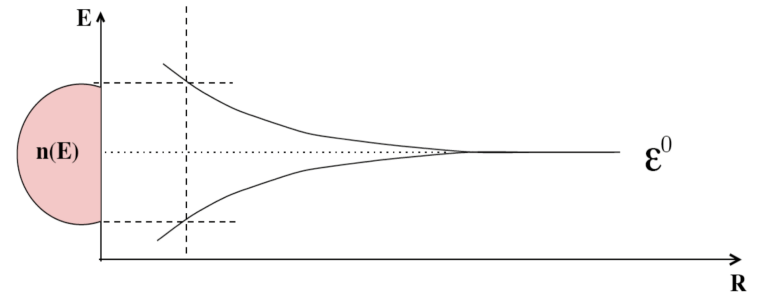
- **Define the basis set :** s, p_x, p_y, p_z

$$d_{xy}, d_{yz}, d_{zx}, d_{x^2-y^2}, d_{3z^2-r^2}$$

...

- **Diagonalization of the tight-binding Hamiltonian**

$$(H) = \begin{pmatrix} \epsilon_n & \beta_{nm} & \dots & \dots \\ \beta_{mn} & \epsilon_n & \beta_{nm} & \dots \\ \dots & \beta_{mn} & \epsilon_n & \beta_{nm} \\ \dots & \dots & \beta_{mn} & \epsilon_n \end{pmatrix} \Rightarrow n(E)$$



$$E_{band} = \int_{-\infty}^{E_f} E n(E) dE$$



$$ss\sigma(r) = ss\sigma_0 \exp\left[-q\left(\frac{r_{ij}}{r_{eq}} - 1\right)\right]$$

$$sp\sigma(r) = sp\sigma_0 \exp\left[-q\left(\frac{r_{ij}}{r_{eq}} - 1\right)\right]$$

➡ **Fitting procedure is necessary**

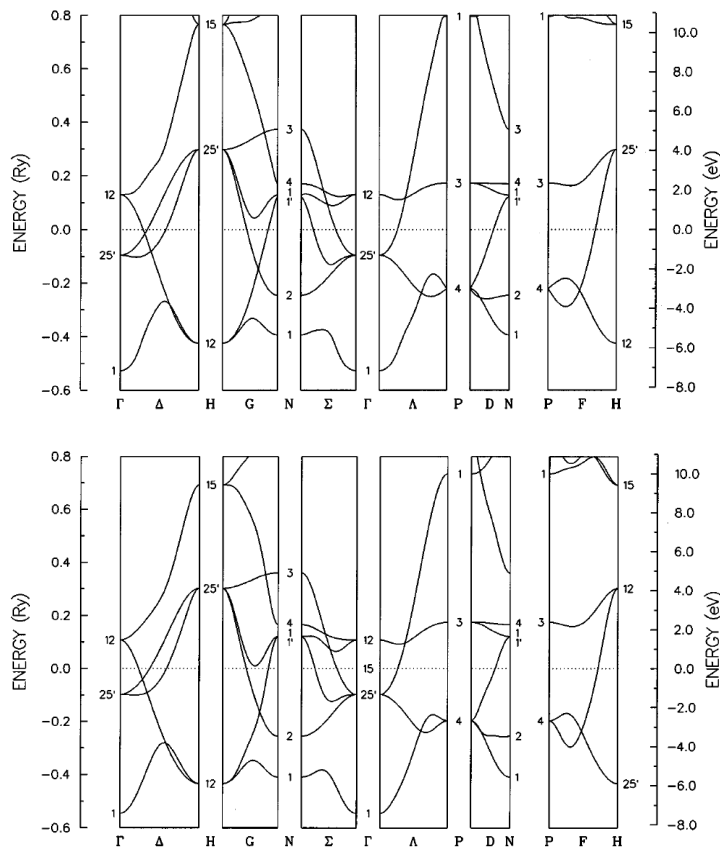
Band structures : Transition metals

basis set : $d_{xy}, d_{yz}, d_{zx}, d_{x^2-y^2}, d_{3z^2-r^2}$

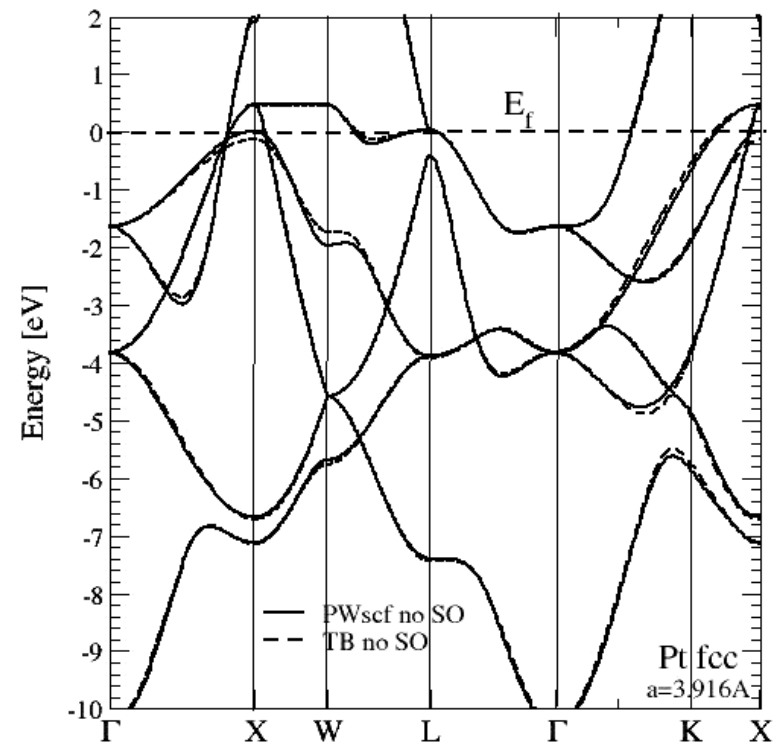
atomic levels : ε_d

hopping integrals : $dd\sigma, dd\pi, dd\delta$

Mo BCC



Pt FCC



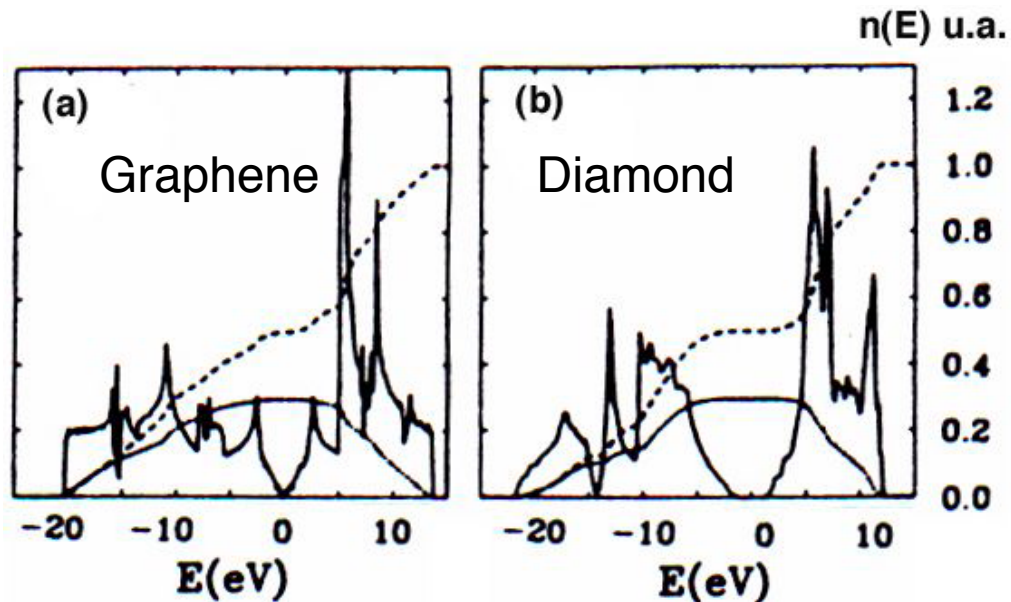
Density of states

• Carbon

basis set : s, p_x, p_y, p_z

atomic levels : $\varepsilon_s, \varepsilon_p$

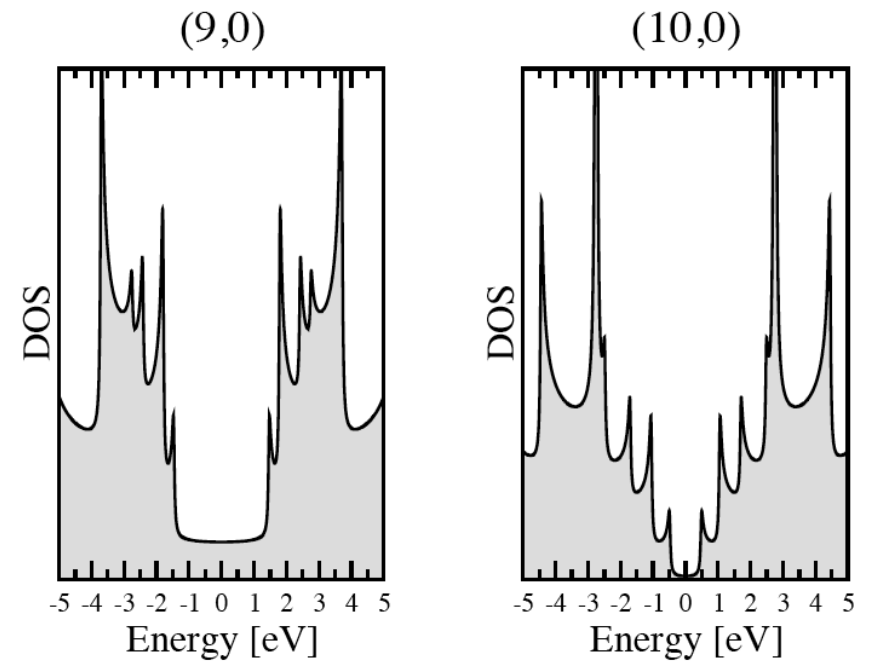
hopping integrals : $ss\sigma, sp\sigma, pp\sigma, pp\pi$



W. Zhong *et al.*, Solid State Comm. **86**, 607 (1993)

basis set : p_z

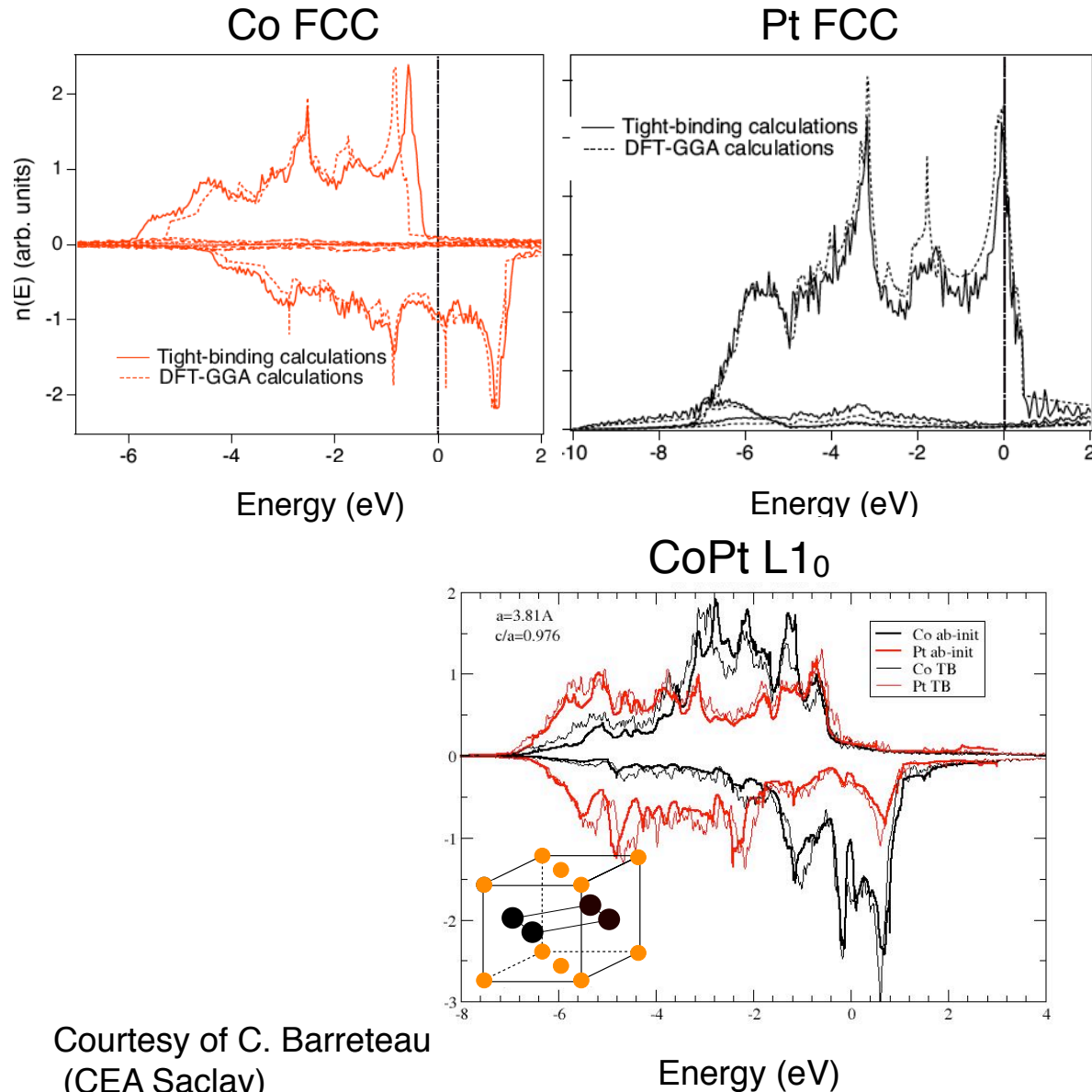
hopping integrals : $pp\pi$



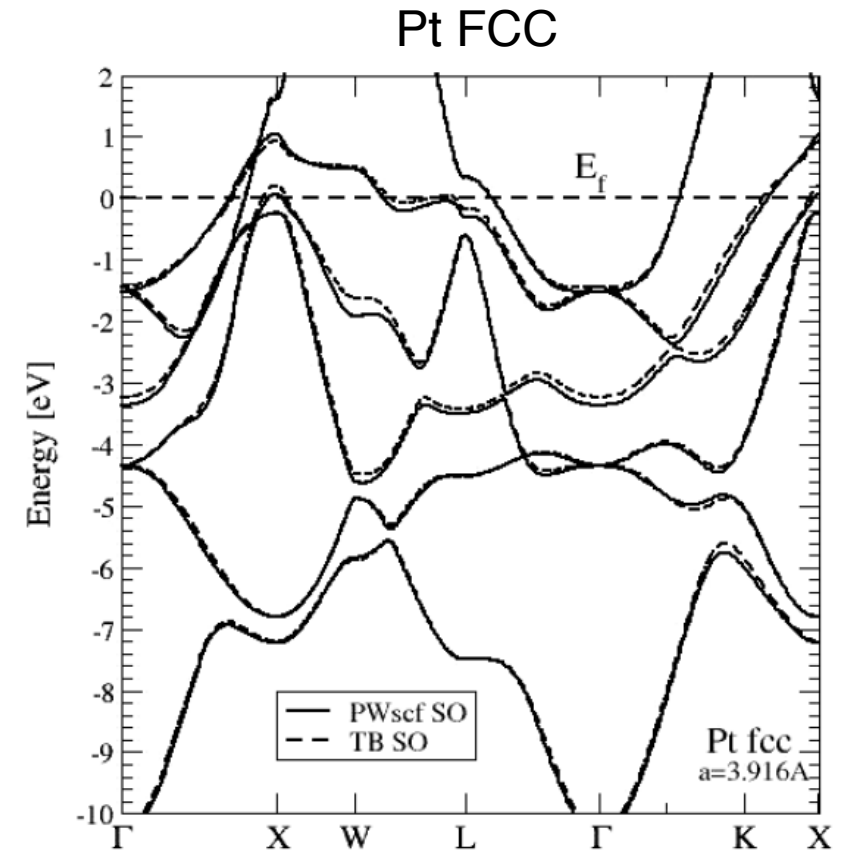
Courtesy of Sylvain Latil (CEA, Saclay)

Electronic properties : some refinements

Magnetism : CoPt



Spin-orbit coupling



C. Barreteau and D. Spanjaard
J. Phys. Condens. Matter **24**, 406004 (2012)

Courtesy of C. Barreteau
(CEA Saclay)

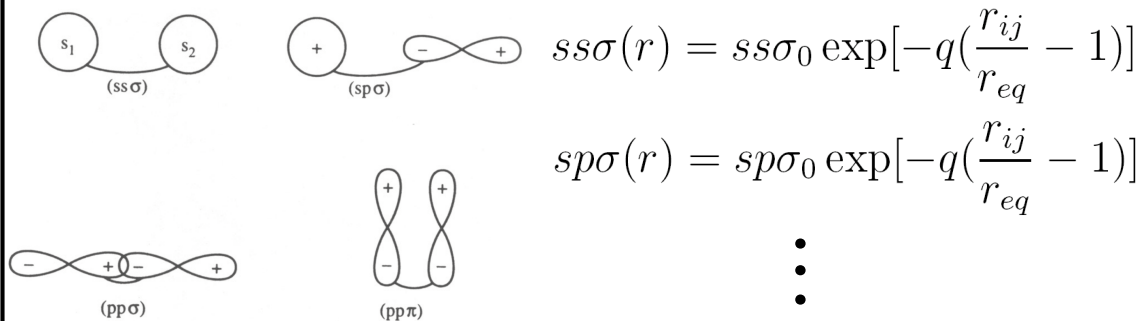
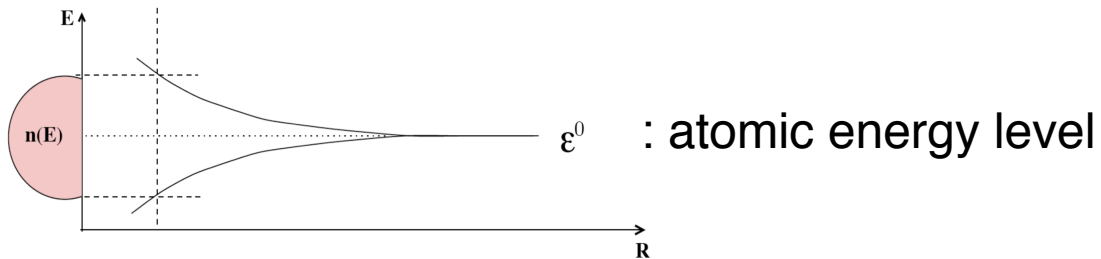
Band term

$$E_{Band} = \int_{-\infty}^{E_f} E n(E) dE \quad n(E): \text{density of states}$$

Tight-binding Hamiltonian

$$H = \sum_n |n\rangle \epsilon_n \langle n| + \sum_{n,m} |n\rangle \beta_{nm} \langle m|$$

$$(H) = \begin{pmatrix} \epsilon_n & \beta_{nm} & \dots & \dots \\ \beta_{mn} & \epsilon_n & \beta_{nm} & \dots \\ \dots & \beta_{mn} & \epsilon_n & \beta_{nm} \\ \dots & \dots & \beta_{mn} & \epsilon_n \end{pmatrix} \implies n(E)$$



Repulsive term

$$E_{Rep} = \sum E_{Rep}^i$$

$$E_{Rep}^i = A \sum_j \exp[-p(\frac{r_{ij}}{r_{eq}} - 1)]$$

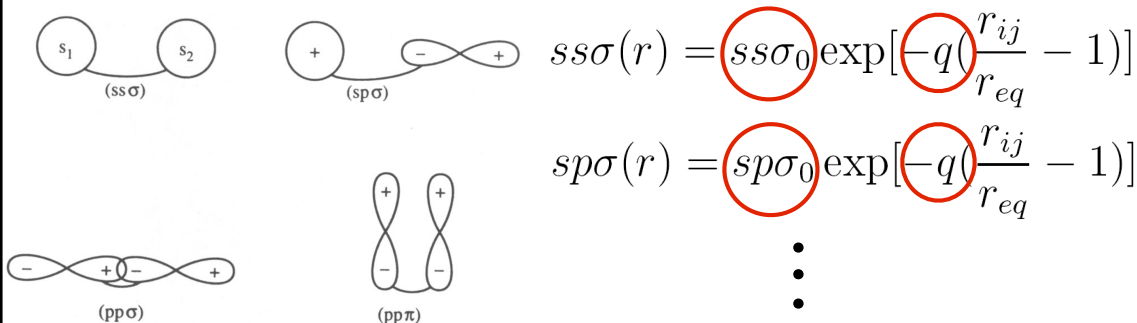
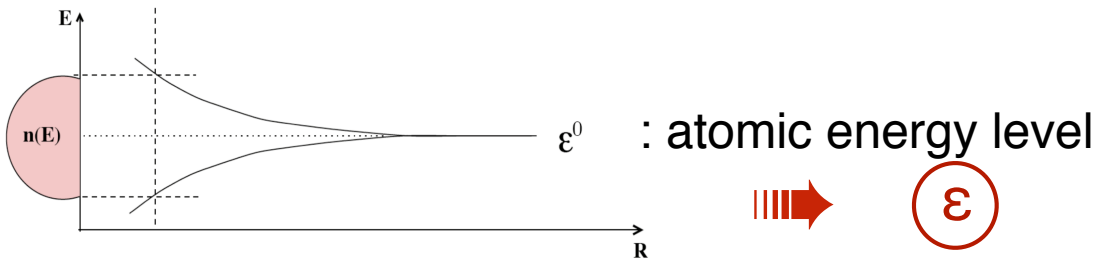
Band term

$$E_{Band} = \int_{-\infty}^{E_f} E n(E) dE \quad n(E): \text{density of states}$$

Tight-binding Hamiltonian

$$H = \sum_n |n\rangle \epsilon_n \langle n| + \sum_{n,m} |n\rangle \beta_{nm} \langle m|$$

$$(H) = \begin{pmatrix} \epsilon_n & \beta_{nm} & \dots & \dots \\ \beta_{mn} & \epsilon_n & \beta_{nm} & \dots \\ \dots & \beta_{mn} & \epsilon_n & \beta_{nm} \\ \dots & \dots & \beta_{mn} & \epsilon_n \end{pmatrix} \implies n(E)$$



Repulsive term

$$E_{Rep} = \sum E_{Rep}^i$$

$$E_{Rep}^i = A \sum_{j \text{ atoms}} \exp\left[-p\left(\frac{r_{ij}}{r_{eq}} - 1\right)\right]$$

Limit : Fitting procedure

- ϵ and β : electronic structure
- A , p , q : physical properties

- cohesive energy
- lattice parameter
- bulk modulus
- elastic constants
- surface energies
- enthalpies of formation
- heat of solution
- segregation energies
- magnetism
- order/disorder temperature
- melting temperature
- formation energies of clusters
- ...

