

# Méthodes multi échelles en mécanique des matériaux hétérogènes

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# Plan

- I. Homogénéisation numérique
- II. Passage échelle atomistique/échelle continue

# Le béton : un matériau fortement multi échelle



380  
Quality

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## I. CSH / anhydrous-cement scale

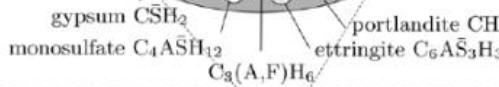
$$\ell = 10^{-8} - 10^{-6} \text{ m}$$

### Ia. anhydrous cement



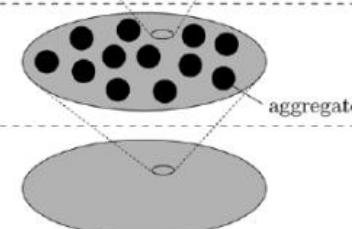
## II. cement-paste scale

$$\ell = 10^{-6} - 10^{-4} \text{ m}$$



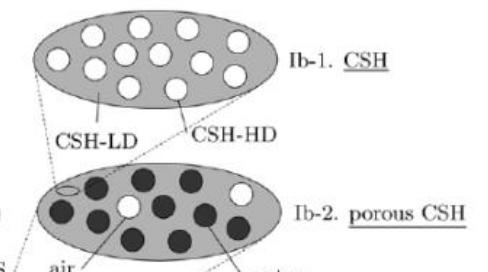
## III. mortar scale

$$\ell = 10^{-2} \text{ m}$$



## IV. macroscale

$$\ell = 10^{-1} \text{ m}$$



Ib-1. CSH

Ib-2. porous CSH

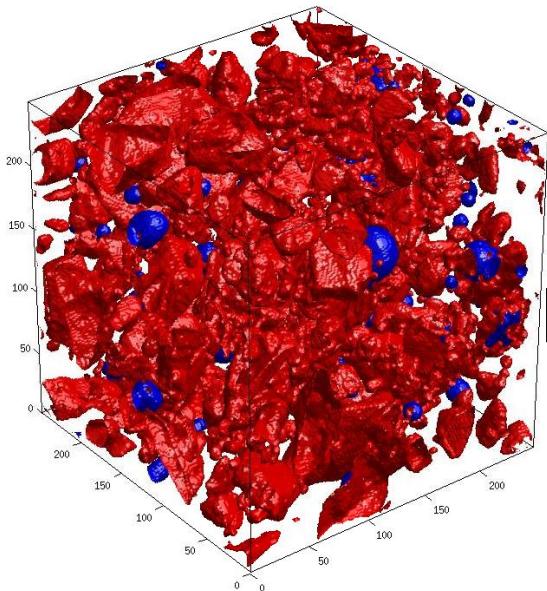
# I. Homogénéisation numérique

# Sommaire

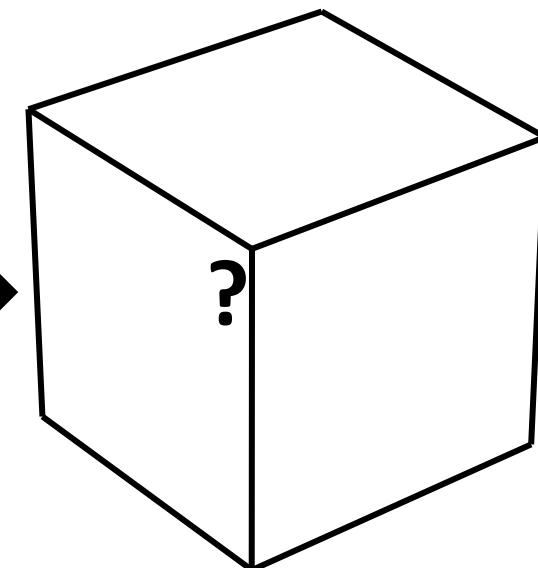
- 1) Objectifs de l'homogénéisation numérique
- 2) Etat de l'art
- 3) Introduction à l'homogénéisation  
numérique : problèmes linéaires
- 4) Milieux poreux
- 5) Problèmes non linéaires
- 6) Modélisation des microstructures complexes
- 7) Contributions

# 1) Homogénéisation numérique : objectifs

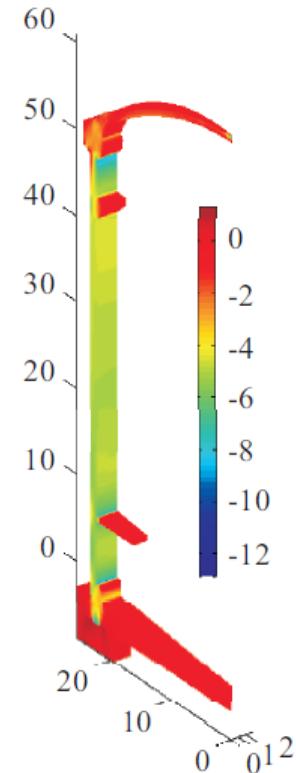
- 1) calcul numérique des propriétés effectives  
(homogénéisées) de matériaux complexes hétérogènes  
dont la microstructure est connue par le biais d'un VER
- 2) Calcul de structure composée du matériau hétérogène



Matériau hétérogène



Matériau homogène équivalent



Calcul de structure

# Homogénéisation numérique/analytique

## Avantages

- Possibilité d'aller **au-delà des limitations associées à l'homogénéisation analytique** (résolution du problème local)
- Prise en compte de **morphologies complexes** et fortes fractions volumiques
- **Comportements non-linéaires**, transitoires
- Prise en compte des incertitudes
- **Calcul de structures**

## Inconvénients

- Analyses difficilement généralisables
- Sensibilité aux paramètres implicite

## 2) Etat de l'art

### Premiers travaux

[Adams and Doner 1967] Différences finies, composites à fibres

[Suquet 1983, 85] Formulation « moderne », Analyses par éléments finis

[Koplik, Needleman 1988] coalescence des vides

[Michel, Moulinec, Suquet, 1999] Article de synthèse sur l'homogénéisation numérique avec FEM et méthode FFT

### Homogénéisation non-linéaire : « FE<sup>2</sup> approaches » (coupled analyses)

[Renard 1987], [Guedes, Kikuchi 1990, Ghosh 1995, Smit and Brekelmans 1995], [Feyel 1999], [Terada et al. 2000], [Terada and Kikuchi 2001], [Miehe et al. 1999]

### Homogénéisation non linéaire : approches découplées

[Dvorak and Rao 1976] TFA

[Michel and Suquet 2003] NTFA

[Temizer and Zhodi 2007], [Yvonnet and He 2009] : approches par interpolation

## 2) Etat de l'art

### Homogénéisation d'ordre supérieur

[Ostoja-Starzewski et al. 1999], [Bouye et al 2001] Modèles couple-contrainte homogénéisé

[Forest and Sab 1998], [Forest et al. 1999], [De Felice and Rizzi 2001], [Yuan et Tomita 2008] Modèle de Cosserat homogénéisé

[Kouznetsova, Geers, Brekelmans, 2002, 2004], [Bouye et al 2002] : conditions aux limites d'ordre supérieur et problèmes non linéaires du second ordre

[Cartraud and Messager 2006], [Coenen, Kouznetsova, Geers IJNME 2010] [Lebée and Sab IJSS 2010] modèle de poutre et plaques homogénéisées

### Méthode FFT

[Moulinec and Suquet CRAS 1994], [Moulinec and Suquet CMAME 1998]

[Muller J. Phys 1996]

[Michel Moulinec and Suquet IJNME] : approche avec multiplicateurs de Lagrange pour contrastes infinis

[Brisard and Dormieux 2010], [Monchiet and Bonnet 2011], [Vinogradov and Milton 2008], [Bonnet 2007] : améliorations de la FFT (convergence)

[Yvonnet IJNME 2012] approche sans Transformée de Fourier

### 3) Introduction à l'homogénéisation numérique : élasticité linéaire

Problème de localisation : approche en déformations

**PB3:** Given a macroscopic strain  $\bar{\epsilon}$ , find the displacement field  $\mathbf{u}(\mathbf{x})$  in  $\Omega$  such that:

$$\nabla \cdot \sigma(\mathbf{u}(\mathbf{x})) = 0 \quad \forall \mathbf{x} \in \Omega \quad (6.1)$$

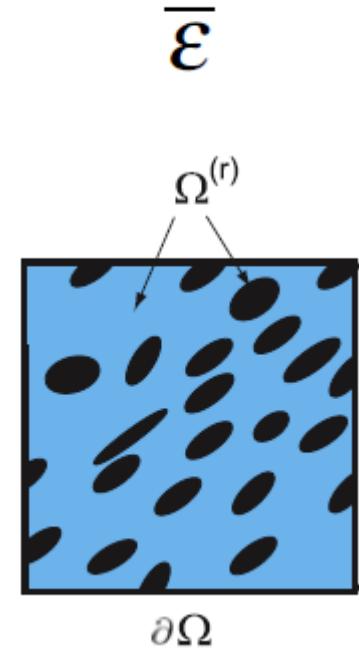
with

$$\sigma(\mathbf{u}(\mathbf{x})) = \mathbb{C}(\mathbf{x}) : \epsilon(\mathbf{u}(\mathbf{x})), \quad (6.2)$$

$$\epsilon(\mathbf{u}(\mathbf{x})) = \frac{1}{2} (\nabla \mathbf{u}(\mathbf{x}) + \nabla^T \mathbf{u}(\mathbf{x})) \quad (6.3)$$

and verifying

$$\langle \epsilon \rangle = \bar{\epsilon}. \quad (6.4)$$



# Approche en déplacements : conditions aux limites

Décomposition du champ de déformation local

$$\boldsymbol{\varepsilon}(\mathbf{x}) = \bar{\boldsymbol{\varepsilon}} + \tilde{\boldsymbol{\varepsilon}}(\mathbf{x})$$

$$\begin{aligned}\langle \boldsymbol{\varepsilon}(\mathbf{x}) \rangle &= \bar{\boldsymbol{\varepsilon}} + \langle \tilde{\boldsymbol{\varepsilon}}(\mathbf{x}) \rangle = \bar{\boldsymbol{\varepsilon}} + \frac{1}{2|\Omega|} \int_{\Omega} \{ \nabla(\tilde{\mathbf{u}}(\mathbf{x})) + \nabla^T(\tilde{\mathbf{u}}(\mathbf{x})) \} d\Omega \\ &= \bar{\boldsymbol{\varepsilon}} + \frac{1}{2|\Omega|} \int_{\partial\Omega} \{ \tilde{\mathbf{u}}(\mathbf{x}) \otimes \mathbf{n} + \mathbf{n} \otimes \tilde{\mathbf{u}}(\mathbf{x}) \} d\Gamma \\ \langle \boldsymbol{\varepsilon}(\mathbf{x}) \rangle &= \bar{\boldsymbol{\varepsilon}}\end{aligned}$$

Vérifié pour

1.  $\tilde{\mathbf{u}}(\mathbf{x}) = 0$  on  $\partial\Omega$ , Kinematically Uniform Boundary Conditions (**KUBC**)  
[Huet JMPS 1990]
2.  $\tilde{\mathbf{u}}(\mathbf{x})$  is periodic on  $\Omega$  **PERIODIC**

# Calcul du tenseur élastique effectif : approche directe, application du principe de superposition

$$\mathbf{u}(\mathbf{x}) = \mathbf{u}^{11}(\mathbf{x})\bar{\varepsilon}_{11} + \mathbf{u}^{22}(\mathbf{x})\bar{\varepsilon}_{22} + \mathbf{u}^{33}(\mathbf{x})\bar{\varepsilon}_{33}$$

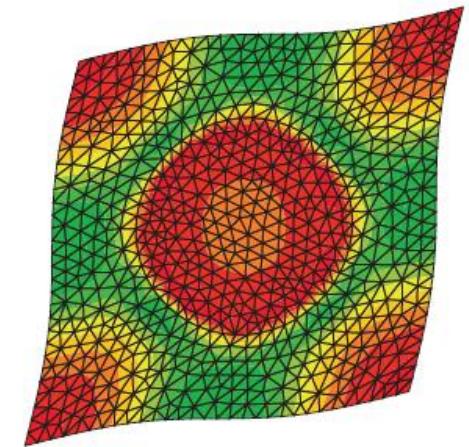
$$+ 2\mathbf{u}^{12}(\mathbf{x})\bar{\varepsilon}_{12} + 2\mathbf{u}^{13}(\mathbf{x})\bar{\varepsilon}_{13} + 2\mathbf{u}^{23}(\mathbf{x})\bar{\varepsilon}_{23}$$

$$\boldsymbol{\varepsilon}(\mathbf{x}) = \varepsilon^{11}(\mathbf{x})\bar{\varepsilon}_{11} + \varepsilon^{22}(\mathbf{x})\bar{\varepsilon}_{22} + \varepsilon^{33}(\mathbf{x})\bar{\varepsilon}_{33}$$

$$+ 2\varepsilon^{12}(\mathbf{x})\bar{\varepsilon}_{12} + 2\varepsilon^{13}(\mathbf{x})\bar{\varepsilon}_{13} + 2\varepsilon^{23}(\mathbf{x})\bar{\varepsilon}_{23}.$$

$$\boldsymbol{\varepsilon}(\mathbf{x}) = \mathbb{A}(\mathbf{x}) : \bar{\boldsymbol{\varepsilon}}$$

$$A_{ijkl}(\mathbf{x}) = \varepsilon_{ij}^{kl}(\mathbf{x})$$



$$\varepsilon = \begin{bmatrix} 0 & 1/2 & 0 \\ 1/2 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

$$\overline{\boldsymbol{\sigma}} = \langle \boldsymbol{\sigma}(\mathbf{x}) \rangle = \langle \mathbb{C}(\mathbf{x}) : \mathbb{A}(\mathbf{x}) \rangle : \bar{\boldsymbol{\varepsilon}}$$

$$\overline{\mathbb{C}}_{KUBC} = \langle \mathbb{C}(\mathbf{x}) : \mathbb{A}_{KUBC}(\mathbf{x}) \rangle$$

## Cas d'un matériau homogène isotrope

$$\bar{\sigma} = \bar{\lambda} \operatorname{Tr}(\bar{\varepsilon}) \mathbf{1} + 2\bar{\mu}\varepsilon$$

let  $\mathbf{u}^{(12)}$  be the solution of the problem PB3 with

$$\bar{\varepsilon} = \begin{bmatrix} 0 & 1/2 & 0 \\ 1/2 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

$$\boxed{\bar{k} = \frac{1}{3} \operatorname{Tr} \langle \mathbb{C}(\mathbf{x}) : \varepsilon(\mathbf{u}^H(\mathbf{x})) \rangle = \frac{1}{3} \operatorname{Tr} \langle \sigma(\mathbf{u}^H(\mathbf{x})) \rangle}.$$

Let  $\mathbf{u}^H$  be the solution of the problem PB3 with

$$\bar{\varepsilon} = \begin{bmatrix} 1/3 & 0 & 0 \\ 0 & 1/3 & 0 \\ 0 & 0 & 1/3 \end{bmatrix}$$

$$\boxed{\bar{\mu} = \left\langle \mathbb{C}(\mathbf{x}) : \varepsilon(\mathbf{u}^{(12)}(\mathbf{x})) \right\rangle_{12} = \left\langle \sigma_{12}(\mathbf{u}^{(12)}(\mathbf{x})) \right\rangle.}$$

## Approche FEM

Forme faible associé à l'équilibre local

Find  $\mathbf{u}^h(\mathbf{x}) \in \mathcal{D}(\Omega)$  such that:

$$\int_{\Omega} \boldsymbol{\sigma}(\boldsymbol{\varepsilon}(\mathbf{u}^h(\mathbf{x}))) : \boldsymbol{\varepsilon}(\delta \mathbf{u}^h(\mathbf{x})) d\Omega = 0 \quad \forall \delta \mathbf{u}^h \in H_0^1(\Omega)$$

Forme vectorielle du tenseur des déformations en élasticité 2D

$$\boldsymbol{\varepsilon}^h(\mathbf{x}) \rightarrow \left[ \boldsymbol{\varepsilon}(\mathbf{u}^h(\mathbf{x})) \right] = \begin{bmatrix} \varepsilon_{11}(\mathbf{x}) \\ \varepsilon_{22}(\mathbf{x}) \\ 2\varepsilon_{12}(\mathbf{x}) \end{bmatrix}$$

Forme matricielle du tenseur élastique en élasticité 2D

$$\mathbb{C}(\mathbf{x}) \rightarrow \mathbf{C}(\mathbf{x}) = \begin{bmatrix} C_{1111}(\mathbf{x}) & C_{1122}(\mathbf{x}) & C_{1112}(\mathbf{x}) \\ C_{1122}(\mathbf{x}) & C_{2222}(\mathbf{x}) & C_{2212}(\mathbf{x}) \\ C_{1112}(\mathbf{x}) & C_{2212}(\mathbf{x}) & C_{1212}(\mathbf{x}) \end{bmatrix}$$

## Calcul numérique des coefficients élastiques effectifs

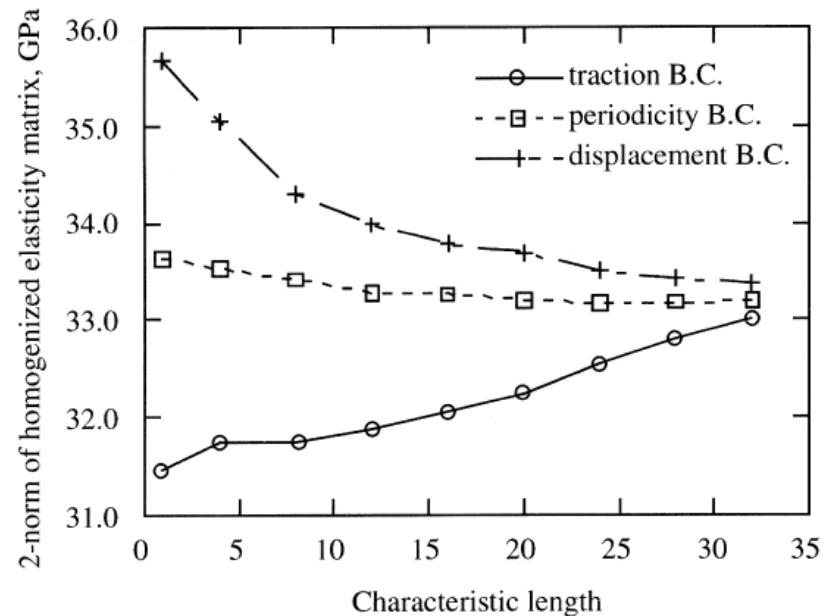
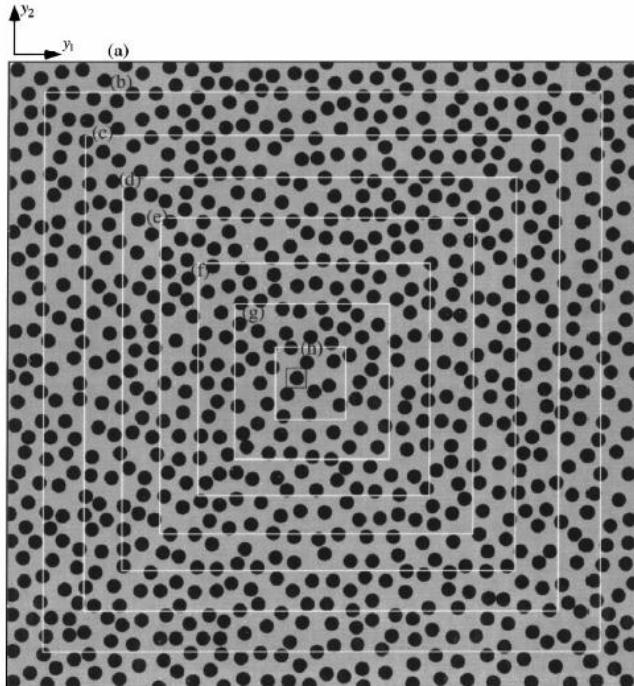
$$\begin{aligned}\overline{\sigma}^h &= \left\langle \boldsymbol{\sigma}^h \right\rangle = \frac{1}{|\Omega|} \left( \sum_e \int_{\Omega^e} \mathbf{C}(\mathbf{x}) \mathbf{D}^{(2)}(\mathbf{x}) \mathbf{u}_i^H d\Omega \right) \frac{\Delta V}{V_0} \\ &= \left( \frac{1}{|\Omega|} \int_{\Omega} \mathbf{C}(\mathbf{x}) \mathbf{D}(\mathbf{x}) \mathbf{u}_i^H d\Omega \right) \frac{\Delta V}{V_0}.\end{aligned}$$

$$\overline{\sigma}^{H,h} = \frac{1}{|\Omega|} \int_{\Omega} \mathbf{C}(\mathbf{x}) \mathbf{D}^{(2)}(\mathbf{x}) \mathbf{u}_i^H d\Omega$$

$$\boxed{\bar{k}^h = \frac{1}{3} Tr \overline{\sigma}^{H,h}}$$

$$\boxed{\bar{\mu}^h = \frac{1}{2} \overline{\sigma}_{12}^{12,h}}$$

# Influence des conditions aux limites

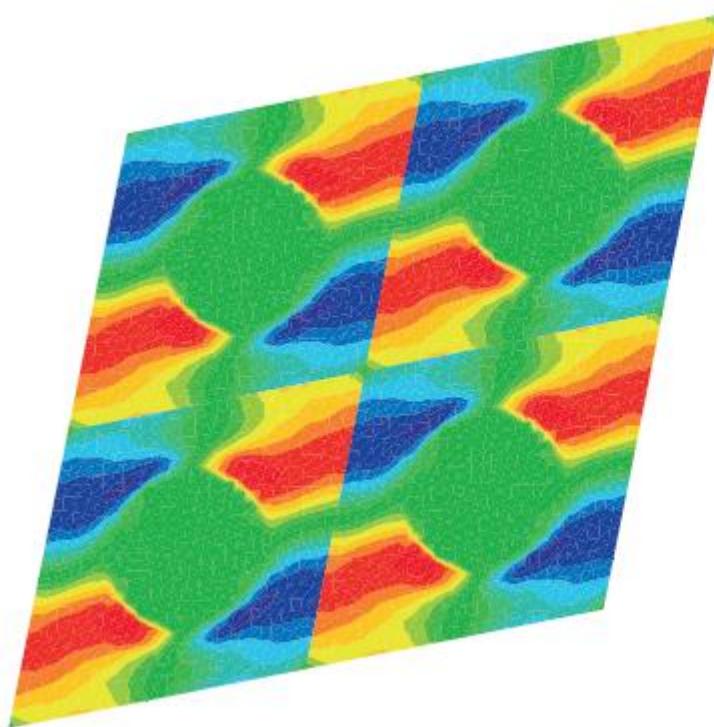


[Terada et al. IJSS 2000]

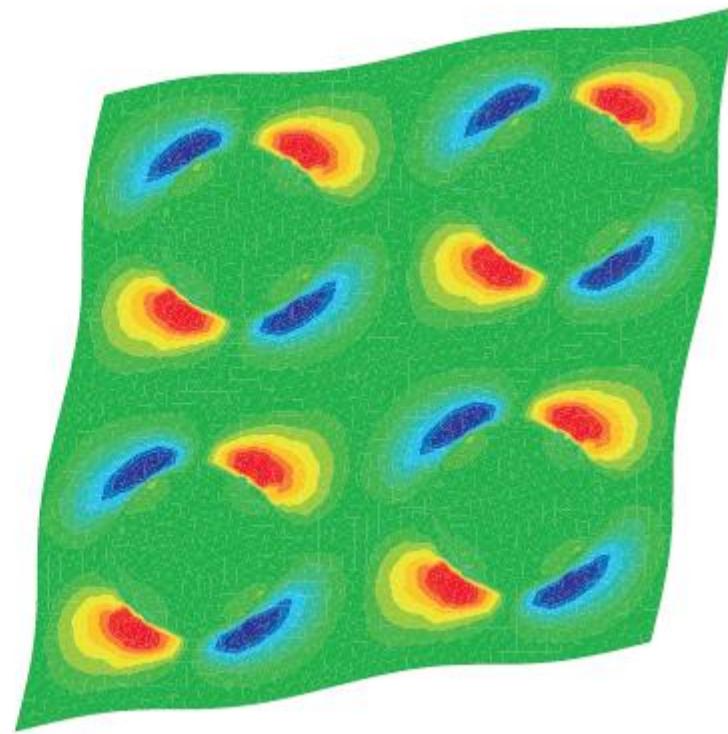
$$\overline{\mathbb{C}}_{SUBC} \leq \overline{\mathbb{C}}_{PER} \leq \overline{\mathbb{C}}_{KUBC}.$$

Théorème de partition [Huet JMPS 90], relations mixtes [Hazanov and Huet 94]

# Influence des conditions aux limites



**KUBC**



**PERIODIC**

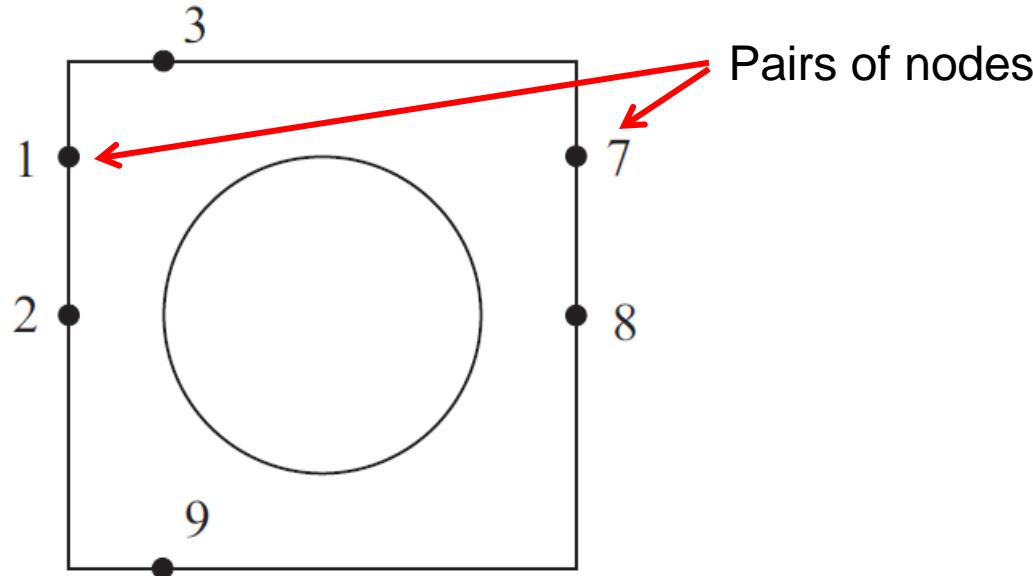
Champs locaux : contraintes

# Prescribing periodic boundary conditions by means of Lagrange multipliers

Periodic boundary conditions: corresponding equations

$$C_i^{\alpha\beta} = u_i^\alpha - u_i^\beta = \bar{\epsilon}_{ij}(x_i^\alpha - x_i^\beta) = 0$$

Example



$$\{\alpha, \beta\} = \{1, 7\}, \{2, 8\}, \{3, 9\}$$

# Prescribing periodic boundary conditions by means of Lagrange multipliers

Can be prescribed by Lagrange multipliers method: minimization of the Energy of the system under the constraints

$$C_i^{\alpha\beta} = u_i^\alpha - u_i^\beta = \bar{\epsilon}_{ij}(x_j^\alpha - x_j^\beta) = 0$$

Can be written as

$$C_i^{\alpha\beta} = P_{ij}u_j - R_i^{\alpha\beta}$$

Constrained minimization problem

$$\underset{\substack{\mathbf{u} \\ C_i=0, i=1,\dots,n_c}}{\text{Inf}} \quad \frac{1}{2} \mathbf{u}^T \cdot \mathbf{K} \mathbf{u}$$

Lagrangian

$$\mathcal{L} = \frac{1}{2} \mathbf{u}^T \cdot \mathbf{K} \mathbf{u} + \lambda \cdot (\mathbf{P} \mathbf{u} - \mathbf{R}) \quad \rightarrow$$

$$\underset{\lambda}{\text{Sup}} \quad \underset{\mathbf{u}}{\text{Inf}} \quad \mathcal{L}$$

# Prescribing periodic boundary conditions by means of Lagrange multipliers

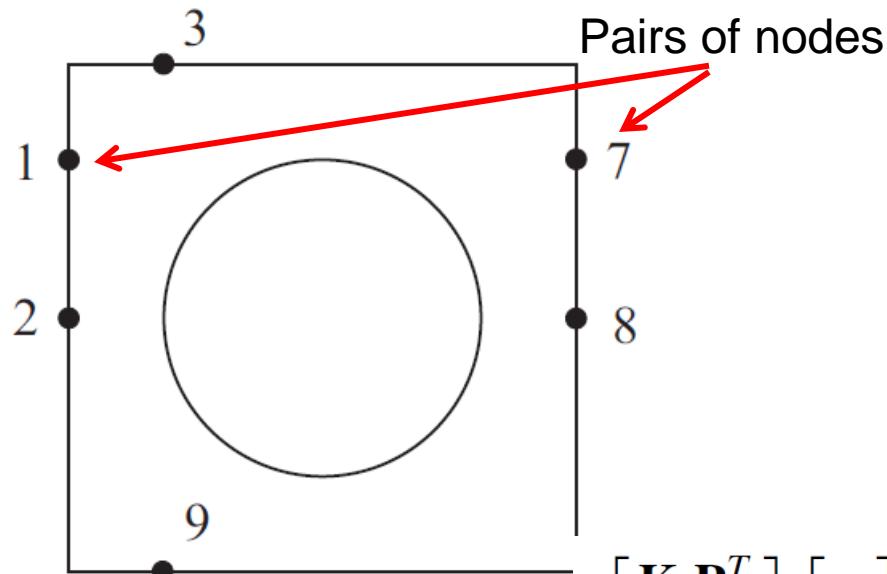
$$\begin{cases} D_{\delta \mathbf{u}} \mathcal{L} = 0 \\ D_{\delta \lambda} \mathcal{L} = 0 \end{cases} \xrightarrow{\hspace{1cm}} \begin{cases} \delta \mathbf{u}^T \cdot (\mathbf{K} \mathbf{u}) + \lambda \cdot \mathbf{P} \delta \mathbf{u} = 0 \\ \delta \lambda \cdot \mathbf{P} \mathbf{u} = \delta \lambda \cdot \mathbf{R} \end{cases}$$

$$\begin{bmatrix} \mathbf{K} & \mathbf{P}^T \\ \mathbf{P} & \mathbf{0} \end{bmatrix} \begin{bmatrix} \mathbf{u} \\ \lambda \end{bmatrix} = \begin{bmatrix} \mathbf{0} \\ \mathbf{R} \end{bmatrix}$$

Linear system

## Example

$$\{\alpha, \beta\} = \{1, 7\}, \{2, 8\}, \{3, 9\}$$



Nodal unknowns corresponding to pair of nodes

$$\begin{bmatrix} \mathbf{K} & \mathbf{P}^T \\ \mathbf{P} & \mathbf{0} \end{bmatrix} \begin{bmatrix} \mathbf{u} \\ \lambda \end{bmatrix} = \begin{bmatrix} \mathbf{0} \\ \mathbf{R} \end{bmatrix}$$

$$\mathbf{q} = [u_1 \ v_1 \ u_2 \ v_2 \ u_3 \ v_3 \ u_4 \ v_4 \ u_5 \ v_5 \ u_6 \ v_6 \ u_7 \ v_7 \ u_8 \ v_8 \ u_9 \ v_9]$$

$$\begin{cases} u^1 - u^7 = \bar{\epsilon}_{11}(x^1 - x^7) + \bar{\epsilon}_{12}(y^1 - y^7) \\ v^1 - v^7 = \bar{\epsilon}_{21}(x^1 - x^7) + \bar{\epsilon}_{22}(y^1 - y^7) \\ u^2 - u^8 = \bar{\epsilon}_{11}(x^2 - x^8) + \bar{\epsilon}_{12}(y^2 - y^8) \\ v^2 - v^8 = \bar{\epsilon}_{21}(x^2 - x^8) + \bar{\epsilon}_{22}(y^2 - y^8) \\ u^3 - u^9 = \bar{\epsilon}_{11}(x^3 - x^9) + \bar{\epsilon}_{12}(y^3 - y^9) \\ v^3 - v^9 = \bar{\epsilon}_{21}(x^3 - x^9) + \bar{\epsilon}_{22}(y^3 - y^9) \end{cases}$$

$$\mathbf{P} = \begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 \end{bmatrix}$$

$$\begin{bmatrix} \mathbf{K} & \mathbf{P}^T \\ \mathbf{P} & \mathbf{0} \end{bmatrix} \begin{bmatrix} \mathbf{u} \\ \lambda \end{bmatrix} = \begin{bmatrix} \mathbf{0} \\ \mathbf{R} \end{bmatrix}$$

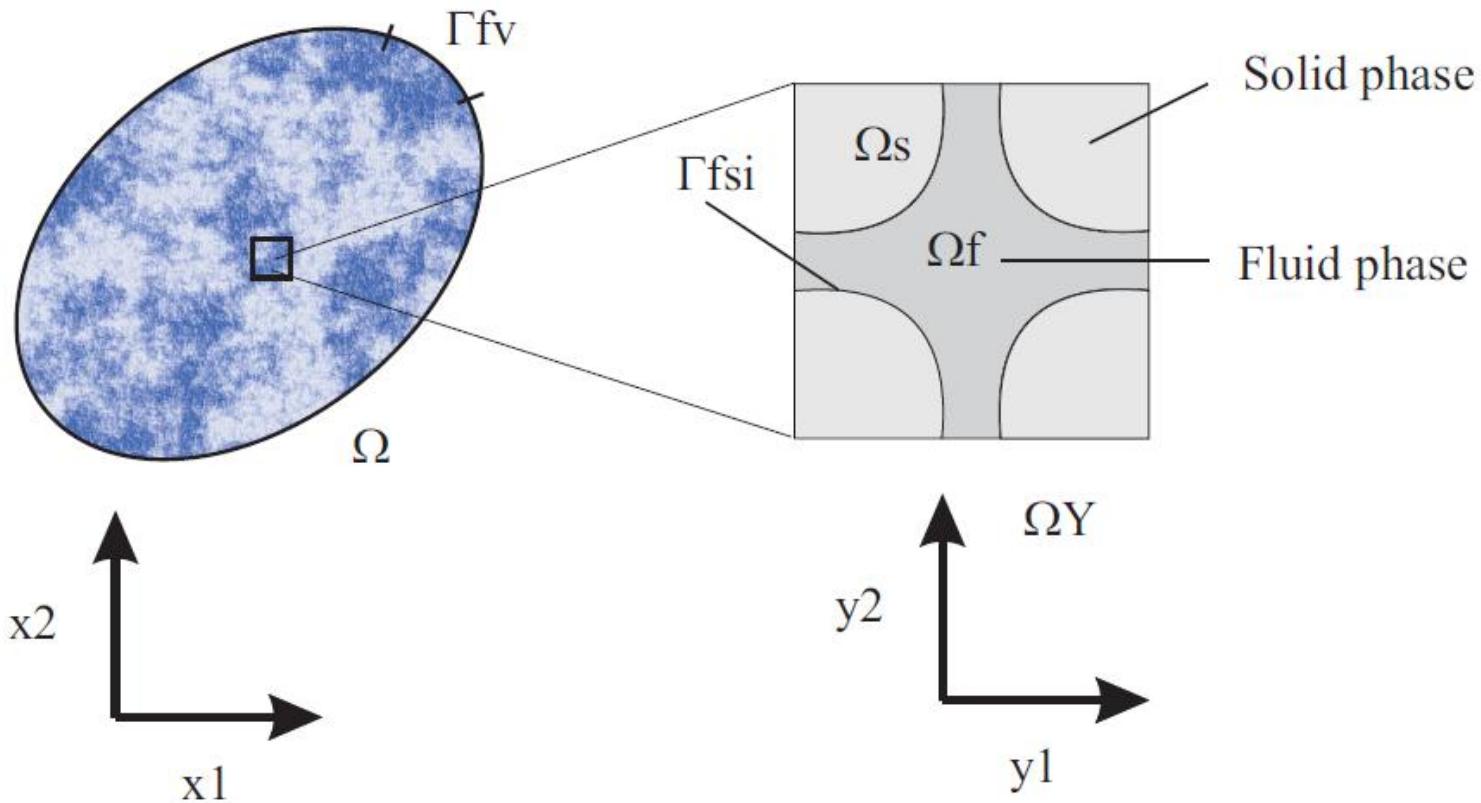
$$\mathbf{q} = [u_1 \ v_1 \ u_2 \ v_2 \ u_3 \ v_3 \ u_4 \ v_4 \ u_5 \ v_5 \ u_6 \ v_6 \ u_7 \ v_7 \ u_8 \ v_8 \ u_9 \ v_9]$$

$$\begin{cases} u^1 - u^7 = \bar{\varepsilon}_{11}(x^1 - x^7) + \bar{\varepsilon}_{12}(y^1 - y^7) \\ v^1 - v^7 = \bar{\varepsilon}_{21}(x^1 - x^7) + \bar{\varepsilon}_{22}(y^1 - y^7) \\ u^2 - u^8 = \bar{\varepsilon}_{11}(x^2 - x^8) + \bar{\varepsilon}_{12}(y^2 - y^8) \\ v^2 - v^8 = \bar{\varepsilon}_{21}(x^2 - x^8) + \bar{\varepsilon}_{22}(y^2 - y^8) \\ u^3 - u^9 = \bar{\varepsilon}_{11}(x^3 - x^9) + \bar{\varepsilon}_{12}(y^3 - y^9) \\ v^3 - v^9 = \bar{\varepsilon}_{21}(x^3 - x^9) + \bar{\varepsilon}_{22}(y^3 - y^9) \end{cases}$$

$$\mathbf{P} = \begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 \end{bmatrix}$$

$$\mathbf{R} = \begin{bmatrix} \bar{\varepsilon}_{11}(x^1 - x^7) + \bar{\varepsilon}_{12}(y^1 - y^7) \\ \bar{\varepsilon}_{21}(x^1 - x^7) + \bar{\varepsilon}_{22}(y^1 - y^7) \\ \bar{\varepsilon}_{11}(x^1 - x^7) + \bar{\varepsilon}_{12}(y^1 - y^7) \\ \bar{\varepsilon}_{21}(x^1 - x^7) + \bar{\varepsilon}_{22}(y^1 - y^7) \\ \bar{\varepsilon}_{11}(x^3 - x^9) + \bar{\varepsilon}_{12}(y^3 - y^9) \\ \bar{\varepsilon}_{21}(x^3 - x^9) + \bar{\varepsilon}_{22}(y^3 - y^9) \end{bmatrix}$$

# Milieux poreux : squelette rigide saturé par un fluide visqueux



# Asymptotic homogenization method

Microscopic and macroscopic quantities

$$\mathbf{y} = \frac{\mathbf{x}}{\varepsilon}$$

Scales ratio  $\varepsilon = \frac{l}{L}$

Expansion of variables (velocities, pressures, displacements)

$$\mathbf{v}^\varepsilon(\mathbf{x}, \mathbf{y}) = \mathbf{v}^{(0)}(\mathbf{x}, \mathbf{y}) + \varepsilon \mathbf{v}^{(1)}(\mathbf{x}, \mathbf{y}) + \varepsilon^2 \mathbf{v}^{(2)}(\mathbf{x}, \mathbf{y}) + \dots$$

$$p^\varepsilon(\mathbf{x}, \mathbf{y}) = p^{(0)}(\mathbf{x}, \mathbf{y}) + \varepsilon p^{(1)}(\mathbf{x}, \mathbf{y}) + \varepsilon^2 p^{(2)}(\mathbf{x}, \mathbf{y}) + \dots$$

$$\mathbf{u}^\varepsilon(\mathbf{x}, \mathbf{y}) = \mathbf{u}^{(0)}(\mathbf{x}, \mathbf{y}) + \varepsilon \mathbf{u}^{(1)}(\mathbf{x}, \mathbf{y}) + \varepsilon^2 \mathbf{u}^{(2)}(\mathbf{x}, \mathbf{y}) + \dots$$

# Asymptotic homogenization method

Differential operators: chain rule

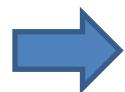
$$\frac{D(\cdot)}{D\mathbf{x}} = \frac{\partial(\cdot)}{\partial\mathbf{x}} + \frac{\partial(\cdot)}{\partial\mathbf{y}} \frac{\partial\mathbf{y}}{\partial\mathbf{x}}$$

$$\mathbf{y} = \frac{\mathbf{x}}{\varepsilon}$$

Gradient operator:

$$\mathbf{grad}_x^\varepsilon p(\mathbf{x}, \mathbf{y}) = \begin{bmatrix} \frac{Dp^\varepsilon(\mathbf{x}, \mathbf{y})}{Dx_1} \\ \frac{Dp^\varepsilon(\mathbf{x}, \mathbf{y})}{Dx_2} \end{bmatrix} = \begin{bmatrix} \frac{\partial p}{\partial x_1} + \frac{\partial p}{\partial y_1} \frac{\partial y_1}{\partial x_1} \\ \frac{\partial p}{\partial x_2} + \frac{\partial p}{\partial y_2} \frac{\partial y_2}{\partial x_2} \end{bmatrix}$$

$$\mathbf{grad}_x^\varepsilon p(\mathbf{x}, \mathbf{y}) = \begin{bmatrix} \frac{\partial p}{\partial x_1} + \varepsilon^{-1} \frac{\partial p}{\partial y_1} \\ \frac{\partial p}{\partial x_2} + \varepsilon^{-1} \frac{\partial p}{\partial y_2} \end{bmatrix}$$



$$\mathbf{grad}_x^\varepsilon(\cdot) = \mathbf{grad}_x(\cdot) + \varepsilon^{-1} \mathbf{grad}_y(\cdot)$$

# Asymptotic homogenization method

Divergence operator:

$$\begin{aligned}\mathbf{div}_x^\varepsilon \boldsymbol{\sigma}(\mathbf{x}, \mathbf{y}) &= \left[ \frac{\frac{D\sigma_{11}^\varepsilon(\mathbf{x}, \mathbf{y})}{Dx_1} + \frac{D\sigma_{12}(\mathbf{x}, \mathbf{y})^\varepsilon}{Dx_2}}{\frac{D\sigma_{21}^\varepsilon(\mathbf{x}, \mathbf{y})}{Dx_1} + \frac{D\sigma_{22}(\mathbf{x}, \mathbf{y})^\varepsilon}{Dx_2}} \right] \\ &= \left[ \frac{\frac{\partial \sigma_{11}}{\partial x_1} + \frac{\partial \sigma_{11}}{\partial y_1} \frac{\partial y_1}{\partial x_1} + \frac{\partial \sigma_{12}}{\partial x_2} + \frac{\partial \sigma_{12}}{\partial y_2} \frac{\partial y_2}{\partial x_2}}{\frac{\partial \sigma_{21}}{\partial x_1} + \frac{\partial \sigma_{21}}{\partial y_1} \frac{\partial y_1}{\partial x_1} + \frac{\partial \sigma_{22}}{\partial x_2} + \frac{\partial \sigma_{22}}{\partial y_2} \frac{\partial y_2}{\partial x_2}} \right] \\ &= \left[ \frac{\frac{\partial \sigma_{11}}{\partial x_1} + \frac{\partial \sigma_{12}}{\partial x_2} + \varepsilon^{-1} \left( \frac{\partial \sigma_{11}}{\partial y_1} + \frac{\partial \sigma_{12}}{\partial y_2} \right)}{\frac{\partial \sigma_{21}}{\partial x_1} + \frac{\partial \sigma_{22}}{\partial x_2} + \varepsilon^{-1} \left( \frac{\partial \sigma_{21}}{\partial y_1} + \frac{\partial \sigma_{22}}{\partial y_2} \right)} \right]\end{aligned}$$



$$\mathbf{div}_x^\varepsilon(.) = \mathbf{div}_x(.) + \varepsilon^{-1} \mathbf{div}_y(.)$$

# Asymptotic homogenization method

Governing equations:

$$\begin{cases} \operatorname{div}_x^\varepsilon \sigma_f^\varepsilon + \rho_f \mathbf{g} = 0 & \text{in } \Omega_f^\varepsilon \\ \operatorname{div}_x^\varepsilon \mathbf{v}^\varepsilon = 0 & \text{in } \Omega_f^\varepsilon \end{cases}$$

$$\begin{cases} \mathbf{v}^\varepsilon = \mathbf{v}^* & \text{on } \Gamma_{fv} \setminus \Gamma_{fsi}^\varepsilon \\ \mathbf{v}^\varepsilon = 0 & \text{on } \Gamma_{fsi}^\varepsilon \end{cases}$$

Boundary conditions

$$\sigma_f^\varepsilon = -p^\varepsilon \mathbf{1} + 2\mu_f^\varepsilon \mathbf{D}^\varepsilon$$

$$\mathbf{D}^\varepsilon = \frac{1}{2} \left( \operatorname{grad}^\varepsilon \mathbf{v}^\varepsilon + \{\operatorname{grad}^\varepsilon \mathbf{v}^\varepsilon\}^T \right)$$

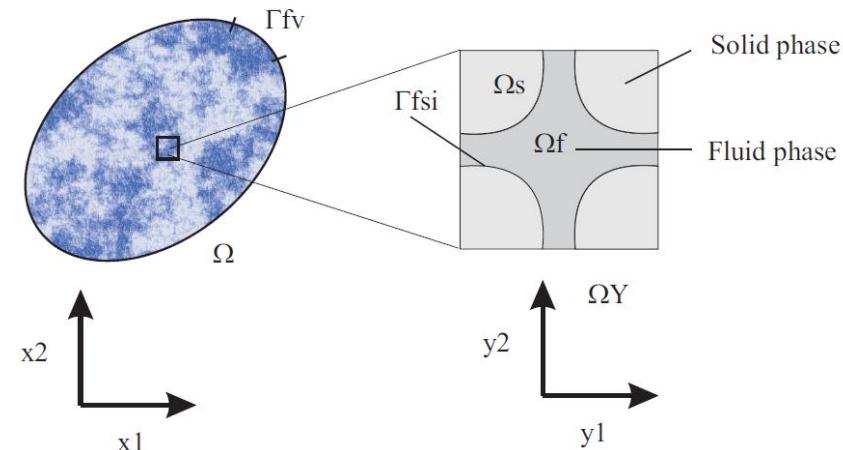
and

$$\mu_f^\varepsilon = \varepsilon^2 \mu_f$$

$$\begin{cases} \operatorname{div}^\varepsilon \left( -p^\varepsilon \mathbf{1} + 2\mu_f^\varepsilon \mathbf{D}^\varepsilon \right) + \rho_f \mathbf{g} = 0 & \text{in } \Omega_f^\varepsilon \\ \operatorname{div}^\varepsilon \mathbf{v}^\varepsilon = 0 & \text{in } \Omega_f^\varepsilon \end{cases}$$

or

→ 
$$\begin{cases} -\operatorname{grad}^\varepsilon p^\varepsilon + 2\mu_f^\varepsilon \operatorname{div}^\varepsilon (\operatorname{grad}_S^\varepsilon \mathbf{v}^\varepsilon) + \rho_f \mathbf{g} = 0 \\ \operatorname{div}^\varepsilon \mathbf{v}^\varepsilon = 0 & \text{in } \Omega_f^\varepsilon \end{cases}$$



# Asymptotic homogenization method

$$\operatorname{div}^\varepsilon \mathbf{v}^\varepsilon = 0 \text{ in } \Omega_f^\varepsilon$$

Chain rule+asymptotic expansion of variables



$$\operatorname{div}_x \mathbf{v}^0 + \varepsilon \operatorname{div}_x \mathbf{v}^1 + \dots + \varepsilon^{-1} \operatorname{div}_y \mathbf{v}^0 + \operatorname{div}_y \mathbf{v}^1 + \dots = 0$$

$$\begin{cases} \mathbf{v}^\varepsilon = \mathbf{v}^* & \text{on } \Gamma_{fv} \setminus \Gamma_{fsi}^\varepsilon \\ \mathbf{v}^\varepsilon = 0 & \text{on } \Gamma_{fsi}^\varepsilon \end{cases}$$



$$\begin{cases} \mathbf{v}^0 + \varepsilon \mathbf{v}^1 + \dots = \mathbf{v}^* & \text{on } \Gamma_{fv} \setminus \Gamma_{fsi}^\varepsilon \\ \mathbf{v}^0 + \varepsilon \mathbf{v}^1 + \dots = 0 & \text{on } \Gamma_{fsi}^\varepsilon \end{cases}$$

# Asymptotic homogenization method

Governing equations:

$$-\mathbf{grad}^\varepsilon p^\varepsilon + 2\mu_f^\varepsilon \mathbf{div}^\varepsilon (\mathbf{grad}_S^\varepsilon \mathbf{v}^\varepsilon) + \rho_f \mathbf{g} = 0$$

Chain rule+asymptotic expansion of variables



$$\begin{aligned} & - \{ \mathbf{grad}_x p^0(\mathbf{x}, \mathbf{y}) + \varepsilon \mathbf{grad}_x p^1(\mathbf{x}, \mathbf{y}) + \dots \} \\ & - \{ \varepsilon^{-1} \mathbf{grad}_y p^0(\mathbf{x}, \mathbf{y}) + \mathbf{grad}_y p^1(\mathbf{x}, \mathbf{y}) + \dots \} \\ & + 2\mu_f \varepsilon^2 \{ \mathbf{div}_x (\mathbf{grad}_x^S \mathbf{v}^0) + \varepsilon \mathbf{div}_x (\mathbf{grad}_y^S \mathbf{v}^1) + \dots \\ & + \varepsilon^{-2} \mathbf{div}_y (\mathbf{grad}_y^S \mathbf{v}^0) + \varepsilon^{-1} \mathbf{div}_y (\mathbf{grad}_y^S \mathbf{v}^1) + \dots \} + \rho_f \mathbf{g} = 0 \end{aligned}$$

# Asymptotic homogenization method

Grouping terms with same exponents (same « order »)

$$\begin{aligned} & - \left\{ \boxed{\mathbf{grad}_x p^0(\mathbf{x}, \mathbf{y})} + \boxed{\varepsilon \mathbf{grad}_x p^1(\mathbf{x}, \mathbf{y})} + \dots \right\} \\ & - \left\{ \boxed{\varepsilon^{-1} \mathbf{grad}_y p^0(\mathbf{x}, \mathbf{y})} + \boxed{\mathbf{grad}_y p^1(\mathbf{x}, \mathbf{y})} + \dots \right\} \\ & + 2\mu_f \varepsilon^2 \left\{ \mathbf{div}_x (\mathbf{grad}_x^S \mathbf{v}^0) + \varepsilon \boxed{\mathbf{div}_x (\mathbf{grad}_y^S \mathbf{v}^1)} + \dots \right. \\ & \left. + \varepsilon^{-2} \mathbf{div}_y (\mathbf{grad}_y^S \mathbf{v}^0) + \varepsilon^{-1} \boxed{\mathbf{div}_y (\mathbf{grad}_y^S \mathbf{v}^1)} + \dots \right\} + \boxed{\rho_f \mathbf{g}} = \boxed{0} \end{aligned}$$

$$\boxed{\mathbf{div}_x \mathbf{v}^0} + \boxed{\varepsilon \mathbf{div}_x \mathbf{v}^1} + \dots + \boxed{\varepsilon^{-1} \mathbf{div}_y \mathbf{v}^0} + \boxed{\mathbf{div}_y \mathbf{v}^1} + \dots = 0$$

$$\begin{cases} \boxed{\mathbf{v}^0} + \boxed{\varepsilon \mathbf{v}^1} + \dots = \mathbf{v}^* & \text{on } \Gamma_{fv} \setminus \Gamma_{fsi}^\varepsilon \\ \boxed{\mathbf{v}^0} + \boxed{\varepsilon \mathbf{v}^1} + \dots = 0 & \text{on } \Gamma_{fsi}^\varepsilon \end{cases}$$

# Asymptotic homogenization method

Grouping terms with same exponents (same « order »)

$$p^0(\mathbf{x}, \mathbf{y}) = p^0(\mathbf{x})$$

$$\left\{ \begin{array}{l} \mathbf{grad}_y p^0 = 0 \\ div_y \mathbf{v}^0 = 0 \\ -\mathbf{grad}_y p^1 + 2\mu_f div_y (\mathbf{grad}_y^S v^0) = \mathbf{grad}_x p^0 - \rho_f \mathbf{g} \\ div_x \mathbf{v}^0 = -div_y \mathbf{v}^1 \end{array} \right.$$



$$\int_{\Omega_Y} div_x \mathbf{v}^0 d\Omega = \int_{\Omega_Y} -div_y \mathbf{v}^1 d\Omega$$

As  $\mathbf{v}^{(1)}$  is periodic on  $\Omega_Y$  it yields:

$$\int_{\Omega_Y} div_x \mathbf{v}^0 d\Omega = 0$$

Furthermore:

$$div_x \bar{\mathbf{v}} = div_x \langle \mathbf{v} \rangle = 0$$



$$\int_{\Omega_Y} div_x \mathbf{v}^0 d\Omega = div_x \int_{\Omega_Y} \mathbf{v}^0 d\Omega = div_x \frac{1}{|\Omega_Y|} \int_{\Omega_Y} \mathbf{v}^0 d\Omega = 0$$

# Asymptotic homogenization method

$$\begin{aligned} \operatorname{div}_y \mathbf{v}^0 &= 0 \\ -\mathbf{grad}_y p^1 + 2\mu_f \operatorname{div}_y (\mathbf{grad}_y^S \mathbf{v}^0) &= \mathbf{grad}_x p^0 - \rho_f \mathbf{g} \end{aligned}$$

Coupled system of equations allowing determining  $p^1$  and  $\mathbf{v}^0$

Using superposition principle we have:

$$\mathbf{v}^{(0)}(\mathbf{x}, \mathbf{y}) = \mathbf{k}(\mathbf{y}) [\mathbf{grad} p^0(\mathbf{x}) - \rho_f \mathbf{g}]$$

$$p^{(1)}(\mathbf{x}, \mathbf{y}) = \mathbf{r}(\mathbf{y}) [\mathbf{grad} p^0(\mathbf{x}) - \rho_f \mathbf{g}]$$

$$\mathbf{v}^{(0)}(\mathbf{x}, \mathbf{y}) = \mathbf{k}(\mathbf{y}) [\mathbf{grad} p^0(\mathbf{x}) - \rho_f \mathbf{g}]$$

$$p^{(1)}(\mathbf{x}, \mathbf{y}) = \mathbf{r}(\mathbf{y}) [\mathbf{grad} p^0(\mathbf{x}) - \rho_f \mathbf{g}]$$

Space averaging

$$\langle \mathbf{v}^{(0)}(\mathbf{x}, \mathbf{y}) \rangle = \bar{\mathbf{v}}(\mathbf{x}) = \langle \mathbf{k}(\mathbf{y}) \rangle [\mathbf{grad} \bar{p}(\mathbf{x}) - \rho_f \mathbf{g}]$$

By identification with the Darcy law :

$$\langle \mathbf{v}(\mathbf{x}) \rangle = -\bar{\mathbf{K}} [\mathbf{grad} \bar{p}(\mathbf{x}) - \rho_f \mathbf{g}]$$

Macroscopic tensor of permeability

$$\boxed{\bar{\mathbf{K}} = -\langle \mathbf{k}(\mathbf{y}) \rangle}$$

# Numerical solving using FEM

Notations       $\mathbf{u}^i = [\mathbf{v}^0]^{(i)}, \quad \boldsymbol{\pi}^i = [p^1]^{(i)}$

Problem to be solved

$$\begin{cases} -\mathbf{grad}\boldsymbol{\pi}^i + 2\mu_f \operatorname{div}(\mathbf{grad}_S \mathbf{u}^i) = \mathbf{G}^i - \rho_f \mathbf{g} \\ \operatorname{div} \mathbf{u}^i = 0 \end{cases}$$

$$\begin{cases} -\mathbf{grad}\boldsymbol{\pi}^i + 2\mu_f \operatorname{div}(\mathbf{grad}_S \mathbf{u}^i) = \mathbf{G}^i - \rho_f \mathbf{g} \\ \operatorname{div} \mathbf{u}^i = 0 \end{cases} \quad (4.401)$$

Multiplying each equation by a test function and integrating over  $\Omega_Y$  we obtain:

$$\begin{cases} -\int_{\Omega_Y} \mathbf{grad}\boldsymbol{\pi}^i \cdot \delta \mathbf{v} d\Omega + \int_{\Omega_Y} 2\mu_f \operatorname{div}(\mathbf{grad}_S \mathbf{u}^i) \cdot \delta \mathbf{v} d\Omega = \int_{\Omega_Y} [\mathbf{G}^i - \rho_f \mathbf{g}] \cdot \delta \mathbf{v} d\Omega \\ \int_{\Omega_Y} \operatorname{div} \mathbf{u}^i \delta \boldsymbol{\pi} d\Omega = 0 \end{cases}$$

the first term in Eq. (4.402<sub>1</sub>) can be transformed into:

$$-\int_{\Omega_Y} \mathbf{grad}\pi^i \cdot \delta\mathbf{v} d\Omega = -\int_{\Omega_Y} \operatorname{div}(\pi\delta\mathbf{v}) d\Omega + \int_{\Omega_Y} \pi \operatorname{div}(\delta\mathbf{v}) d\Omega$$

Using the divergence theorem and as  $\delta\mathbf{v} = 0$  on  $\partial\Omega_Y$  we have:

$$\int_{\Omega_Y} \operatorname{div}(\pi\delta\mathbf{v}) d\Omega = \int_{\partial\Omega_Y} (\pi\delta\mathbf{v}) \cdot \mathbf{n} d\Omega = 0$$

Then:

$$-\int_{\Omega_Y} \mathbf{grad}\pi^i \cdot \delta\mathbf{v} d\Omega = \int_{\Omega_Y} \pi \operatorname{div}(\delta\mathbf{v}) d\Omega$$

Using the equality:

$$\text{div}(\text{grad}(\mathbf{u})) \cdot \mathbf{v} = \text{div}(\text{grad}(\mathbf{u})\mathbf{v}) - \text{grad}(\mathbf{u}) : \text{grad}(\mathbf{v})$$

we obtain:

$$\begin{aligned} & \int_{\Omega_Y} 2\mu_f \text{div}(\text{grad}_S(\mathbf{u})^i) \cdot \delta \mathbf{v} d\Omega \\ &= \int_{\Omega_Y} 2\mu_f \text{div}(\text{grad}(\mathbf{u}^i) \delta \mathbf{u}^i) d\Omega - \int_{\Omega_Y} 2\mu_f \text{grad}_S(\mathbf{u}^i) : \text{grad}_S(\delta \mathbf{v}) d\Omega \\ &= - \int_{\Omega_Y} \mu_f \text{grad}_S(\mathbf{u}^i) : \text{grad}_S(\delta \mathbf{v}) d\Omega \\ &= - \int_{\Omega_Y} 2\mu_f \boldsymbol{\varepsilon}(\mathbf{u}^i) : \boldsymbol{\varepsilon}(\delta \mathbf{v}) d\Omega. \end{aligned}$$

Final weak form (classical form for viscous incompressible fluids)

$$\int_{\Omega_Y} \pi \operatorname{div}(\delta \mathbf{v}) d\Omega - \int_{\Omega_Y} 2\mu_f \boldsymbol{\varepsilon}(\mathbf{u}^i) : \boldsymbol{\varepsilon}(\delta \mathbf{v}) d\Omega$$

$$= \int_{\Omega_Y} [\mathbf{G}^i - \rho_f \mathbf{g}] \cdot \delta \mathbf{v} d\Omega$$

$$\int_{\Omega_Y} \operatorname{div}(\mathbf{u}^i) \cdot \delta \pi d\Omega = 0$$

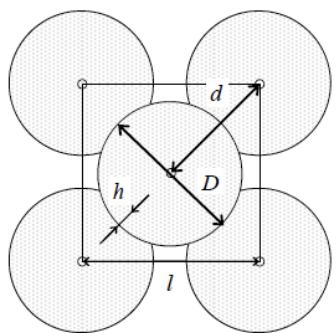
Discrete system of equations

$$\begin{bmatrix} \mathbf{K} & \mathbf{G}^T \\ \mathbf{G} & \mathbf{0} \end{bmatrix} \begin{bmatrix} [\mathbf{u}_i] \\ [\pi_i] \end{bmatrix} = \begin{bmatrix} \mathbf{F} \\ \mathbf{0} \end{bmatrix}$$

# Summary

To compute the effective permeability  $\bar{\mathbf{K}}$ :

1. Solve for each  $\mathbf{G}^i$  the problem (4.415)
2. Construct  $[\mathbf{k}] = \{\mathbf{u}^1; \mathbf{u}^2; \mathbf{u}^3\}$
3. Compute  $\bar{\mathbf{K}} = \frac{1}{|\Omega_Y|} \int_{\Omega_Y} [\mathbf{k}] d\Omega$

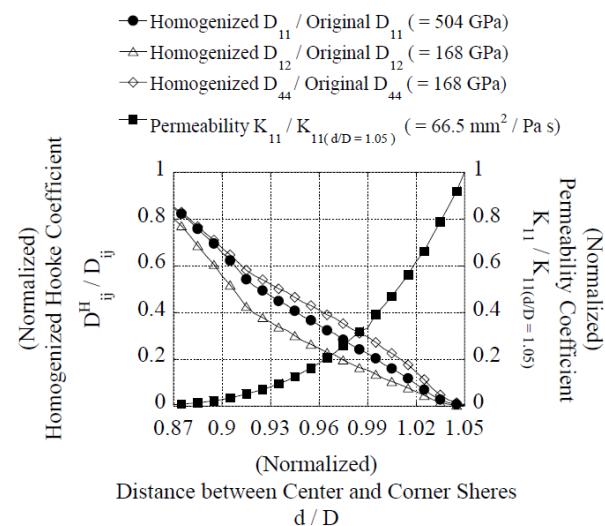
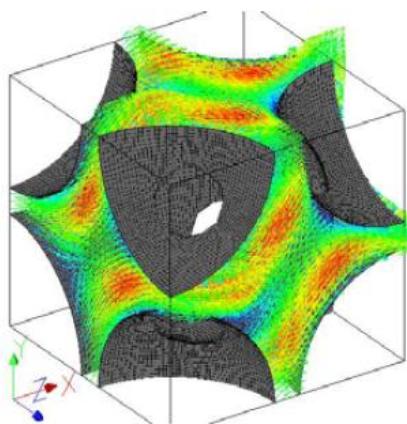


Diameter of ceramics particle:  
 $D = 1.0 \text{ mm}$ .

Distance between centers of ceramics particle:  
 $d = 0.87D \sim 1.05D$ .

Depth of sintered part:  
 $h = D - d$ .