Some transition metals : Pt

Parameters fitted to reproduce the fcc structure

TB parameters : $dd\sigma = -1.086 \text{ eV}$ / $dd\pi = 0.543 \text{ eV}$ / $dd\delta = 0.0 \text{ eV}$
 $q = 3.95$ / $p = 12.47$
 $A = 0.053 \text{ eV}$

Lattice parameter : **3.92 Å (3.92 Å)**

Cohesive energy : **-5.85 eV/at (-5.85 eV/at)**

Bulk modulus : **277 GPa (289 GPa)**



Elastic constant C_{11} : **358 GPa (347 GPa)**

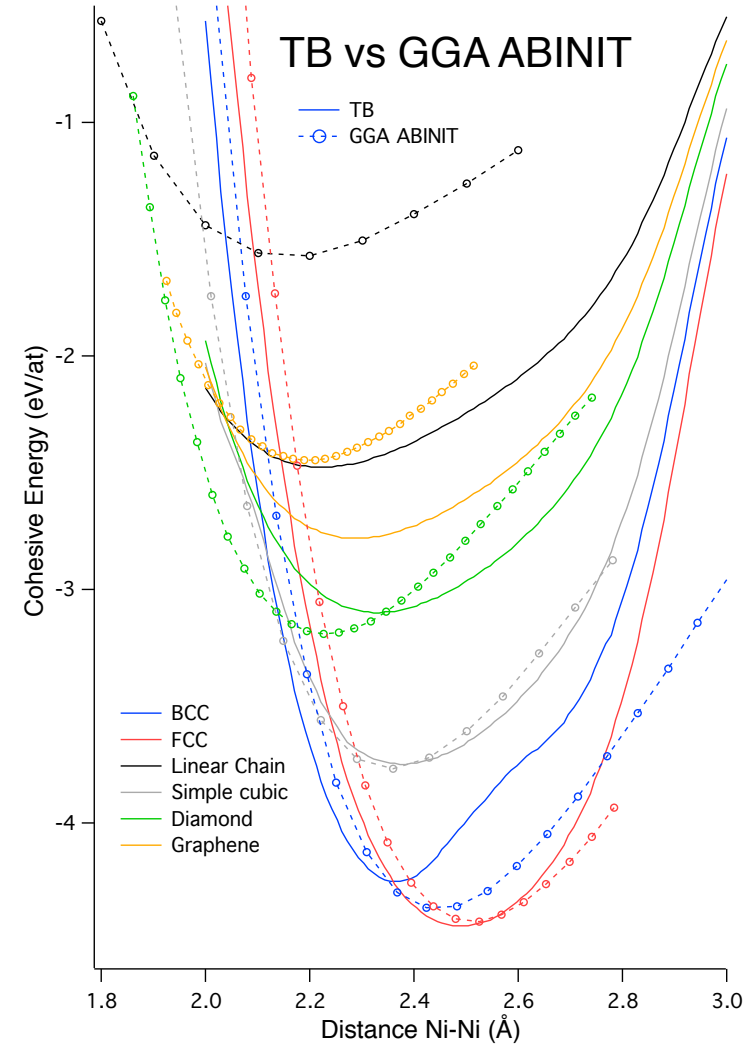
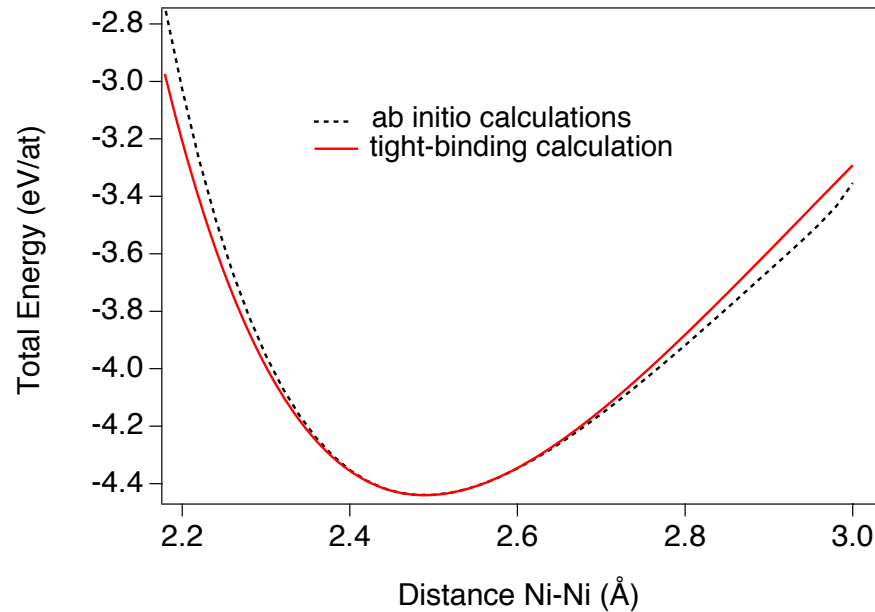
Elastic constant C_{12} : **254 GPa (260 GPa)**

Elastic constant C_{44} : **77 GPa (91 GPa)**

Melting temperature : **2041 K (2142 K)**

Some transition metals : Ni

Parameters fitted to reproduce the fcc structure

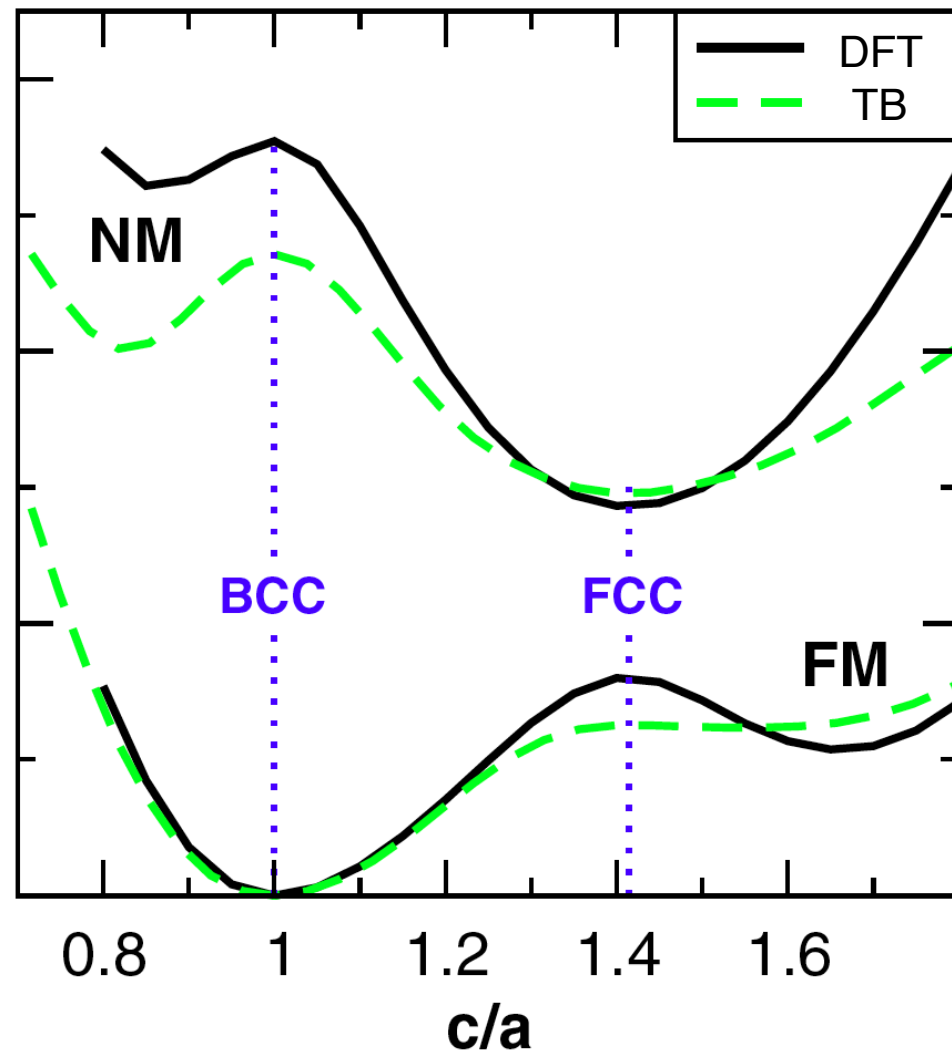


	Structure	Lattice parameter (Å)	Cohesive energy (eV/atom)	B (GPa)	C' (GPa)	C_{44} (GPa)	Surface energy (mJ/m ²)
Ni	fcc	$a/\sqrt{2}=2.489$	-4.44	187.6	55.2	131.7	1840 (solid) 2385 (liquid)
This work	fcc	$a/\sqrt{2}=2.489$	-4.44	182.1	68.8	96.9	1660 (100) 1560 (111)

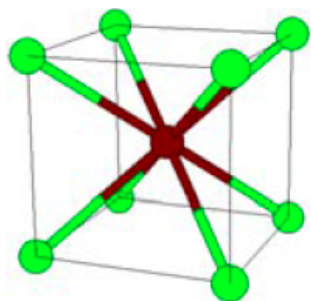
Some transition metals : Fe

Parameters fitted to reproduce the bain path between bcc and fcc

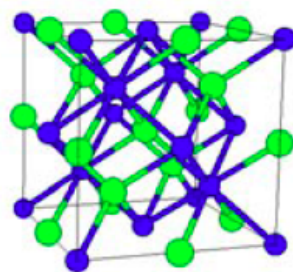
[GPa]	Exp	BCC FM	BCC NM
B	172	177	237
C'	43	49	-116
C ₄₄	116	118	19



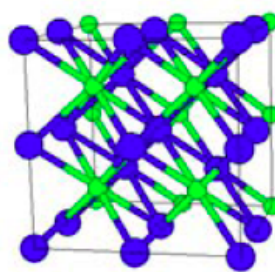
Intermetallic compound : $\text{Fe}_x\text{Al}_{1-x}$



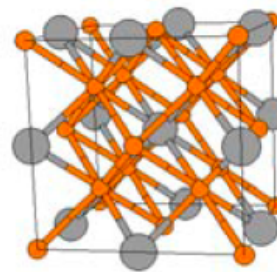
B2 (CsCl)



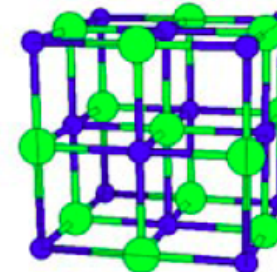
B32 (FeAl)



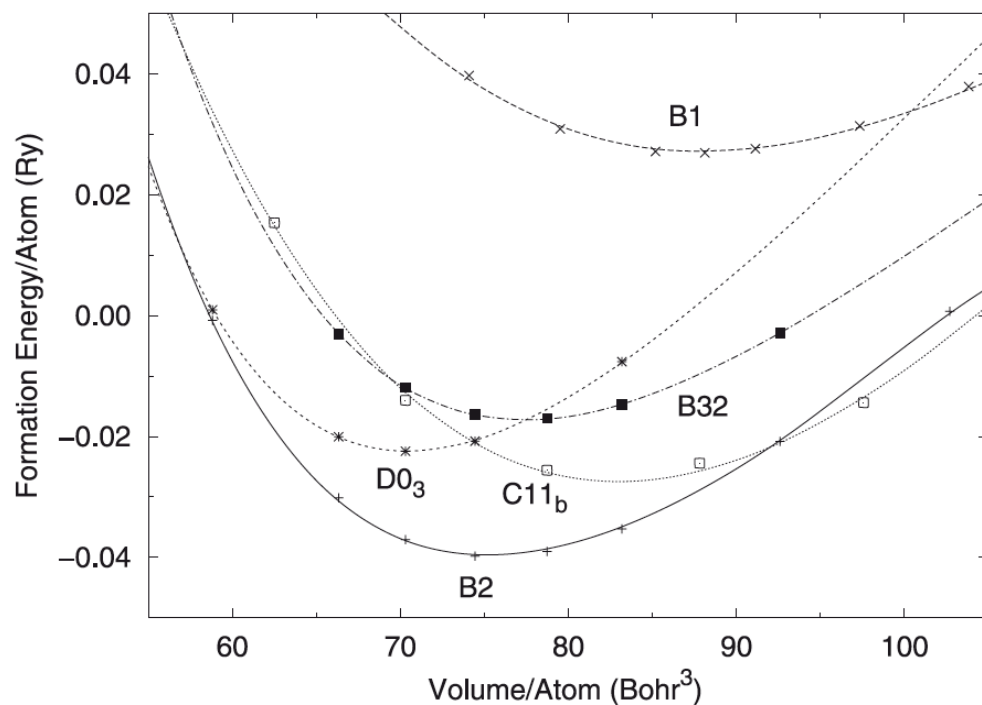
C11_b (FeAl₂)



D0₃ (Fe₃Al)



B1 (NaCl)

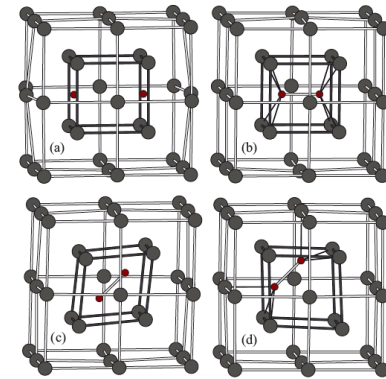
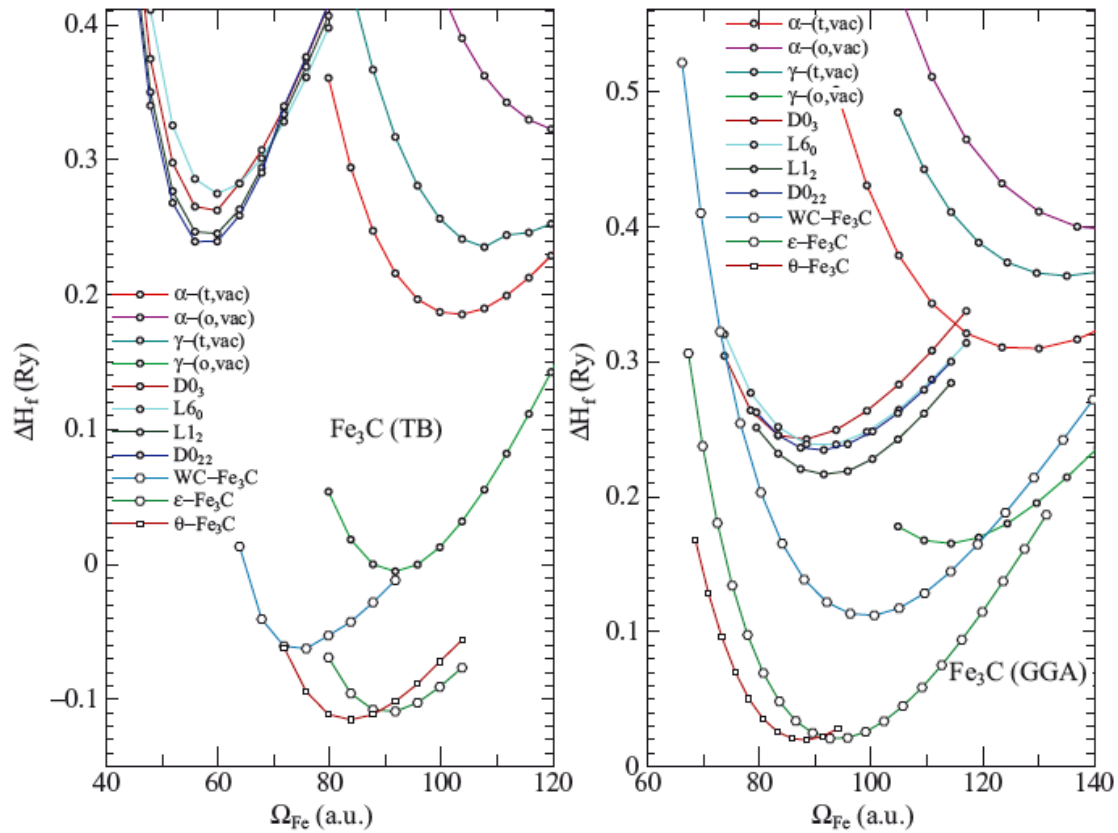


CsCl phase

Property	TB	LAPW
a (Bohr)	5.32	5.33 (5.49 from experiment [1])
B (GPa)	116	113
$C_{11} - C_{12}$ (GPa)	138	104
C_{11} (GPa)	199	182
C_{12} (GPa)	74	78
C_{44} (GPa)	91	45

Steel : FeC

• Fe₃C (cementite) and C dimer in BCC Fe



Approximation

N atoms in the system and 5 orbital atomics (5d) per atom

Diagonalization of a $(5N) \times (5N)$ matrix

Continuous spectrum : density of states $n(E)$

$$E_{band} = \int_{-\infty}^{E_f} E n(E) dE$$

Diagonalization
scheme

not effective for atomic simulations with
large system

Approximation :
➡ **the moment's method or recursion method**

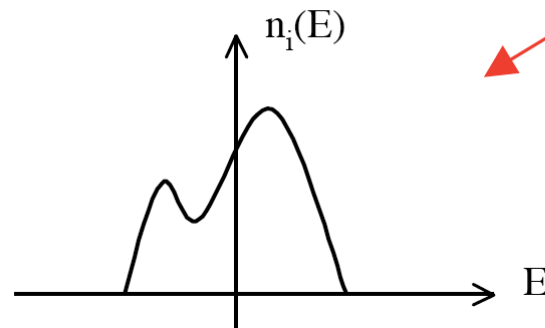
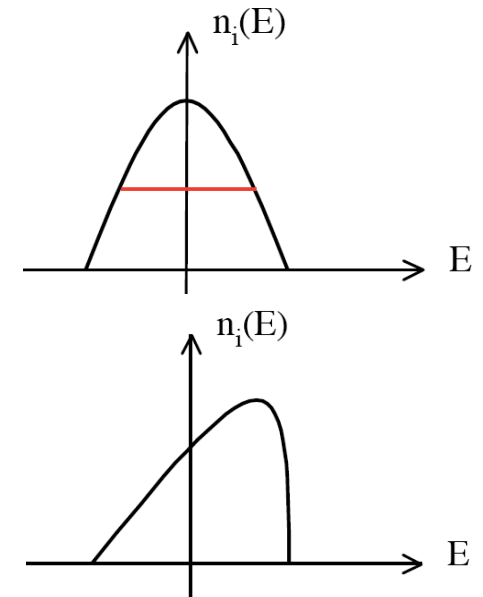
(see F. Ducastelle's lecture)

Moments : definition

The k th moment of a local density of states n_i (to simplify we forget the orbitals) is defined by :

$$\mu_k = \int_{-\infty}^{+\infty} E^k n_i(E) dE \quad (23)$$

- μ_0 gives the total number of states in the eigenspectrum.
- μ_1/μ_0 gives the centre of gravity of the eigenspectrum.
- μ_2/μ_0 gives the mean square width of the eigenspectrum.
- μ_3/μ_0 reflects the skewness of the eigenspectrum.
- μ_4 reflects the presence or not of a gap in the eigenspectrum.