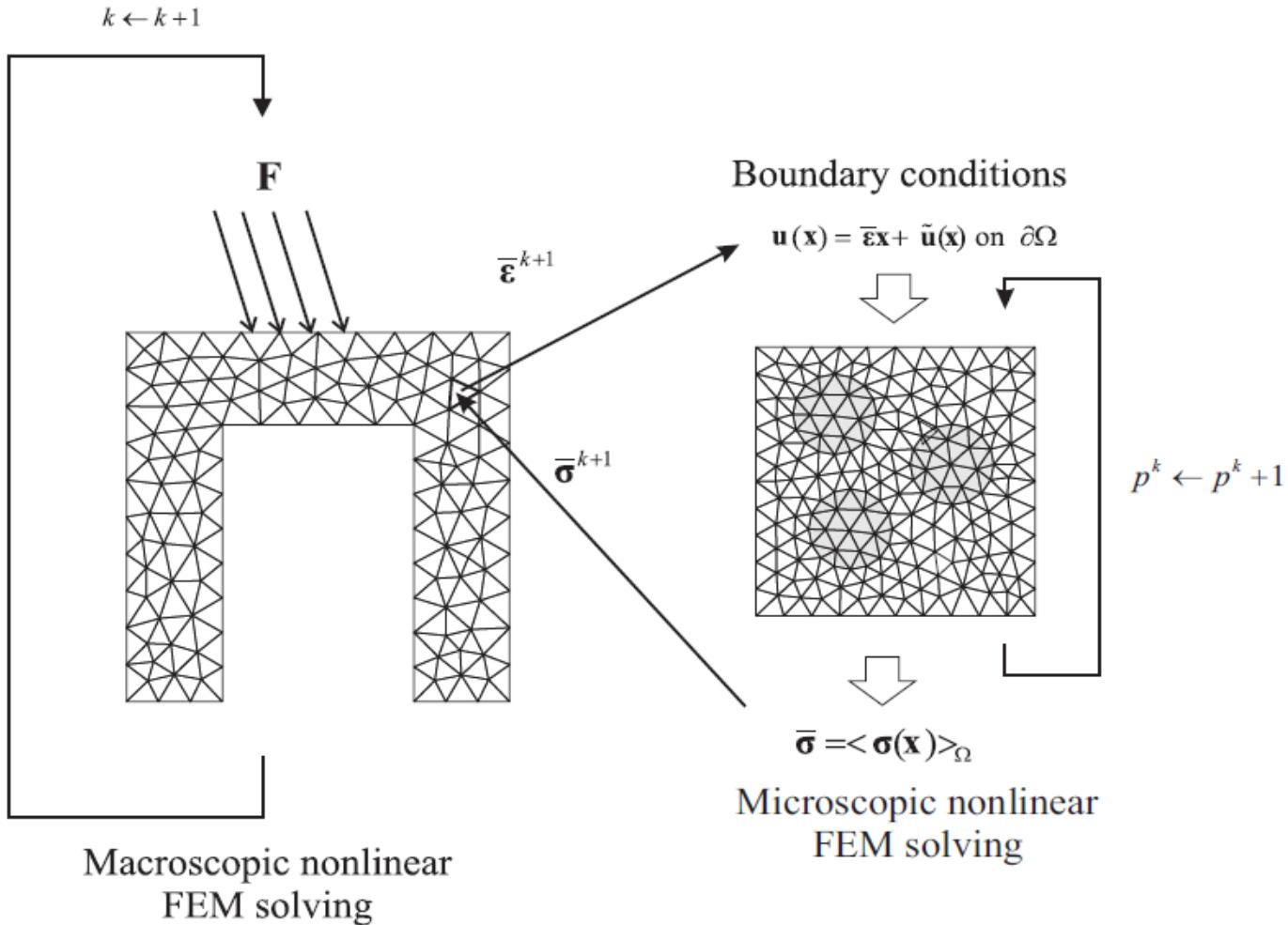
Length of unit cell:  $l$ .



[Sawada et al. IMM 2009]

## 6) Problèmes non linéaires : Homogénéisation non linéaire numérique : « FE2 method »

[Renard 1987], [Guedes, Kikuchi 1990, Ghosh 1995, Smit and Brekelmans 1995], [Feyel 1999], [Miehe et al. 1999], [Terada et al. 2000], [Terada and Kikuchi 2001],



- Nécessité de résoudre un problème non linéaire en chaque point d'intégration, pour chaque itération jusqu'à l'équilibre macroscopique (ex: Newton-Raphson)
- Méthode simple, générale, possibilité de prendre en compte :
  - Evolution de microstructures
  - Toutes lois de comportement, effets d'histoire
- Méthode très coûteuse, la complexité augmente non linéairement (au carré) avec la taille du maillage macro
- module tangent non explicite, calculs supplémentaires nécessaires

# Problèmes non linéaires

## Approches découplées : NTFA

[Dvorak G. Transformation field analysis of inelastic composite materials. Proc Roy Soc Lond A 1992;437:311–27.]

[Michel JC, Suquet P. Nonuniform transformation field analysis. Int J Solids Struct 2003;40:6937–55]

[Michel JC, Suquet P. Computational analysis of nonlinear composite structures using the nonuniform transformation field analysis. Comput Meth Appl Mech Eng 2004;193:5477–502]

[Roussette, Michel, Suquet, CST 2009]

# NTFA : Non uniform transformation analysis

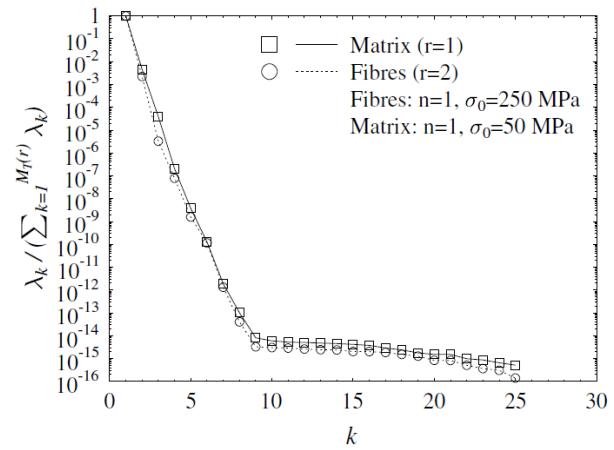
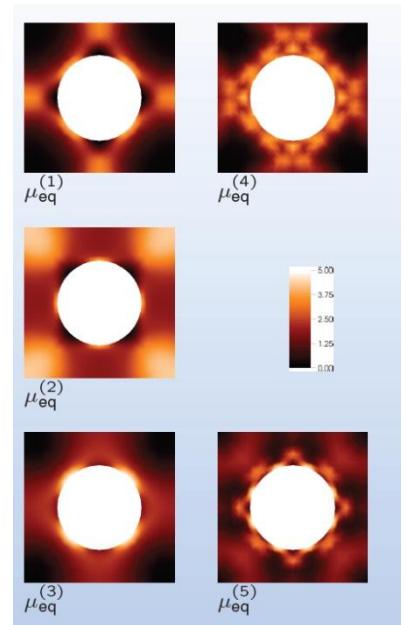
$$\boldsymbol{\varepsilon}(\boldsymbol{x}) = \boldsymbol{A}(\boldsymbol{x}) : \boldsymbol{E} + \frac{1}{|V|} \int_V \boldsymbol{D}(\boldsymbol{x}, \boldsymbol{x}') : \boldsymbol{\varepsilon}^{\text{vp}}(\boldsymbol{x}') d\boldsymbol{x}'$$

$$\boldsymbol{\varepsilon}^{\text{vp}}(\boldsymbol{x}, t) = \sum_{k=1}^M \varepsilon_k^{\text{vp}}(t) \boldsymbol{\mu}^k(\boldsymbol{x}).$$

$$\boldsymbol{\Sigma} = \langle \boldsymbol{L} : \boldsymbol{A} \rangle : \boldsymbol{E} + \sum_{k=1}^M (\langle \boldsymbol{L} : \boldsymbol{D} * \boldsymbol{\mu}^k \rangle - \langle \boldsymbol{L} : \boldsymbol{\mu}^k \rangle) \varepsilon_k^{\text{vp}}$$

$$\sum_{i=1}^{M_T(r)} g_{ij} v_j^k = \lambda_k v_i^k, \quad g_{ij} = \langle \boldsymbol{\theta}^i : \boldsymbol{\theta}^j \rangle$$

Sélection des modes plastiques par POD  
[Roussette et al 2009 ]



# 8) Contributions

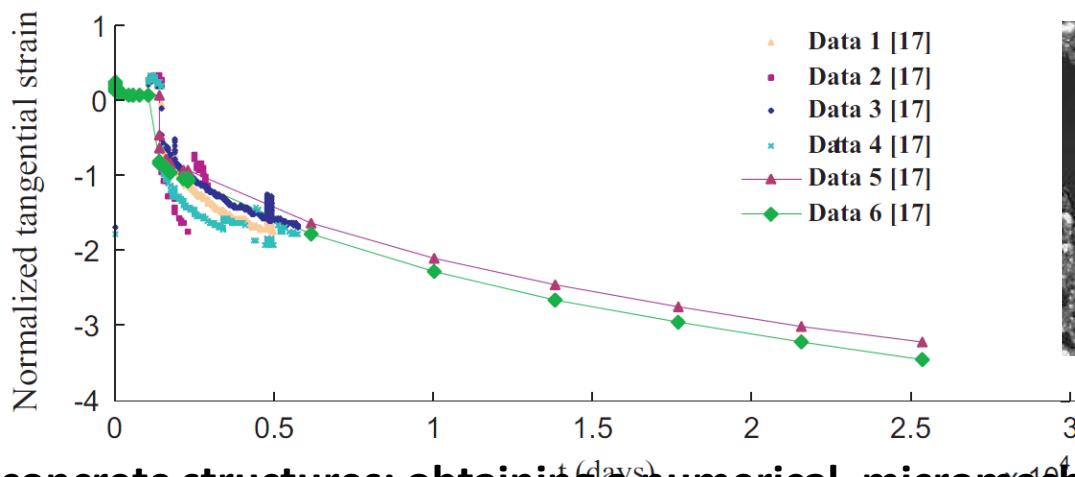
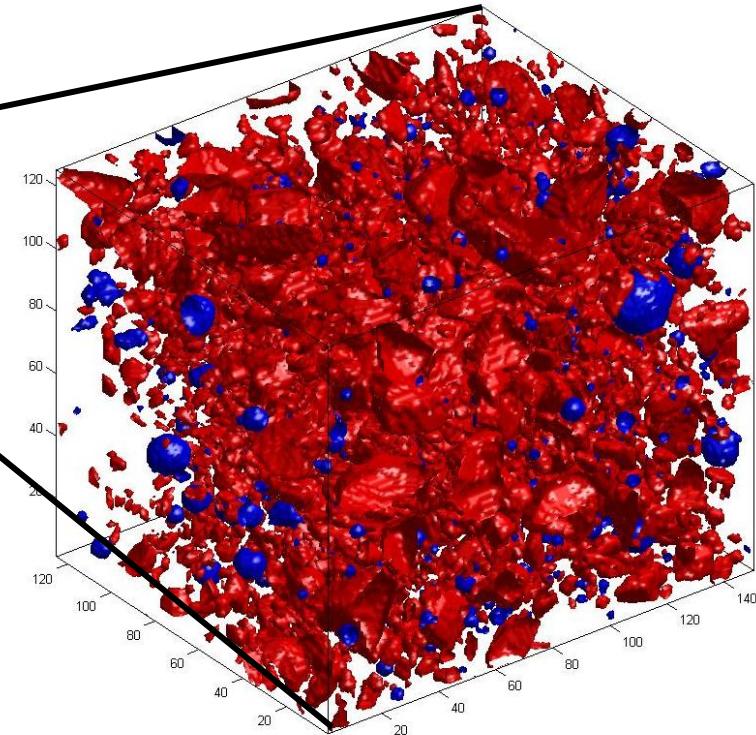
- Homogénéisations des plaques et coques, approche simplifiée avec modèle à 7 paramètres (Thèse Yu Cong)
- **Homogénéisation viscoélastique en temps [Tran et al. CMAME 2011]**
- Homogénéisation stochastique non linéaire [Clément, Soize, JY CMAME 2013], [Clément, Soize, JY, IJNME, 2012]
- Analyse multi échelle des instabilités [Nezamabadi et al. EJCM 2013], [Nezamabadi et al. IJNME 2010], [Nezamabadi et al. CMAME 2009]
- Homogénéisation des surfaces nano
- **Space Lippmann-Schwinger [JY IJNME 2012]**
- Méthode XFEM pour modélisation des microstructures complexes avec interfaces imparfaites (exposé Qi-Chang )
- **Homogénéisation non linéaire avec approches découplées : approche par base de donnée**
- Méthodes FE<sup>2</sup> avec réduction de modèle [JY and He JCP 2007, Monteiro et al. CMS 2008]

# Homogénéisation des matériaux viscoélastiques

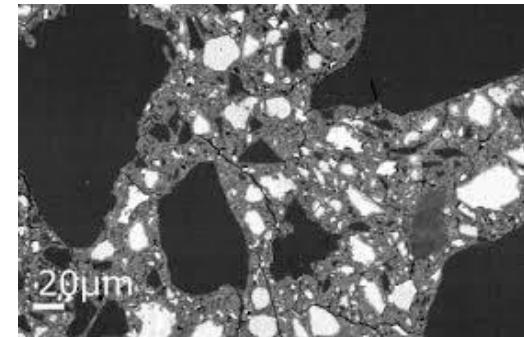
# Motivations



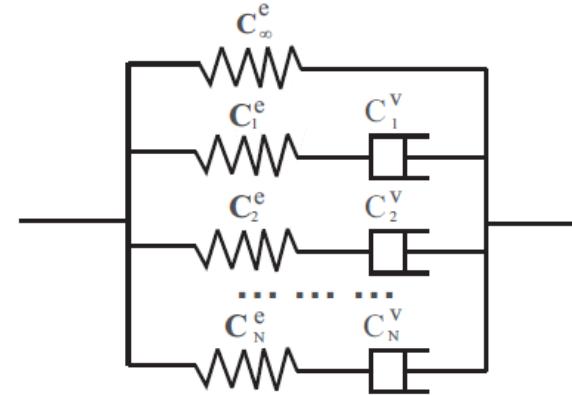
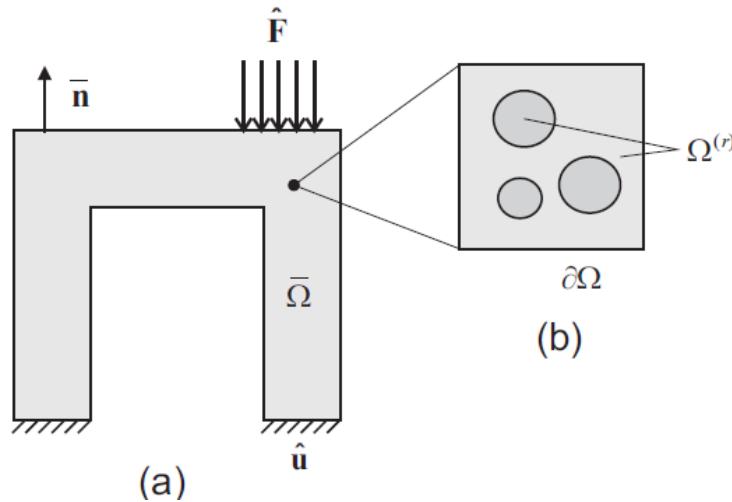
Nam Theun 2 hydrolic dam (Laos)



Creep of concrete structures: obtaining a numerical, micromechanical-based model



# Homogenization of linear viscoelastic materials



Generalized Maxwell model

Multiscale structure problem

Local constitutive expressed as convolution products

$$\begin{cases} \text{tr}(\boldsymbol{\sigma}(t)) = \int_0^t G_k(t-s) \text{tr}(\dot{\boldsymbol{\epsilon}}(s)) ds + G_k(t) \text{tr}(\boldsymbol{\epsilon}(0)) \\ \text{dev}(\boldsymbol{\sigma}(t)) = \int_0^t G_\mu(t-s) \text{dev}(\dot{\boldsymbol{\epsilon}}(s)) ds + G_\mu(t) \text{dev}(\boldsymbol{\epsilon}(0)) \end{cases}$$

$$\begin{cases} G_k(t) = 3k_\infty + \sum_{i=1}^N 3k_i \exp(-t/\tau_k) \\ G_\mu(t) = 2\mu_\infty + \sum_{i=1}^N 2\mu_i \exp(t/\tau_\mu), \end{cases}$$

# Homogenization of linear viscoelastic materials

**A composite whose phase are viscoelastic remains a viscoelastic material [Hashin 65]**

$$\begin{aligned}\bar{\sigma}_{ij}(t) &= \int_{-\infty}^t \bar{\Gamma}_{ijkl}(t-s) \frac{d\bar{\varepsilon}_{kl}(s)}{ds} ds, \\ &= \int_0^t \boxed{\bar{\Gamma}_{ijkl}(t-s)} \frac{d\bar{\varepsilon}_{kl}(s)}{ds} ds + \bar{\Gamma}_{ijkl}(t)\bar{\varepsilon}_{kl}(0)\end{aligned}$$



Unknown functional (Green function related to the macroscopic linear operator in time)

Difficult to explicit in the general case (local constitutive laws, morphologies, anisotropy...)

# Homogenization of linear viscoelastic materials

## Existing approaches

- Laplace transform –based numerical methods
  - Difficulties related to the numerical inverse Laplace transform
  - Difficulties related to the number of local problems to be solved
- Multilevel FE methods (« FE<sup>2</sup> »)
  - Complexity of computations, storage of internal variables...

# Discrete representation of the macroscopic relaxation tensor

Choosing:

$$\bar{\varepsilon}_{ij}(t) = H(t)\bar{\varepsilon}_{ij}^0$$

We obtain:

$$\bar{\sigma}_{ij}^{(pq)}(t) = \int_{-\infty}^t \bar{\Gamma}_{ijkl}(t-s)\bar{\varepsilon}_{kl}^{(pq)}\delta(s)ds$$

$$\bar{\varepsilon}^{(kl)} = \frac{1}{2}\bar{\varepsilon}_0 (\mathbf{e}_k \otimes \mathbf{e}_l + \mathbf{e}_l \otimes \mathbf{e}_k)$$

Using the property:

$$\int_{-\infty}^t f(t-s)\delta(s)ds = f(t)$$

We obtain:

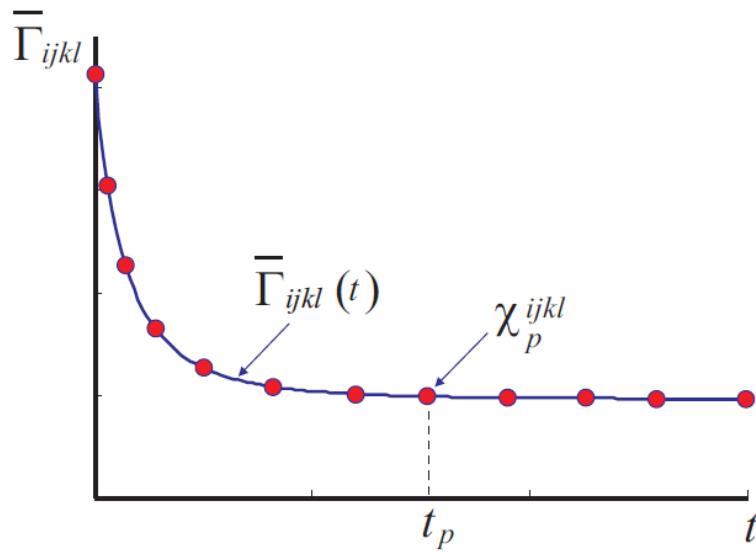
$$\bar{\Gamma}_{ijkl}(t) = \frac{\bar{\sigma}_{ij}^{(kl)}(t)}{\bar{\varepsilon}_0} = \frac{\langle \sigma_{ij}^{(kl)}(\mathbf{x}, t) \rangle}{\bar{\varepsilon}_0},$$

Conclusion :

**Requires solving 3 time-dependent problems on the RVE in 2D and 6 in 3D**

# Discrete representation of the macroscopic relaxation tensor

Sampling of the Effective relaxation tensor in time



Continuous representation for the macroscopic algorithm: interpolation

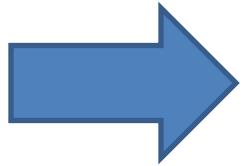
$$\bar{\Gamma}_{ijkl}(t) \simeq \sum_{p=1}^M \phi_p^{ijkl}(t) \chi_p^{ijkl} \quad \bar{\Gamma}_{ijkl}(t_p) \equiv \chi_p^{ijkl}$$

# Implicit algorithm for the macroscopic scale

Implicit time-stepping

$$\begin{aligned}\bar{\sigma}_{ij}^{n+1} &= \int_0^{t^{n+1}} \bar{\Gamma}_{ijkl}(t^{n+1} - s) \frac{d\bar{\varepsilon}_{kl}(s)}{ds} ds + \bar{\Gamma}_{ijkl}(t^{n+1}) \bar{\varepsilon}_{kl}^{(0)} \\ &= \sum_{m=0}^n \int_{t^m}^{t^{m+1}} \bar{\Gamma}_{ijkl}(t^{n+1} - s) \frac{d\bar{\varepsilon}_{kl}(s)}{ds} ds + \bar{\Gamma}_{ijkl}(t^{n+1}) \bar{\varepsilon}_{kl}^{(0)}\end{aligned}$$

$$\frac{d\bar{\varepsilon}_{kl}(t)}{dt} \simeq \frac{\bar{\varepsilon}_{kl}^{m+1} - \bar{\varepsilon}_{kl}^m}{\bar{\Delta}t}$$



$$\bar{\sigma}_{ij}^{n+1} = \sum_{m=0}^n \left\{ \left( \frac{\bar{\varepsilon}_{kl}^{m+1} - \bar{\varepsilon}_{kl}^m}{\Delta t} \right) \int_{t^m}^{t^{m+1}} \bar{\Gamma}_{ijkl}(t^{n+1} - s) ds \right\} + \bar{\Gamma}_{ijkl}(t^{n+1}) \bar{\varepsilon}_{kl}^{(0)}$$

$$= \sum_{m=0}^n (\bar{\varepsilon}_{kl}^{m+1} - \bar{\varepsilon}_{kl}^m) A_{ijkl}^{(m,m+1)}(t^{n+1}) + \bar{\Gamma}_{ijkl}(t^{n+1}) \bar{\varepsilon}_{kl}^{(0)}, \quad (1)$$

$$A_{ijkl}^{(m,m+1)}(t^{n+1}) = \frac{1}{\bar{\Delta}t} \int_{t^m}^{t^{m+1}} \bar{\Gamma}_{ijkl}(t^{n+1} - s) ds$$

$$= \frac{1}{\bar{\Delta}t} \sum_{p=1}^M \chi_p^{ijkl} \int_{t^m}^{t^{m+1}} \boxed{\phi_p^{ijkl}(t^{n+1} - s)} ds.$$

Interpolation functions

Can be expressed in closed-form

Discrete system at time  $t^{n+1}$

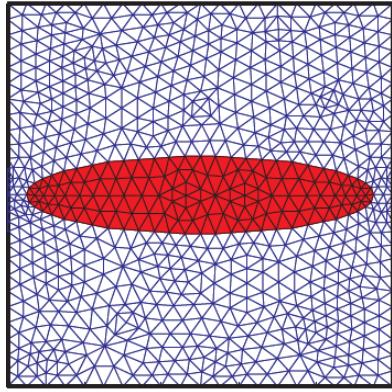
$$\bar{\mathbf{K}}^{n+1} \bar{\mathbf{u}}^{n+1} = \bar{\mathbf{f}}_{ext} - \bar{\mathbf{f}}_V^{n+1}$$

$$\bar{\mathbf{K}}^{n+1} = \int_{\Omega} \mathbf{B}^T [\mathbf{A}]^{(n,n+1)} \mathbf{B} d\Omega$$

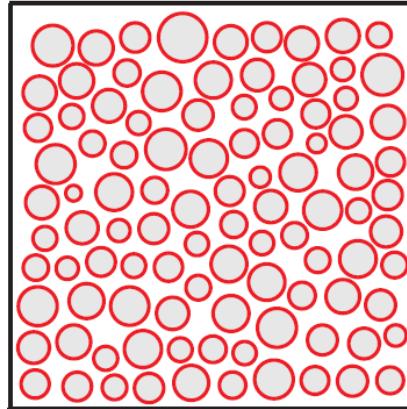
$$\bar{\mathbf{f}}_V^{n+1} = \sum_{m=0}^{n-1} \int_{\Omega} \mathbf{B}^T [\mathbf{A}^{(m,m+1)}(t^{n+1})] ([\bar{\varepsilon}^{m+1}] - [\bar{\varepsilon}^m]) d\Omega$$

$$- \int_{\Omega} \mathbf{B}^T [\mathbf{A}^{(n,n+1)}(t^{n+1})] [\bar{\varepsilon}^n] d\Omega + \int_{\Omega} \mathbf{B}^T [\boldsymbol{\Gamma}(t^{n+1})] [\bar{\varepsilon}^{(0)}] d\Omega.$$

# Numerical examples



RVE (a)



RVE (b)

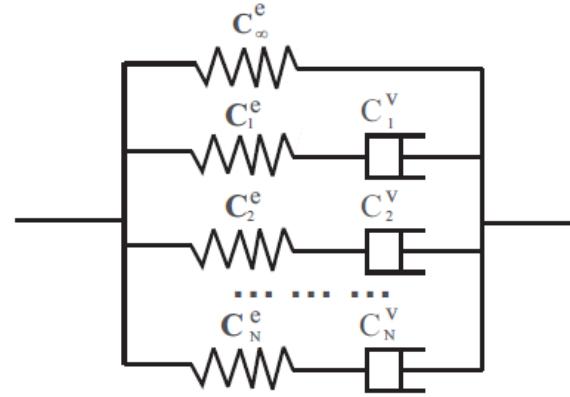


Table 1: Material parameters of viscoelastic phases in RVE of example 4.1.1.

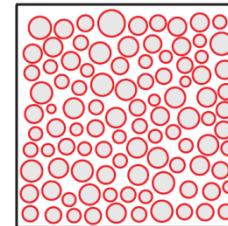
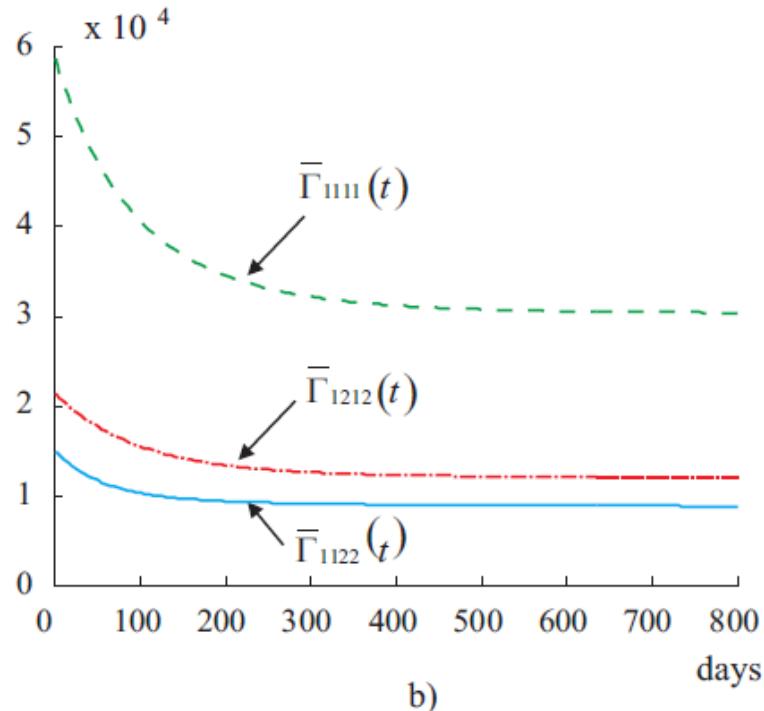
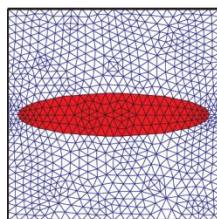
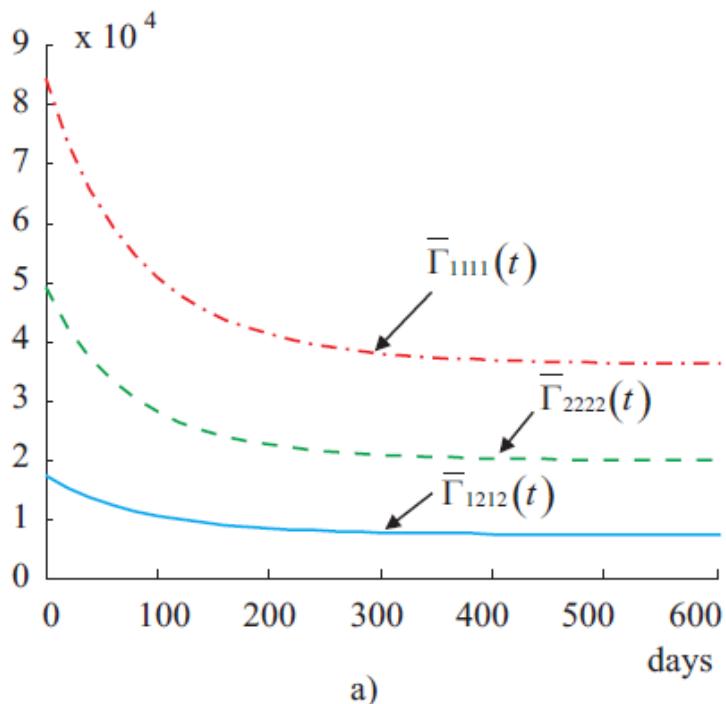
Matrix parameters

$E_{\infty,m}$ (MPa.days)	13909
$\nu_{\infty,m}$	0.256
$E_m^e$ (MPa.days)	231      322      425      630      577
$\nu_m^e$	0.1      0.2      0.3      0.1      0.25
$E_m^v$ (MPa.days)	201200    255500    348900    503000    657700
$\nu_m^v$	0.1      0.2      0.3      0.1      0.25

Inclusion parameters

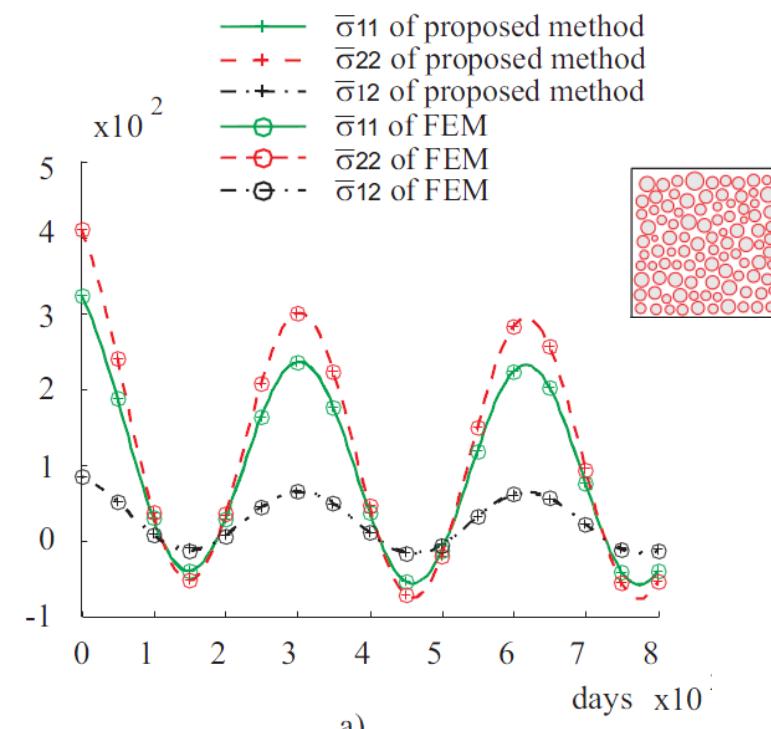
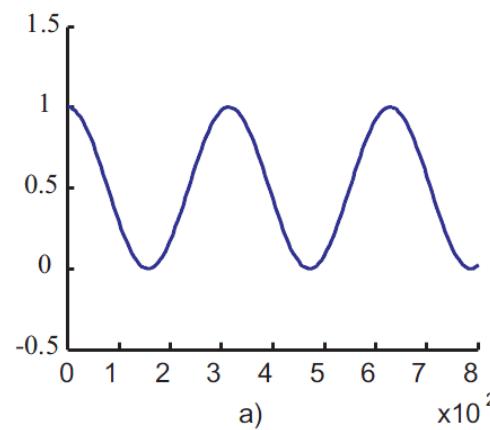
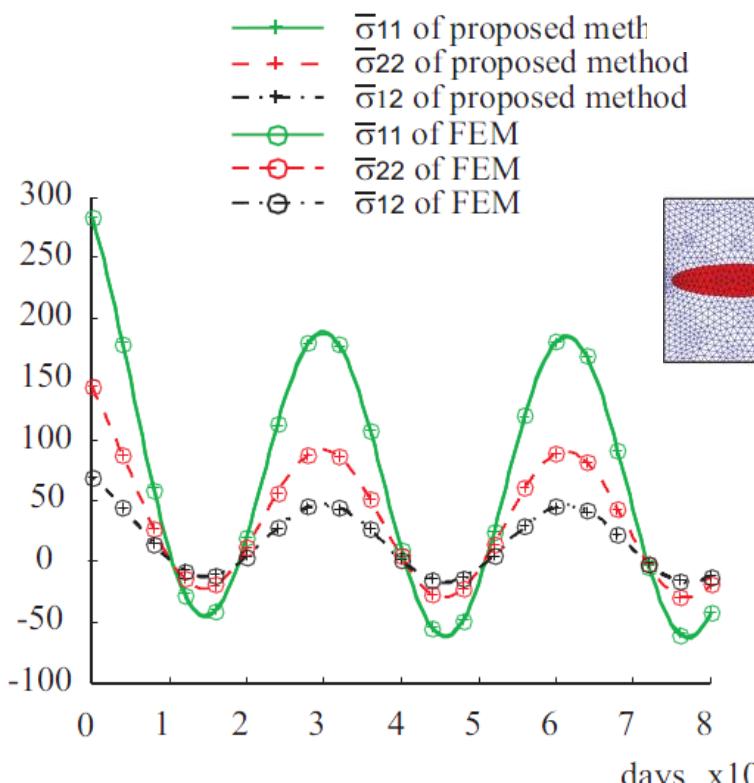
$E_i^e$ (MPa)	2398400
$\nu_i^e$	0.28

# Components of the effective relaxation tensor



# Validation: comparison with direct FEM calculations

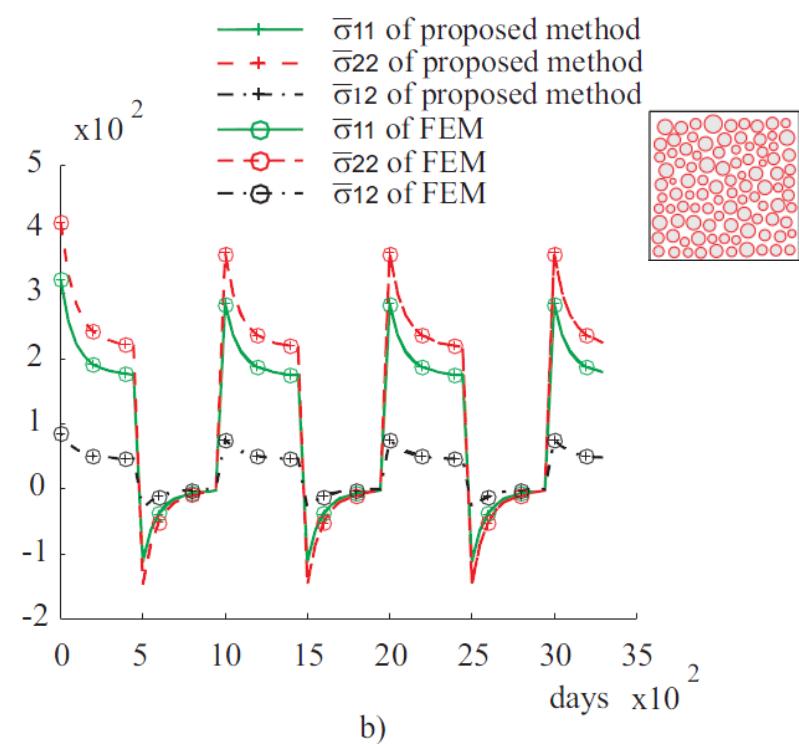
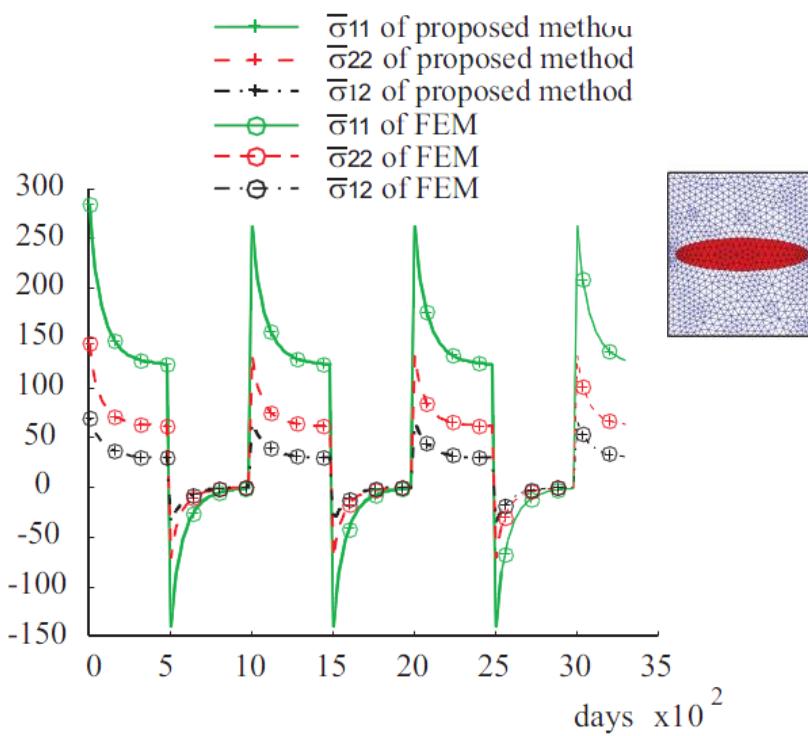
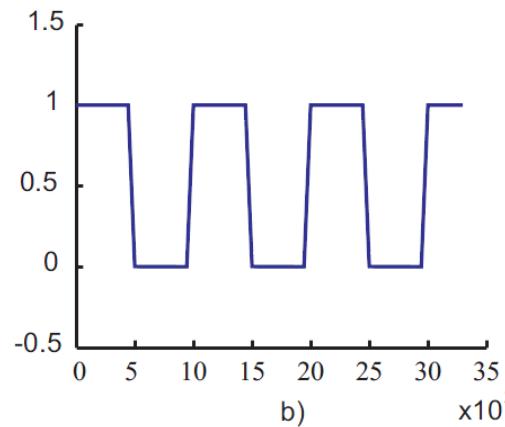
Prescribed macroscopic strains



Macroscopic stress

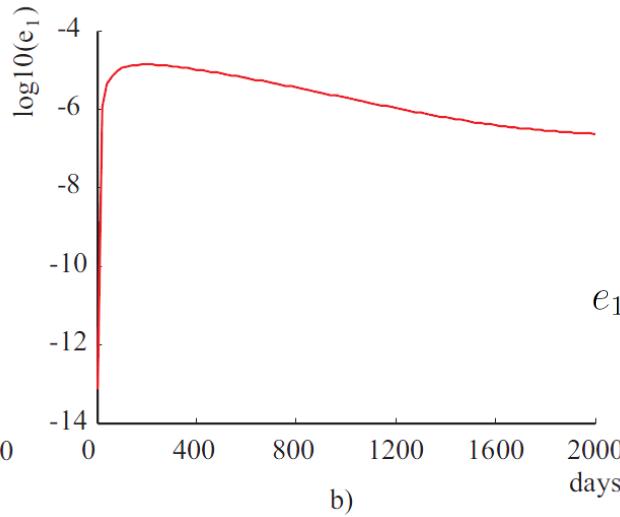
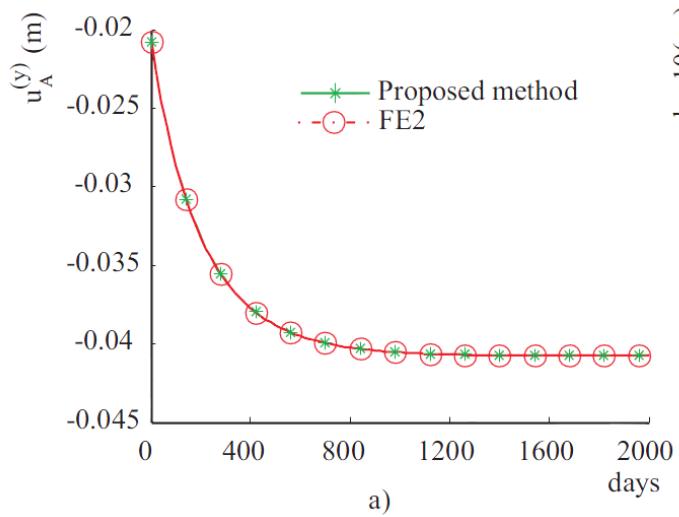
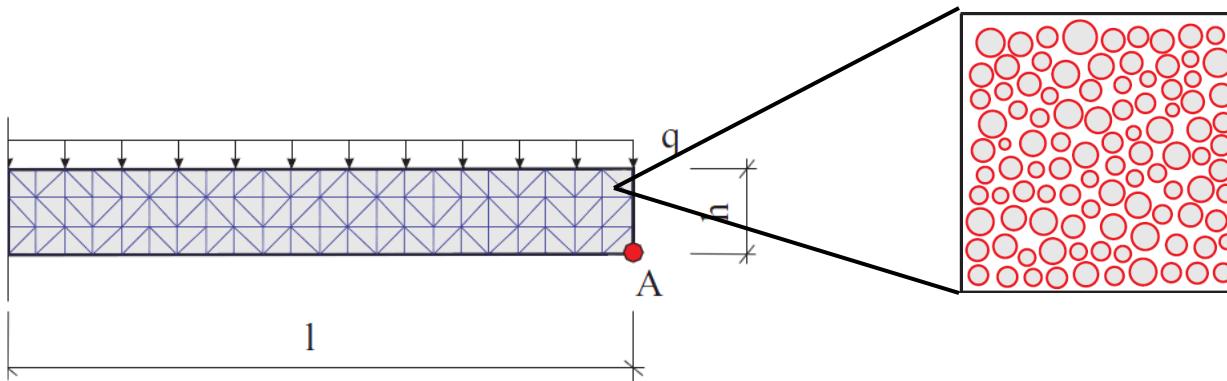
# Validation: comparison with direct FEM calculations

Prescribed macroscopic strains



Macroscopic stress

# Example: structure calculation



$$e_1 = \frac{|u_A^{(y)}(t) - u_{A,FE2}^{(y)}(t)|}{|u_{A,FE2}^{(y)}(t)|}$$

Comparison with a  $FE^2$  calculation

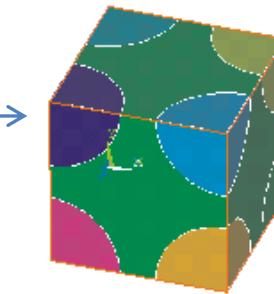
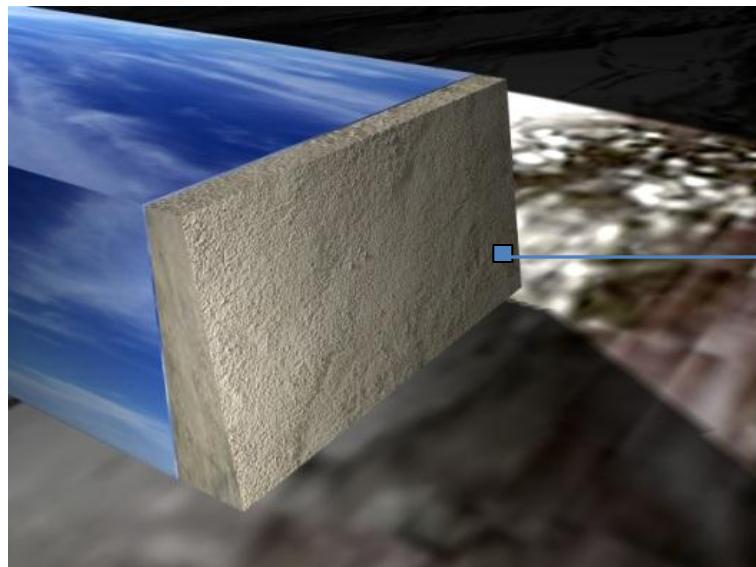
# 3D numerical example: Creep of a dam

## Matrix parameters

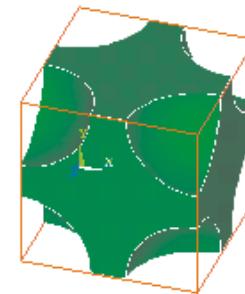
$E_{\infty,m}$ (MPa.days)	13909				
$\nu_{\infty,m}$	0.256				
$E_m^e$ (MPa.days)	6930	9660	12750	18900	17310
$\nu_m^e$	0.1	0.2	0.3	0.1	0.25
$E_m^v$ (MPa.days)	2012000	2555000	3489000	5030000	6577000
$\nu_m^v$	0.1	0.2	0.3	0.1	0.25

## Inclusion parameters

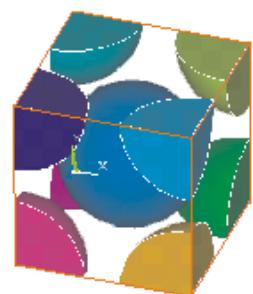
$E_i$ (MPa)	1098400
$\nu_i$	0.28



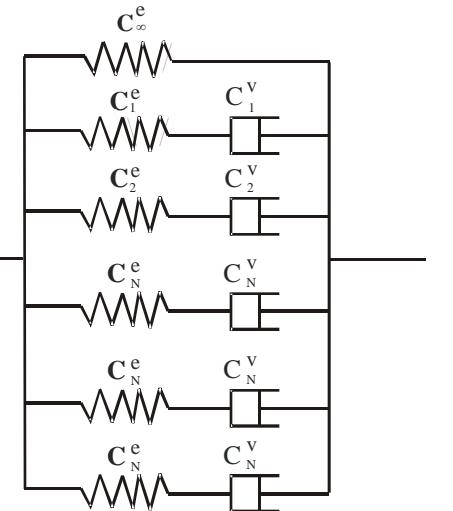
RVE  
R



Matrix

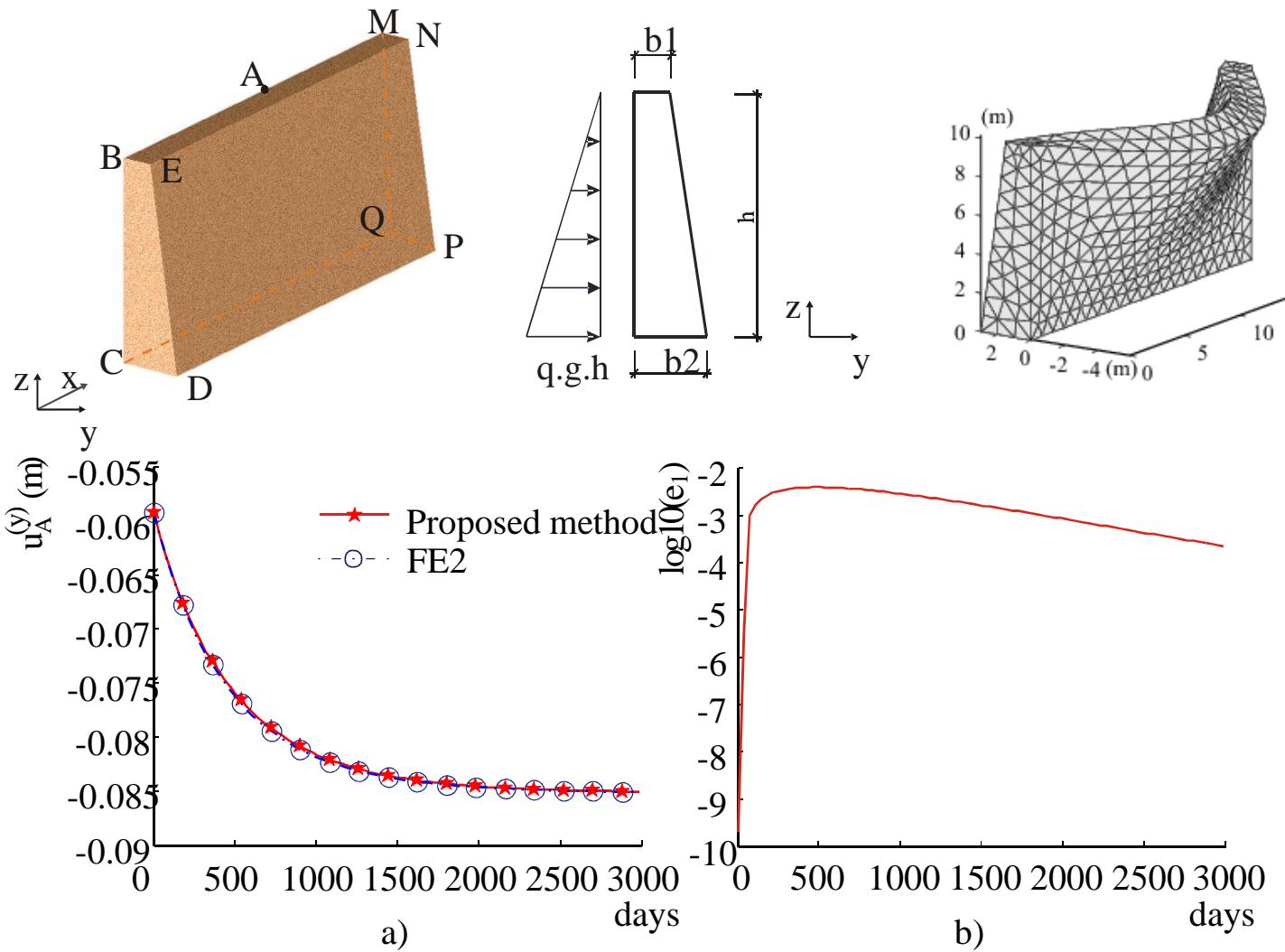


Inclusions

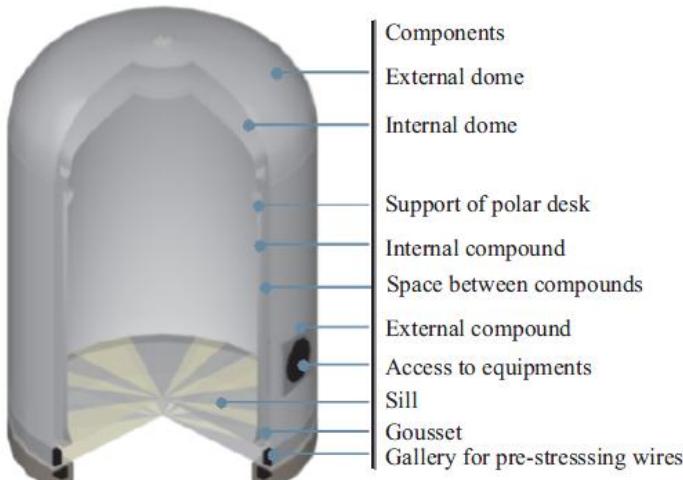


Generalized Maxwell  
model

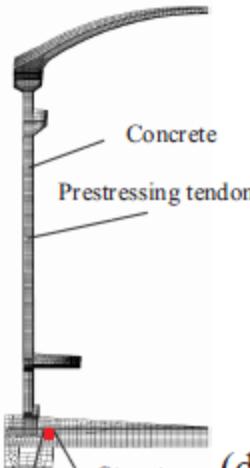
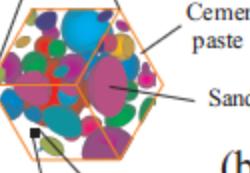
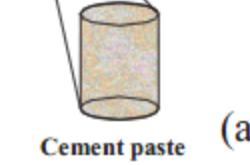
# 3D numerical example: Creep of a dam



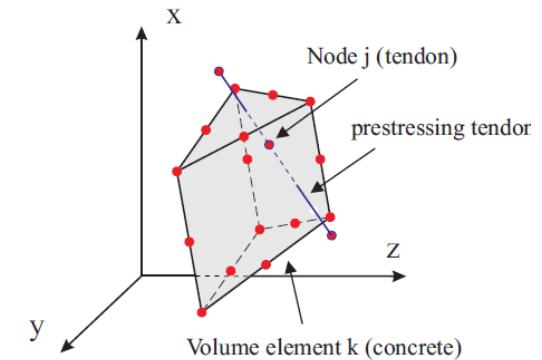
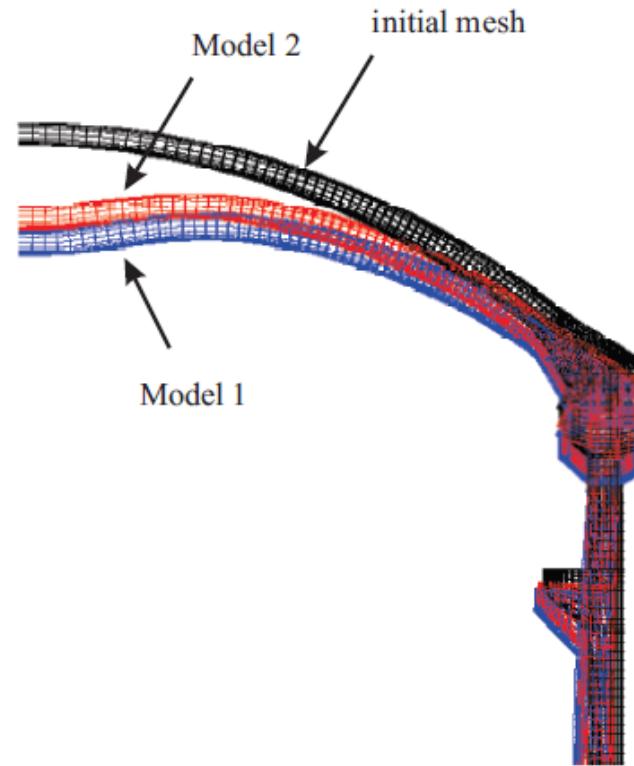
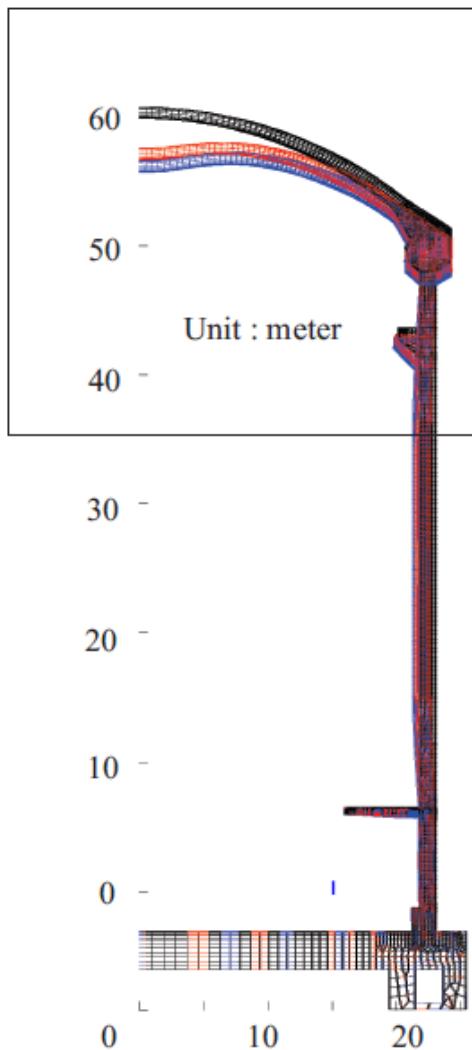
# 4 scales creep analysis of a concrete nuclear containment structure



nuclear reactor REPP1300

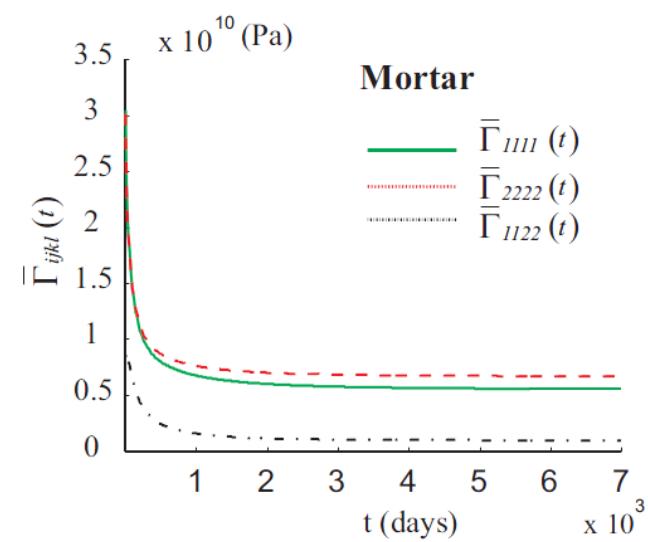
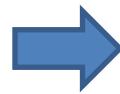
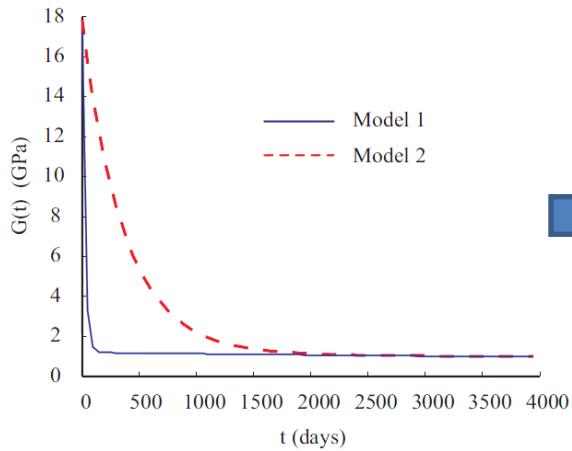
		Constituents and characterization of constitutive laws	Result
Scale 4: structure		Concrete (numerical constitutive law) Tendons (experimental constitutive law)	Response of the structure
Scale 3: concrete		Mortar (numerical constitutive law) Gravels (experimental constitutive law)	Constitutive law of concrete
Scale 2: mortar		Cement paste (experimental constitutive law) Sand (experimental constitutive law)	Constitutive law of mortar
Scale 1: cement paste		Cement paste (experimental constitutive law)	Constitutive law of cement paste

# Structure response



Prestressing  
tendons

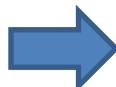
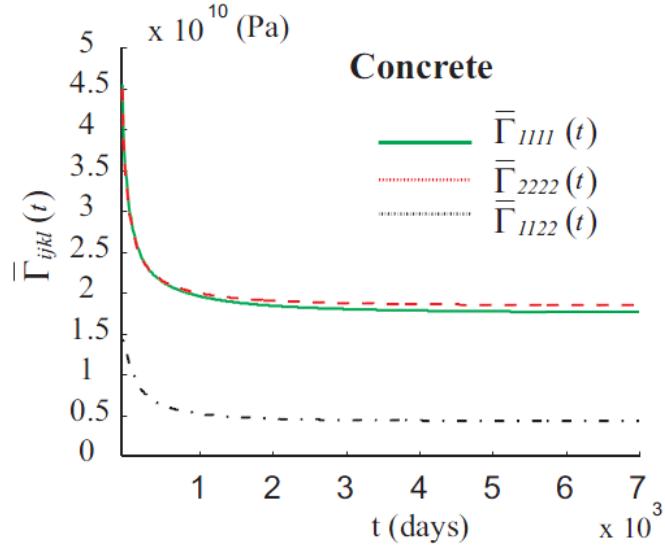
# Relaxation tensors at the different scales



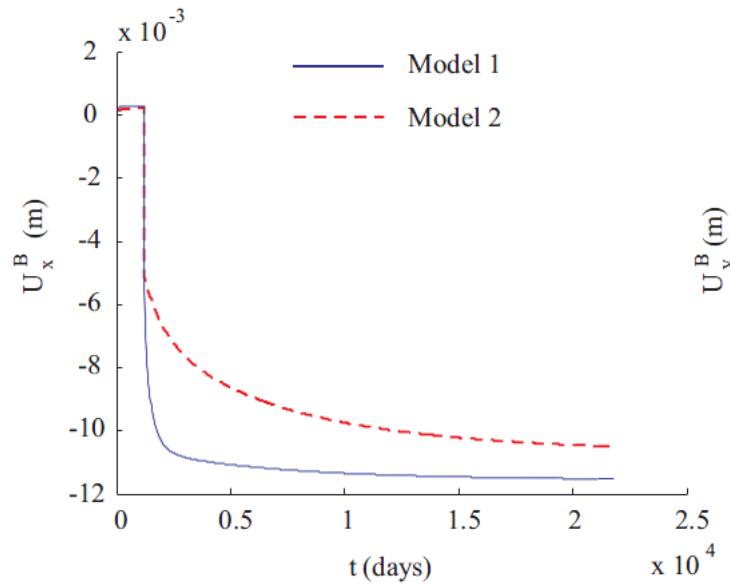
Scale 1 : cement paste (experimental)



Scale 2 : Mortar



Scale 3 : concrete



Scale 4 : structure

# Conclusions

- New computational homogenization method for linear viscoelastic materials
  - No Laplace transform
  - Only involves 3(6) simulations on a 2D (3D) RVE
  - Highly accurate
  - Fast as compared to FE<sup>2</sup> computation (reduction by 100 of CPU times on small meshes)
  - Sequential approach: Allows handling more than 2 scales

Limitations: linear viscoelasticity

[A. B. Tran, J. Yvonnet, Q-C. He, C. Toulemonde, J. Sanahuja, A simple computational homogenization method for structures made of heterogeneous linear viscoelastic materials, CMAME 2011]

[A. B. Tran, J. Yvonnet, Q-C. He, C. Toulemonde, J. Sanahuja, A four scales-creep analysis of a nuclear containment structure, Nuclear Engineering and Design, 2014, in press]

# Homogénéisation non linéaire : approches découplées

# Approches découplées : méthode d'interpolations

[Hill J.M.P.S 1963]

Définition des contraintes et du tenseur élastique tangent effectifs à partir d'un potentiel macroscopique

$$\bar{\sigma} = \frac{\partial \bar{w}(\bar{\epsilon})}{\partial \bar{\epsilon}}$$