Moments : tight-binding approach

In a tight-binding approach, the determination of the first moments is easy :

$$\begin{aligned}\mu_1^i &= \int_{-\infty}^{+\infty} E n_i(E) dE = \sum_n \int_{-\infty}^{+\infty} E |\langle i|n\rangle|^2 \delta(E - E_n) dE \\ &= \sum_n E_n |\langle i|n\rangle|^2 = \langle i|H|i\rangle = \epsilon_i .\end{aligned}\quad (23)$$

The second moment is :

$$\mu_2^i = \int_{-\infty}^{+\infty} E^2 n_i(E) dE \quad (24)$$

$$= \sum_j H_{ij} H_{ji} . \quad (25)$$

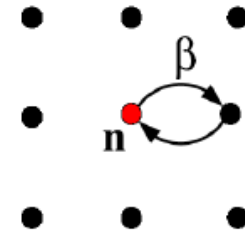
H_{ij} is different to zero if i and j are first neighbours. Thus,

$$\mu_2^i = Z_i \beta_{i,j}^2 \quad (26)$$

Thus, we can easily generalize :

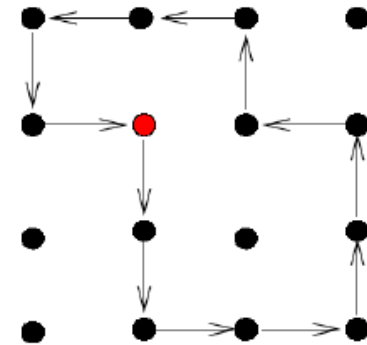
$$\mu_k^i = (H)_{ii}^k = \sum_{j_1, j_2, \dots, j_{k-1}} H_{ij_1} H_{j_1 j_2} \dots H_{j_{k-1} i} .$$

Second moment



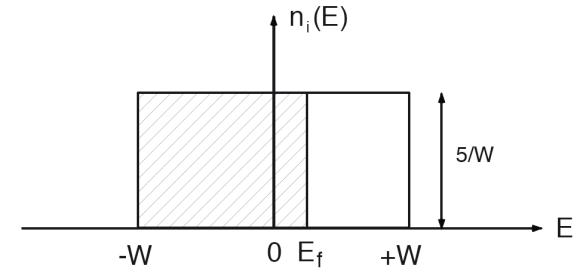
Path of length two hops from atom i

k^{th} moment



The k th moment of the LDOS of an atom i is the sum of all paths of length k hops starting and ending at site i

$$\mu_2 = \int_{-\infty}^{+\infty} E^2 n_d(E) dE = \frac{10W^2}{3}$$

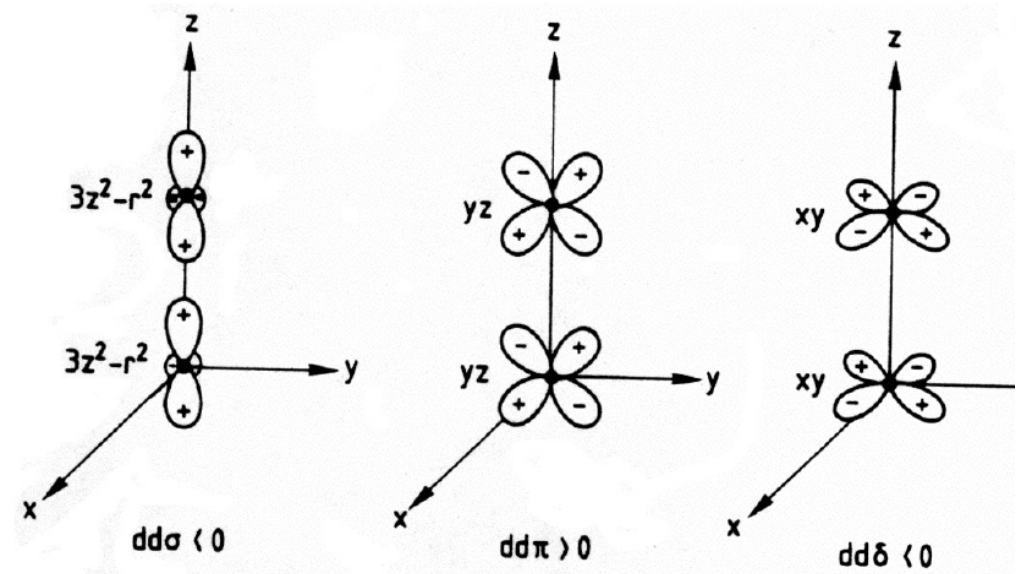


$$E_{bande}^i = \frac{N_d(N_d - 10)}{10} \sqrt{\frac{3\mu_2}{10}}$$

$$\mu_2 = Z(dd\sigma^2 + 2dd\pi^2 + 2dd\delta^2)$$

$$dd\sigma_0 = -2dd\pi_0$$

$$dd\delta_0 \simeq 0$$



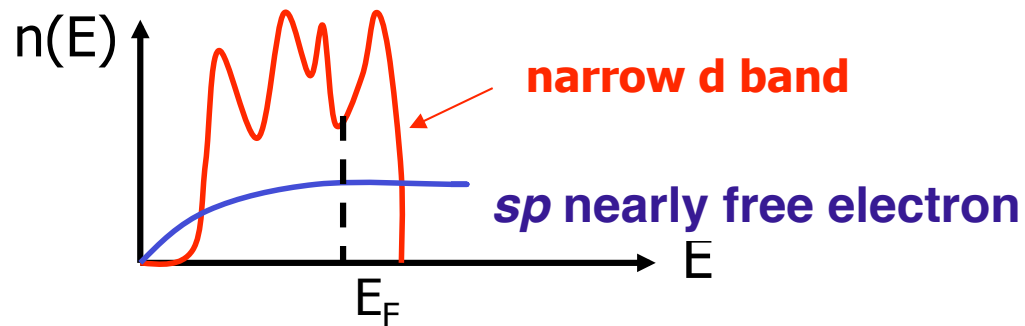
$$E_{bande}^i = N_d(N_d - 10) \left(\frac{3}{5}\right)^{\frac{3}{2}} \sqrt{2} dd\pi_0 \exp(-qr_{ij})$$

$$E_{rep}^n = \sum A \exp(-pr_{ij})$$

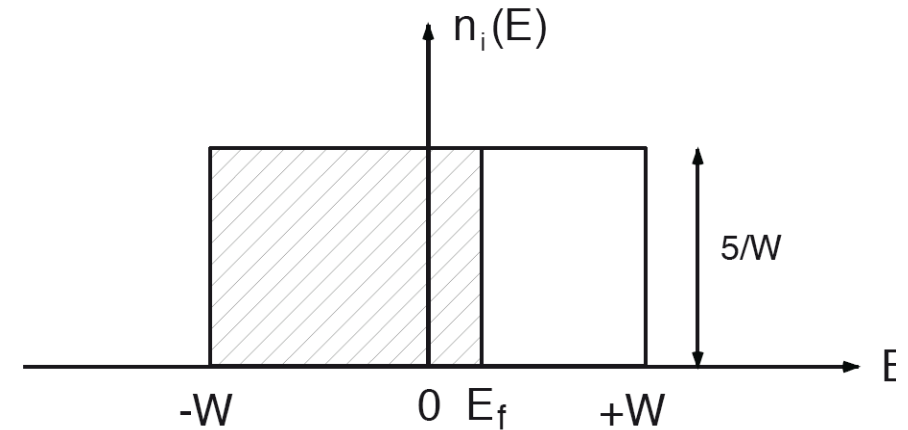
$$E_{Tot} = \sum_{i < j} A \exp[-p(\frac{r_{ij}}{r_0} - 1)] - \left\{ \sum_{i < j} \xi^2 \exp[-2q(\frac{r_{ij}}{r_0} - 1)] \right\}^{1/2}$$

Example : transition metals

- Transition metals
 - Cohesion result from *d* band
 - *sp* band is neglected



Friedel's model



Second Moment Approximation



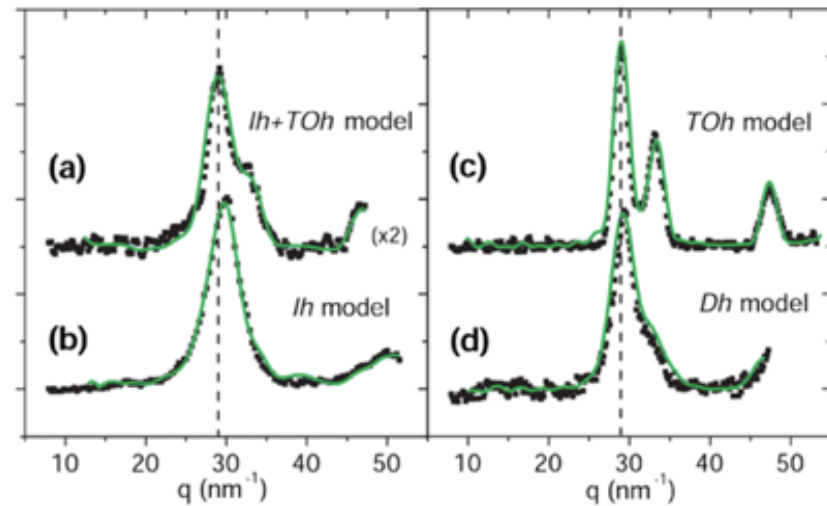
$$E_{tot}^i = - \sqrt{\sum_{i \neq j} \xi^2 \exp \left[-2q \left(\frac{r_{ij}}{r_0} - 1 \right) \right]} + \sum_{i \neq j} A \exp \left[-p \left(\frac{r_{ij}}{r_0} - 1 \right) \right]$$

SMA : some examples

Structure and morphology of CoPt NPs



Comparison between experimental (black) and calculated (green) diffraction patterns

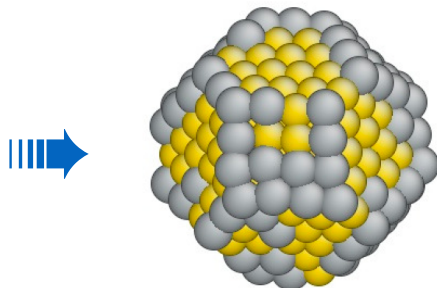


J. Penuelas *et al.*, Phys. Rev. Lett. **100**, 115502 (2008)

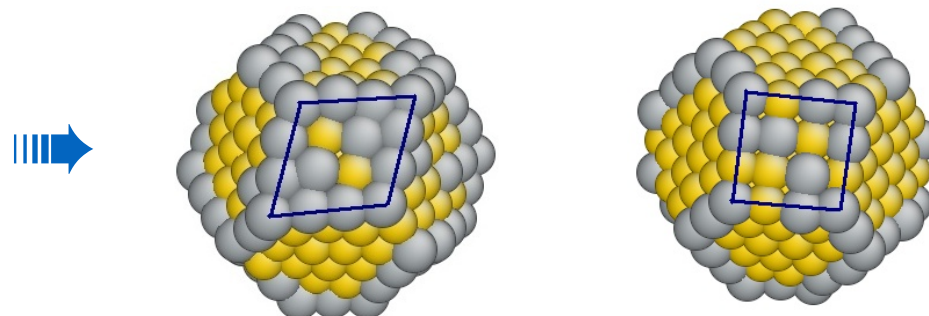
Structure of CuAg NPs (500 K)

Isolated cluster

(or a set of isolated clusters) for a nominal concentration



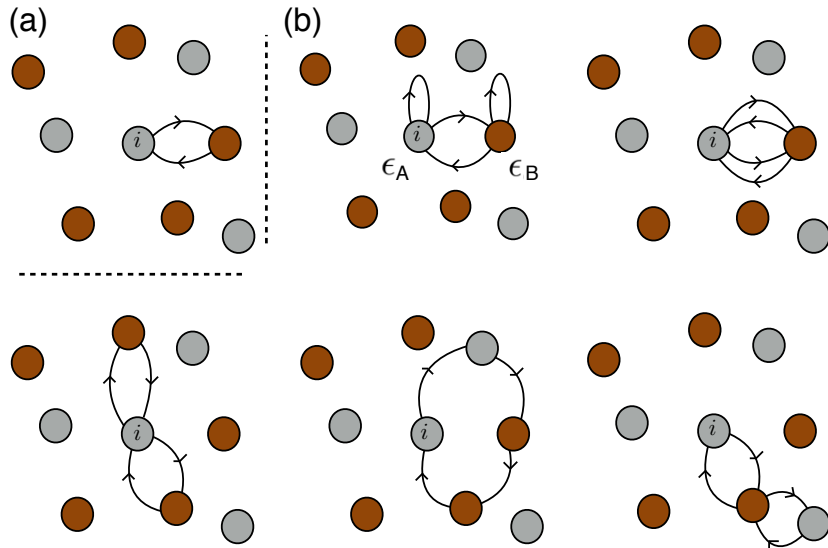
Clusters in mutual equilibrium or in equilibrium with reservoir (gas phase, ...)



L. Defour *et al.*, Phys. Rev. Lett. **103**, 205701 (2009)
Mohamed Briki, Thèse de Doctorat, Univ. Paris Orsay, (2013)

Beyond SMA

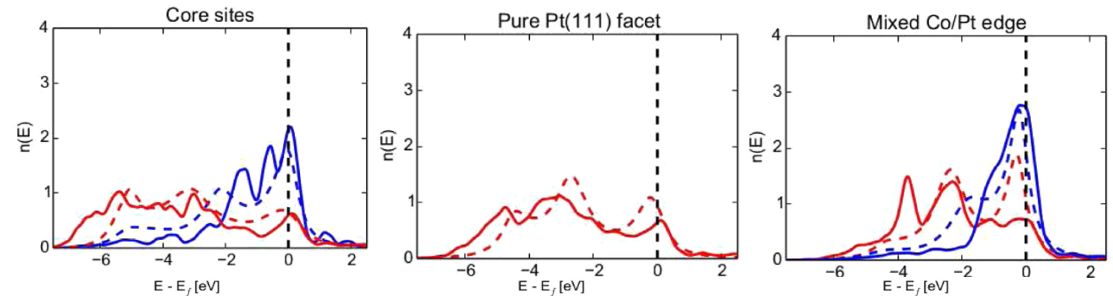
• More neighbors



• Bond Order Potential

(see F. Ducastelle's lecture)

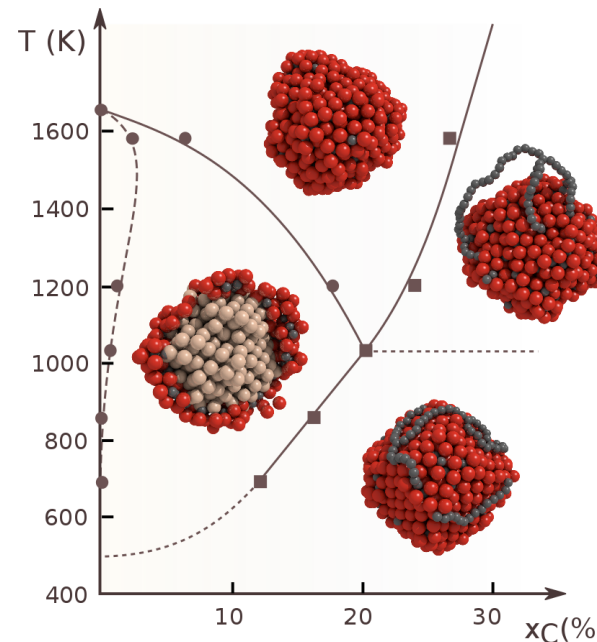
Electronic properties of CoPt NPs



L Zosiak *et al.*, J. Phys.: Condens. Matter **27**, 455503 (2015)

good agreement between DFT and TB For NP containing 561 atoms

Phase diagram for Ni-C NPs



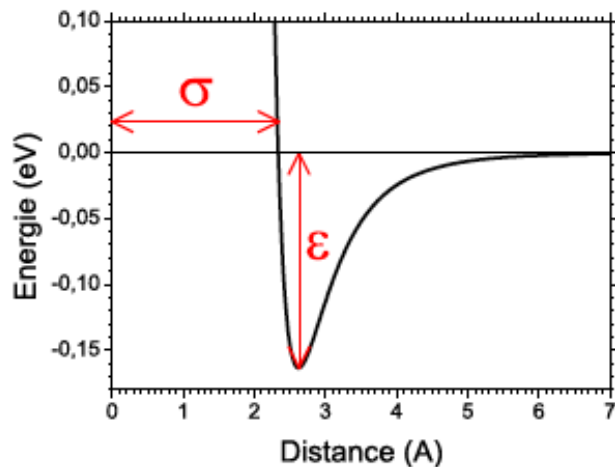
Y. Magnin *et al.*,
Phys. Rev. Lett. **115**,
205502 (2015)

different states are identified in agreement with experimental observations

Lennard-Jones potential

$$U = \frac{1}{2} \sum_{i,j=1}^N V_{ij}(|\vec{r}_{ij}|) \quad V_{ij}^{\alpha\beta}(|\vec{r}_{ij}|) = -4\varepsilon^{\alpha\beta} \left[\left(\frac{\sigma^{\alpha\beta}}{r_{ij}} \right)^6 - \left(\frac{\sigma^{\alpha\beta}}{r_{ij}} \right)^{12} \right]$$

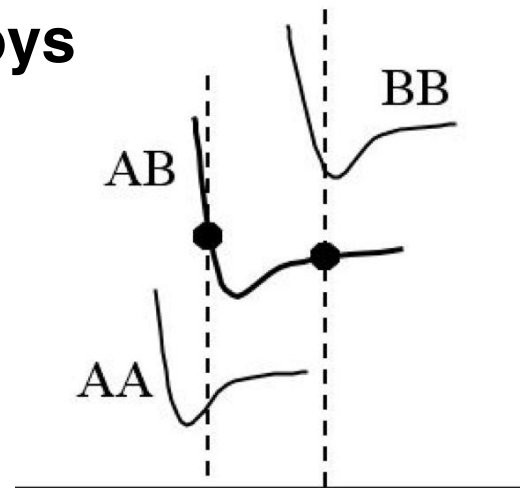
Pure



σ : atomic radius

ε : cohesive energy

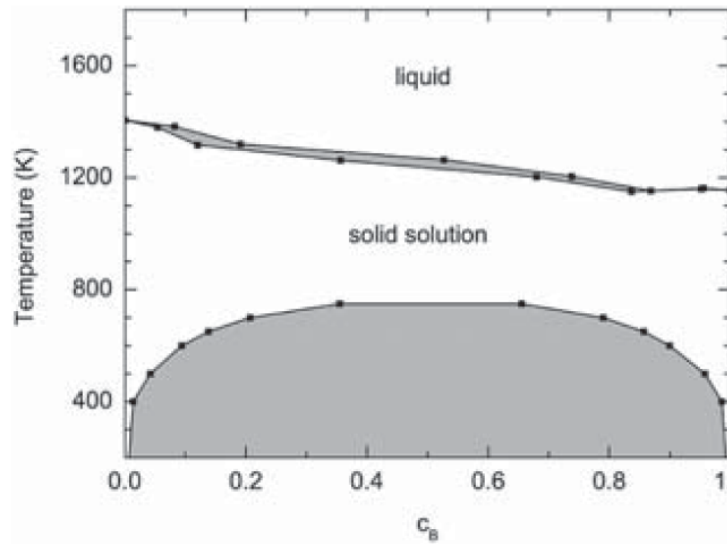
Alloys



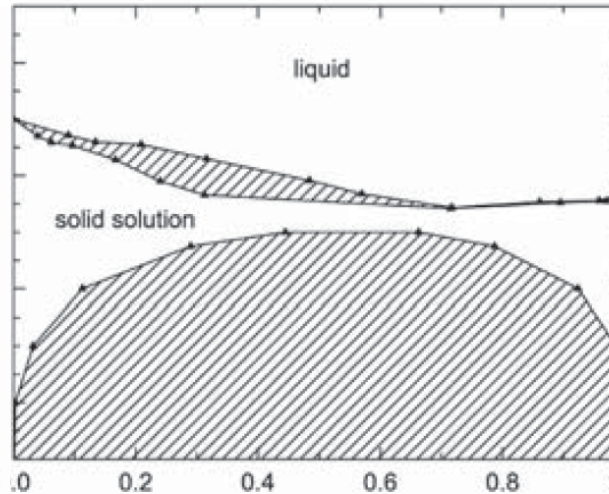
- very simple formula
- parameters control some physical quantities

AB alloy : phase diagram in volume

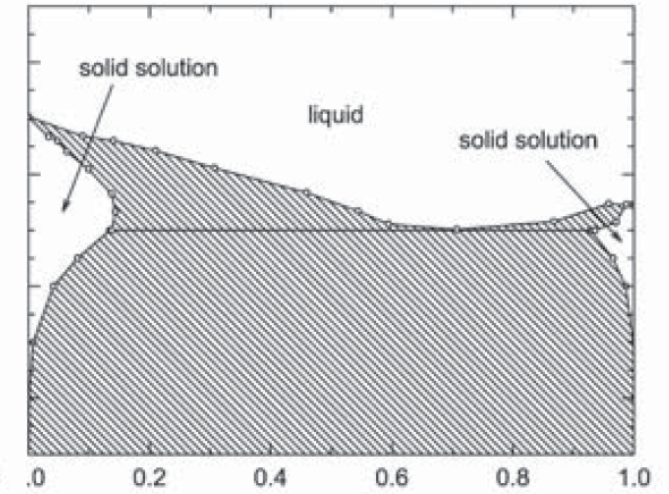
$\Delta a/a = 0\%$



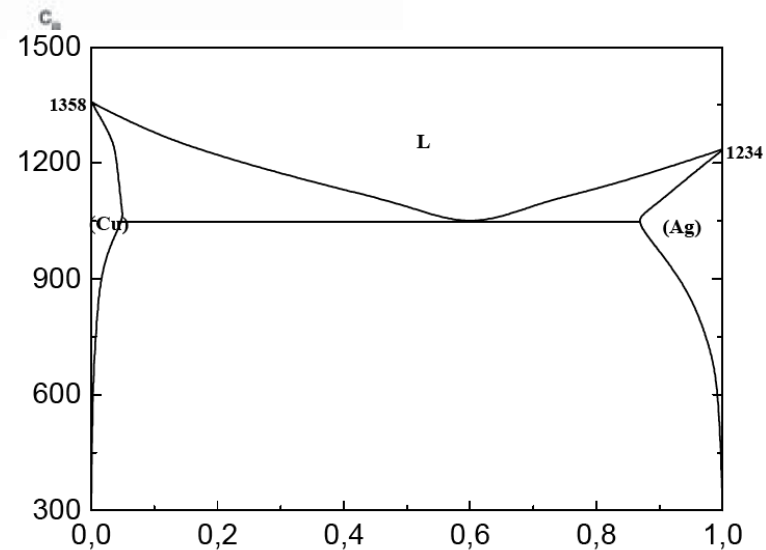
$\Delta a/a = 8\%$



$\Delta a/a = 12\%$

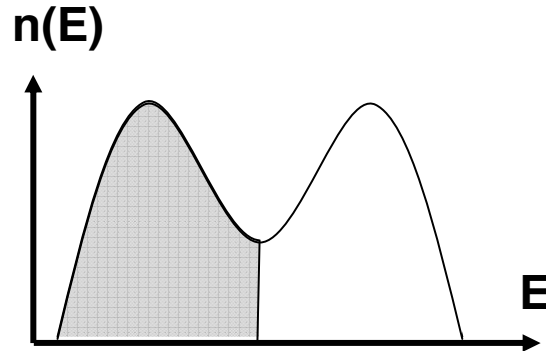


➡ $\Delta a/a = 12\%$
close to Cu-Ag



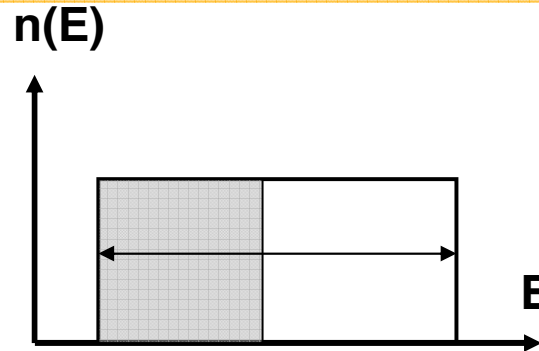
Potentiels empiriques pour les métaux de transition

Liaisons Fortes



- Forces angulaires
- Propriétés dépendent du remplissage de la bande d

Approximation du Second moment



$$E^i = E_{\text{paire}}^i + E_{\text{bande}}^i$$

$$E_{\text{bande}}^i = -\sqrt{\rho_i}$$

- Propriétés normalisées indépendantes du remplissage
- Pas de forces angulaires
- 4 paramètres ajustés sur données expérimentales (E_{coh} , C_{ij} , a)

Potentiel EAM

$$E^i = E_{\text{paire}}^i + F(\rho_i)$$

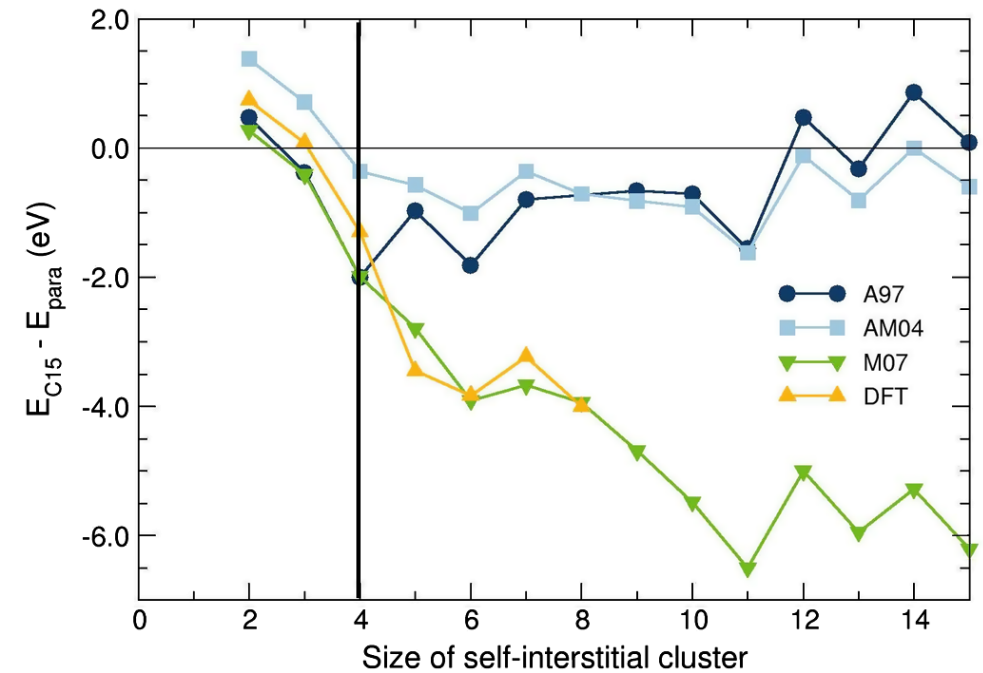
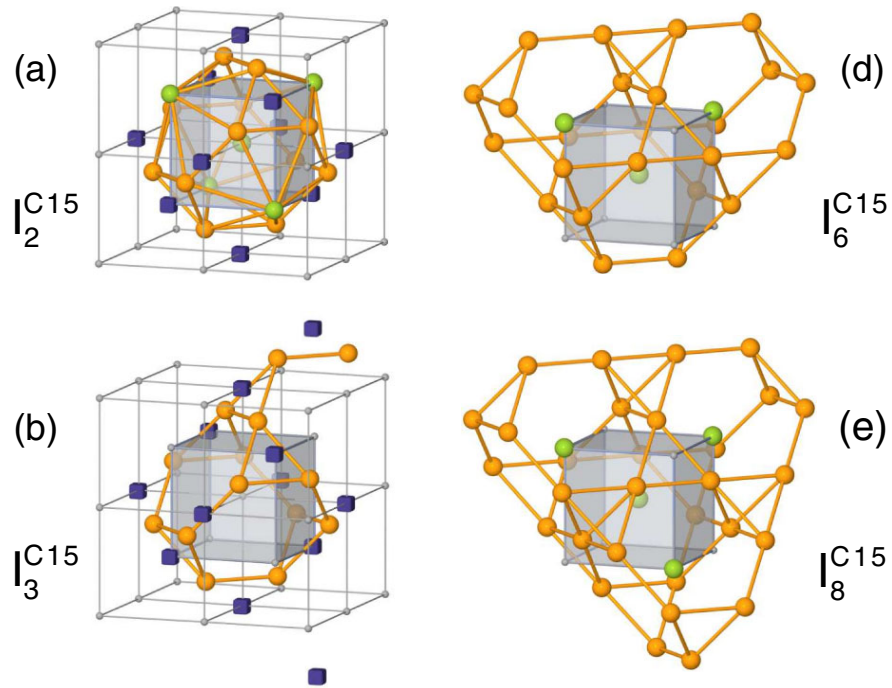
Mendelev et al. (2003):

$$F(\rho_i) = -\sqrt{\rho_i} + a\rho_i^2$$

- = généralisation empirique du second-moment
- + de flexibilité dans dépendance en distance
- Ajustement des paramètres (10-15) sur résultats DFT (défauts, "liquide")

EAM potentials

• Importance de tester les potentiels



Example : carbon

- Phenomenological (classic) potential :

$$E_{Tot} = E_{Att} + E_{Rep}$$

- Example C-C interaction : Brenner potential

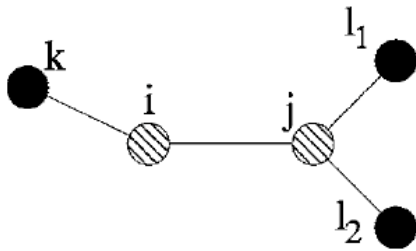
$$E_{Tot} = \sum_i \sum_{j(i < j)} [V_R(r_{ij}) - B_{ij}^* V_A(r_{ij})]$$

$$V_R = f(r) \frac{D_e}{S-1} \exp\{-\beta\sqrt{2S}(r - R_e)\}$$

$$V_A = f(r) \frac{D_e S}{S-1} \exp\{-\beta\sqrt{2/S}(r - R_e)\}$$

$$B_{ij}^* = \frac{B_{ij} + B_{ji}}{2}, \quad B_{ij} = \left(1 + \sum_{k(\neq i, j)} G_c(\theta_{ijk}) f(r_{ik})\right)^{-\delta}$$

$$G_c(\theta) = a_0 \left(1 + \frac{c_0^2}{d_0^2} - \frac{c_0^2}{d_0^2 + (1 + \cos \theta)^2}\right)$$



Example : carbon

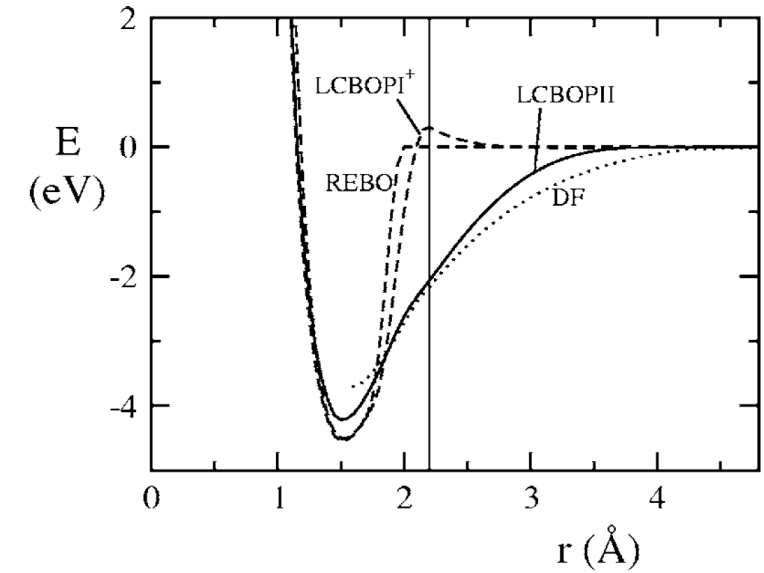
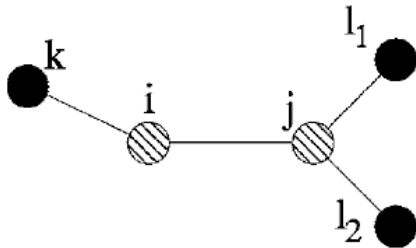
- REBO, LCBOP, LCBOP II, ...

$$E_{Tot} = \frac{1}{2} \sum_{i,j}^N (S_{sr,ij}^{down} V_{ij}^{sr} + S_{sr,ij}^{up} V_{ij}^{lr} + \frac{1}{Z_i^{mr}} S_{mr,ij}^{up} V_{ij}^{mr})$$

$$V_{ij}^{sr} = V_{R,ij}^{sr} - B_{ij} V_{A,ij}^{sr}$$

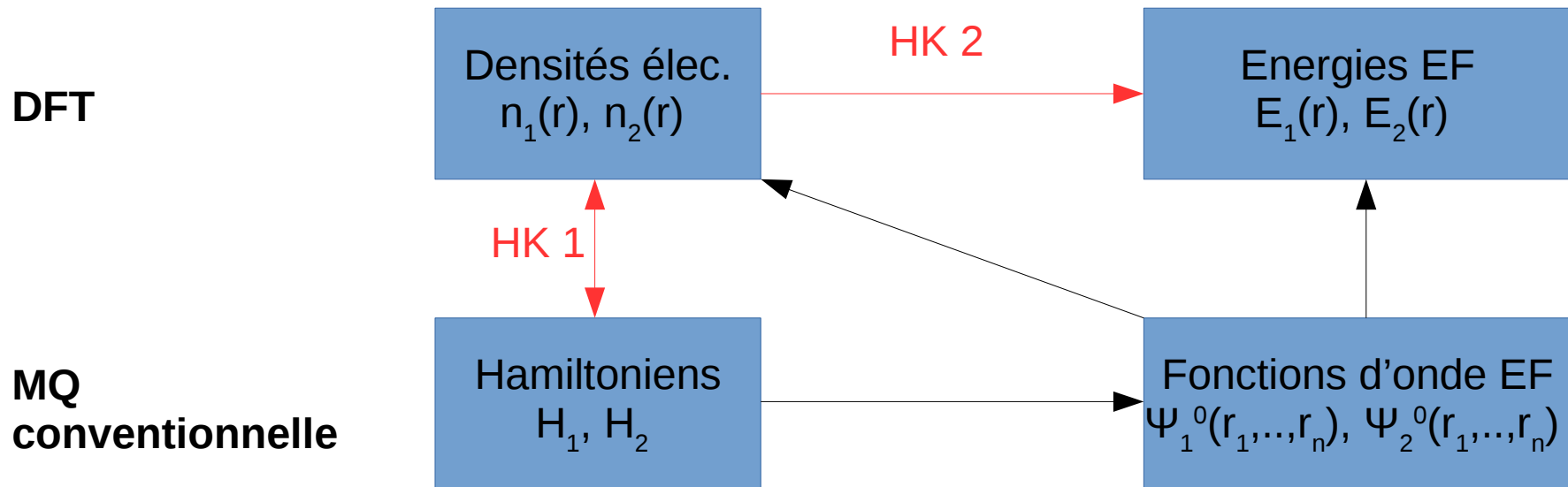
B_{ij} : bond order

S_{ij} : screening term



Calculs DFT

- Théorie de la fonctionnelle de la densité : Hohenberg et Kohn (1964)



- Kohn et Sham (1965) : système virtuel d'e⁻ indépendants de même n(r)

$$\left(-\frac{1}{2} \nabla^2 + v_s(r) + \int \frac{n(r')}{|r-r'|} dr' + v_{xc}(r) \right) \phi_i(r) = \epsilon_i \phi_i(r)$$

$$n^{(t)}(r) \rightarrow v_s^{(t)}(r) \rightarrow \Phi_i^{(t)} \rightarrow n^{(t+1)}(r)$$

- Résolution auto-cohérente

Calculs DFT

Voir le cours de F. Ducastelle

- “Esprit” de la DFT :

- Théorie effective pour décrire l'état fondamental : $E_0 = \min E[n(r)]$
- Problème de N e⁻ en interaction ↔ jeu d'équations auto-cohérentes à 1 e⁻
- Exact en principe, mais approximations nécessaires

- *Ab initio*, {Z_i, r_i} suffisent... avec des choix à faire

- $E_{xc}[n]$: LDA, **GGA**, B3LYP, ...
- Traitement des e⁻ de coeur (**PP**, **PAW**, calculs tous électrons)
- Bases : localisées, **ondes planes**
- Magnétisme électronique (ou pas) : polarisation en spin
- Maillage de point k

- **Réflexes à avoir :**

- Pas de calcul de gap
- Attentions aux systèmes fortement corrélés
- Limitations à ~100 atomes : “size effects”
- Température : difficile

→ **Il faut connaître son matériau d'étude (sens physique, données expérimentales...)**

Machine Learning potentials

- Pas de structure électronique !

Voir le cours de A. Bartok

- But :

- Efficacité des potentiels empiriques, précision de l'*ab initio*
- Méthode $O(N)$

- Une classification possible :

Pot. Emp. traditionnels

Peu de paramètres, nb. fixé a priori

Pas d'amélioration systématique

Potentiels ML

Pas de nb paramètres fixé a priori

Amélioration systématique possible (coût de calcul $\uparrow$)

- Différentes catégories de potentiels :

Classe	Réprésentation environnements atomiques	Modèle de régression
NNP	Fonctions radiales + dépendance angulaire	Réseaux neurones
GAP	Densité atomique développée sur base d'harmoniques sphériques	Processus gaussien
MTP	Polynômes invariants	Linéaire

Machine Learning potentials

- Pas de structure électronique !
- But :
 - Efficacité des potentiels empiriques, précision de l'*ab initio*
 - Méthode O(N)
- Une classification possible :

Pot. Emp. traditionnels

Peu de paramètres, nb. fixé a priori

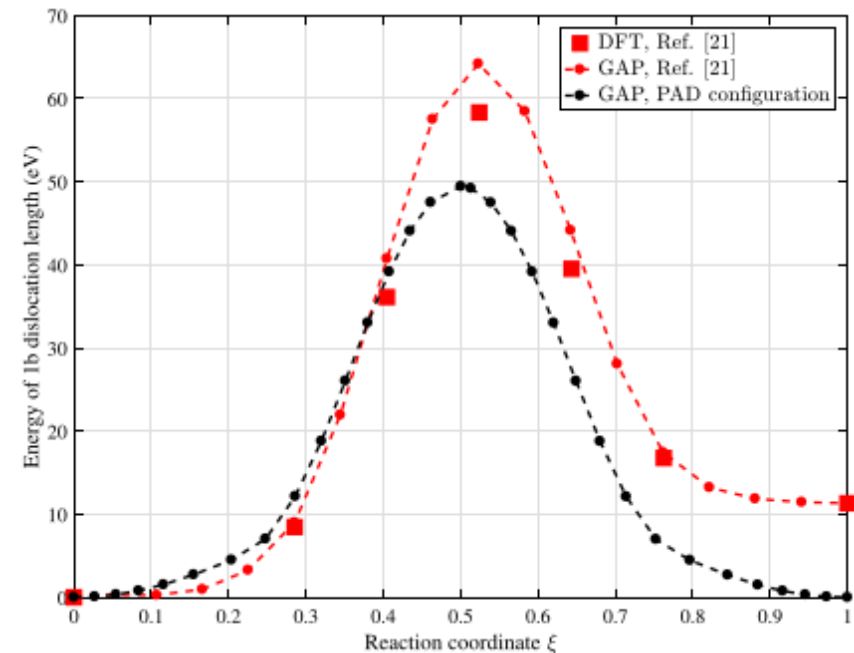
Pas d'amélioration systématique

- Exemple de la dislocation vis dans Fe cc*

Potentiel GAP

- Bon accord avec la DFT dans le même arrangement quadrupolaire
- Artefact d'effet de taille : surmonté via le GAP (NB : des approches correctives existent**)

Potentiers ML

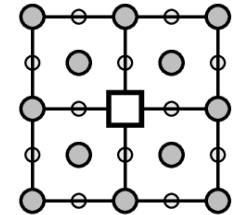


*F. Maresca *et al.*, npj Comp. Mat. 4:69 (2018) ; **L. Dezerald *et al.*, Phys. Rev. B 91 (2015)

Types de calculs atomistiques

- **Statique moléculaire (T=0K)**

- Minimisation $E_{tot}(\{R_i\})$ par rapport aux positions atomiques $\{R_i\}$
- Calculs en déformations homogènes, relaxations (CG, FIRE, etc.)
- $C_{ij}(T=0K)$, a_0 , structure et énergétique de défauts
- Mécanismes élémentaires sous déformations / contraintes statiques



- **Dynamique moléculaire :**

- Trajectoire des atomes → intégration des équations de Newton discrétisées

$$R_i(t + \Delta t) = 2 R_i(t) - R_i(t - \Delta t) + \frac{F_i(t)}{m_i} \Delta t^2$$

- *Forces nécessaires*

- *Choix de Δt (!)*

- Mécanismes de diffusion, $C_{ij}(T)$, mécanismes élémentaires de la plasticité...

- Évolutions temporelles (courtes, ou accélérées !)