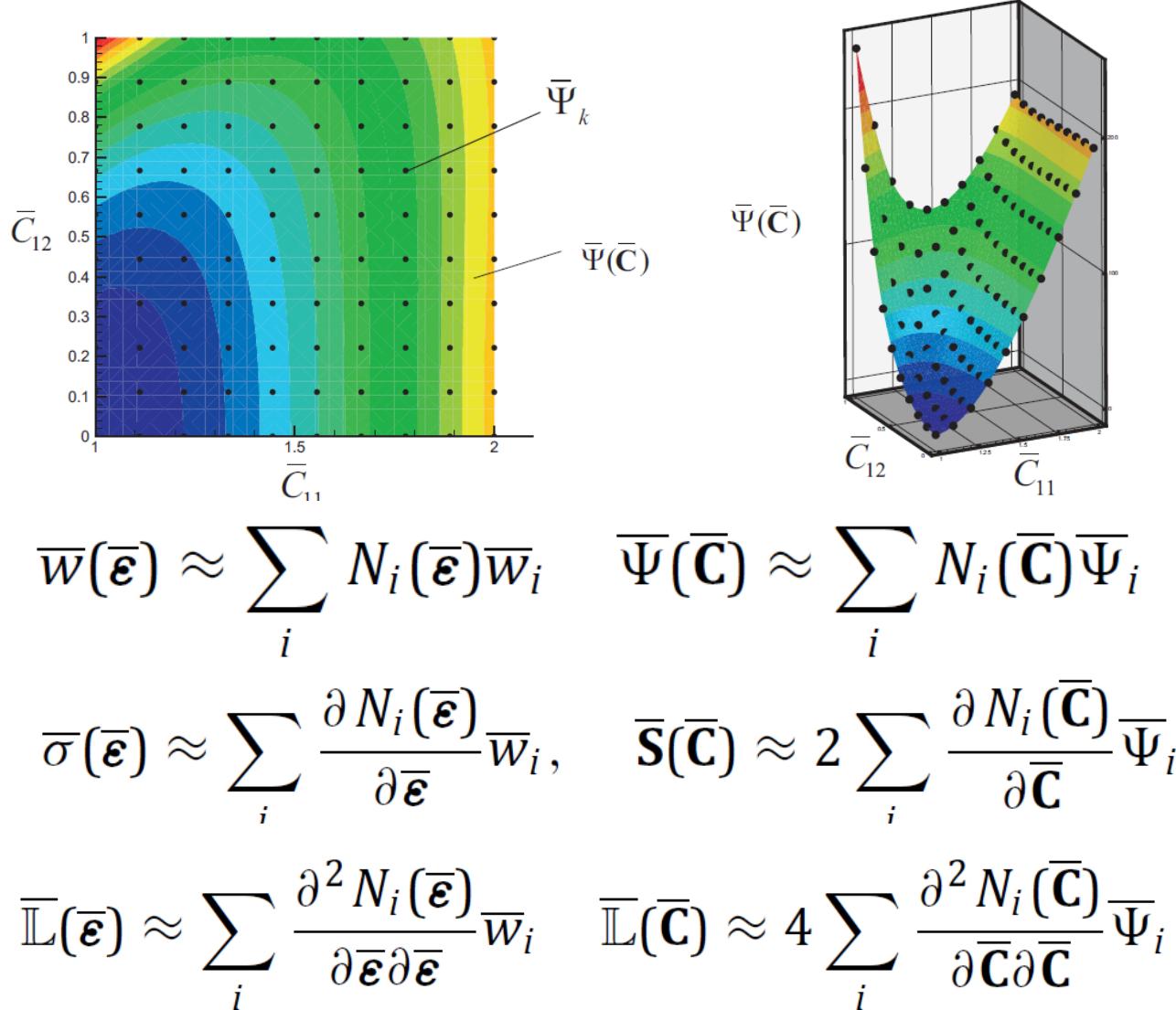
$$\bar{w}(\bar{\epsilon}) = \inf_{\mathbf{v} \in \mathcal{K}(\bar{\epsilon})} \langle w(\mathbf{x}, \boldsymbol{\epsilon}(\mathbf{v})) \rangle$$

$$\bar{\mathbf{s}} = 2 \frac{\partial \bar{\Psi}(\bar{\mathbf{C}})}{\partial \bar{\mathbf{C}}}$$

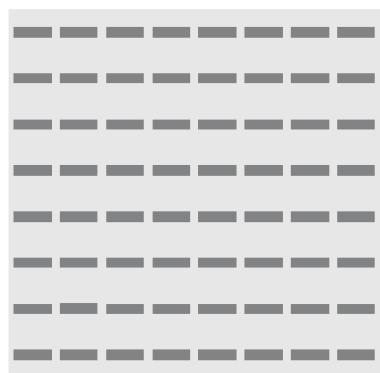
$$\bar{\Psi}(\bar{\mathbf{C}}) = \inf_{\mathbf{C} \in \mathcal{K}(\bar{\mathbf{C}})} \langle \Psi(\mathbf{X}, \mathbf{C}) \rangle = \inf_{\mathbf{C} \in \mathcal{K}(\bar{\mathbf{C}})} \sum_{r=1}^N c^{(r)} \langle \Psi^{(r)}(\mathbf{C}) \rangle_r$$

$$\bar{\mathbb{L}} = 4 \frac{\partial^2 \bar{\Psi}(\bar{\mathbf{C}})}{\partial \bar{\mathbf{C}}^2}$$

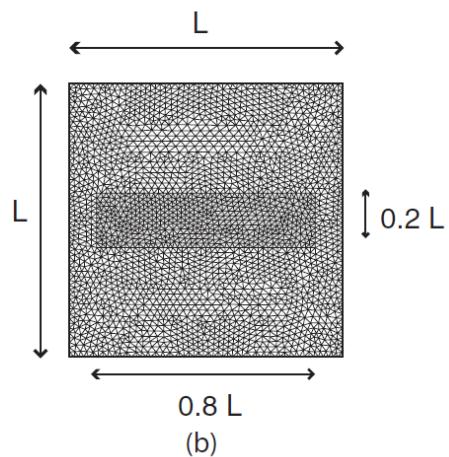
Approches découplées utilisant des interpolations : méthode de potentiels numériques [JY, Gonzalez, He, CMAME 2008, JY and HE, EJCM 2010], [JY, Monteiro, He, IJMCE in press], [Clément, Soize, JY, CMAME 2012, IJNME 2013]



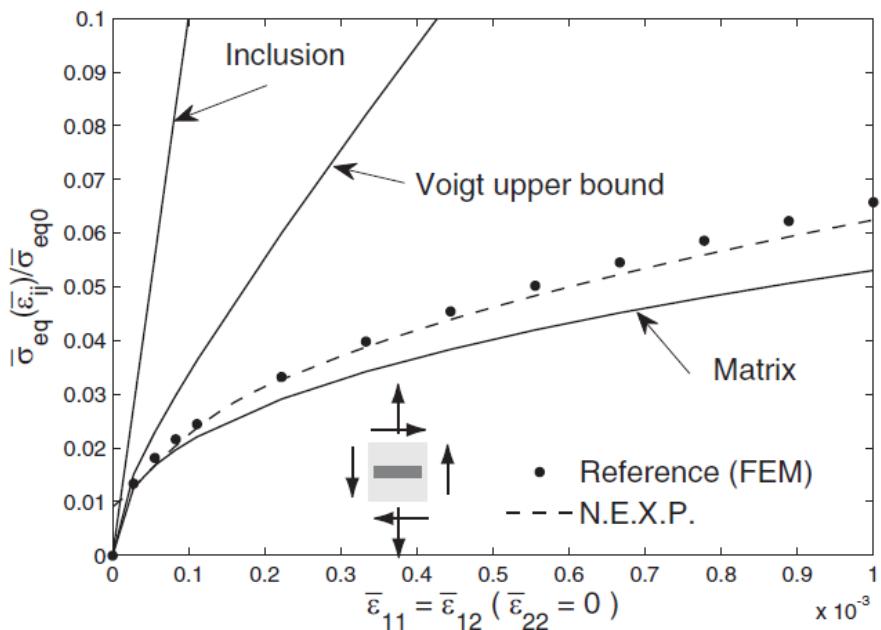
# Petites déformations non linéaires



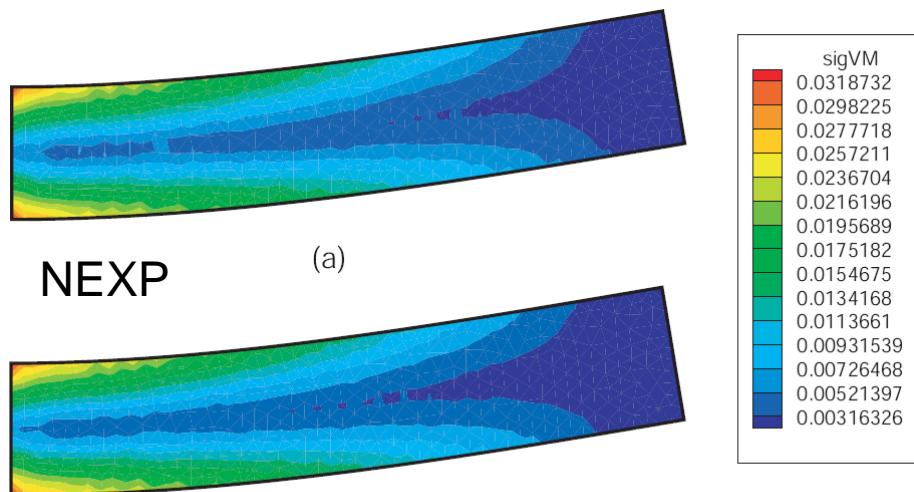
(a)



(b)

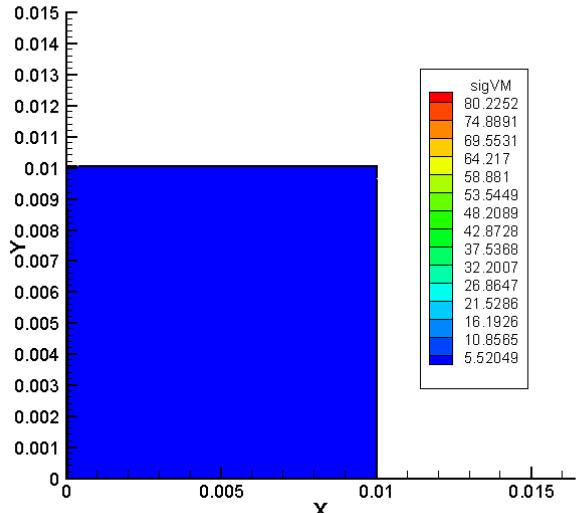


## Calcul de structure

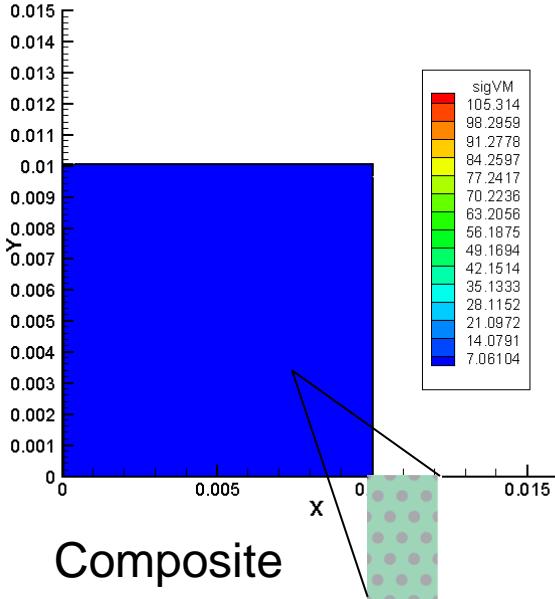


von Mises stress field

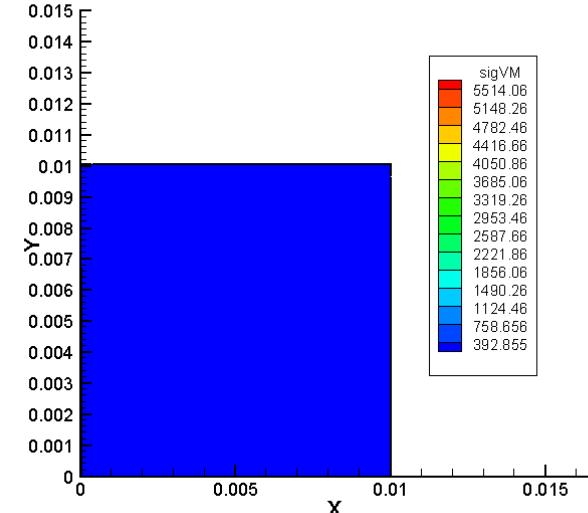
# Grandes déformations non linéaires



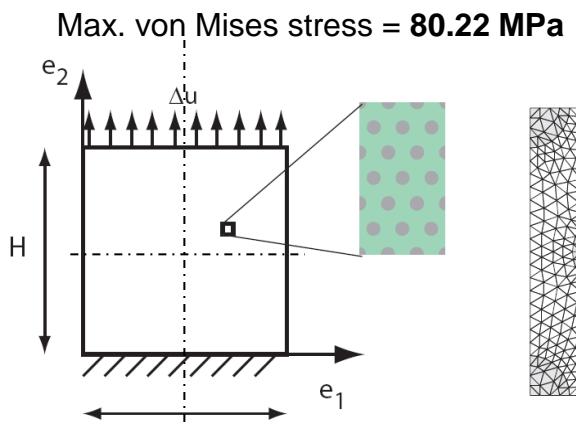
Matrix



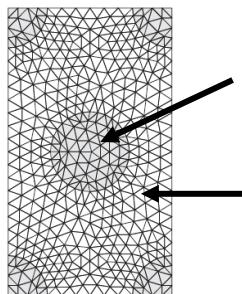
Composite



Inclusion



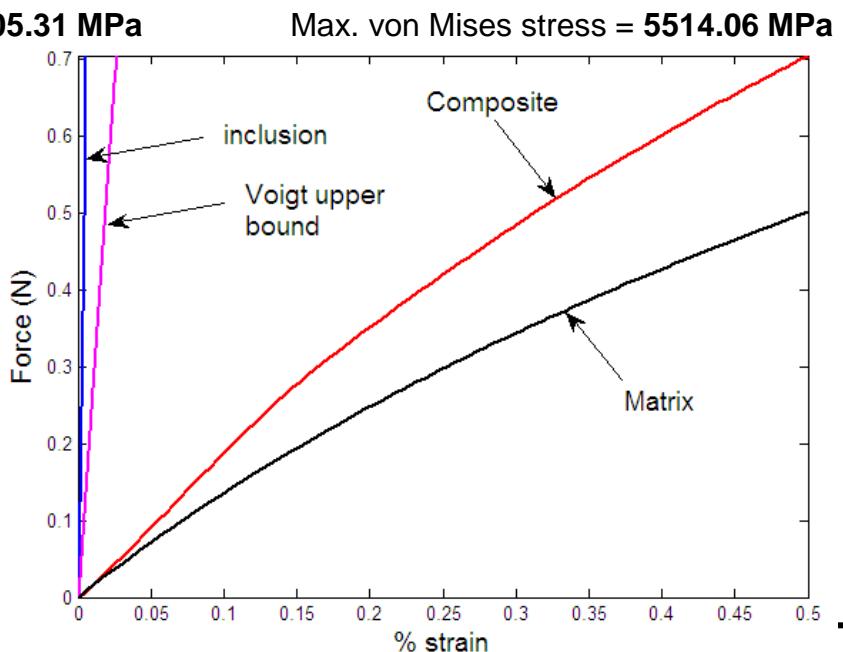
Max. von Mises stress = **105.31 MPa**



**50%**  
stretching

Elastic,  
stiff  
  
Compressible  
Mooney-  
Rivlin, soft

[JY He EJCM 2010, JY, Monteiro and He, IJMCE 2012]



## II. Passage échelle atomique/échelle continue

# Sommaire

- 1) Dynamique Moléculaire**
- 2) Méthodes ab initio**
- 3) Calcul de propriétés volumiques à partir de calculs atomistiques**
- 4) Modélisation des effets nanométriques dans le cadre de la mécanique des milieux continus**
- 5) Calcul des coefficients de surfaces par calculs atomistiques**
- 6) Exemples numériques (contributions)**

# Modélisations atomistiques : vocabulaire

Dynamique moléculaire

Statique moléculaire

Calculs ab initio

Calculs de type «Premier principe»

Dynamique moléculaire quantique

Calculs atomistiques...

# Dynamique moléculaire

# Dynamique moléculaire

Énergie potentielle d'un système de  $N$  particules de coordonnées  $\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N$

$$U = U(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$$

Force induite par le potentiel  $U$

$$\mathbf{F}_i = -\frac{dU}{d\mathbf{r}_i}$$

L'énergie dépend des positions seulement (pas des vitesses)

Seconde loi de Newton

$$m_i \ddot{\mathbf{r}}_i = -\nabla_i U + \mathbf{F}_i, \quad i = 1, 2, \dots, N$$



Force non conservatives ou forces extérieures exercées sur une particule  $i$



## 1.2. Echelle nanométriques/atomique

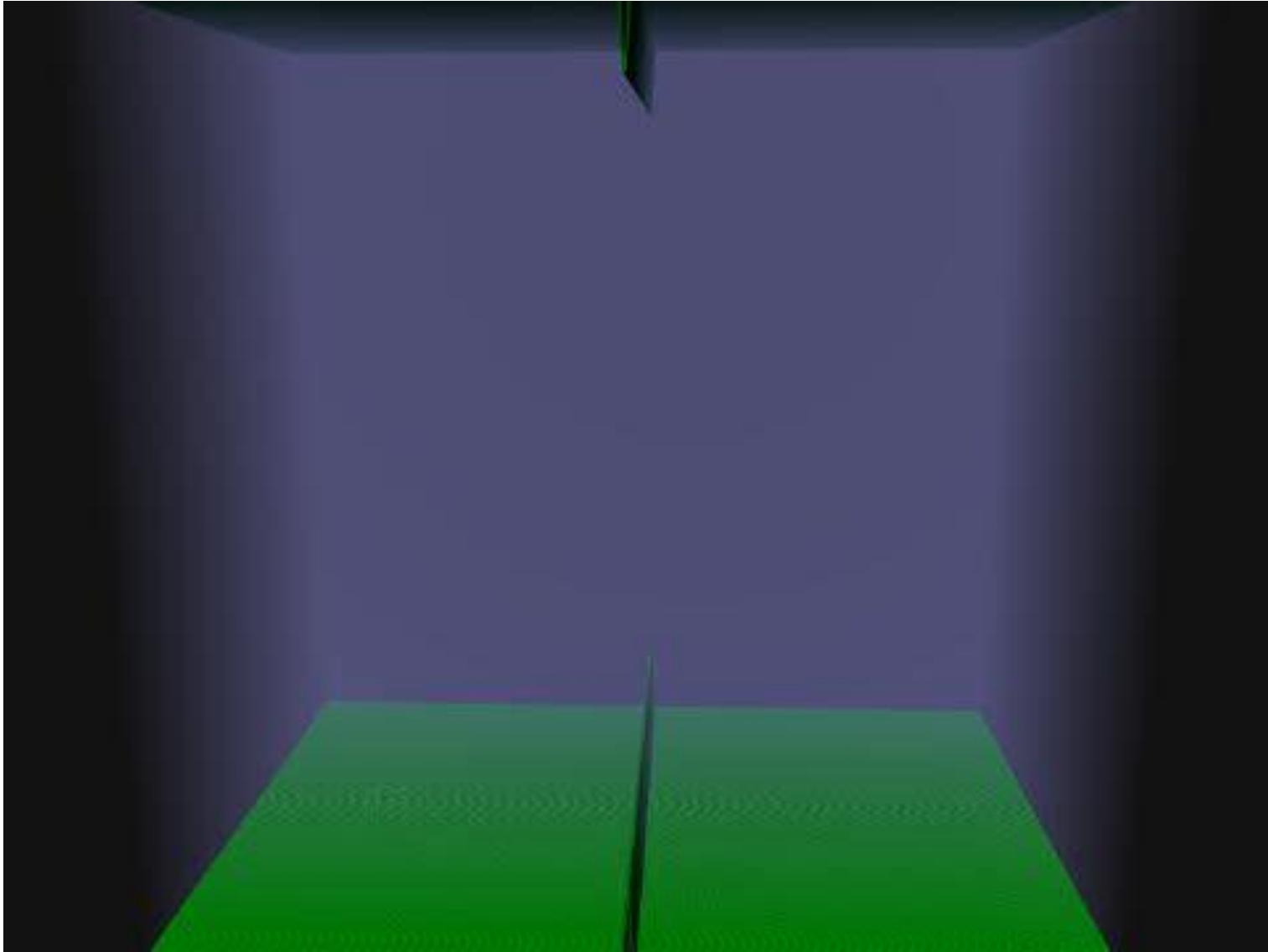
### Dynamique moléculaire

#### 3 objectifs principaux de la DM

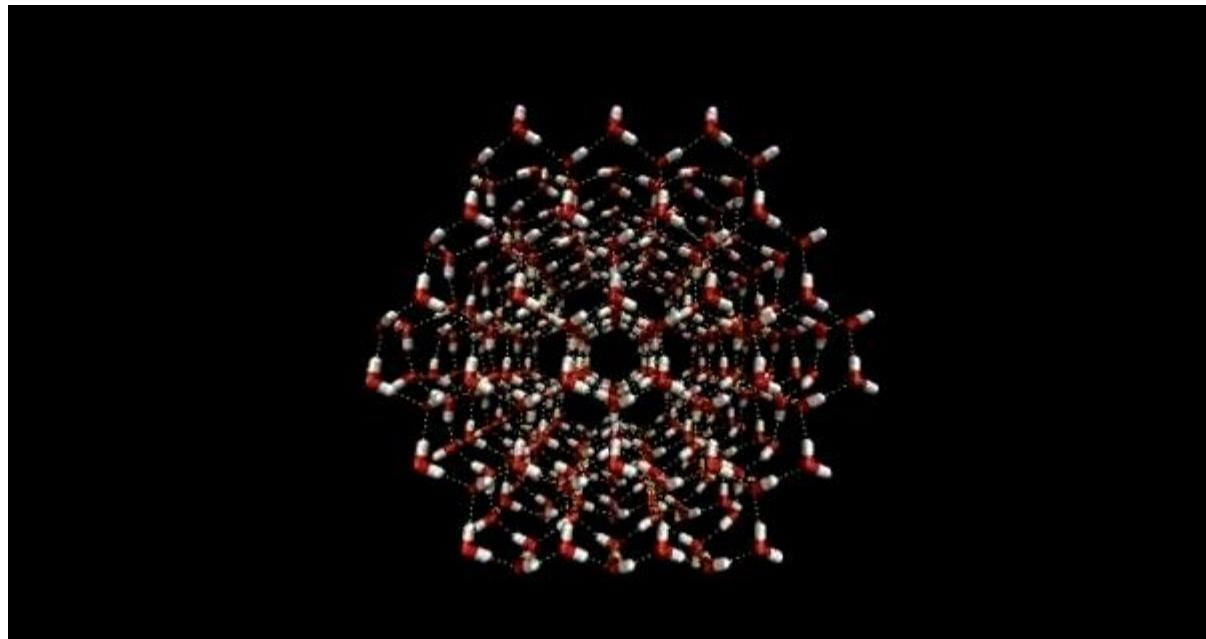
- Réaliser des moyennes sur des ensembles (thermodynamique) pour calculer des paramètres macroscopiques
- Simuler l'évolution de systèmes atomiques pour mieux comprendre certains mécanismes (fissuration, dislocation, changement de phase...)
- Déterminer l'état d'équilibre de structures moléculaires complexes (optimisation)

### Limitations

- Echelles temporelles (pas de temps de l'ordre de  $10^{-15}$  s !!)
- Echelles spatiales ( $1 \mu\text{m}^3$ ) de métal contient  $\sim 10^{12}$  atomes !!
- Choix des potentiels, les potentiels ne peuvent reproduire les réactions chimiques



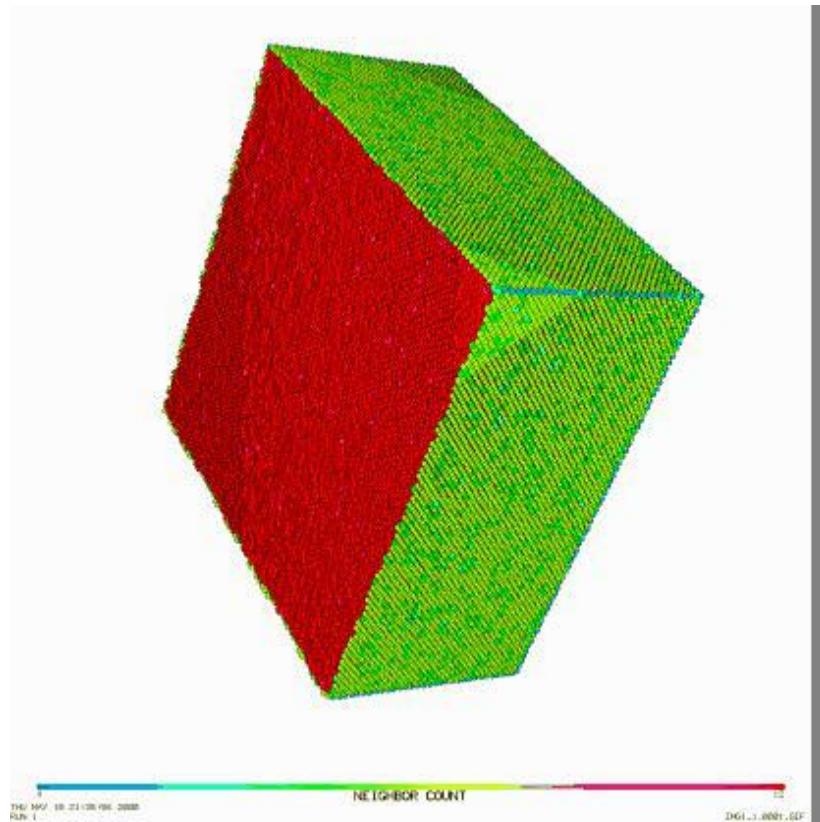
Propagation de dislocations: simulation avec  
plusieurs milliards d'atomes



Simulation du changement de phase glace/eau



Fissuration



Transformations  
structurales dues à un  
changement de phase  
martensitique

## 1.2. Echelle nanométriques/atomique

### Dynamique moléculaire

Système dissipatif

$$m_i \ddot{\mathbf{r}}_i = -\nabla_i U - m_i \gamma_i \dot{\mathbf{r}}_i, \quad i = 1, 2, \dots, N$$

↳ Constante d'amortissement

**Extension : effet dus au mouvement Brownien**

$$m_i \ddot{\mathbf{r}}_i = -\nabla_i U - m_i \gamma_i \dot{\mathbf{r}}_i + \mathbf{R}_i(t), \quad i = 1, 2, \dots, N$$



Force aléatoire liée à la collision entre la particule i et d'éventuelles molécules du solvant

## 1.2. Echelle nanométriques/atomique

### Dynamique moléculaire

#### Équation de Langevin

$$m_i \ddot{\mathbf{r}}_i = -\nabla_i U - m_i \gamma_i \dot{\mathbf{r}}_i + \mathbf{R}_i(t), \quad i = 1, 2, \dots, N$$

$$\lim_{t \rightarrow \infty} \frac{1}{t} \int_0^t \mathbf{R}(\tau) d\tau = 0 \longrightarrow$$

Les forces dues au mouvement Brownien n'impliquent pas de directions préférentielles

$$\lim_{t \rightarrow \infty} \frac{1}{t} \int_0^t \mathbf{R}_i(\tau) \cdot \mathbf{R}_{i'}(t_0 + \tau) d\tau = a \delta(t_0) \delta_{ii'}$$

La force exercée par la particule  $i$  n'est pas corrélée avec la force exercée sur une autre particule  $i'$

## 1.2. Echelle nanométriques/atomique

### Dynamique moléculaire

#### Potentiels

Structure générale :

$$U(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \sum_i V_1(\mathbf{r}_i) + \sum_{i,j>i} V_2(\mathbf{r}_i, \mathbf{r}_j) + \sum_{i,j>i,k>j} V_3(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k) + \dots$$

Champ extérieur ex :  $V(\mathbf{r}) = mgx$ ,  
champ de gravité

Potentiel par paires d'atomes

Interactions multiples entre atomes

## 1.2. Echelle nanométriques/atomique

Interactions par paires d'atomes

$$V_2(\mathbf{r}_i, \mathbf{r}_j) = V_2(r), \quad r = |\mathbf{r}_{ij}| = |\mathbf{r}_i - \mathbf{r}_j|$$



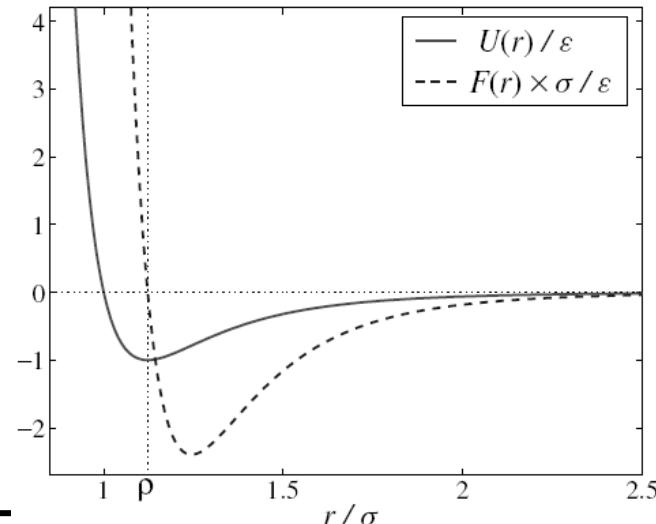
**Interactions à longues distances** : ex: interaction électrostatique de Coulomb

$$V_C(\mathbf{r}_1, \mathbf{r}_2) = V_C(r) = \frac{1}{4\pi\epsilon_0} \frac{e_1 e_2}{r} \quad F_C(r) = -\frac{\partial V(r)}{\partial r} = \frac{1}{4\pi\epsilon_0} \frac{e_1 e_2}{r^2}$$

**Interactions à courtes distances** : ex: Potentiel de Lennard-Jones

$$V_{LJ}(r) = 4\epsilon \left( \frac{\sigma^{12}}{r^{12}} - \frac{\sigma^6}{r^6} \right)$$

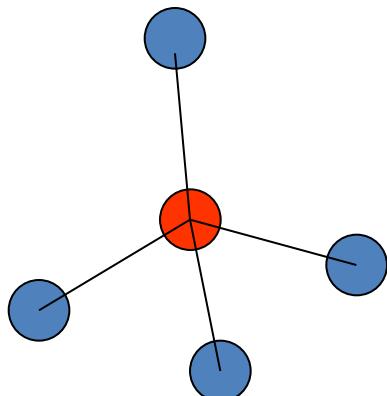
$$F_{LJ}(r) = 24\epsilon \left( \frac{2\sigma^{12}}{r^{13}} - \frac{\sigma^6}{r^7} \right)$$



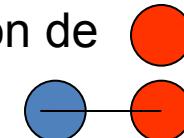
## 1.2. Echelle nanométriques/atomique

### Les défauts principaux des potentiels par paires (Type Lennard-Jones, Morse...)

- Pas de stabilité en cisaillement
- Pas de dépendance à l'angle entre les liaisons
- Les liaisons ne se « voient pas » entre elles



L'énergie de liaison de  
Est 4 fois celle de



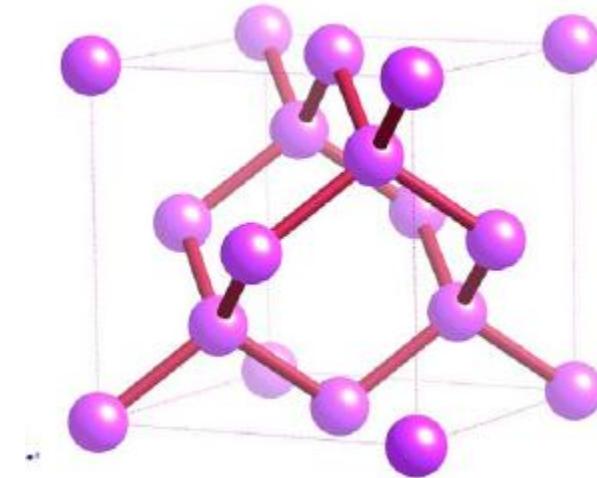
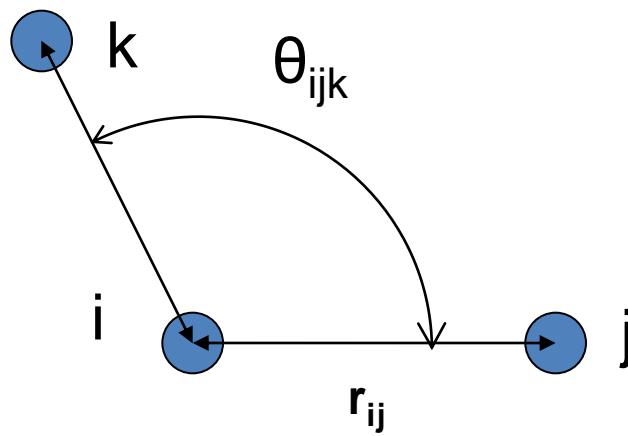
Contradiction avec  
l'expérimentation ET les calculs  
plus précis de mécanique  
quantique !