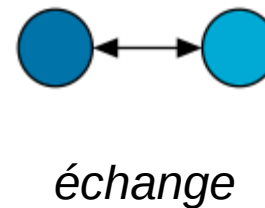
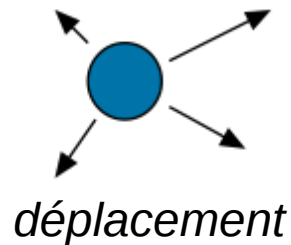
Voir le cours de N. Combes

Types de calculs atomistiques

- **Méthode Monte Carlo**

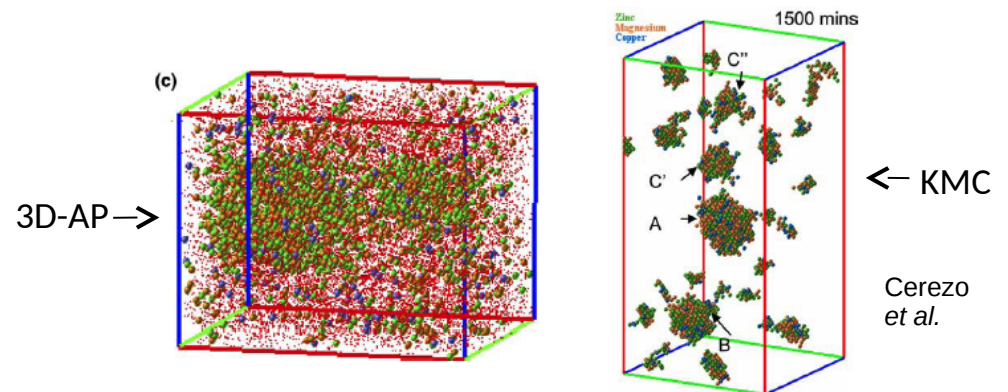
Voir le cours de N. Combes

- Dynamique aléatoire sur l'espace des configurations
- Ensemble statistique de travail (Canonique, Grand Canonique, SCG...)
- Mise oeuvre :



- Probabilité d'acceptation adaptée

- Structures d'équilibre global
- Diagrammes de phases
- Cinétiques : KMC sur / hors réseau

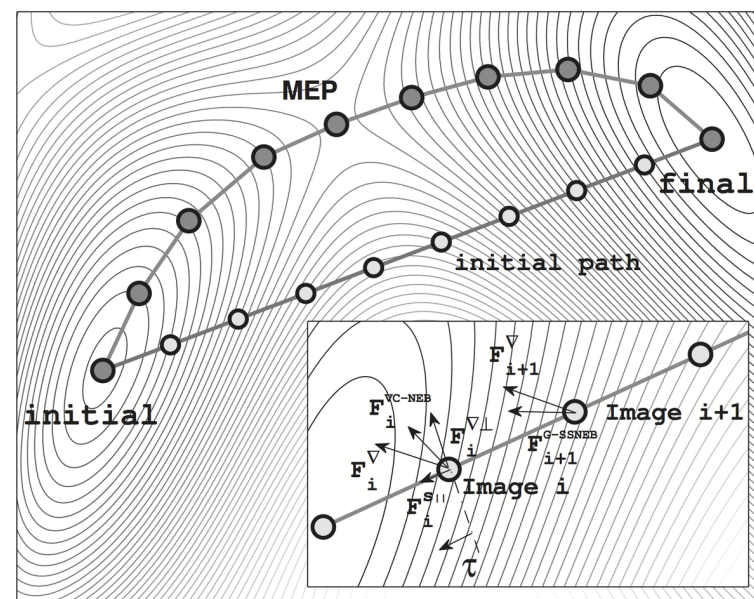
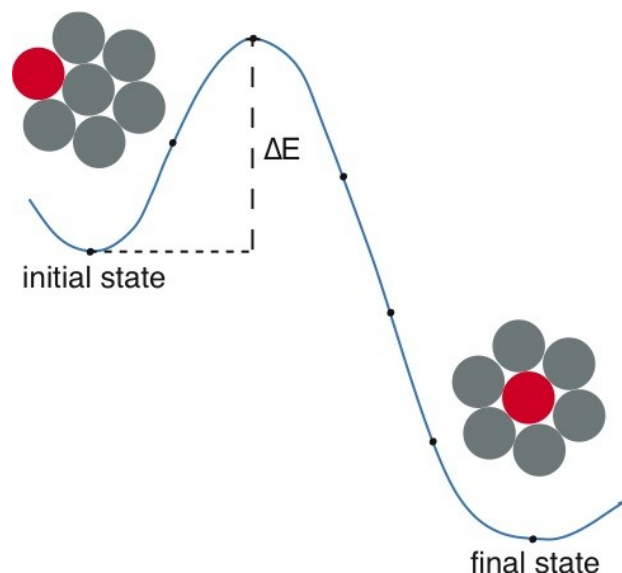


Types de calculs atomistiques

- Méthodes d'exploration de paysages d'énergie

Voir le cours de N. Mousseau

→ Etats initiaux et finaux connus, e.g. NEB, CI-NEB



→ Exploration automatisée, sans connaissance *a priori* : e.g. ART nouveau

- D'autres types de calculs existent (intégration thermodynamique, temperature accelerated dynamics, méthodes de changement d'échelle, etc.)

Plan

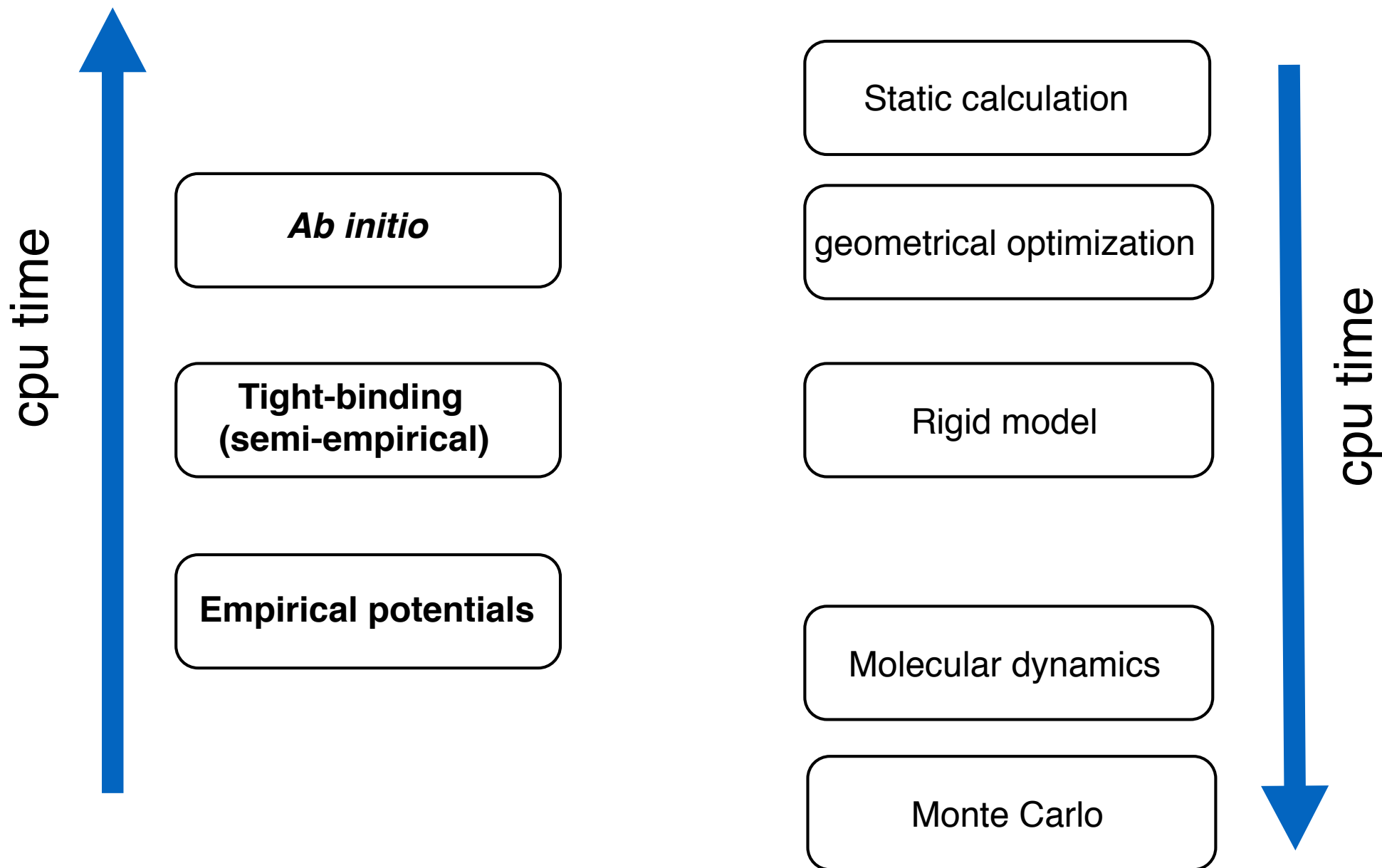
I) Introduction : les nanoparticules

II) Les outils

III) Exercices

- 1) **Comment modéliser les problèmes physiques présentés en Introduction**
- 2) Amas lacunaires dans Zr hcp
- 3) Croissance de structures carbonées à partir d'un catalyseur métallique

What is possible to study ?



Plan

I) Introduction : les nanoparticules

II) Les outils

III) Exercices

- 1) Comment modéliser les problèmes physiques présentés en Introduction
- 2) Amas lacunaires dans Zr hcp**
- 3) Croissance de structures carbonées à partir d'un catalyseur métallique

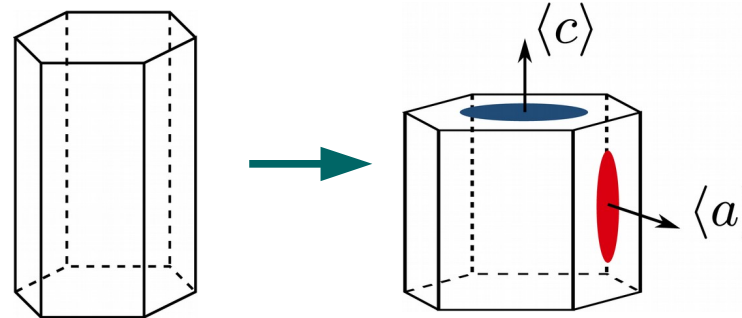
Exo : amas lacunaires dans Zr hcp

• Gaine entourant le combustible nucléaire : alliages de Zr hcp

- **Irradiation growth** : dimensional change without applied stress

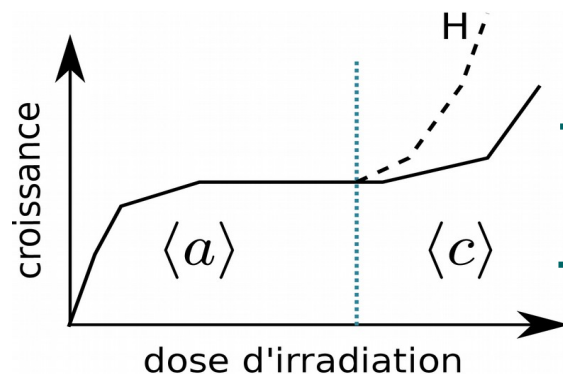
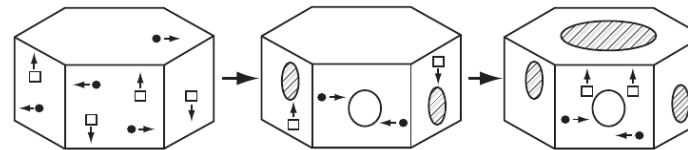
Monocristal de Zr :

- Elongation selon $\langle a \rangle$
- Contraction selon $\langle c \rangle$



- **Défauts d'irradiation :**

- SIAs, V
- Formation d'amas



Caractéristiques de la croissance ↔ microstructure de défauts

H accentue l'accélération de croissance

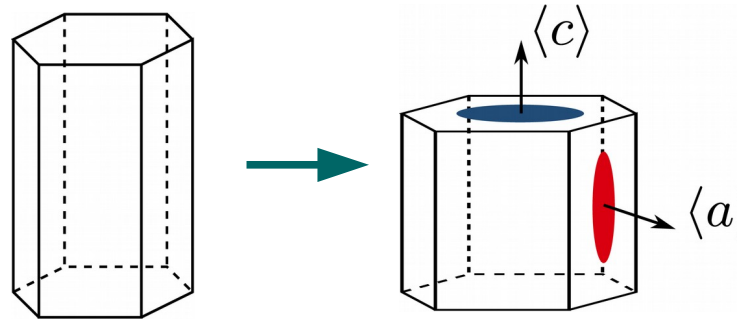
Exo : amas lacunaires dans Zr hcp

• Gaine entourant le combustible nucléaire : alliages de Zr hcp

- **Irradiation growth** : dimensional change without applied stress

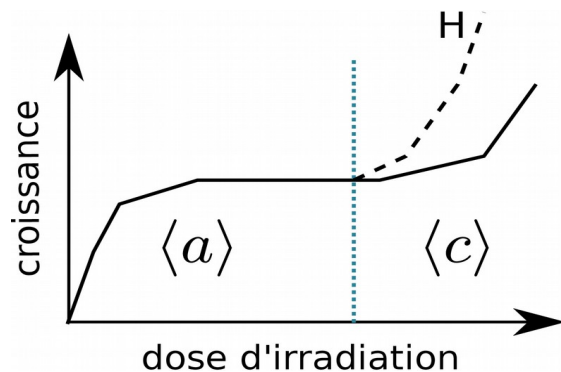
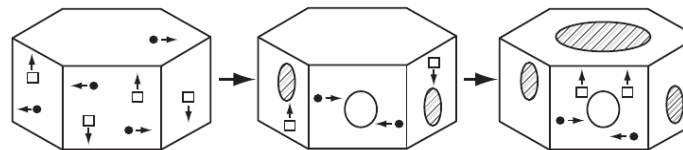
Monocristal de Zr :

- Elongation selon $\langle a \rangle$
- Contraction selon $\langle c \rangle$



- **Défauts d'irradiation :**

- SIAs, V
- Formation d'amas



→ **Formation privilégiée des boucles $\langle a \rangle$ vs boucles $\langle c \rangle$ et cavités ?**

→ **Action de H en solution solide diluée ?**

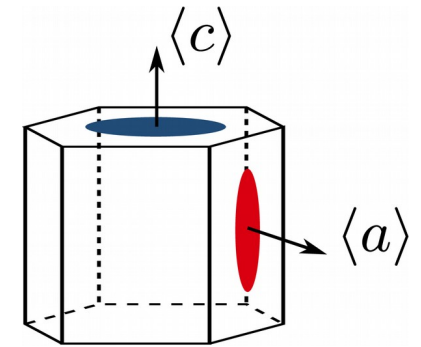
Context

Nuclear fuel cladding : hcp Zr alloys

- Goal : kinetic evolution under irradiation (Cluster Dynamics)

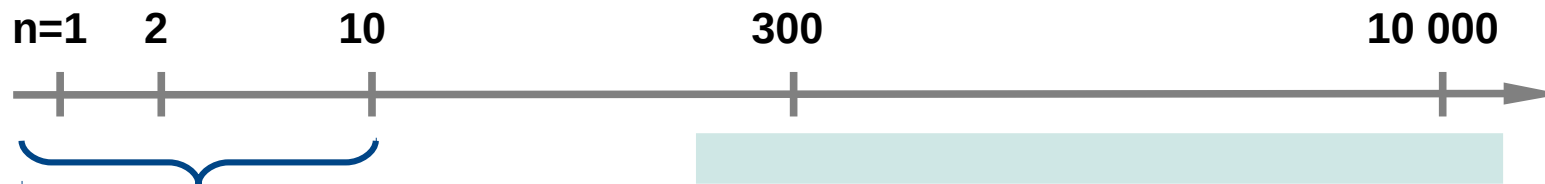
- Diffusion coefficients for PDs
- Absorption biases
- Energetics of SIAs, V, H, clusters.

- Focus on V-clusters
- Influence of H



- Dislocation loops
- Cavities

Approach :



- Ab initio calculations

- Continuous models

- Line tension,
- Surface, stacking fault energies

Main inputs
from DFT

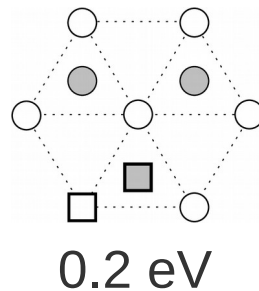
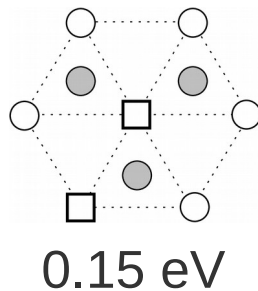
- EAM #2 and #3 :

M. Mendelev & G. Ackland, *Philos. Mag. Lett.* **87**, (2007)

I. Small V-clusters and H-V_n complexes

Elementary interactions between point defects

- V-clusters :

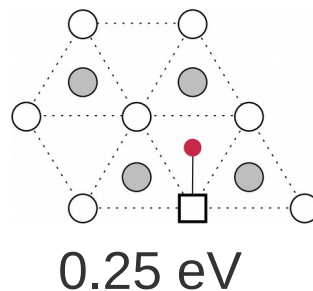
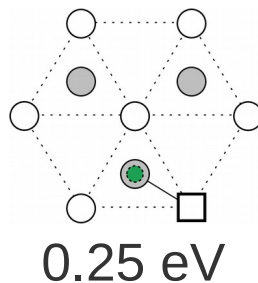


→ Only 1nn interactions attractive

→ Clustering : compact clusters

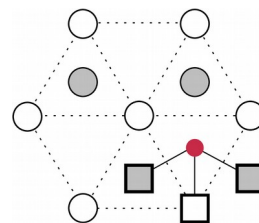
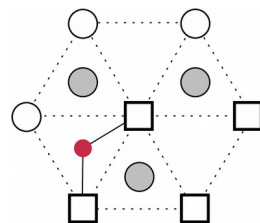
- H-V_n complexes :

- H-V :



→ 1nn interaction dominant

- Position of H :

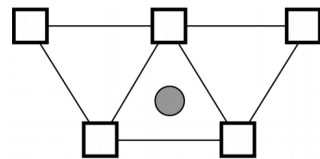


→ O site with 2 or 3 nn Vacancies ($E^b \sim 0.4\text{eV}$)

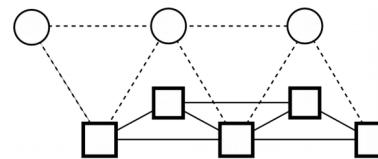
I. Small V-clusters and H- V_n complexes

Relative stability of small V-clusters :

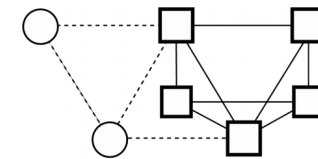
Strategy : keeping only the most stable configurations



Basal $\equiv <c>$

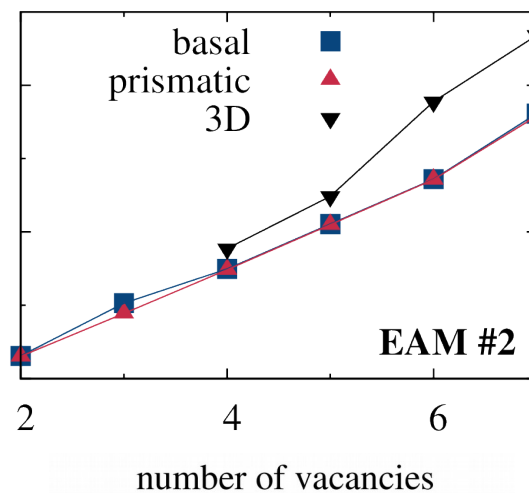
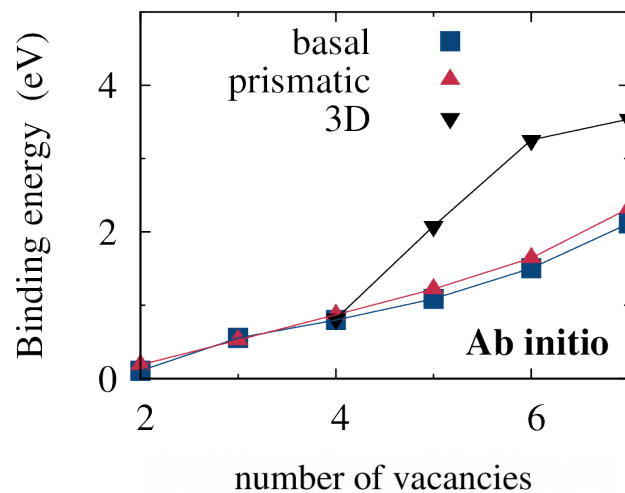


Prismatic $\equiv <a>$



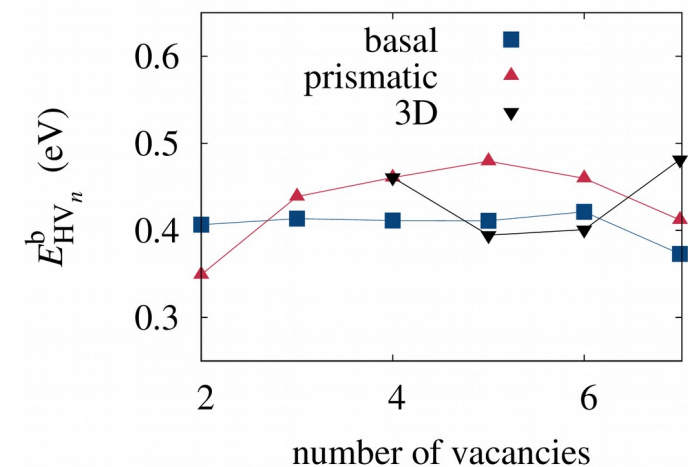
Cavities $\equiv 3D$

Small clusters :



- **Ab initio** : most stable defects = 3D clusters
- **EAM #2** : qualitative agreement

With H



- **H binds to V_n**
- **No discriminating effect**

II. Energetics of large clusters

Modeling approach:

Rely on classical expressions carefully parameterized

- Cavities :

$$E^f(R) = 4\pi R^2 f \sigma \rightarrow \text{surface energy model}$$

- Vacancy loops :

$$E^f(R) = 2\pi f K b^2 \ln \frac{R}{r_c} + 2\pi R^2 \gamma_{SF} \rightarrow \text{stacking fault energy}$$

↓
Line tension term

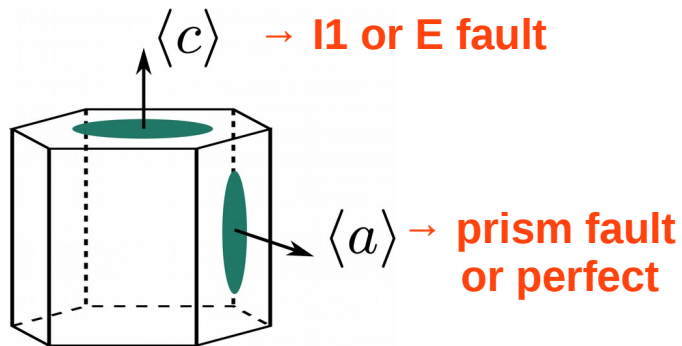
Strategy :

- 1) Calculation of the surface and fault energies (DFT and EAM #2)
- 2) EAM validation of the classical expressions
- 3) Parameterization using DFT data

II. Energetics of large clusters

1) Planar defects

- Stacking fault energies :



- Surface energies :

	DFT	EAM #2
Basal E	274 mJ/m ²	164 mJ/m ²
Basal I1	147	55
Prism	211	357

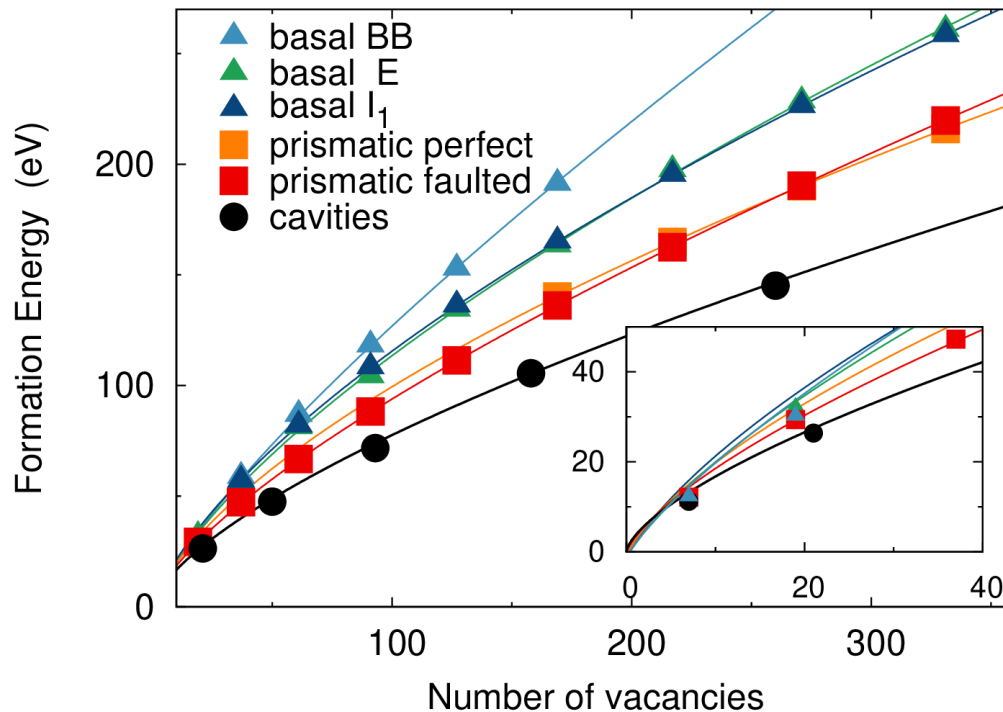
↓
Different
relative order

	DFT	EAM #2
Basal	1600 mJ/m ²	1270 mJ/m ²
Prism	1670	1340
Pyramidal (1 st)	1550	1340
Wulff construction	1690	1420

→ Underestimated
with EAM #2

II. Energetics of large clusters

2) EAM Validation



- Cavities : $E^f(R) = 4\pi R^2 f \sigma$

with $\frac{4\pi R^3}{3} = n\Omega$

- Dislocation loops :

$$E^f(R) = 2\pi f K b^2 \ln \frac{R}{r_c} + 2\pi R^2 \gamma_{SF}$$

with $\pi R^2 b_e = n\Omega$

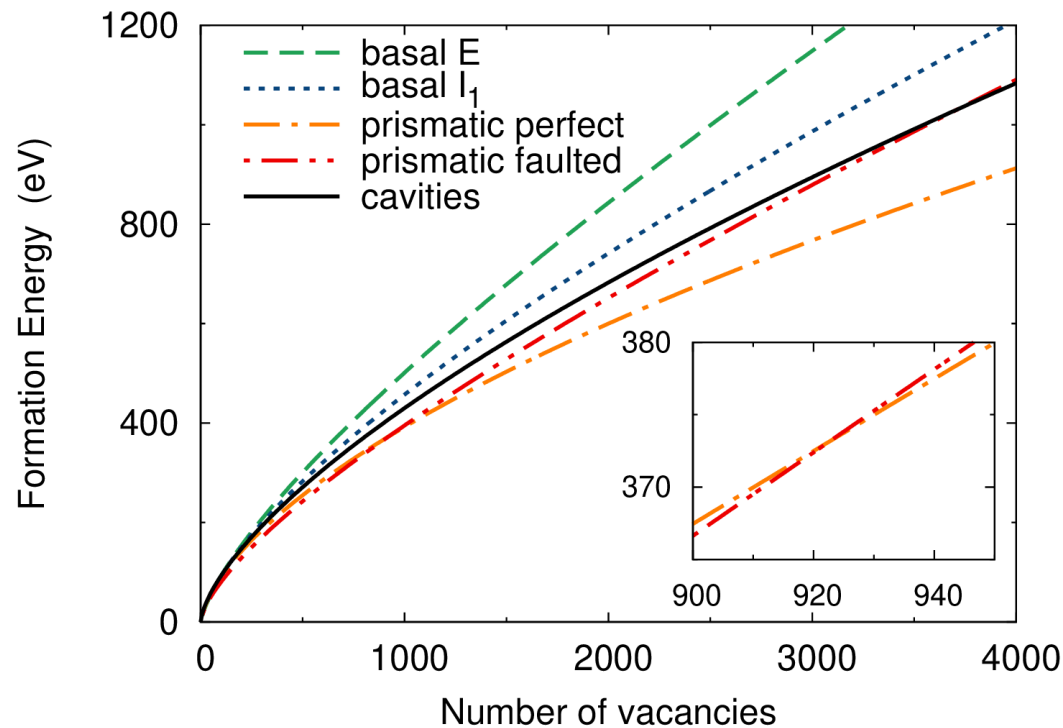
- Atomistic computation of cluster energetics (EAM#2)
- Classical laws : ajustement of f , r_c on EAM#2 results

→ Good agreement

→ Values of f , r_c

II. Energetics of large clusters

3) DFT Parameterization :



▪ Cavities : $E^f(R) = 4\pi R^2 f \sigma$

with $\frac{4\pi R^3}{3} = n\Omega$

▪ Dislocation loops :

$$E^f(R) = 2\pi f K b^2 \ln \frac{R}{r_c} + 2\pi R^2 \gamma_{SF}$$

with $\pi R^2 b_e = n\Omega$

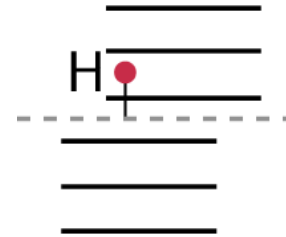
- Most stable defect = <a> loops, faulted at small sizes

- In agreement with experiments
- DFT parameterization necessary

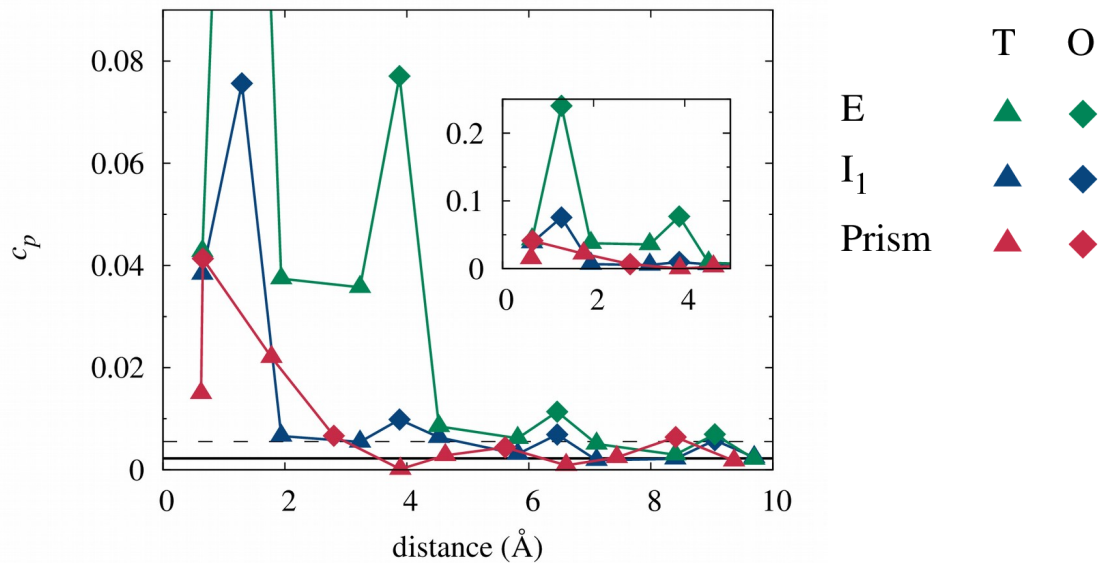
II. Energetics of large clusters

Influence of H

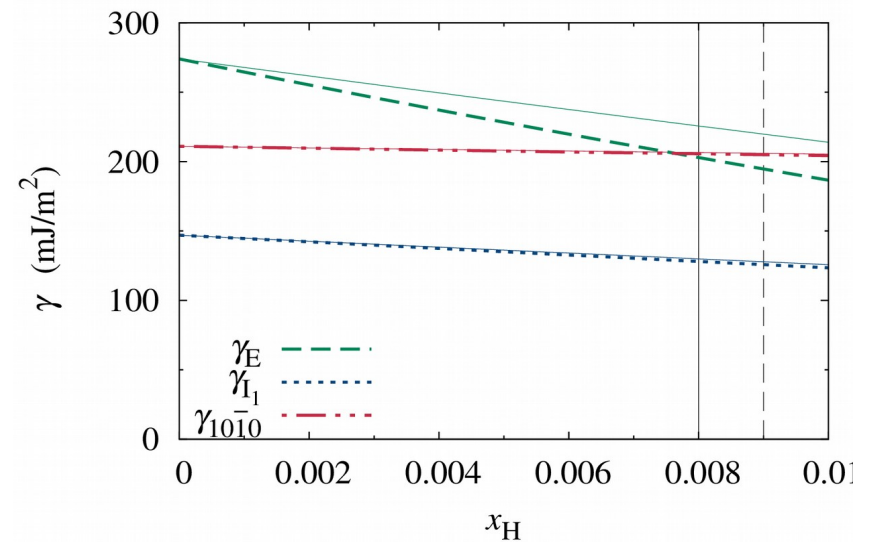
- H binds to the SFs (E_b : DFT computed)



Segregation profiles $T=600\text{K}$, $x_H=0.01$



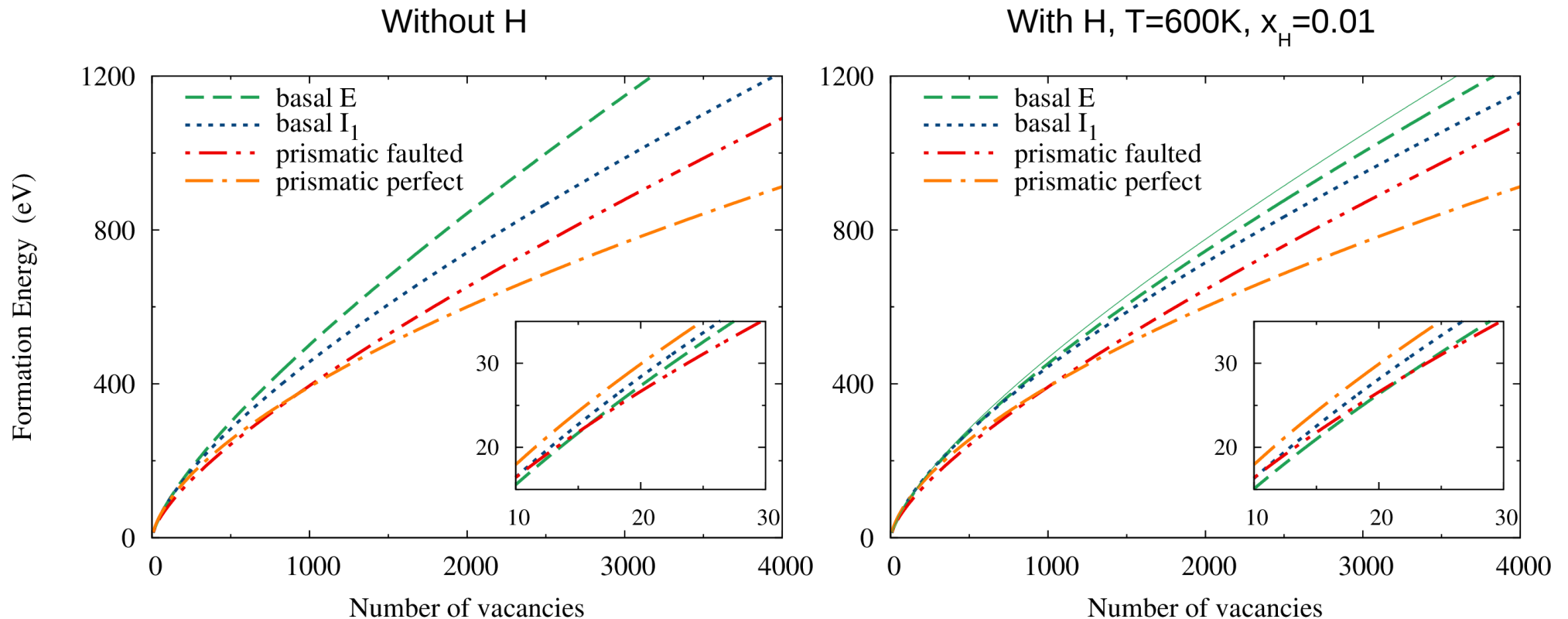
Variation of SFEs



- Discriminating effect of H
- E fault strongly impacted by H

II. Energetics of large clusters

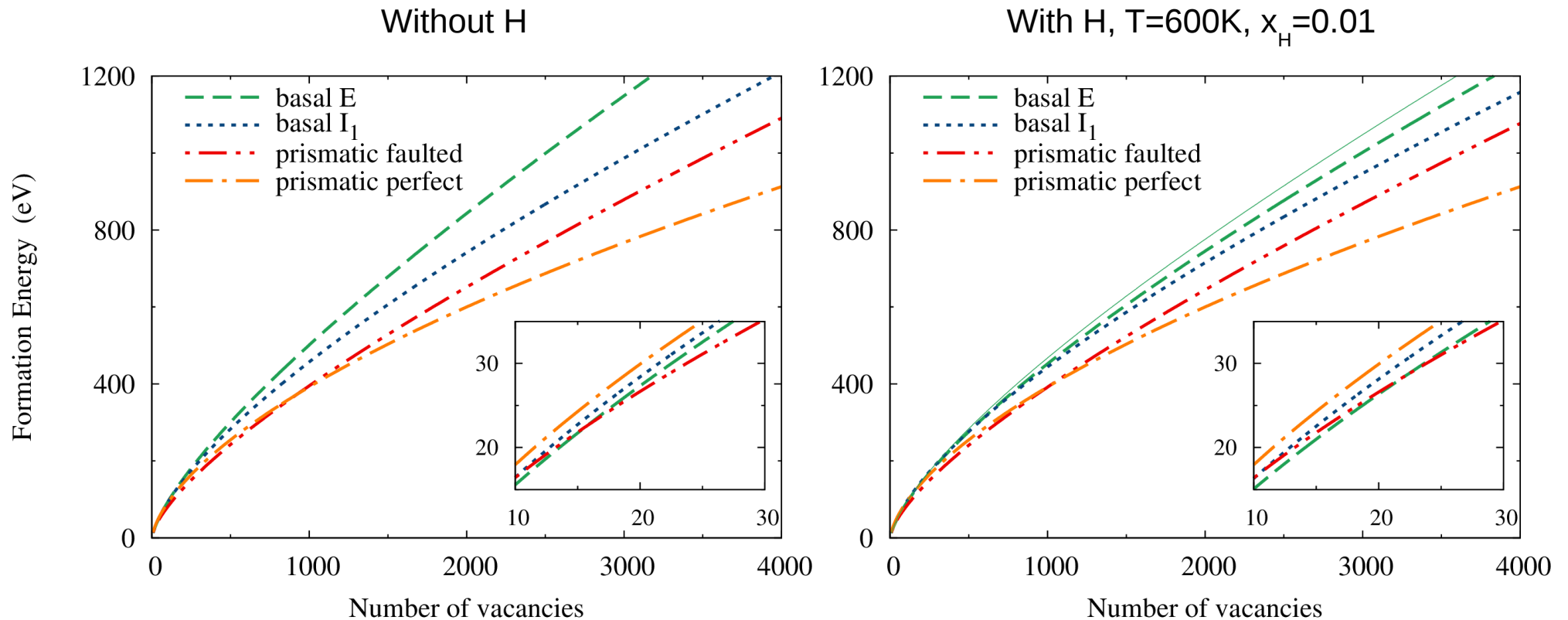
Influence of H :



- **Hydrogen stabilizes <c> loops**
- **in agreement with experimental observations (H-induced enhancement of the breakaway growth)**

II. Energetics of large clusters

Influence of H :



Mais étude forcément incomplète :

- modélisation sur défauts de morphologies postulées *a priori* (d'autres peuvent exister)
- Aspects cinétiques non abordés
- Quid des interstitiels ?
- ...