Dans la réalité, les liaisons deviennent plus « faibles » quand plus d'atomes sont liés à l'atome central

## 1.2. Echelle nanométriques/atomique

Interactions multiples

$$V_3(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k) = V_3(\cos \theta_{ijk})$$



Silcone

Exemple : potentiel de Stillinger Webber pour le Si

$$V_3 = \lambda \exp \left[ \gamma(r_{ij} - a)^{-1} + \gamma(r_{ik} - a)^{-1} \right] \cos \theta_{ijk} + \frac{1}{3}$$
$$V_2 = A \left[ Br^{-p} - r^{-q} \right] \exp \left[ (r - a)^{-1} \right]$$

- Impraticable pour les calculs de DM la complexité de calcul croît avec  $N^3$  ( $N=\text{Nb atomes}$ )
- Ce type de potentiel ne peut décrire toutes les configurations [Biswas and Hamann, 1985, 1987], [Tersoff (1988)]
- Prendre en compte des interactions  $O(N>3)$  entraîne trop de paramètres libres dans les modèles

## 1.2. Echelle nanométriques/atomique

Comment réparer les potentiels par paires ?

Solution : Ecrire l'énergie par atome comme  $E=f(\text{nb de liaisons})$  ou  $f$  est une fonction non-linéaire

Représentation des liaisons métalliques : The Embedded Atom Model (EAM) [Daw 1989], [Daw et al. 1993], [Johnson, 1988]

$$U = \sum_i G_i \left( \sum_{j \neq i} \rho_j^a(r_{ij}) \right) + \sum_{i, j > i} V_C(r_{ij})$$

Chaque atome est incorporé dans un nuage d'électron créé par tous les atomes du voisinage

$G$  : fonction « d'incorporation » de l'atome  $i$

$\rho_j^a$  : densité moyenne d'électrons pour un atome  $j$

## 1.2. Echelle nanométriques/atomique

### Dynamique moléculaire : mise en œuvre numérique

#### Etapes:

- 1) Initialiser les positions et les vitesses des particules
- 2) Intégrer : calculer les forces, déterminer les nouvelles positions
- 3) Équilibrer : laisser le système atteindre une position d'équilibre
- 4) Moyenner les quantités désirées

#### **1) Initialisation :**

EDP du second ordre : des C.L. sont nécessaires sur les positions et les vitesses initiales

Positions : Raisonnables avec la structure à étudier : éviter les faibles distances entre atomes

Vitesses : nulles ou très faibles, puis imposer la température par méthodes de thermostats

## 1.2. Echelle nanométriques/atomique

### Dynamique moléculaire : mise en œuvre numérique

#### Intégration

- Schéma de Verlet, leap-frog, velocity Verlet, Gear predictor-corrector...
- Imposition de la température par un thermostat
  - Stochastique (Langevin)
  - Contrainte (Velocity rescaling)
  - Système étendu (Nose-Hoover)

#### Un intégrateur simple : Schéma de Verlet

$$\mathbf{r}(t + \Delta t) = \mathbf{r}(t) + \mathbf{v}(t)\Delta t + (1/2)\mathbf{a}(t)\Delta t^2 + (1/6)\mathbf{b}(t)\Delta t^3 + O(\Delta t^4)$$

$$+ \frac{\mathbf{r}(t - \Delta t) = \mathbf{r}(t) - \mathbf{v}(t)\Delta t + (1/2)\mathbf{a}(t)\Delta t^2 - (1/6)\mathbf{b}(t)\Delta t^3 + O(\Delta t^4)}{=}$$

$$= \mathbf{r}(t + \Delta t) = 2\mathbf{r}(t) - \mathbf{r}(t - \Delta t) + \mathbf{a}(t)\Delta t^2 + O(\Delta t^4)$$

$$- \mathbf{a}(t) = -(1/m)\nabla V(\mathbf{r}(t)) \qquad \qquad \mathbf{v}(t) = \frac{\mathbf{r}(t + \Delta t) - \mathbf{r}(t - \Delta t)}{2\Delta t} -$$

## 1.2. Echelle nanométriques/atomique

### Dynamique moléculaire : mise en œuvre numérique

#### Algorithme

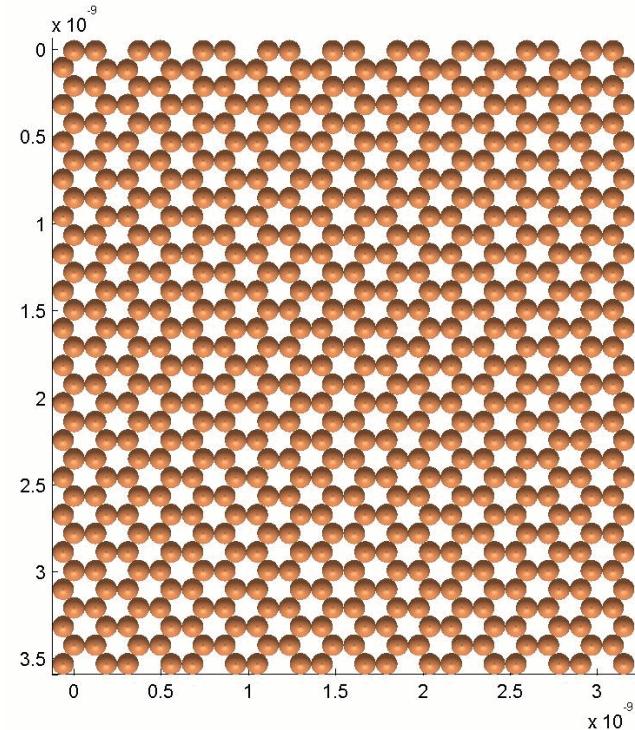
1) Initialiser  $v^0, r^0$

→ 2) Calculer  $V(r_1^n, r_2^n, \dots, r_s^n)$

Calculer  $F^n = -\nabla V$

Calculer  $a^n = F^n/m$

3) Actualiser  $r^{n+1} = 2r^n - r^{n-1} + a^n \Delta t$

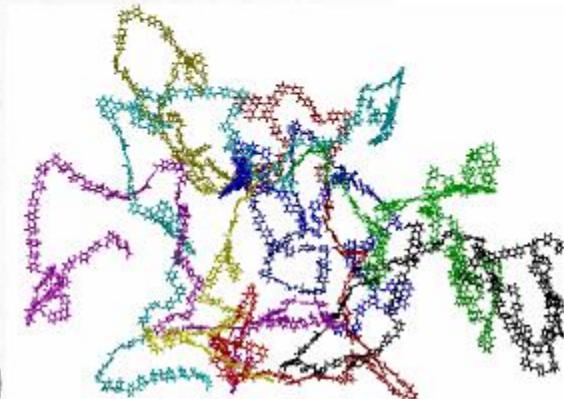


## 1.2. Echelle nanométriques/atomique

Conclusion : la plus grosse difficulté pour mettre en œuvre la Dynamique Moléculaire : Bien choisir les potentiels !

$$\mathcal{U} = \sum_{chains} \left\{ \sum_{ijk} \mathcal{U}_{valence,ijk} + \sum_{ijkl} \mathcal{U}_{torsion,ijkl} + \sum_{ijkl} \mathcal{U}_{improper\ torsion,ijkl} + \frac{1}{2} \sum_{ij} \mathcal{U}_{vdW,ij} + \frac{1}{2} \sum_{ij} \mathcal{U}_{Coulomb,ij} \right\}$$

where



$$\mathcal{U}_{valence,ijk} = \frac{1}{2} k_v (\theta_{ijk} - \theta_{ijk,0})$$

$$\mathcal{U}_{torsion,ijkl} = \sum_{m=1}^4 H_m \phi (1 - \cos(m\phi_{ijkl}))$$

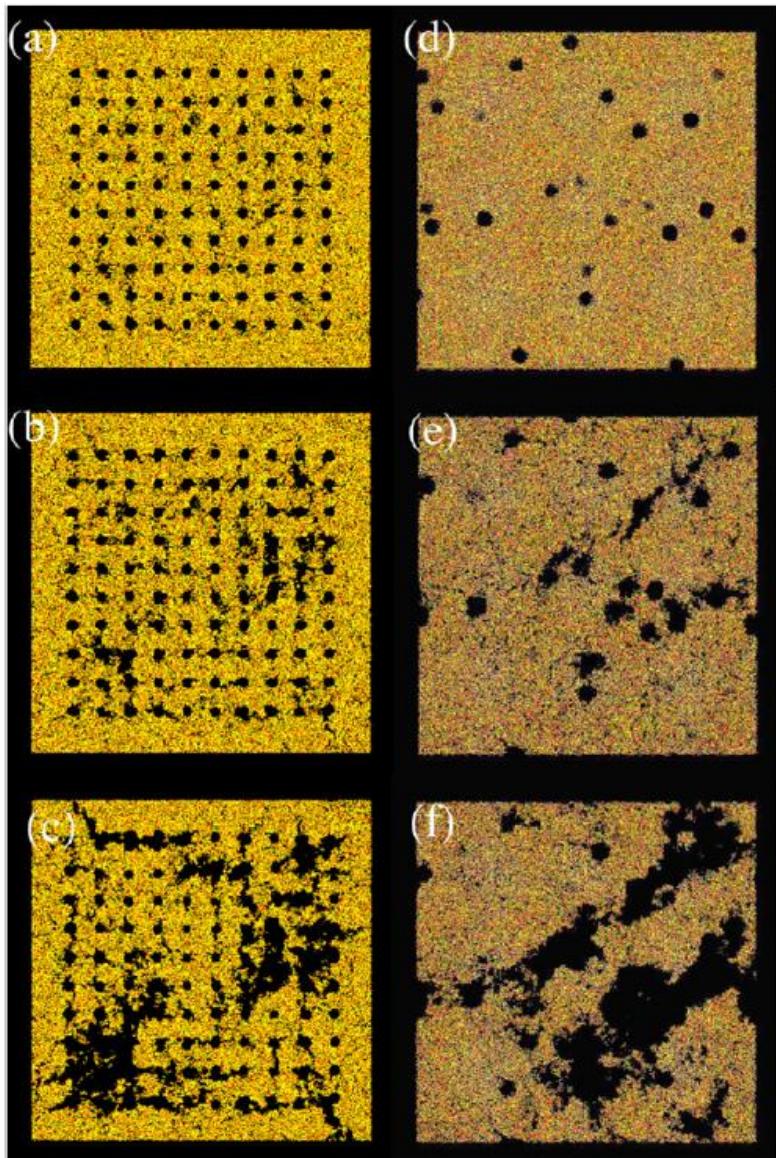
$$\mathcal{U}_{improper\ torsion,ijkl} = H_{2\Phi} (1 - \cos(2\Phi_{ijkl}))$$

$$\mathcal{U}_{vdW,ij} = 4\epsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^6 \right]$$

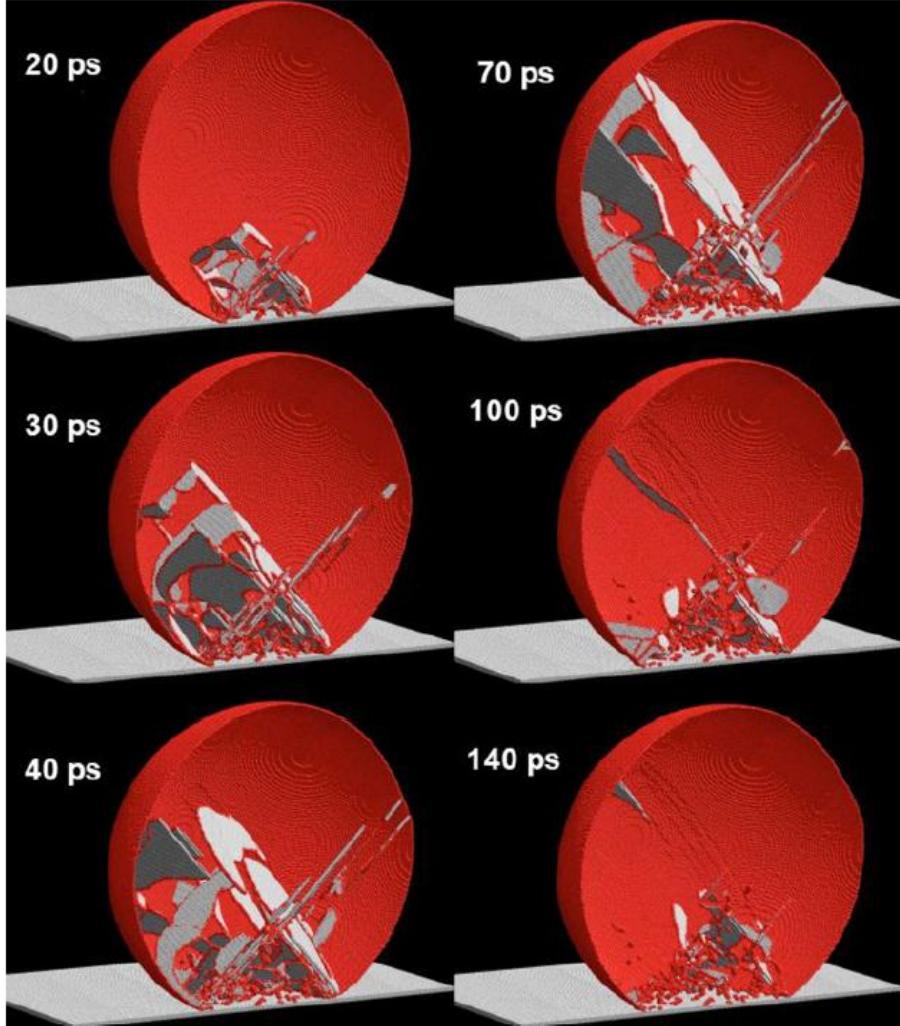
$$\mathcal{U}_{Coulomb,ij} = (4\pi\epsilon_0 r_{ij})^{-1} q_i q_j.$$

---

Exemple : acide Poly-Hydroxybezoïque



Growth of void and void coalescence  
 [J. Phys. D. Appl. Phys. 2001]



Impact of particle  
 [T.C. Germann, Int. J. Impact Engineering 2006]

## 2.2. Nano/macro : thermodynamique et mécanique statistique

### Imposer la température dans la DM

Thermostat de Nosé-Hoover

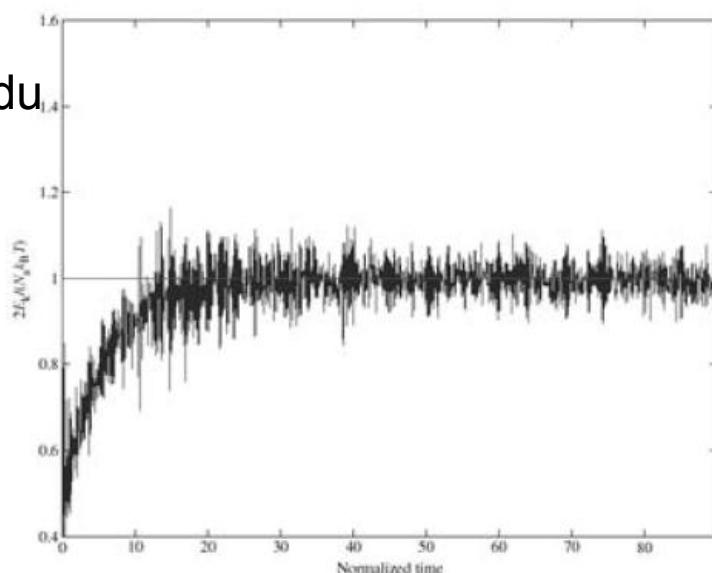
$$m\ddot{\mathbf{r}} = -\nabla U - m\zeta(t)\dot{\mathbf{r}}$$

$$\dot{\zeta}(t) = \frac{1}{Q} \left( \underbrace{\sum_j^{3N} m_j v_j^2}_{\text{Différence entre l'énergie cinétique visée et l'énergie du système}} - (3N + 1)k_B T_0 \right)$$

Coefficient de friction dynamique

Différence entre l'énergie cinétique visée et l'énergie du système

Evolution d'un système pour une température visée  $T=300$  K

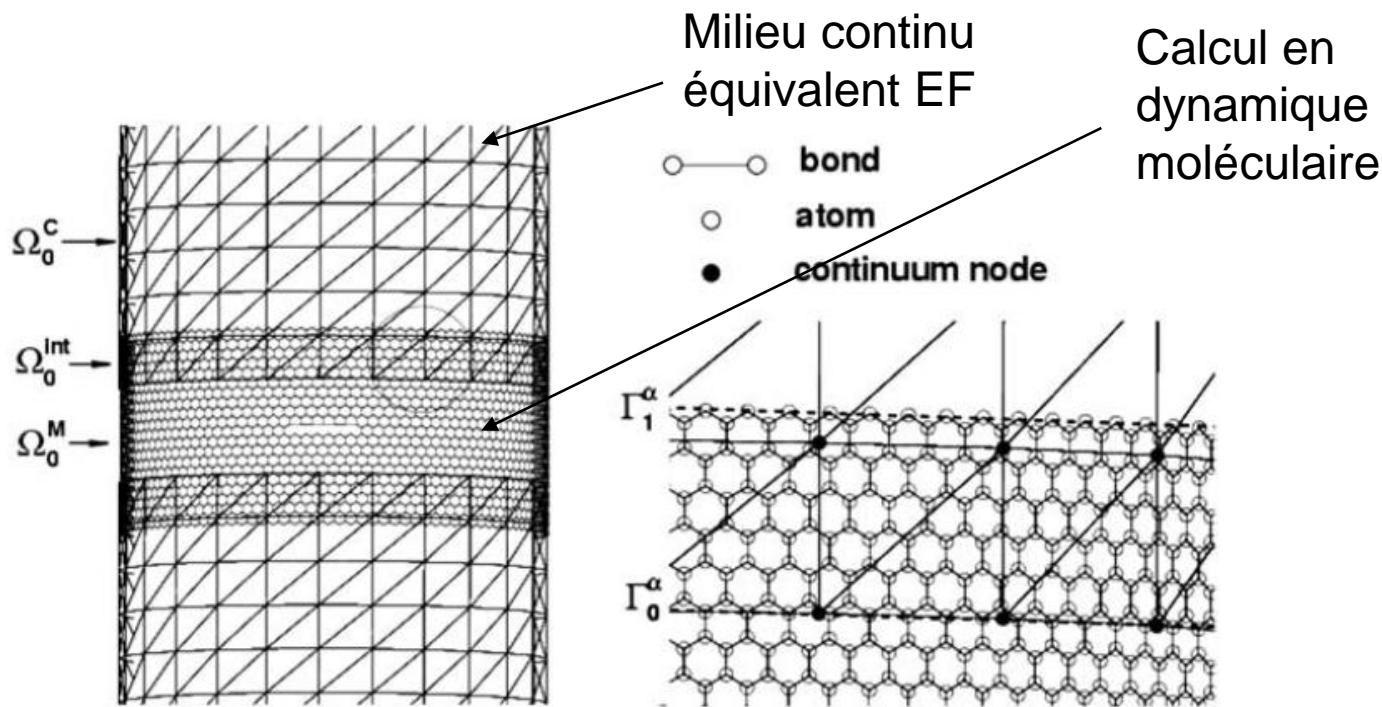


## 2.3. Couplages entre échelles : méthodes « multi-échelles »

### 3) Couplage direct méthodes avec zones « hand-shake »

Que faire quand les cinématiques ne sont pas les mêmes aux différentes échelles ?

Idée : décomposer le domaine spatial en une partie continue, une partie atomique, et une partie « interface » (hand-shake)

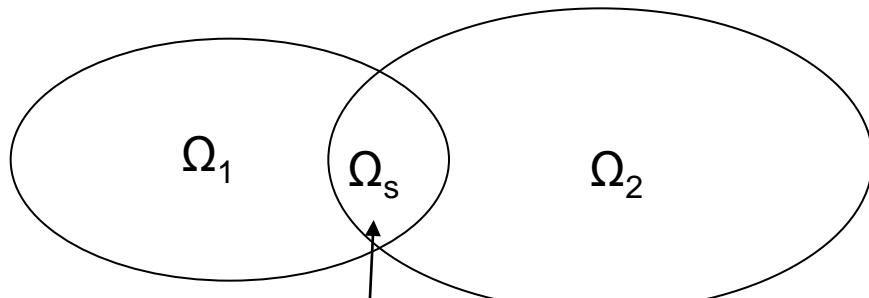


Exemple : étude d'un défaut dans un nano tube de carbone [Xiao, T. Belytschko 2004]

## 2.3. Couplages entre échelles : méthodes « multi-échelles »

### 3) Couplage direct méthodes avec zones « hand-shake »

La méthode Arlequin [Ben Dhia 2001]



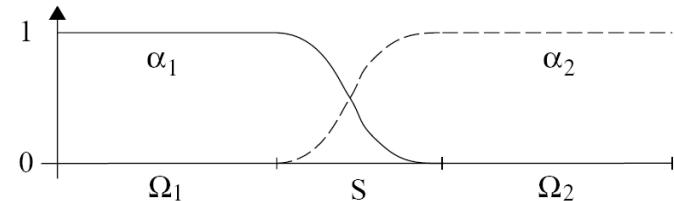
Modèle 1

Champ  
solution  $u_1$

Zone de  
collage

Modèle 2

Champ  
solution  $u_2$



$$\alpha_1 = 1 \text{ sur } \Omega_1 \setminus \Omega_2$$

$$\alpha_2 = 1 \text{ sur } \Omega_2 \setminus \Omega_1$$

$$\alpha_1 + \alpha_2 = 1 \text{ sur } \Omega_1 \cap \Omega_2$$

$$W = W^{(\Omega_1 / \Omega_2)}(u_1) + W^{(\Omega_2 / \Omega_1)}(u_2) + \alpha_1 \cdot W^{(\Omega_s)}(u_1) + (\alpha_2) \cdot W^{(\Omega_s)}(u_2)$$

Energie totale

## 2.3. Couplages entre échelles : méthodes « multi-échelles »

### 3) Couplage direct méthodes avec zones « hand-shake »

$$W = W^{(\Omega^1 / \Omega^2)}(u_1) + W^{(\Omega^2 / \Omega^1)}(u_2) + \alpha_1 \cdot W^{(\Omega^s)}(u_1) + (\alpha_2) \cdot W^{(\Omega^s)}(u_2)$$

Energie totale

Principe de la méthode : Trouver  $u_1, u_2$  tels que:

Min  $W$

$u_1, u_2$

Sous la contrainte :

$u_1 = u_2$  dans  $\Omega_s$

Système à résoudre

Trouver  $(\mathcal{U}_1, \mathcal{U}_2, \Lambda) \in \mathbb{R}^{N_1 \times d} \times \mathbb{R}^{N_2 \times d} \times \mathbb{R}^{N_c \times d}$

$$\begin{bmatrix} \mathcal{K}_1 & 0 & \mathcal{C}_1^T \\ 0 & \mathcal{K}_2 & -\mathcal{C}_2^T \\ \mathcal{C}_1 & -\mathcal{C}_2 & 0 \end{bmatrix} \begin{bmatrix} \mathcal{U}_1 \\ \mathcal{U}_2 \\ \Lambda \end{bmatrix} = \begin{bmatrix} \mathcal{F}_1 \\ \mathcal{F}_2 \\ 0 \end{bmatrix}$$

Méthode des multiplicateurs de Lagrange :

$$\min_{u_1, u_2, \lambda} (W + \int_{\Omega_s} \lambda(u_1 - u_2) d\Omega)$$

$u_1$  et  $u_2$  peuvent être des cinématiques différentes

## 2.3. Couplages entre échelles : méthodes « multi-échelles »

### 3) Couplage direct méthodes avec zones « hand-shake »

Couplage milieu continu/dynamique moléculaire [Xiao, Belytschko 2004]

Bridging domains method == Méthode Arlequin

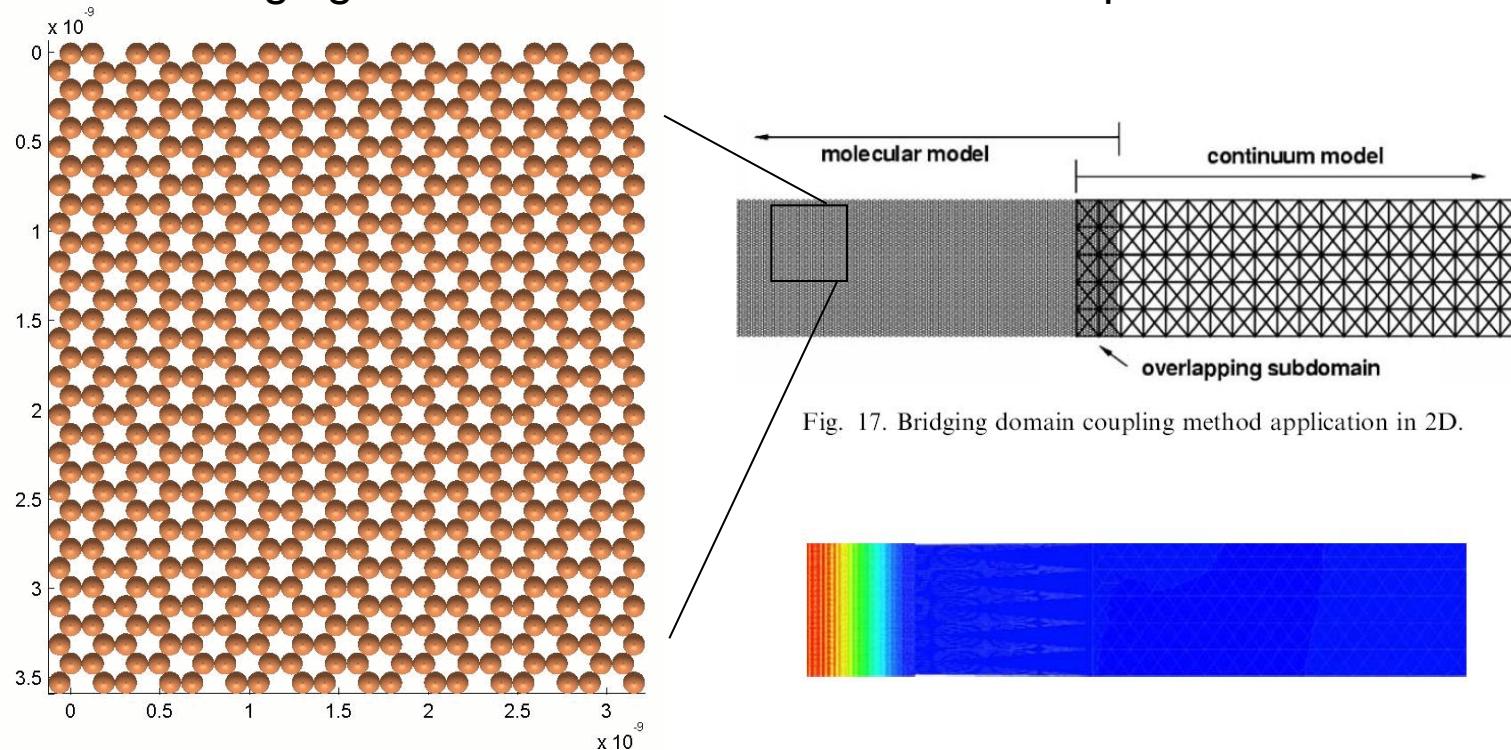


Fig. 17. Bridging domain coupling method application in 2D.