Plan

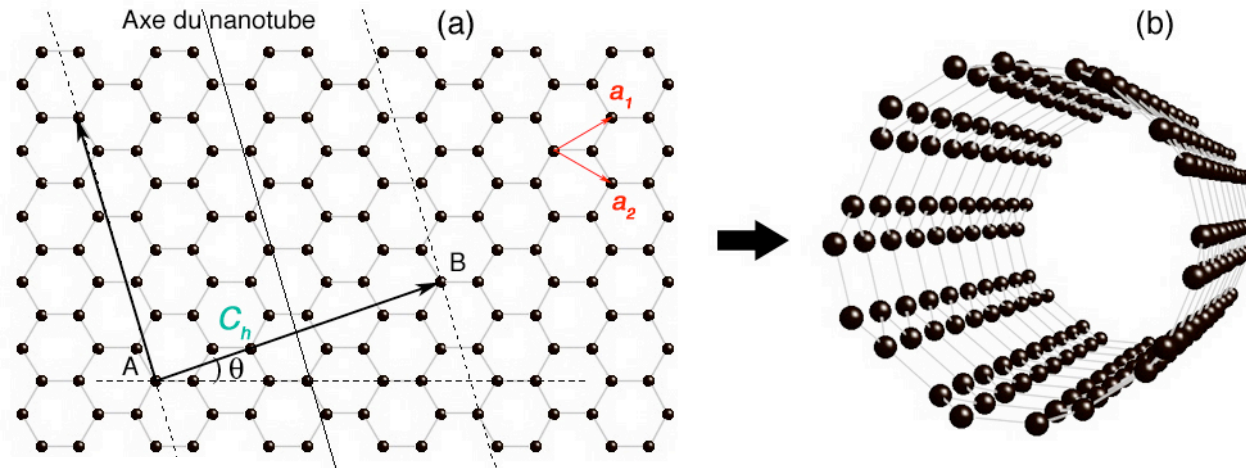
I) Introduction : les nanoparticules

II) Les outils

III) Exercices

- 1) Comment modéliser les problèmes physiques présentés en Introduction
- 2) Amas lacunaires dans Zr hcp
- 3) **Croissance de structures carbonées à partir d'un catalyseur métallique**

Carbon nanotubes : definition



$$C_h = na_1 + ma_2.$$

$$\theta = \arctan(\sqrt{3}n/(2m + n)).$$

Diameter : 0.6 - 20 nm
Length : few mm



(n,n): armchair



(n,0) : zigzag
(0,m) :

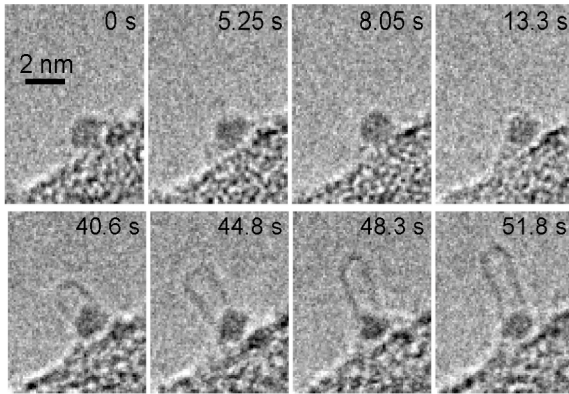


(n,m): chiral

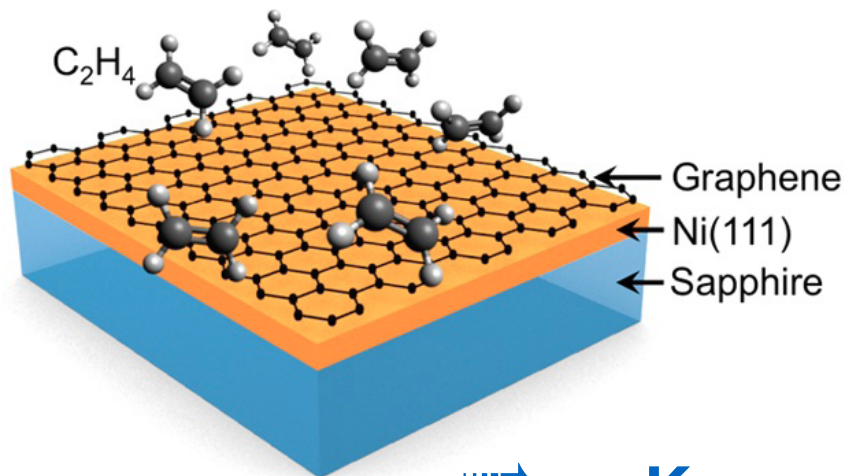
Motivations

Focus on CVD synthesis

- **CVD synthesis** : decomposition of a C-rich gas feedstock at the catalyst surface (Cu, Ir, Ni, ...)



Yoshida *et al.*, Nanolett. 2008



Key point : Carbon-Metal interaction

Open questions :

- role of the metal catalyst
- state of metal catalyst : solid or molten
- carbide or not carbide
- diffusion of C : surface and/or volume
- ...
- **control the number of layers**
- **control the quality of the material**
- **control the geometry of the tube**

Cahier des charges

- Modèle énergétique (énergie de cohésion, paramètre de maille, module de compressibilité, constantes élastiques, ΔH , ...)
 - Description correcte des liaisons C-C, Ni-Ni et Ni-C
 - ~ 1000 atomes
 - Couplage avec un code Monte Carlo pour étudier les propriétés thermodynamiques
- |||➡
- Méthode d'ordre N
 - Approche locale
 - Calcul des forces n'est pas nécessaire

Procédure :

**Ajustement de
paramètres
sur certaines
propriétés**



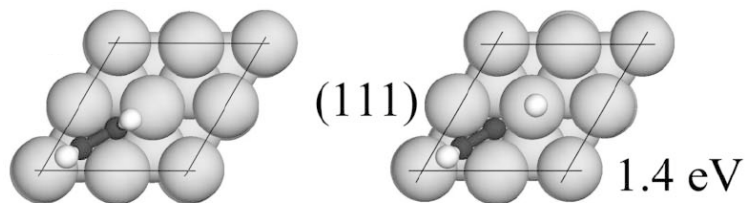
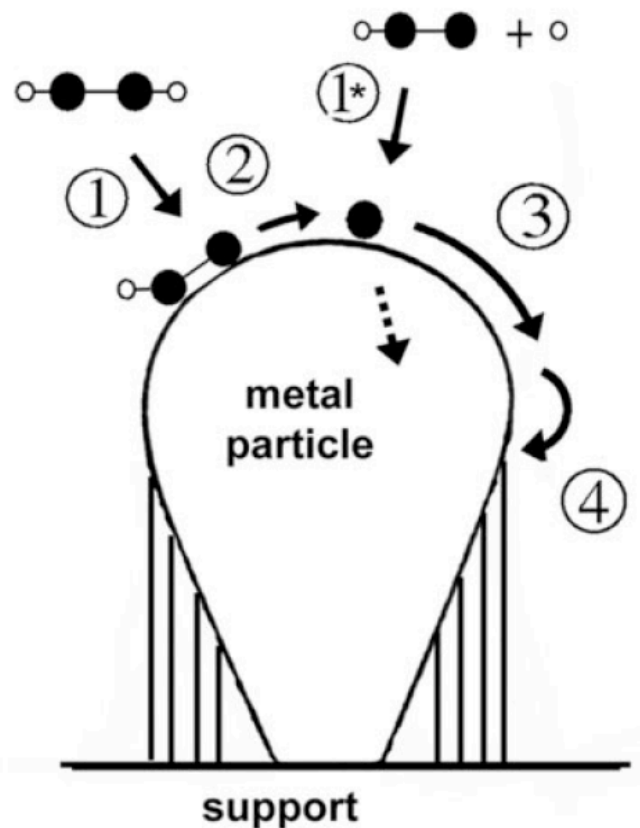
**Tester la
transférabilité
du modèle**



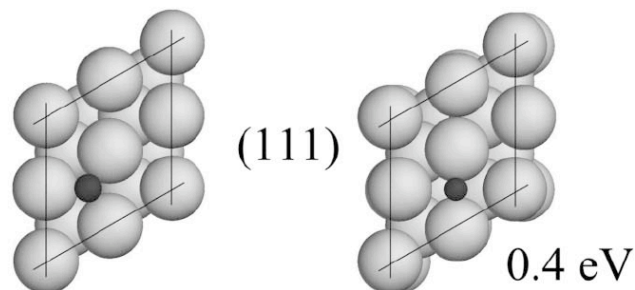
**Effectuer des
études
pertinentes ...**

ab initio ground state calculations

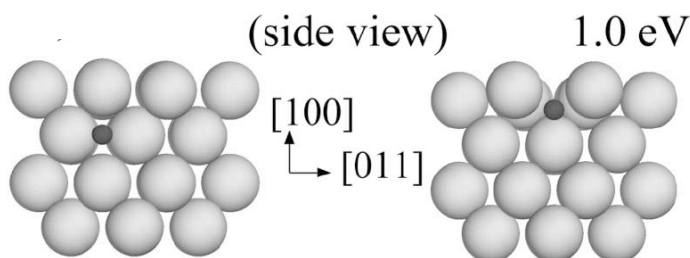
Dissociation and diffusion barriers



dissociation of C₂H₂
on Ni(111)



diffusion of a C atom on
Ni(111)



a subsurface pathway
one layer below the
Ni surface

S. Hofmann *et al.*,
Phys. Rev. Lett **95**, 036101 (2005)



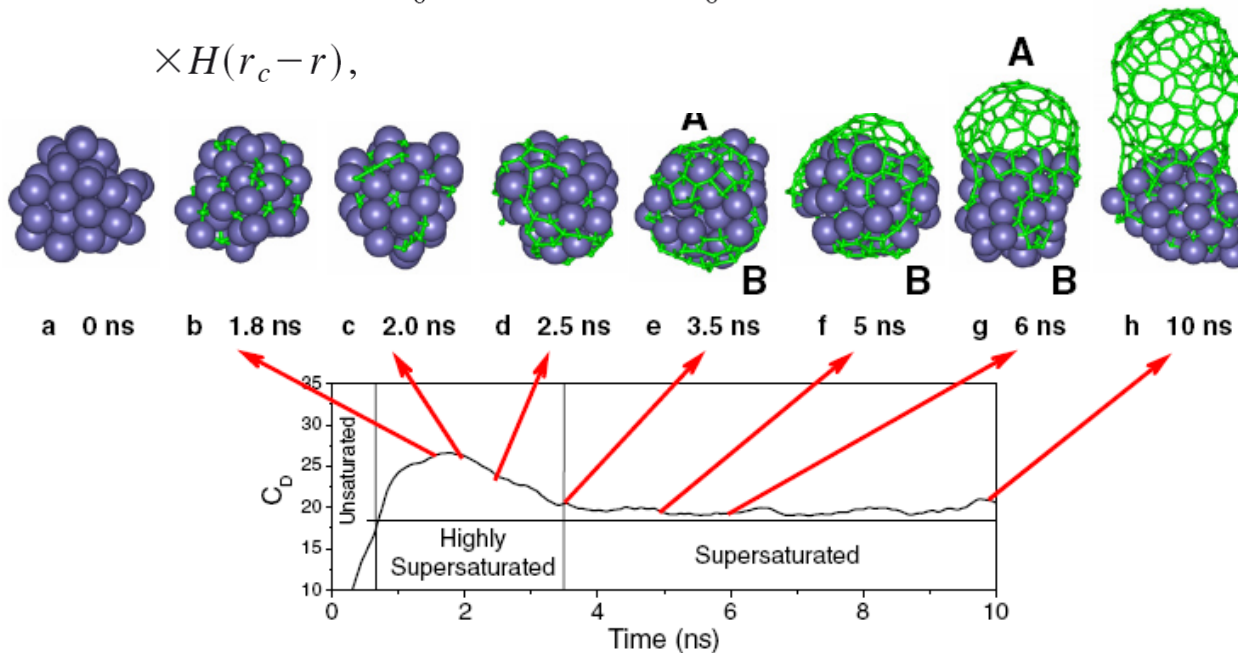
- diffusion on surface
- solid catalyst particle

Empirical potentials and Molecular Dynamics

Nucleation of carbon nanotubes : example I

$$E_{\text{Fe-C}} = \sum_{i \neq j} -\epsilon \left[2 \left(\frac{\frac{r_{ij} - r_c}{r_0 - r_0}}{\frac{r_c}{r_0} - 1} \right)^3 - 3 \left(\frac{\frac{r_{ij} - r_c}{r_0 - r_0}}{\frac{r_c}{r_0} - 1} \right)^2 \right] H(x) \times H(r_c - r),$$

$$H(x) = \begin{cases} 1, & \text{if } x \geq 0 \\ 0, & \text{if } x < 0 \end{cases}$$



- dissolution and segregation of C in liquid Fe cluster
- time of simulation : 10 ns
- ad hoc potential

Empirical potentials and Molecular Dynamics

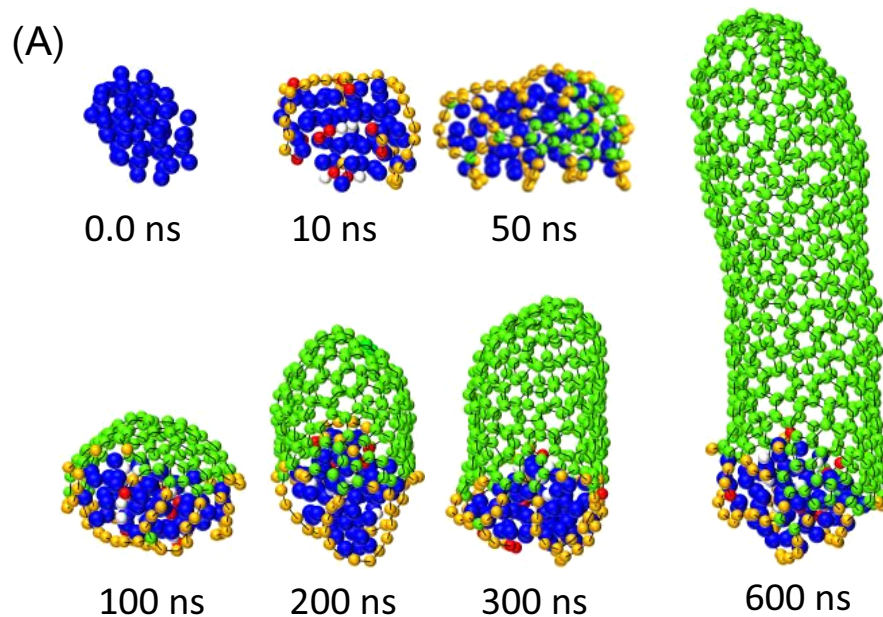
Nucleation of carbon nanotubes : example II

$$E_{Tot} = \sum_i \sum_{j(i < j)} [V_R(r_{ij}) - B_{ij}^* V_A(r_{ij})]$$

$$B^* = \{1 + b(N^C - 1)\}^\delta$$

$$N^C = 1 + \sum_{\text{carbon } k (\neq j)} f(r_{ik})$$

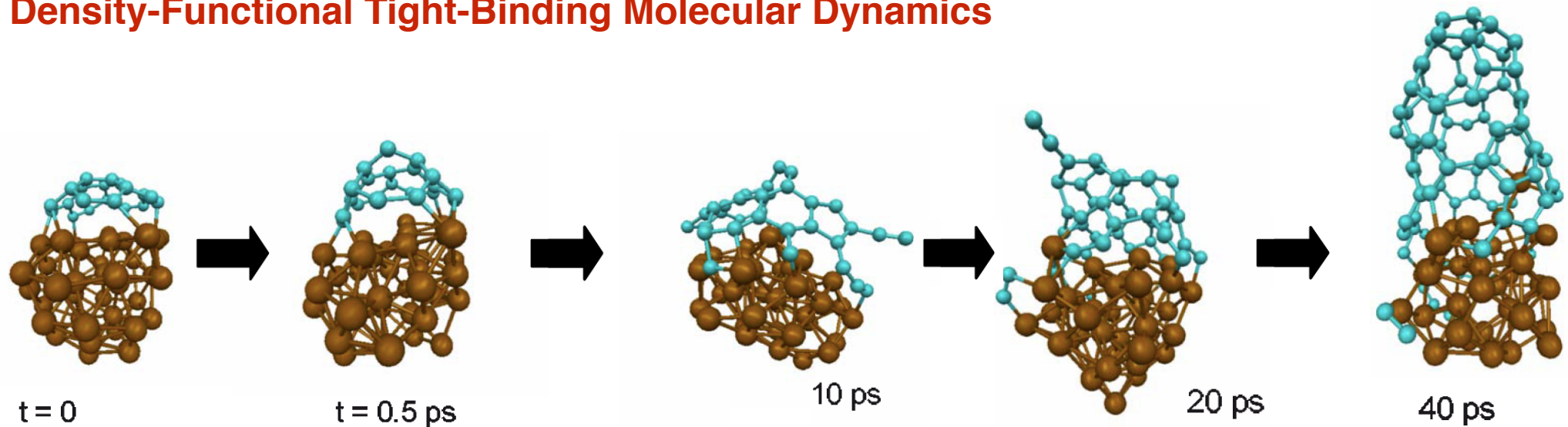
N^C : carbon coordinate number



- dissolution and segregation of C in Ni cluster
- time of simulation : 600 ns

Tight-binding potential and Molecular Dynamics

Density-Functional Tight-Binding Molecular Dynamics



Y. Ohta *et al.*, ACS Nano **2**, 1437 (2008)

A. Page *et al.*, Rep Prog Phys **78**, 36501 (2015)

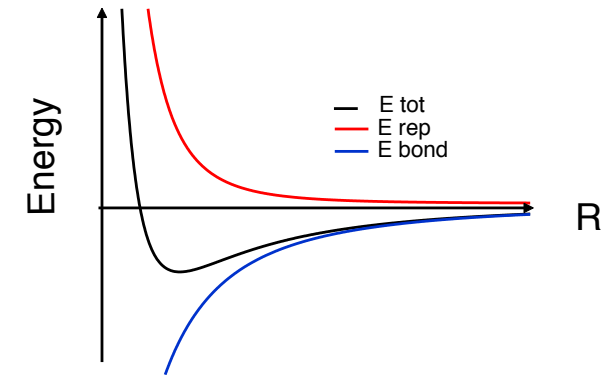
- Nucleation of short and defected tubes from a Fe₃₈ cluster
- Time of simulation : 50 ps

Tight-binding model

Total energy : $E_{Total} = E_{Band} + E_{Rep}$

The band energy E_{band} is given by

$$E_{band} = \int_{-\infty}^{E_F} (E - \varepsilon) n(E) dE,$$



Minimal basis set

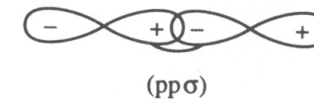
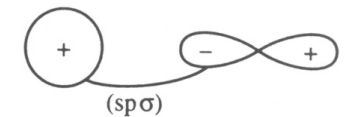
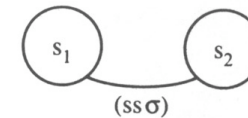
- C s and p electrons
- Ni d electrons

ε_s , ε_p and ε_d

- price to pay :
- parameters

Hopping integrals

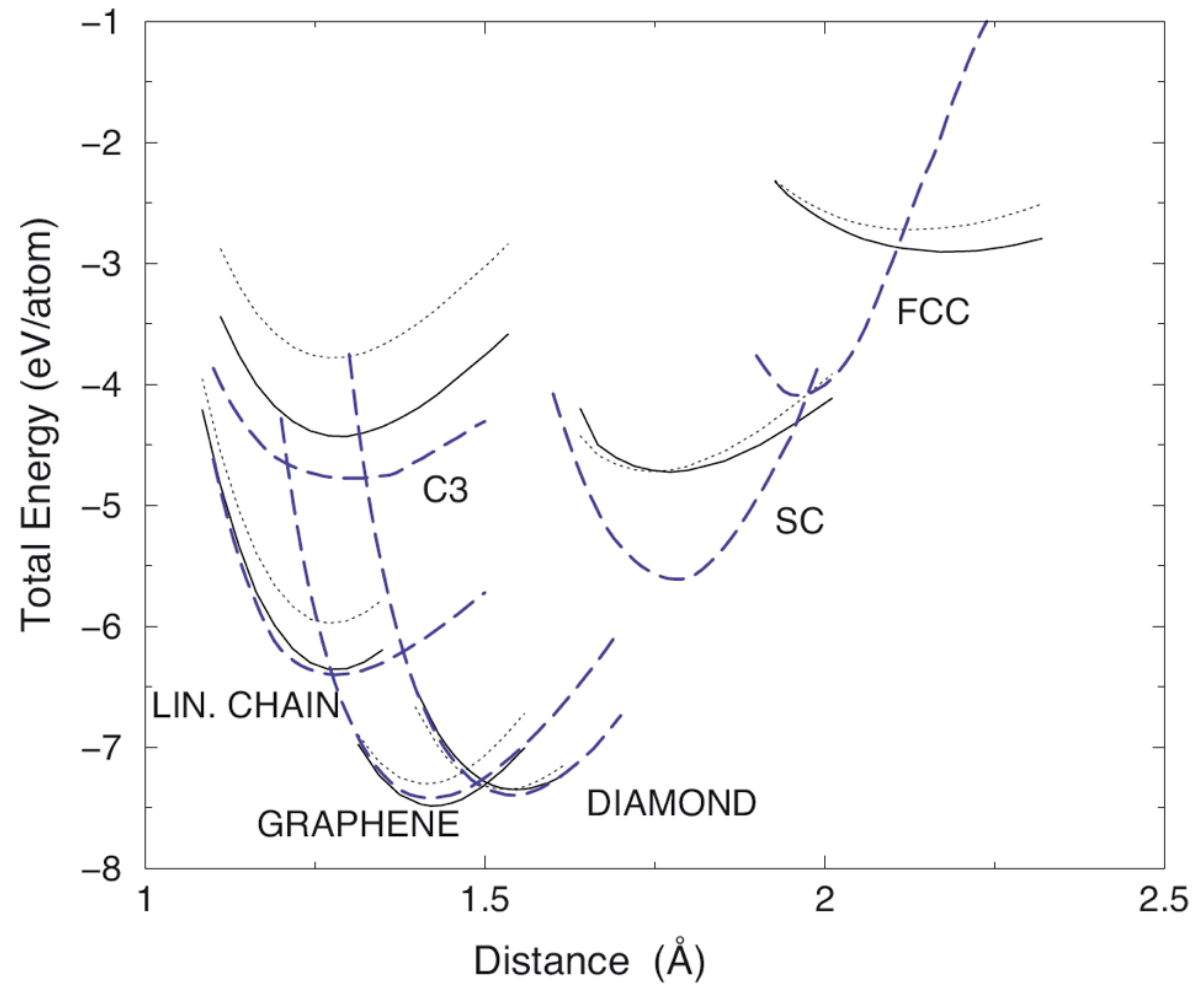
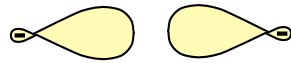
- C-C : $ss\sigma$, $sp\sigma$, $pp\sigma$, $pp\pi$
- Ni-Ni : $dd\sigma$, $dd\pi$, $dd\delta$
- Ni-C : $sd\sigma$, $pd\sigma$, $pd\pi$