## 1.2. Echelle nanométriques/atomique

### B) Mécanique quantique

## 1.2. Echelle nanométriques/atomique

### Mécanique quantique

#### Pourquoi descendre à cette échelle ?

- 1) Obtenir les propriétés de liaisons atomiques et prédiction des structures moléculaires
- 2) Accéder aux propriétés macroscopiques sans aucun potentiel empirique ni modèle :

#### **1 seule équation : EQUATION DE SCHRÖDINGER**

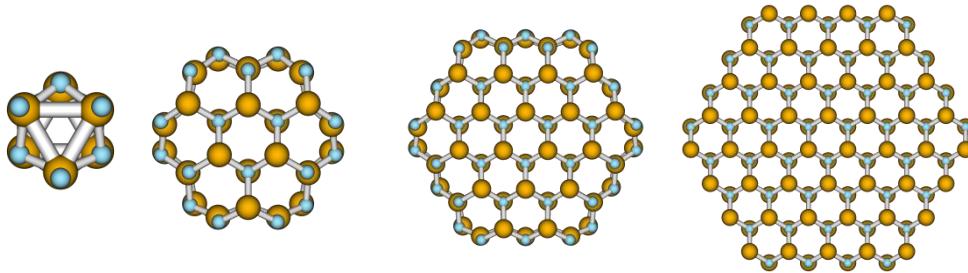
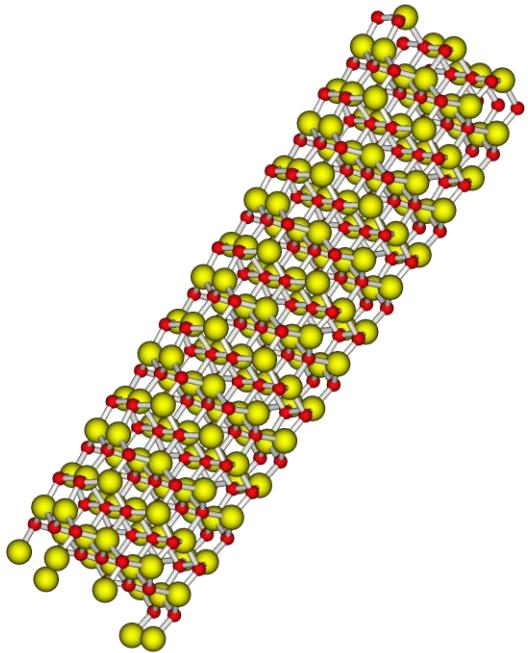
Calculs « **ab initio** » (à partir de « rien ») ou basés sur les « premiers principes »

- 3) Simuler des réactions chimiques
- 4) Accéder aux propriétés électroniques, optiques, magnétiques

# 1.2. Nano/atomistic scale

## Quantum mechanics

Example of Ab initio computations: determining lattice and piezoelectric constants of piezoelectrical nanowires



Computations with two solid-states softwares : CRYSTAL and SIESTA

ZnO			
	lattice parameters in Å, $e_{33}^a$ in $10^{-16} \mu\text{C Å/ion}$		
	PWGGA, Crystal	LDA, Siesta [4]	Expt [5]
Bulk, $a$	3.264	3.170	3.250
Bulk, $c$	5.270	5.180	5.207
Bulk, $e_{33}^a$	<b>1055</b>	<b>1453</b>	<b>1143</b>
Wire A, $c$	5.488	5.335	
Wire A, $e_{33}^a$	<b>2002</b>	<b>2025</b>	
Wire B, $c$	5.430	5.302	
Wire B, $e_{33}^a$	<b>1704</b>	<b>1837</b>	

ZnO and AlN nanowire

[Mitrushchenkov et al 2009]

## 1.2. Nano/atomistic scale

### Quantum mechanics

Time-dependent Schrödinger equation for a particle

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi(x,t)}{\partial x^2} + V(x)\Psi(x) = -\frac{\hbar}{i} \frac{\partial \Psi(x,t)}{\partial t}$$

Stationary Schrödinger equation for a particle

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi(x)}{\partial x^2} + V(x)\Psi(x) = E\Psi(x)$$

Potential

Wave function

Energy

Planck's constant

$$\hbar \equiv \frac{h}{2\pi}$$

## 1.2. Nano/atomistic scale

### Quantum mechanics

#### Interpretation of the Quantum wavefunction

$\|\psi(\mathbf{r}, t)\|^2$  Is the probability of finding an electron in  $\mathbf{r}$  and  $t$

$$\left\| \varphi(\mathbf{r}) \exp\left(-\frac{i}{\hbar} Et\right) \right\|^2 = \|\varphi(\mathbf{r})\|^2$$

## 1.2. Nano/atomistic scale

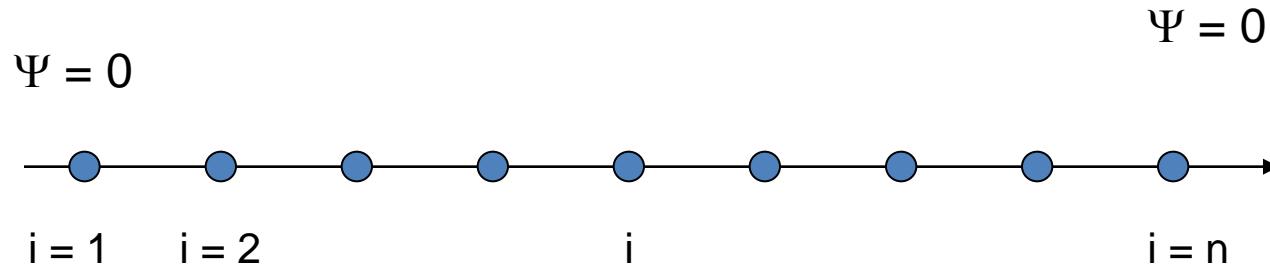
### Quantum mechanics

Numerical solution : a particle alone (1D problem)

Stationnary schrödinger equation:

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi(x)}{\partial x^2} + V(x) \Psi(x) = E \Psi(x)$$

Finite difference approximation:



$$-\frac{\hbar^2}{2m} \frac{(\Psi_k^{i+1} - 2\Psi_k^i + \Psi_k^{i-1})}{\Delta x^2} + V^i \Psi_k^i = E_k \Psi_k^i$$

## 1.2. Nano/atomistic scale

$$-\frac{\hbar^2}{2m} \frac{(\Psi_k^{i+1} - 2\Psi_k^i + \Psi_k^{i-1})}{\Delta x^2} + V^i \Psi_k^i = E_k \Psi_k^i$$

$$-\frac{\hbar^2}{2m} \frac{(\Psi_k^3 - 2\Psi_k^2 + \Psi_k^1)}{\Delta x^2} + V^2 \Psi_k^2 = E_k \Psi_k^2$$

$$-\frac{\hbar^2}{2m} \frac{(\Psi_k^4 - 2\Psi_k^3 + \Psi_k^2)}{\Delta x^2} + V^3 \Psi_k^3 = E_k \Psi_k^3$$

⋮  
⋮

$$-\frac{\hbar^2}{2m} \frac{(\Psi_k^n - 2\Psi_k^{n-1} + \Psi_k^{n-2})}{\Delta x^2} + V^{n-1} \Psi_k^{n-1} = E_k \Psi_k^{n-1}$$

## 1.2. Nano/atomistic scale

### Quantum mechanics

$$-\frac{\hbar^2}{2m\Delta x^2} \mathbf{M}\Psi_k + \mathbf{V}\Psi_k = E_k \Psi_k$$

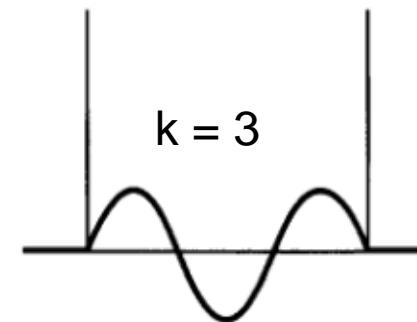
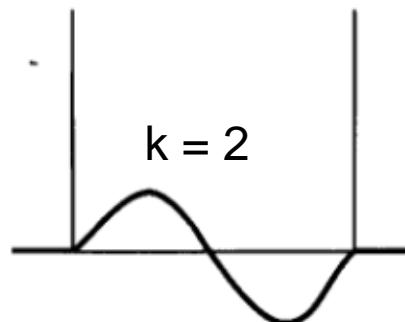
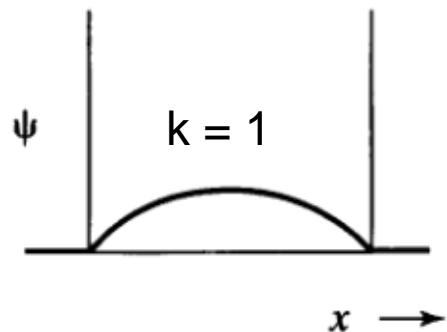
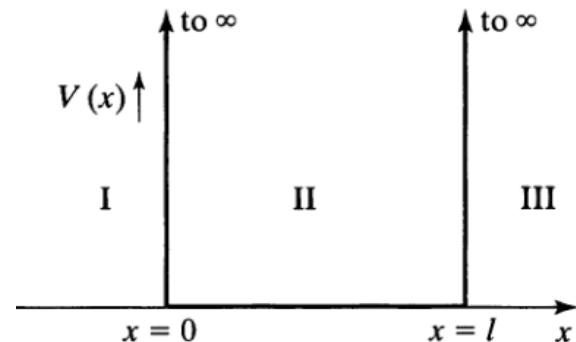
$$\mathbf{K}\Psi_k = E_k \Psi_k$$

Eigenvalue problem

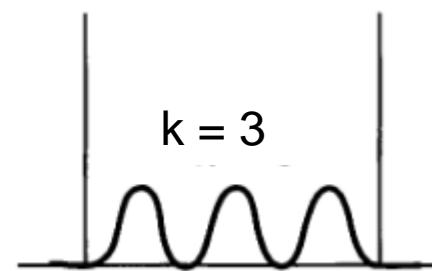
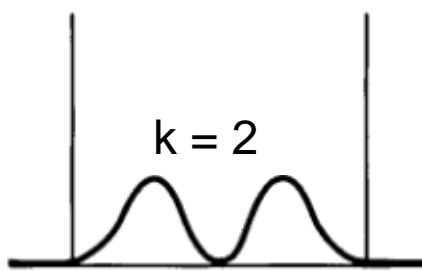
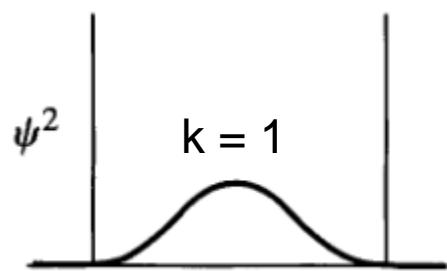
## 1.2. Nano/atomistic scale

### Quantum mechanics

Example: particle in a one-dimensional box



Solution  $\psi(x)$  for the lowest energy states



Solution  $\psi^2(x)$  for the lowest energy states

## 1.2. Nano/atomistic scale

### Quantum mechanics

#### Variational approach

$$E(\psi) = \frac{\int_{\Omega} \psi \hat{H} \psi d\Omega}{\int_{\Omega} \psi \psi d\Omega}$$

Energy

#### Variational principle

$$E(\psi) \geq E_0$$

$$D_{\delta\psi} E(\psi) = 0 \quad \text{Gateaux variation (directional derivative)}$$

After integration by parts

$$\int_{\Omega} \frac{\hbar^2}{2m} \nabla \psi \cdot \nabla \delta\psi d\Omega + \int_{\Omega} V \psi \delta\psi d\Omega = E \int_{\Omega} \psi \delta\psi d\Omega$$

## 1.2. Nano/atomistic scale

### Quantum mechanics

Variational approach

$$\int_{\Omega} \frac{\hbar^2}{2m} \nabla \psi \cdot \nabla \delta\psi d\Omega + \int_{\Omega} V\psi \delta\psi d\Omega = E \int_{\Omega} \psi \delta\psi d\Omega$$

Galerkin method

$$\psi = N\psi_i \quad \delta\psi = N\delta\psi_i$$

$$K = \int_{\Omega} \frac{\hbar^2}{2m} B^T B d\Omega$$

$$\nabla \psi = B\psi_i \quad \nabla \delta\psi = B\delta\psi_i$$

$$V = \int_{\Omega} V(\mathbf{x}) N^T N d\Omega$$

$$(K + V)\Psi_k = E_k M \Psi_k$$

$$M = \int_{\Omega} N^T N d\Omega$$

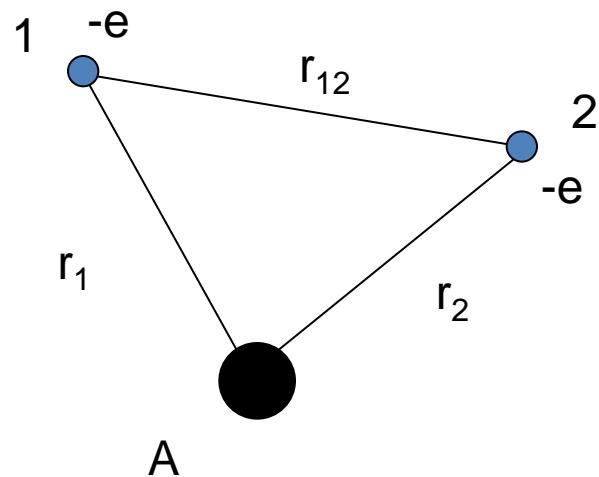
Generalized eigenvalue problem

## 1.2. Nano/atomistic scale

### Quantum mechanics

Stationnary Schrödinger equation for an atom and two electrons (He), or H<sup>-</sup>, Li<sup>+</sup>, Be<sup>2+</sup>

$$\left[ -\frac{\hbar^2}{2m_e} \nabla_1^2 - \frac{\hbar^2}{2m_e} \nabla_2^2 - \frac{Ze^{12}}{r_1} - \frac{Ze^{12}}{r_2} + e^{12} \right] \psi = E \psi$$



$$\nabla_1^2 = \frac{\partial}{\partial x_1^2} + \frac{\partial}{\partial y_1^2} + \frac{\partial}{\partial z_1^2}$$

$$\nabla_2^2 = \frac{\partial}{\partial x_2^2} + \frac{\partial}{\partial y_2^2} + \frac{\partial}{\partial z_2^2}$$

## 1.2. Nano/atomistic scale

### Quantum mechanics

Stationnary Schrödinger equation for an atom and two electrons (He), or H<sup>-</sup>, Li<sup>+</sup>, Be<sup>2+</sup>

$$\left[ -\frac{\hbar^2}{2m_e} \nabla_1^2 - \frac{\hbar^2}{2m_e} \nabla_2^2 - \frac{Ze^{12}}{r_1} - \frac{Ze^{12}}{r_2} + e^{12} \right] \psi = E \psi$$

$$\psi = \psi(x_1, y_1, z_1, x_2, y_2, z_2, x_A, y_A, z_A)$$

Eigenvalue problem in 9 dimensions !

Discretization (FD, EF...)

Size of K :

$$(K + V) \Psi_k = E_k M \Psi_k$$

$$n^9 \times n^9$$

## 1.2. Nano/atomistic scale

### Quantum mechanics

Schrödinger equation for a N particles system (atoms and electrons)

Assumption : we neglect spin orbitals and relativistic interactions

$$\hat{H}\Psi = E\Psi$$

$$\hat{H} = \boxed{-\frac{\hbar^2}{2} \sum_{\alpha} \frac{1}{m_{\alpha}} \nabla_{\alpha}^2} \quad \text{(A)} \quad \boxed{-\frac{\hbar^2}{2m_e} \sum_i \nabla_i^2} \quad \text{(B)} \quad \boxed{+ \sum_{\alpha} \sum_{\beta} \frac{Z_{\alpha} Z_{\beta} e'^2}{r_{\alpha\beta}}} \quad \text{(C)}$$

$$- \sum_{\alpha} \sum_i \frac{Z_{\alpha} e'^2}{r_{\alpha i}} + \sum_j \sum_{i>j} \frac{e'^2}{r_{ij}}$$

(D)

(E)

- (A) Operator associated with nuclei kinetic energy  
(B) Operator associated with electrons kinetic energy  
(C) Operator associated with nuclei  $\alpha, \beta$  repulsion potential energy  
(D) Operator associated with attraction/electrons potential energy  
(E) Operator associated with electrons repulsion potential energy

$$e' \equiv \bar{e}/(4\pi\epsilon_0)^{1/2},$$

## 1.2. Nano/atomistic scale

### Quantum mechanics

The Born-oppenheimer approximation :

Electrons move way faster than nuclei : we can assume that nuclei are fixed with respect to the electrons

Purely electronic Hamiltonian

$$\hat{H}_{el} + V_{NN}$$

$$\hat{H}_{el} = (B) + (D) + (E)$$

$$V_{NN} = (C)$$

$$(A) \approx 0$$

(A) Operator associated with nuclei kinetic energy

(B) Operator associated with electrons kinetic energy

(C) Operator associated with nuclei  $\alpha, \beta$  repulsion potential energy

(D) Operator associated with attraction/electrons potential energy

(E) Operator associated with electrons repulsion potential energy

## 1.2. Nano/atomistic scale

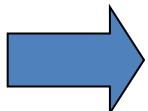
Schrôdinger equation for electron motion:

$$(\hat{H}_{el} + V_{NN}) \psi_{el} = U \psi_{el}$$

$$V_{NN} = C^{te} \text{ if nuclei are fixed}$$

It can be shown that;

$$(H + C^{te}) \phi = E \phi$$

  $H \phi = E' \phi$        $E = E' + C^{te}$

We can solve

$$(\hat{H}_{el}) \psi_{el} = E_{el} \psi_{el} \quad U = E_{el} + V_{NN}$$

## 1.2. Echelle nanométriques/atomique

### Mécanique quantique

#### Différentes méthodes de résolution disponibles

- **Méthode de Hartree-Fock**
- Post-Hartree-Fock methods
  - Møller-Plesset perturbation theory
  - Configuration Interaction...
- **Density Functional Theory**
- Valence bond methods
- Quantum Monte Carlo methods....

## 1.2. Echelle nanométriques/atomique

### Mécanique quantique

#### Hartree method :

- Modèle de particules indépendentes (Hartree) : chaque électron se déplace dans un potentiel moyen représentant l'attraction du noyau et les effets moyens des attractions et interactions des autres électrons

$$\left[ -\frac{1}{2} \nabla_i^2 + \sum_I V(\vec{R}_I - \vec{r}_i) + \boxed{\sum_{j \neq i} \int |\varphi_j(\vec{r}_j)|^2 \frac{1}{|\vec{r}_j - \vec{r}_i|} d\vec{r}_j} \right] \varphi_i(\vec{r}_i) = \varepsilon \varphi_i(\vec{r}_i)$$

Potentiel moyen créé par les électrons  $j \neq i$

Ecriture de la solution comme un produit de fonctions dépendant d'une seule dimension

$$\psi(\vec{r}_1, \dots, \vec{r}_n) = \varphi_1(\vec{r}_1) \varphi_2(\vec{r}_2) \cdots \varphi_n(\vec{r}_n)$$

---

## 1.2. Echelle nanométriques/atomique

### Mécanique quantique

Hartree method :

$$\left[ -\frac{1}{2} \nabla_i^2 + \sum_I V(\vec{R}_I - \vec{r}_i) + \boxed{\sum_{j \neq i} \int |\varphi_j(\vec{r}_j)|^2 \frac{1}{|\vec{r}_j - \vec{r}_i|} d\vec{r}_j} \right] \varphi_i(\vec{r}_i) = \varepsilon \varphi_i(\vec{r}_i)$$

Problème en 1 dimension ! : trouver  $\varphi_i(r_i)$

Résolution itérative : connaissant les autres fonctions  $\varphi_j(r_j)$ , on calcule le nouveau potentiel, et calcul de  $\varphi_i(r_i)$ , jusqu'à convergence (si convergence !!)

## 1.2. Echelle nanométriques/atomique

### Mécanique quantique

#### Hartree method :

##### Problèmes de la méthode de Hartree:

- Pas de corrélation (la fonction d'onde est un produit de fonctions en 1D)
- La fonction d'onde n'est pas antisymétrique (pour les fermions), notion de SPIN
- Problème pour les atomes de type hydrogène : on supprime artificiellement nl dégénérescences

# 1.2. Nano/atomistic scale

## Quantum mechanics

### The Pauli principle

**The wave function of a system of electrons must be antisymmetric with respect to interchange of any two electrons**

$$\psi(q_1, q_2, \dots, q_n) = -\psi(q_2, q_1, \dots, q_n) \quad q = \{x, y, z, m_s\}$$

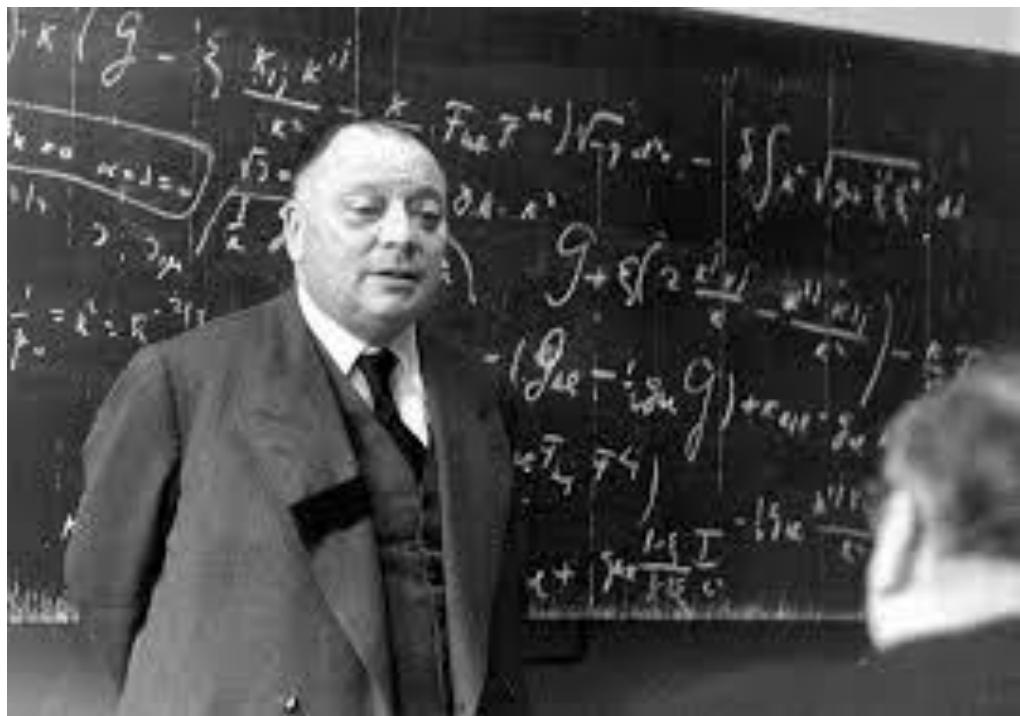
$$q_2 \equiv q_1 \longrightarrow \psi(q_1, q_1, \dots, q_n) = -\psi(q_1, q_1, \dots, q_n)$$

$$2\psi(q_1, q_1, \dots, q_n) = 0$$

$$\psi(q_1, q_1, \dots, q_n) = 0$$

Two electrons with the same spin have zero probability of being found at the same point in three-dimensional space

Spin  
↑



Wolfgang Pauli  
(Prix Nobel Physique 1945)



## 1.2. Nano/atomistic scale

### Quantum mechanics

**Hartree method : the wave function is not antisymmetric by construction**

$$\psi(\vec{r}_1, \dots, \vec{r}_n) = \varphi_1(\vec{r}_1) \varphi_2(\vec{r}_2) \cdots \varphi_n(\vec{r}_n)$$

Solution : **Hartree-Fock method** : the wave function is expressed as a Slater determinant

$$\psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_n) = \frac{1}{\sqrt{n!}} \begin{vmatrix} \varphi_\alpha(\vec{r}_1) & \varphi_\beta(\vec{r}_1) & \cdots & \varphi_\nu(\vec{r}_1) \\ \varphi_\alpha(\vec{r}_2) & \varphi_\beta(\vec{r}_2) & \cdots & \varphi_\nu(\vec{r}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \varphi_\alpha(\vec{r}_n) & \varphi_\beta(\vec{r}_n) & \cdots & \varphi_\nu(\vec{r}_n) \end{vmatrix}$$

## 1.2. Echelle nanométriques/atomique

### Mécanique quantique

#### Hartree-Fock method :

##### Améliorations

- Méthodes semi-empiriques (approximation des potentiels d'interactions (coûteux à calculer)
- Configuration Interaction, Méthodes de perturbation...

## 1.2. Nano/atomistic scale

### Quantum mechanics

#### Density Functional Theory (DFT)

Hohenberg-Kohn theorems (1965)

- I) Electronic density is the unknown variable: the external potential uniquely determines the electronic density, and the electronic density uniquely determines the external potential.
- II) A new Schrödinger -type equation can be written as a function of the electron density only

DFT : only works for the GROUND STATE

The most popular and versatile method available in condensed matter physics, computational physics, and computational chemistry



Walter Kohn  
(Prix Nobel chimie  
1998)



## 1.2. Nano/atomistic scale

### Quantum mechanics

#### Density Functional Theory (DFT)

Main objective:

replace the many-body electronic wavefunction with the electronic density as the basic quantity

-> Replace a  $3N$ -dimensional problem by a 3-D problem !

## 1.2. Nano/atomistic scale

### Quantum mechanics

#### Density Functional Theory (DFT)

Particle density function

$$n(\vec{r}) = N \int \int \dots \int \psi^*(\vec{r}, \vec{r}_2, \dots, \vec{r}_N) \psi(\vec{r}, \vec{r}_2, \dots, \vec{r}_N) dr_2^3 dr_3^3 \dots dr_N^3$$

Hohenberg and Kohn (1964) : for a given ground state density  $n_0(r)$ , it is (in principle) possible to find the corresponding ground state wave function

Knowing  $n(\vec{r})$  We can deduce  $\psi(\vec{r}, \vec{r}_2, \dots, \vec{r}_N)$

## 1.2. Nano/atomistic scale

### Quantum mechanics

#### Density Functional Theory (DFT)

Kohn-Sham equations: non interacting system

$$\left[ -\frac{\hbar^2}{2m} \nabla^2 + V_S(\vec{r}) \right] \phi_i(\vec{r}) = \varepsilon_i(\vec{r})$$

Effective potential

$$V_S = V + \int \frac{e^2 n_S(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}'^3 + V_{XC}(n_S(\vec{r}))$$



Exact BUT  $V_{XC}$  is unknown and must be approximated

-> LIMITATIONS OF DFT (Is DFT a « truly ab initio method ? »<sub>24</sub>)

## 1.2. Nano/atomistic scale

### Density Functional Theory (DFT)

Algorithm:

0) Initialize  $n(r) = n^0(r)$

→ 1) Calculate  $V_s$  using

$$V_s = V + \int \frac{e^2 n_s(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}'^3 + V_{XC}(n_s(\vec{r}))$$

2) Solve the Kohn-Sham equations for  $\phi_i$

$$\left[ -\frac{\hbar^2}{2m} \nabla^2 + V_s(\vec{r}) \right] \phi_i(\vec{r}) = \varepsilon_i(\vec{r})$$

3) Calculate the new density using

$$n(\vec{r}) = n_s(\vec{r}) = \sum_i |\phi_i(\vec{r})|^2$$

4) Test convergence

IF NOT: go to (1)

## 1.2. Nano/atomistic scale

# Density Functional Theory (DFT)

## Limitations of DFT

- Ground state theory (the excited states can not be predicted)
- The exchange correlation function is approximated: DFT can yield energy below the true ground state (not variational)
- The currently available DFT functionals don't give good results for activation energies of reactions, fail for some van der Waals molecules

# Conclusions and issues

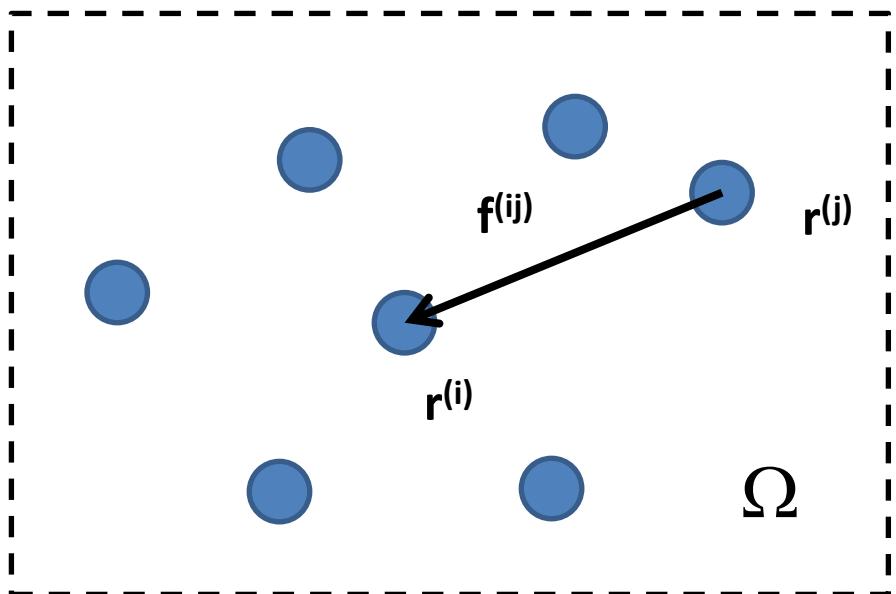
## Existing numerical methods: be carreful !

- Continuum models require parameters from lower scales (ex: MD)
- MD must be used with caution (validity of empirical potentials)
- MD requires ab initio (ex DFT) calculations for obtaining realistic forces fields
- Ab initio calculations are highly costly (in 2013...)
- DFT is an exact method in theory, but we approximate the exchange correlation function: not valid in any case !
- Thermodynamics properties: averages must be performed on large cells/large times: costly operations
- Need for continuum/mesoscale models to study clusters of nanoparticles

# Notions de contraintes et de force à l'échelle atomique

## Contraintes « Virielles »

$$\bar{\sigma}_{ij} = \frac{1}{|\Omega|} \sum_{k \in \Omega} \left( -m^{(k)} \left[ \dot{u}_i^{(k)} - \dot{\bar{u}}_i^{(k)} \right] \left[ \dot{u}_i^{(k)} - \dot{\bar{u}}_i^{(k)} \right] + \frac{1}{2} \sum_{l \in \Omega} \left[ r_i^{(l)} - r_i^{(k)} \right] f_j^{kl} \right)$$



DM

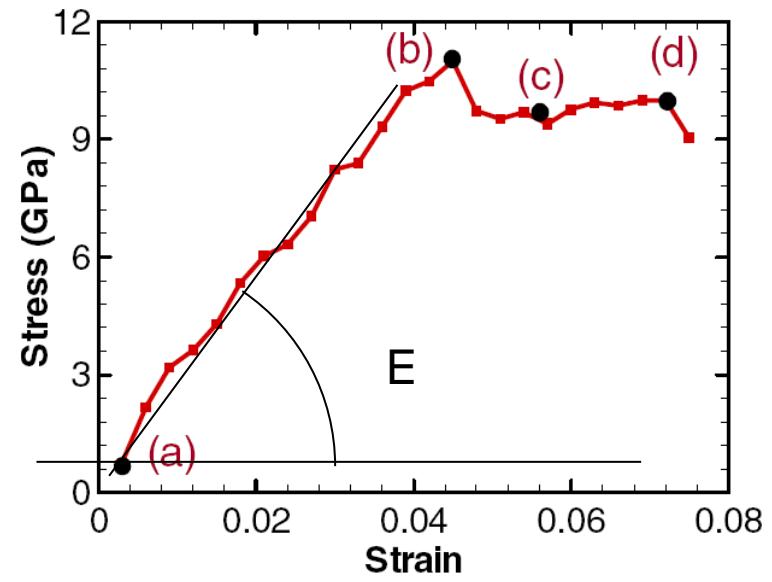
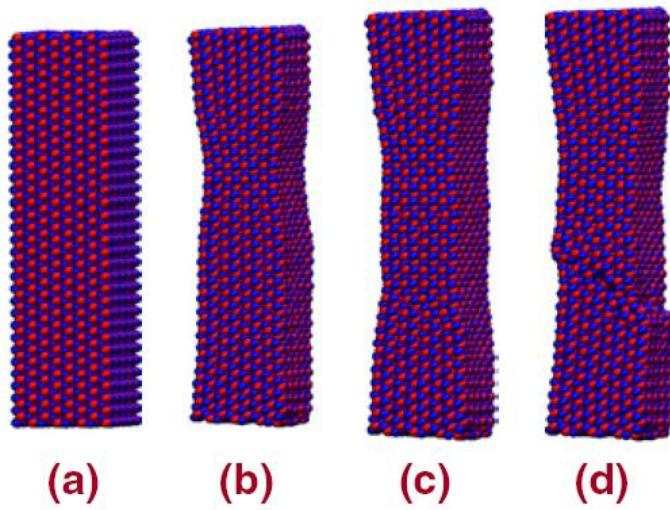
$$f_i^{(kl)} = \frac{\partial V(r^{(kl)})}{\partial r_i^{(kl)}} \frac{r_i^{(kl)}}{r^{(kl)}}$$

# Contrainte locale [Zhou 03]

$$\sigma_{ij}(\mathbf{r}) = \sum_{k \in \Omega} \left( -m^{(k)} \dot{u}_i^{(k)} \dot{u}_j^{(k)} + \frac{1}{2} \sum_{l \neq k} r_i^{(kl)} f_j^{kl} \right) \times \delta(\mathbf{r} - \mathbf{r}^{(k)})$$

Régularisation  
possible

$$\langle \sigma_{ij}(\mathbf{r}) \rangle_{\Omega} = \overline{\sigma}_{ij}^{virial}$$



Exemple : détermination du module d'Young d'un nanofil de ZnO [Kulkarni et al.2005]

# Mécanique quantique : pas de notion de potentiel

## Comment calculer les forces ?

### Generalized Hellmann Feynman theorem

$$\frac{\partial E_n}{\partial \lambda} = \int \psi_n^* \frac{\partial \hat{H}}{\partial \lambda} \psi_n d\Omega$$

Born-Hoppenheimer approximation

$$\hat{H}\psi_{el} = (\hat{T}_{el} + \hat{V})\psi_{el} = U\psi_{el}$$

$$\hat{V} = \hat{V}_{el} + \hat{V}_{NN}$$

$\hat{H}$  depends on nuclear coordinates  $x_j$  as parameters

$$\frac{\partial U}{\partial x_j} = \int \psi_{el}^* \frac{\partial \hat{H}}{\partial x_j} \psi_{el} d\Omega$$