C-C interaction

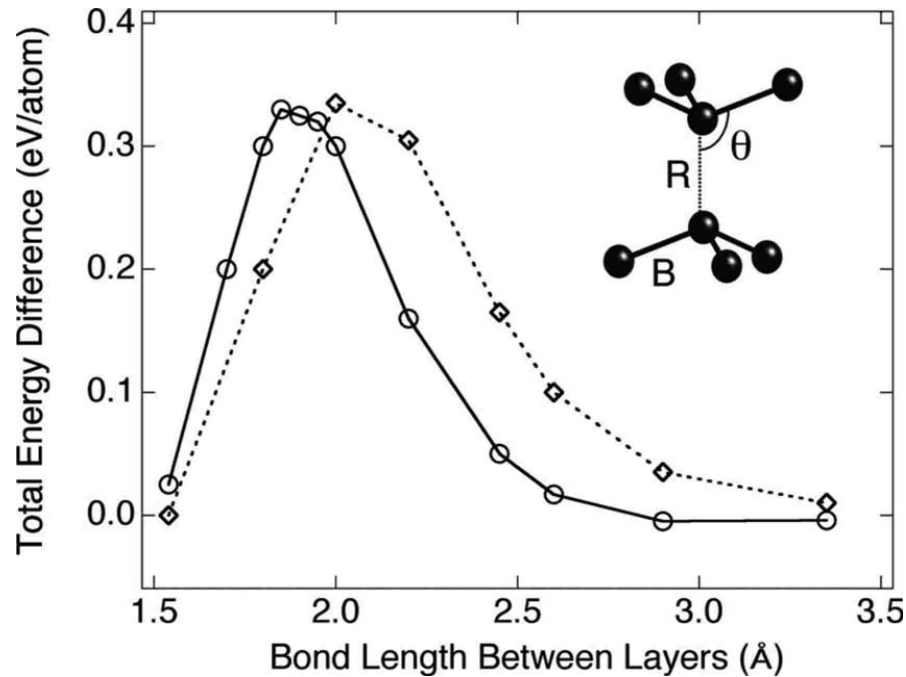
- fitted to reproduce the competition between the different bonds:
 sp , sp^2 , sp^3

C-C interaction

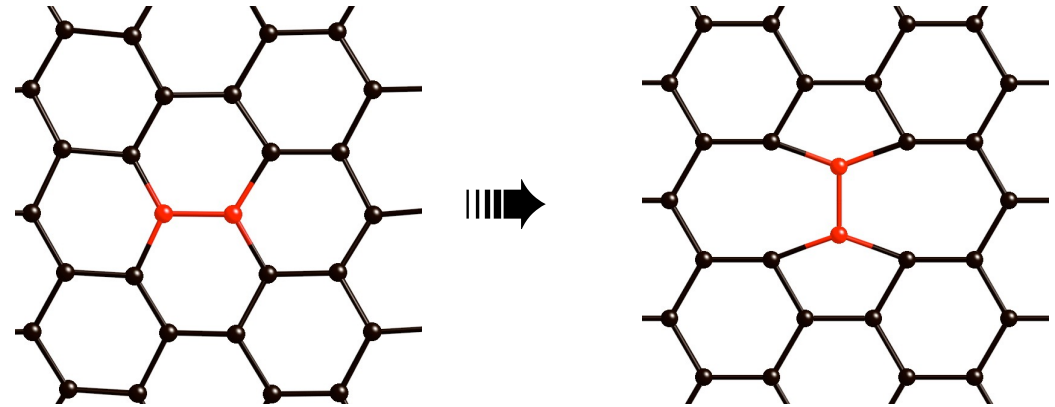


Validation de l'interaction C-C

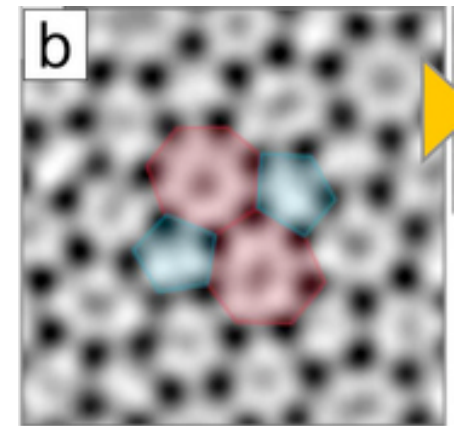
Diamond to graphite



Stone-Wales defect



	ΔE (eV)
<i>ab initio</i> (code ABINIT)	4.99
<i>ab initio</i> (code SIESTA)	5.17
liaisons fortes	6.01



T. Björkman *et al.*,
Scientific Reports **3**, 3482 (2013)

Ni-Ni interaction

- fitted to reproduce the fcc structure

Ni-Ni interaction

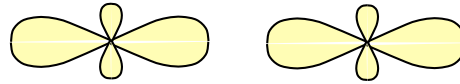
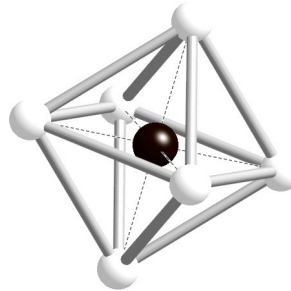
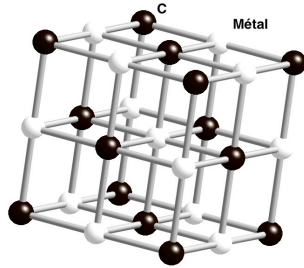


TABLE I. Comparison of our tight-binding d model with experimental data. The experimental values for fcc Ni and hcp Co are taken from Ref. 49, those for fcc Co from Ref. 50, and the surface energies from Ref. 51.

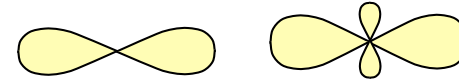
	Structure	Lattice parameter (Å)	Cohesive energy (eV/atom)	B (GPa)	C' (GPa)	C_{44} (GPa)	Surface energy (mJ/m ²)
Ni	fcc	$a/\sqrt{2}=2.489$	-4.44	187.6	55.2	131.7	1840 (solid) 2385 (liquid)
Co	hcp	$a=2.50$ $c=4.07$	-4.39	193			1884 (liquid)
Co	fcc			182	32.5	92	
This work	fcc	$a/\sqrt{2}=2.489$	-4.44	182.1	68.8	96.9	1660 (100) 1560 (111)

Ni-C interaction

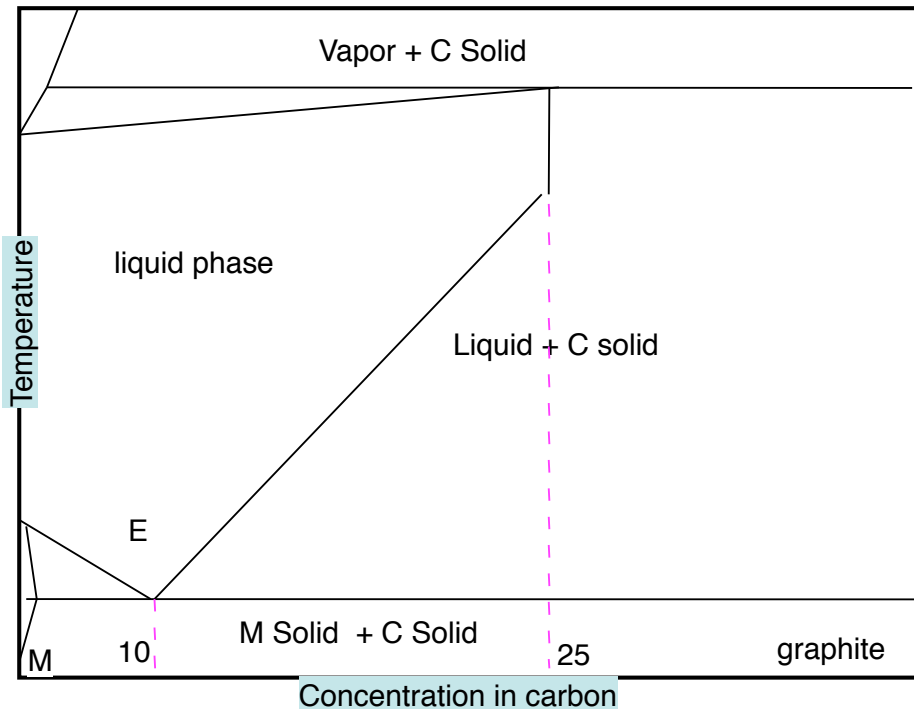
- fitted to reproduce the theoretical NaCl structure



Ni-C interaction



- experimentally we expect a phase separation between a liquid metallic phase containing a few percent of carbon and a solid pure carbon phase



ab initio data :

enthalpy of formation of the carbide $\Delta H \approx +0.9$ eV/at
weak phase separation

$$\Delta H = (E_{\text{NiC}}^{\text{NaCl}} - E_{\text{C}} - E_{\text{Ni}})/2$$

	Lattice parameter (Å)	ΔH (eV/atom)	B (GPa)
<i>Ab initio</i>	4.01	0.93	304
Present work	4.17	0.93	350

Carbon on Ni(111) : adsorption or formation energies

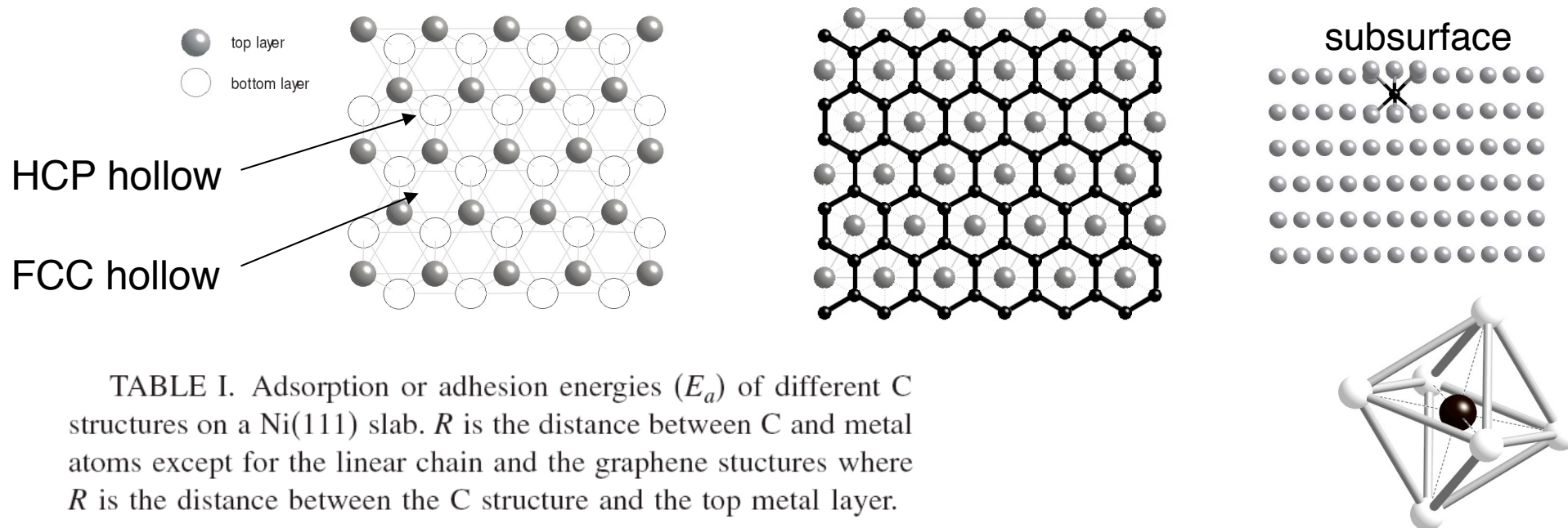


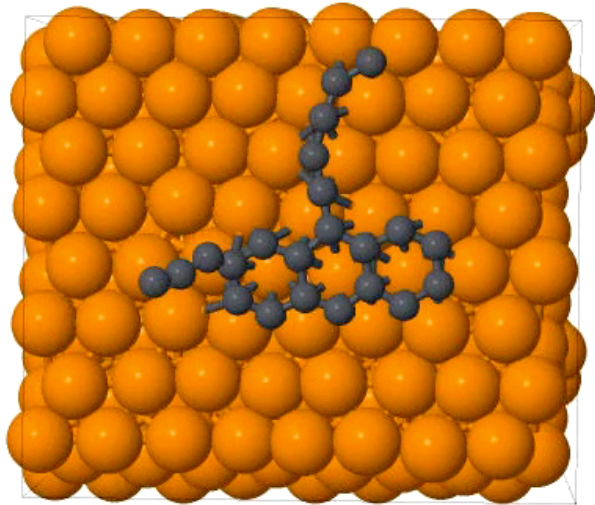
TABLE I. Adsorption or adhesion energies (E_a) of different C structures on a Ni(111) slab. R is the distance between C and metal atoms except for the linear chain and the graphene structures where R is the distance between the C structure and the top metal layer.

Site	<i>Ab initio</i> ^a		Present work	
	E_a (eV)	R (Å)	E_a (eV)	R (Å)
Top	-4.38	2.11	-3.56	1.78
Bridge	-5.99, -8.38 ^b	1.75	-4.98	1.84
hcp hollow	-6.68, -8.59, ^b -7.18 ^c	1.79	-6.52	1.87
fcc hollow	-5.97, -7.25 ^c	1.89	-6.43	1.83
Subsurface	-7.30	1.85	-8.25	1.89
Linearchain			-0.71	1.98
Graphene	-0.08, -0.05, ^d -0.09 ^c	2.1, 3.2 ^d	-0.03	2.19

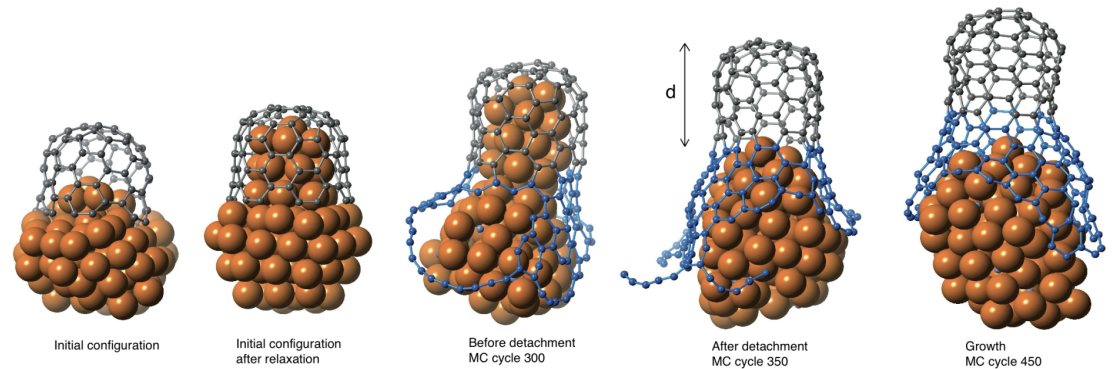
- $\Delta H_{\text{dissolution}} = 0.45$ eV
(*ab initio* : 0.35 eV, experimental : 0.4 eV)
- distortion : 8% (*ab initio* : 5%)
⇒ size effect

Some applications

Graphene growth from Ni slab



Nanotube growth from Ni NP



M. Diarra *et al.*, Phys. Rev. Lett. **109**, 185501 (2012)

M.-F. Fiawoo *et al.*, Phys. Rev. Lett. **108**, 195503 (2012)

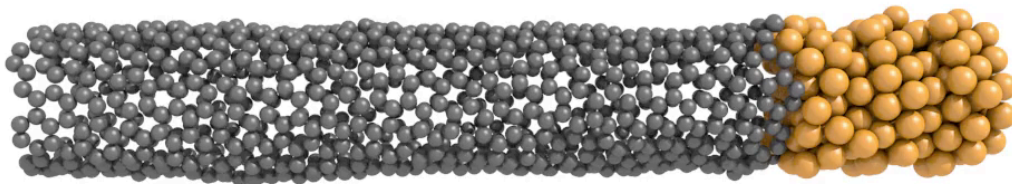
H. Amara *et al.*, Phys. Rev. B **73**, 113404 (2006)

R. Weatherup *et al.*, J. Am. Chem. Soc. **111**, 13698 (2014)

R. Martinez-Gordillo, Phys. Rev. B **97**, 205431(2018)

Jmol

Wetting properties between NP and tube

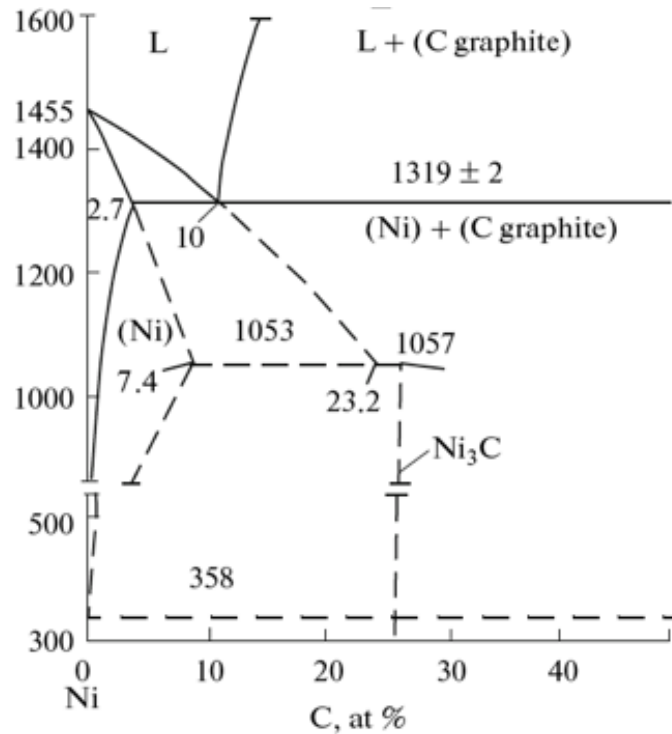


M. He *et al.* Nanoscale **10**, 6744 (2018)

Y. Magnin *et al.*, Science **362**, 212 (2018)

A reality that is difficult to admit ...

Bulk phase diagram



V. K. Portnoi,
Phys. Met. Metallogr. **109**, 153 (2010)

Ni₃C

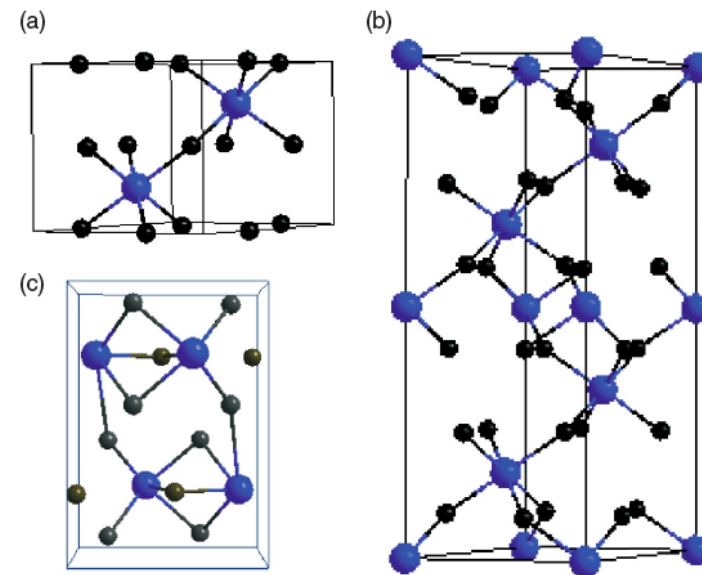


FIG. 1. (Color online) Schematic structures of Ni₃X for the hcp phase (a), 3R phase (b), and θ phase (c).

C.M. Fang *et al.*, Phys. Rev. B 86, 134114 (2012)



- Ni₃C is metastable (DFT calculations : $\Delta H_f \gtrsim 0$)
- What about our TB model ?

A reality that is difficult to admit ...

TB calculations

$\Delta H_f \gg 0$  **Where is the problem ??**

V_{C-C} calculations inside Ni

DFT

TB

V_{CC}^1 (eV)

0.22

1.06

V_{CC}^2 (eV)

0.16

0.54

 **strongly overestimates the C-C repulsion within nickel that destabilizes the Ni_3C structure**



Restart the procedure by including this physical quantity

...jusqu'où aller dans le côté obscur ?

- **Ab initio / DFT**

- Clair
- Néanmoins à tester (E_{xc} , comparaison données exp...)
- Transférabilité

- **Liaisons Fortes / BOP :**

- Assez clair
- Ajustement difficile pour l'instant
- On apprend de la physique des systèmes étudiés !
- ~ transférable

- **Potentiels empiriques LJ / EAM / MEAM / Tersoff...**

- Obscurs mais légers
- Ajustement...
- Transférabilité ?
- Plusieurs potentiels pour un système / calculs systématiques

- **Potentiels Machine Learning**

- Très très très obscurs
- Ajustement / amélioration systématique possible
- Transférabilité ?



...