The part of the potential associated with kinetic energy  $H$  does not depend on nuclei cartesian coordinates

$$\frac{\partial U}{\partial x_j} = \int \psi_{el}^* \frac{\partial \hat{H}}{\partial x_j} \psi_{el} d\Omega \rightarrow \frac{\partial U}{\partial x_j} = \int \psi_{el}^* \frac{\partial \hat{V}}{\partial x_j} \psi_{el} d\Omega$$

$$\frac{\partial \hat{V}}{\partial x_j} = \frac{\partial \hat{V}_{el}}{\partial x_j} + \frac{\partial \hat{V}_{NN}}{\partial x_j}$$

$$\frac{\partial \hat{V}_{el}}{\partial x_j} = - \sum_i \frac{Z_j (x_i - x_j) e'^2}{r_{ij}^3} \quad \frac{\partial \hat{V}_{NN}}{\partial x_j} = - \sum_{\alpha \neq j} \frac{Z_\alpha Z_j e'^2}{r_{ij}^3} \frac{(x_\alpha - x_j)}{r_{\alpha j}^2}$$

$$\boxed{\mathbf{F} = - \frac{\partial U}{\partial \mathbf{x}}}$$

Forces acting on  
nucleus i

$$\boxed{F_i = - \int_{\Omega} \psi \left( - \frac{d\hat{V}}{dR_i} \right) \psi d\Omega}$$

# Ab initio Molecular Dynamics

Born-Oppenheimer molecular dynamics

$$m_i \ddot{R}_i = F_i = - \int_{\Omega} \psi \left( - \frac{d\hat{V}}{dR_i} \right) \psi d\Omega$$

Algorithm:

→ For each time step:

    For fixed positions of nuclei R

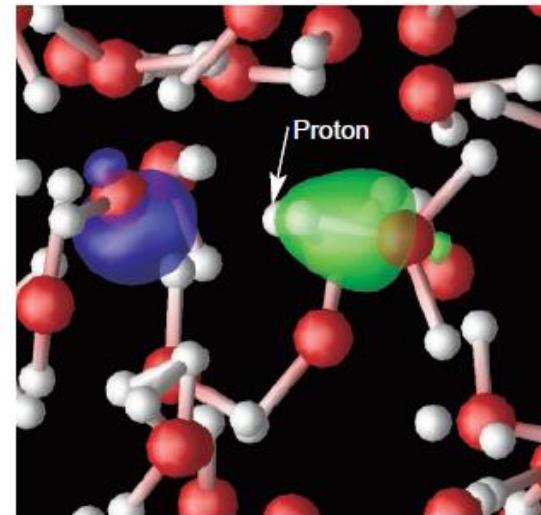
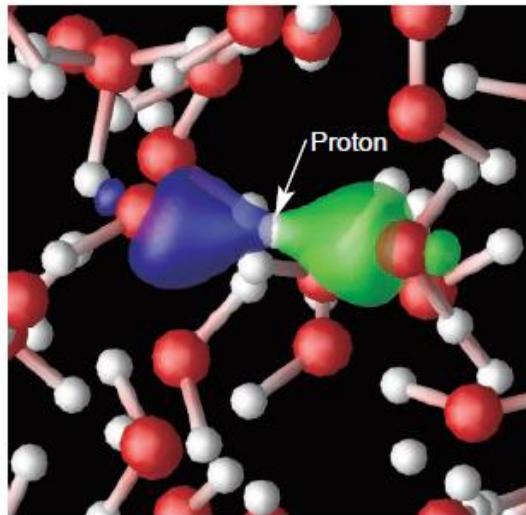
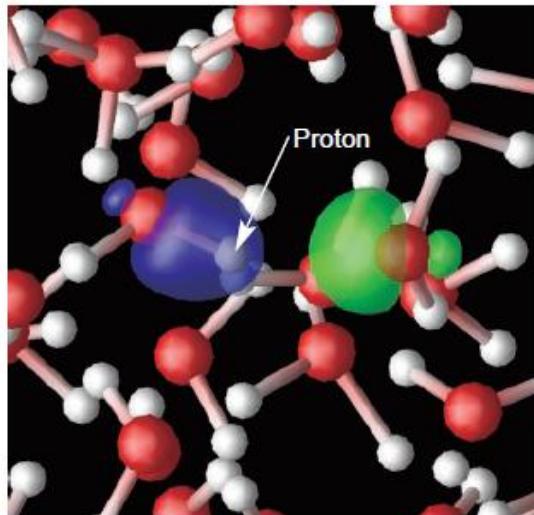
        Compute  $\psi$  Using quantum mechanics

        Compute  $F_i = - \int_{\Omega} \psi \left( - \frac{d\hat{V}}{dR_i} \right) \psi d\Omega$

        Compute accelerations

        Update positions and velocities

# Ab initio molecular dynamics



Simulation des réactions chimiques : Dislocation d'une molécule  
d'eau à haute pression, formation de  $\text{OH}^-$  et  $\text{H}_3\text{O}^+$

# Modélisations atomistiques

## Vocabulaire employé dans la littérature

**Dynamique moléculaire** = Potentiels empiriques+dynamique

**Statique moléculaire** = Potentiels empiriques + équilibre statique

**Calculs ab initio** = Résolution de l'Eq. De Schrödinger avec approches sans modèles empiriques (Hartree-Fock)

**Calculs de type «Premier principe»** = Résolution de l'Equation de Schrödinger avec modèle empirique (DFT)

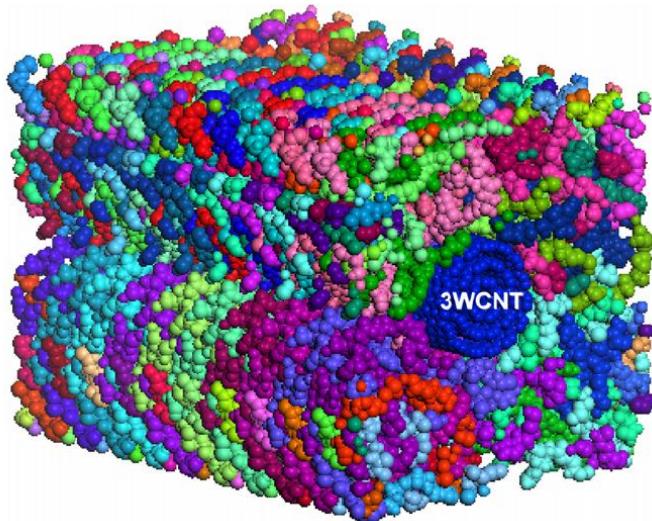
**Dynamique moléculaire quantique** = DM+calcul des forces par résolution de l'Eq. De Scrödinger

**Calculs atomistiques** : ensemble des méthodes de calcul à l'échelle atomistique (MD/ab initio)

# Calcul de propriétés de volume à partir de calculs atomistiques

$$\bar{C}_{ijkl} = \frac{1}{\Omega} \frac{\partial^2 E}{\partial \bar{\varepsilon}_{ij} \partial \bar{\varepsilon}_{kl}}, \quad E = \sum_i \sum_j \phi^{ij}(r_{ij}) \quad \bar{C}_{ijkl} = \frac{1}{\Omega T} \int_0^T \frac{\partial^2 E(t)}{\partial \bar{\varepsilon}_{ij} \partial \bar{\varepsilon}_{kl}} dt.$$

Température finie

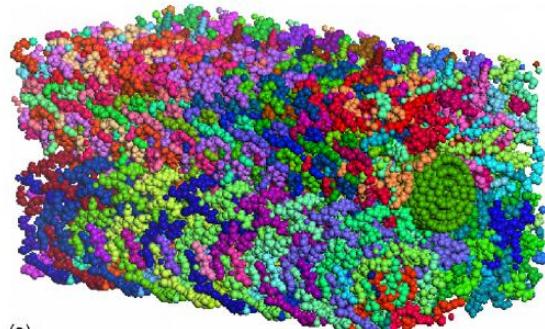


VER : matrice polymère contenant un nanotube

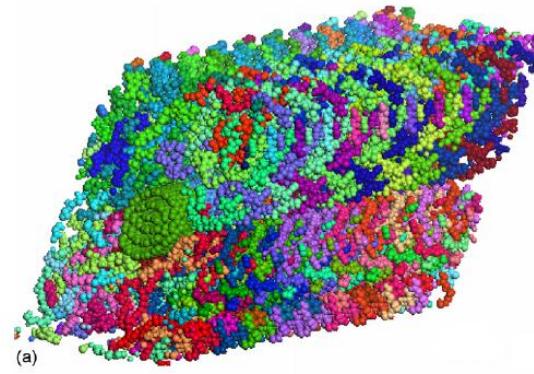
$$\begin{bmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_3 \\ \sigma_{23} \\ \sigma_{31} \\ \sigma_{12} \end{bmatrix} = \underbrace{\begin{bmatrix} c_{11} & c_{12} & c_{13} & c_{14} & c_{15} & c_{16} \\ c_{12} & c_{22} & c_{23} & c_{24} & c_{25} & c_{26} \\ c_{13} & c_{23} & c_{33} & c_{34} & c_{35} & c_{36} \\ c_{14} & c_{24} & c_{34} & c_{44} & c_{45} & c_{46} \\ c_{15} & c_{25} & c_{35} & c_{45} & c_{55} & c_{56} \\ c_{16} & c_{26} & c_{36} & c_{46} & c_{56} & c_{66} \end{bmatrix}}_{\text{Tenseur élastique de comportement}} \begin{bmatrix} \varepsilon_1 \\ \varepsilon_2 \\ \varepsilon_3 \\ \varepsilon_{23} \\ \varepsilon_{31} \\ \varepsilon_{12} \end{bmatrix}$$

Tenseur élastique de comportement

# Conditions aux limites linéaires sur le bord, imposition d'états de déformation macroscopiques

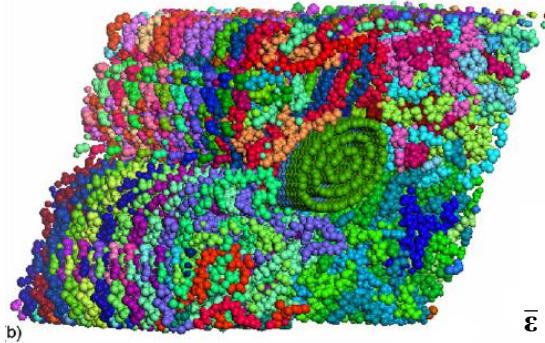


(a)



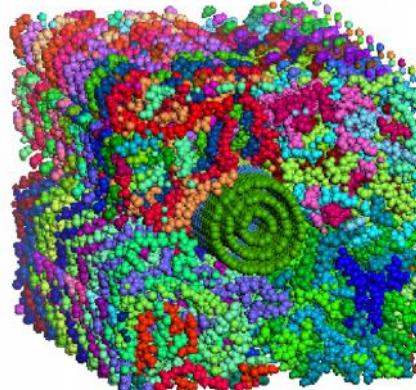
(a)

$$\bar{\boldsymbol{\varepsilon}} = \begin{bmatrix} \varepsilon_{11} & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$



b)

$$\bar{\boldsymbol{\varepsilon}} = \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & \frac{\varepsilon_{23}}{2} \\ 0 & \frac{\varepsilon_{23}}{2} & 0 \end{bmatrix}$$



$$\bar{\boldsymbol{\varepsilon}} = \begin{bmatrix} 0 & 0 & 0 \\ 0 & \varepsilon_{22} & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

# Conductivité thermique

Loi de conduction de Fourier

$$\mathbf{q} = -\mathbf{k}\nabla T$$

Formule de Green-Kubo

$$\mathbf{k} = \frac{1}{3Vk_bT^2} \int_0^\infty \langle \mathbf{j}(0)\mathbf{j}(t) \rangle dt$$

$$\mathbf{j}(t) = \sum_i \mathbf{V}_j \varepsilon_i + \frac{1}{2} \sum_{i,j} \mathbf{r}_{ij} (\mathbf{F}_{ij} \cdot \mathbf{v}_i)$$

$$\varepsilon_i = \frac{1}{2} m_i |\mathbf{v}_i|^2 + \frac{1}{2} \sum_j \phi(\mathbf{r}_{ij})$$

# Propriétés piézoélectriques par calculs ab initio

## Approche des phases de Berry

$$e_{ik} = -\frac{1}{2\pi V} \sum_{\alpha} \frac{\partial \phi_{\alpha}}{\partial \varepsilon_k} a_{\alpha i}$$

## Phases de Berry

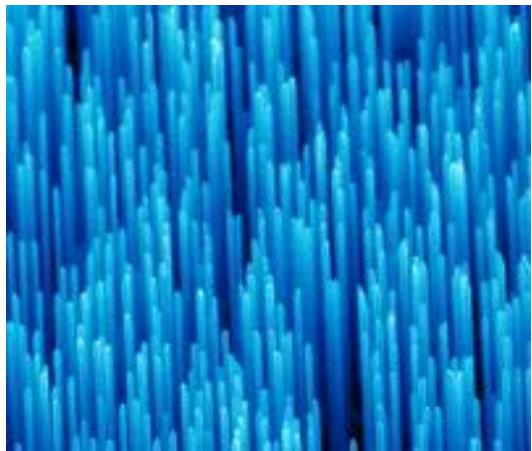
$$\phi_{\alpha} = \phi_{\alpha}^{nuc} + \phi_{\alpha}^{elec}$$

$$\phi_{\alpha}^{nuc} = \sum_{iA} B_{\alpha i} R_{Ai} Z_A$$

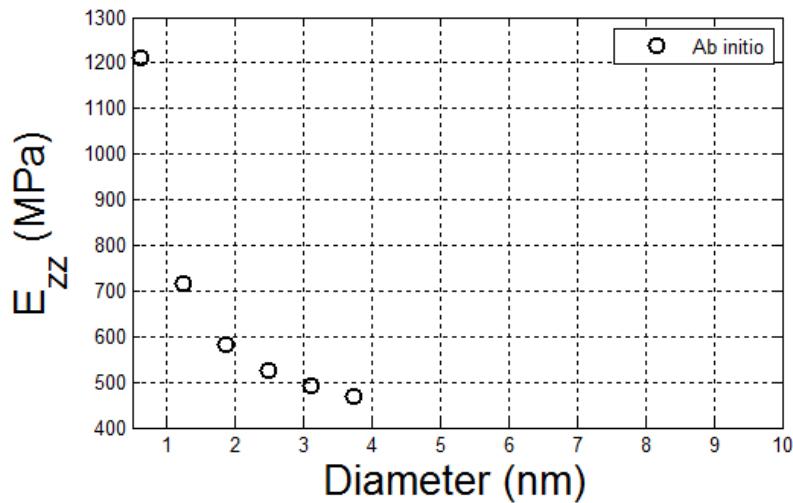
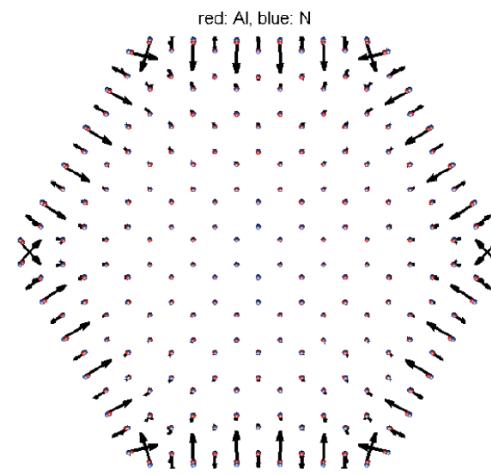
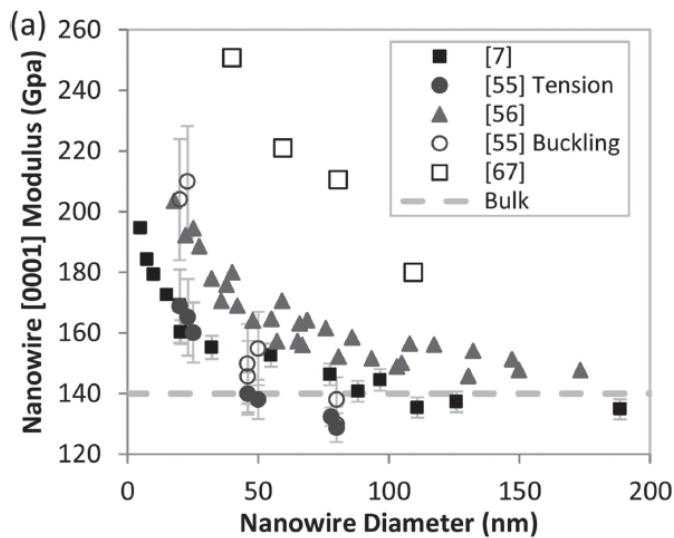
$$\phi_{\alpha}^{elec} = \frac{1}{\Omega} \sum_n \int_{BZ} \langle u_{n\mathbf{k}} | -i\mathbf{B}_{\alpha} \nabla_{\mathbf{k}} | u_{n\mathbf{k}} \rangle d\mathbf{k}$$

# Modélisation continue des effets de surface dans les nanostructures

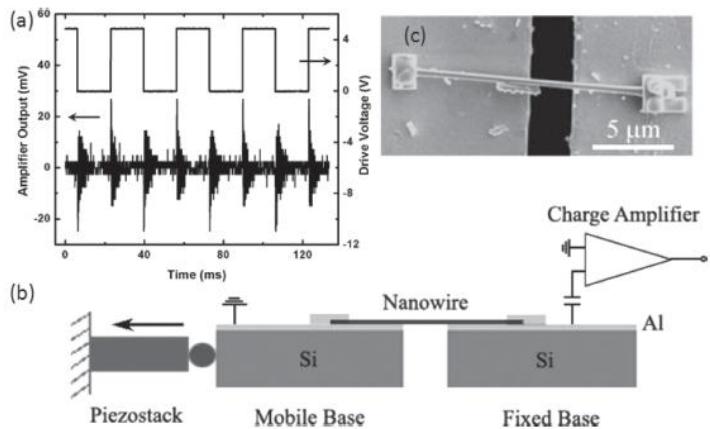
# Effets de surface dans les nanofils



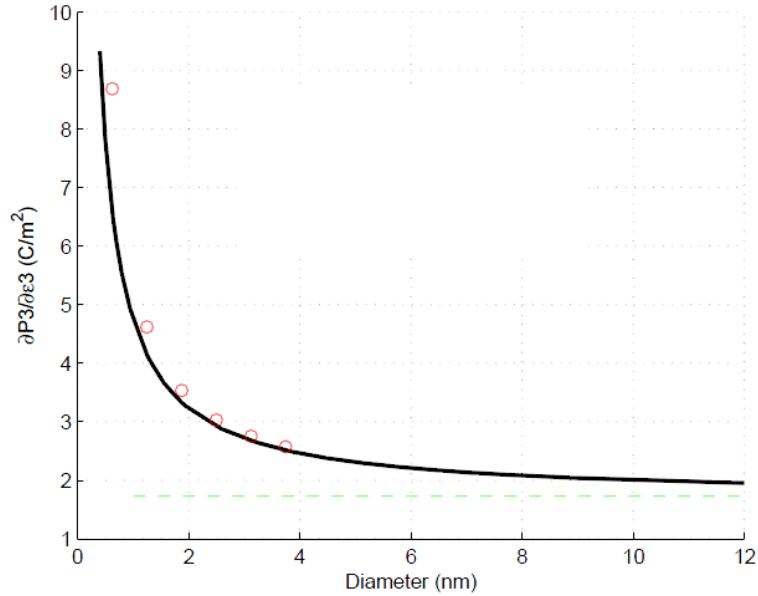
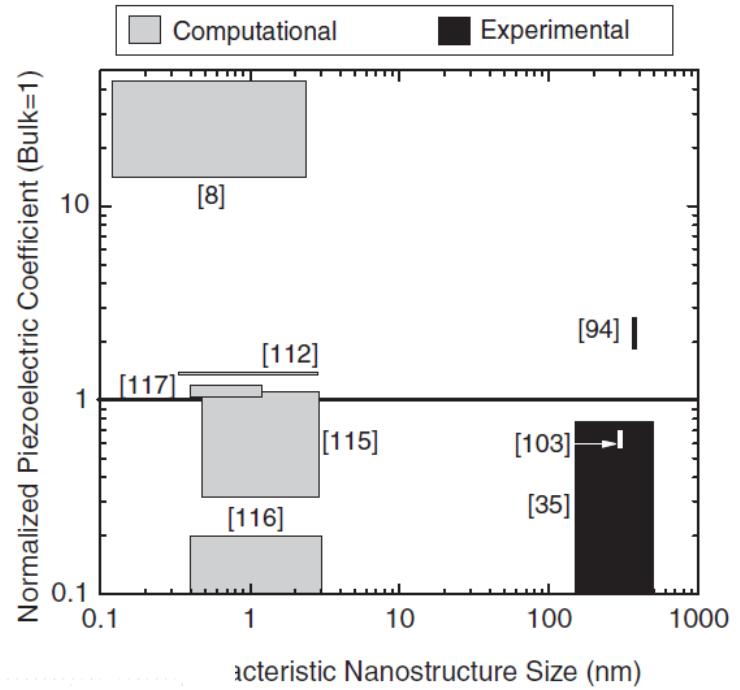
ZnO nanowires  
(monocrystal wurtzite structure)



Ab initio calculations  
[ Yvonnet et al. CMAME 2010],



## Piezoelectric properties in ZnO nanowires [Espinoza et al. Adv. Mat. 2012]



Ab initio calculation of  
effective piezoelectric  
coefficients  
[Hoang et al. In preparation]

# Intérêt des modélisations continues/calculs atomistiques

Ab initio model with 500 atoms (simple elastic relaxation)

50 CPUs  
Computational time = 1 month

Equivalent continuum (Finite element)

1 CPU, laptop  
Computational time = <1 s

Construct a continuum model for nanowires (and in general for nanoparticles) able to:

- Capture size-dependent mechanical properties
- Capture electromechanical (piezoelectric) properties
- Being identified from ab initio calculations at low computational costs
- Operate in a large range of scale, from nanometers to micrometers

# The Gurtin-Murdoch surface elasticity theory for modeling free surface effects in nanosystems

$$\nabla \cdot \boldsymbol{\sigma} + \mathbf{b} = 0 \quad \text{in } \Omega,$$

$$\nabla^s \cdot \boldsymbol{\sigma}^s + \boldsymbol{\sigma} \mathbf{n} = 0 \quad \text{on } \Gamma$$

Bulk and surface equilibrium

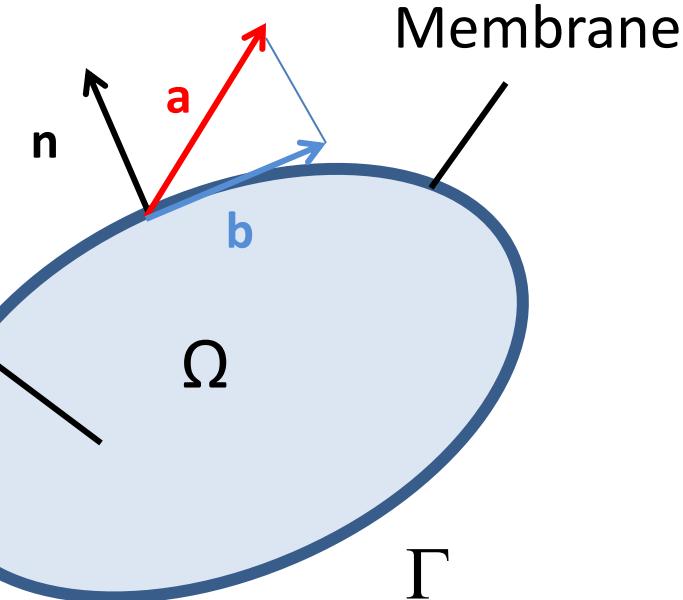
$$[\![\mathbf{u}]\!] = 0 \quad \text{on } \Gamma$$

Adherence of the surface on the bulk

$$\boldsymbol{\sigma}^s = \frac{\partial \gamma_0^s(\boldsymbol{\varepsilon}^s)}{\partial \boldsymbol{\varepsilon}^s} + \frac{\partial \gamma^s(\boldsymbol{\varepsilon}^s)}{\partial \boldsymbol{\varepsilon}^s}$$

Surface stress-surface strain relationship

$$\gamma_0^s(\boldsymbol{\varepsilon}^s) = \boldsymbol{\tau}^s : \boldsymbol{\varepsilon}^s, \quad \gamma^s(\boldsymbol{\varepsilon}^s) = \frac{1}{2} \boldsymbol{\varepsilon}^s : \mathbb{C}^s : \boldsymbol{\varepsilon}^s$$



$$\mathbf{b} = \mathbf{P}\mathbf{a}$$

$$\nabla^s \mathbf{T} = \nabla \mathbf{T} : \mathbf{P}$$

$$\boldsymbol{\sigma}^s = \mathbf{P} \boldsymbol{\sigma} \mathbf{P}, \quad \boldsymbol{\varepsilon}^s = \mathbf{P} \boldsymbol{\varepsilon} \mathbf{P}$$

$$\mathbf{P}(\mathbf{x}) = \mathbf{1} - \mathbf{n}(\mathbf{x}) \otimes \mathbf{n}(\mathbf{x})$$

# Enriched energetic model

Virtual work of internal forces (bulk)

$$\int_{\Omega} \boldsymbol{\varepsilon}(\mathbf{u}) : \mathbb{C}^{bulk} : \boldsymbol{\varepsilon}(\delta \mathbf{u}) d\Omega$$

Virtual work of internal forces  
(surface)

$$\int_{\Gamma} \boldsymbol{\varepsilon}^s(\mathbf{u}) : \mathbb{C}^s : \boldsymbol{\varepsilon}^s(\delta \mathbf{u}) d\Gamma$$

$$= \int_{\Gamma_F} \bar{\mathbf{F}} \cdot \delta \mathbf{u} d\Gamma + \int_{\Omega} \mathbf{b} \cdot \delta \mathbf{u} d\Omega - \int_{\Gamma} \boldsymbol{\tau}^s : \delta \boldsymbol{\varepsilon}^s(\delta \mathbf{u}) d\Gamma$$

Virtual work of external forces

Virtual work of residual surface  
stress

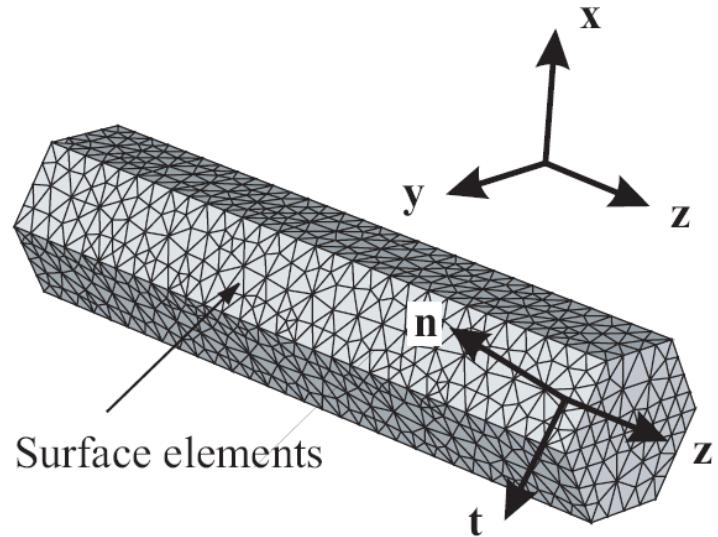
# FEM discretization

Linear system of equations

$$(\mathbf{K} + \mathbf{K}^s) \mathbf{q} = \mathbf{F} - \mathbf{F}^s$$

Surface rigidity matrix

$$\mathbf{K}^s = \int_{\Gamma} \mathbf{B}^T \mathbf{M}_p^T \mathbf{C}^s \mathbf{M}_p \mathbf{B} d\Gamma$$



Forces related to surface residual stress

$$\mathbf{F}^s = \int_{\Gamma} \mathbf{B}^T \mathbf{M}_p^T \boldsymbol{\tau}^s d\Gamma$$

$$[\boldsymbol{\varepsilon}^s] = \mathbf{M}_p [\boldsymbol{\varepsilon}]$$

$$\mathbf{M}_p = \begin{bmatrix} P_{11}^2 & P_{12}^2 & P_{13}^2 & P_{12}P_{13} & P_{11}P_{13} & P_{11}P_{12} \\ P_{12}^2 & P_{22}^2 & P_{23}^2 & P_{22}P_{23} & P_{12}P_{23} & P_{12}P_{22} \\ P_{13}^2 & P_{23}^2 & P_{33}^2 & P_{23}P_{33} & P_{13}P_{33} & P_{13}P_{23} \\ 2P_{12}P_{13} & 2P_{22}P_{23} & 2P_{23}P_{33} & (P_{23}^2 + P_{22}P_{33}) & (P_{23}P_{13} + P_{12}P_{33}) & (P_{22}P_{13} + P_{12}P_{23}) \\ 2P_{11}P_{13} & 2P_{12}P_{23} & 2P_{13}P_{33} & (P_{13}P_{23} + P_{12}P_{33}) & (P_{13}^2 + P_{11}P_{33}) & (P_{12}P_{13} + P_{11}P_{23}) \\ 2P_{11}P_{12} & 2P_{12}P_{22} & 2P_{13}P_{23} & (P_{13}P_{22} + P_{12}P_{23}) & (P_{11}P_{23} + P_{13}P_{12}) & (P_{11}P_{22} + P_{12}^2) \end{bmatrix}$$

Avoiding local surface coordinates

$$\mathbf{K}^s \simeq \sum_{e \in \mathcal{S}^\Gamma} \mathbf{B}^T(\mathbf{x}_\Omega^e) \mathbf{M}_p^T(\mathbf{x}_\Gamma^e) \mathbf{C}^s(\mathbf{x}_\Gamma^e) \mathbf{M}_p(\mathbf{x}_\Gamma^e) \mathbf{B}(\mathbf{x}_\Omega^e) |\Gamma^e|$$

# Surface parameters

$$\mathbf{K}^s \simeq \sum_{e \in \mathcal{S}^\Gamma} \mathbf{B}^T(\mathbf{x}_\Omega^e) \mathbf{M}_p^T(\mathbf{x}_\Gamma^e) \mathbf{C}^s(\mathbf{x}_\Gamma^e) \mathbf{M}_p(\mathbf{x}_\Gamma^e) \mathbf{B}(\mathbf{x}_\Omega^e) |\Gamma^e|$$

$$\mathbb{C}^s = C_{11}^s \mathbf{t} \otimes \mathbf{t} \otimes \mathbf{t} \otimes \mathbf{t} + C_{33}^s \mathbf{z} \otimes \mathbf{z} \otimes \mathbf{z} \otimes \mathbf{z}$$

$$+ C_{13}^s (\mathbf{t} \otimes \mathbf{t} \otimes \mathbf{z} \otimes \mathbf{z} + \mathbf{z} \otimes \mathbf{z} \otimes \mathbf{t} \otimes \mathbf{t}) + C_{55}^s (\mathbf{t} \otimes \mathbf{z} \otimes \mathbf{t} \otimes \mathbf{z} + \mathbf{z} \otimes \mathbf{t} \otimes \mathbf{z} \otimes \mathbf{t})$$

For wurtzite (1010) surfaces

$$\begin{bmatrix} \sigma_1^s \\ \sigma_3^s \\ \sigma_5^s \end{bmatrix} = \begin{bmatrix} C_{11}^s & C_{13}^s & 0 \\ C_{13}^s & C_{33}^s & 0 \\ 0 & 0 & C_{55}^s \end{bmatrix} \begin{bmatrix} \varepsilon_1^s \\ \varepsilon_3^s \\ 2\varepsilon_5^s \end{bmatrix} + \begin{bmatrix} \tau_1^s \\ \tau_3^s \\ 0 \end{bmatrix}$$

To be identified via atomistic simulations

(local form)

# Extracting surface coefficients via ab initio calculations

Schrödinger equation with Born-Hoppenheimer assumption

$$\hat{H}_{el}(\mathbf{r}, \mathbf{R})\Psi_k(\mathbf{r}, \mathbf{R}) = E(\mathbf{R})\Psi_{el}(\mathbf{r}, \mathbf{R})$$

$$\hat{H}_{el} = -\frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 + \sum_{\alpha} \sum_{\beta} \frac{Z_{\alpha} Z_{\beta} e'^2}{d_{\alpha\beta}}$$

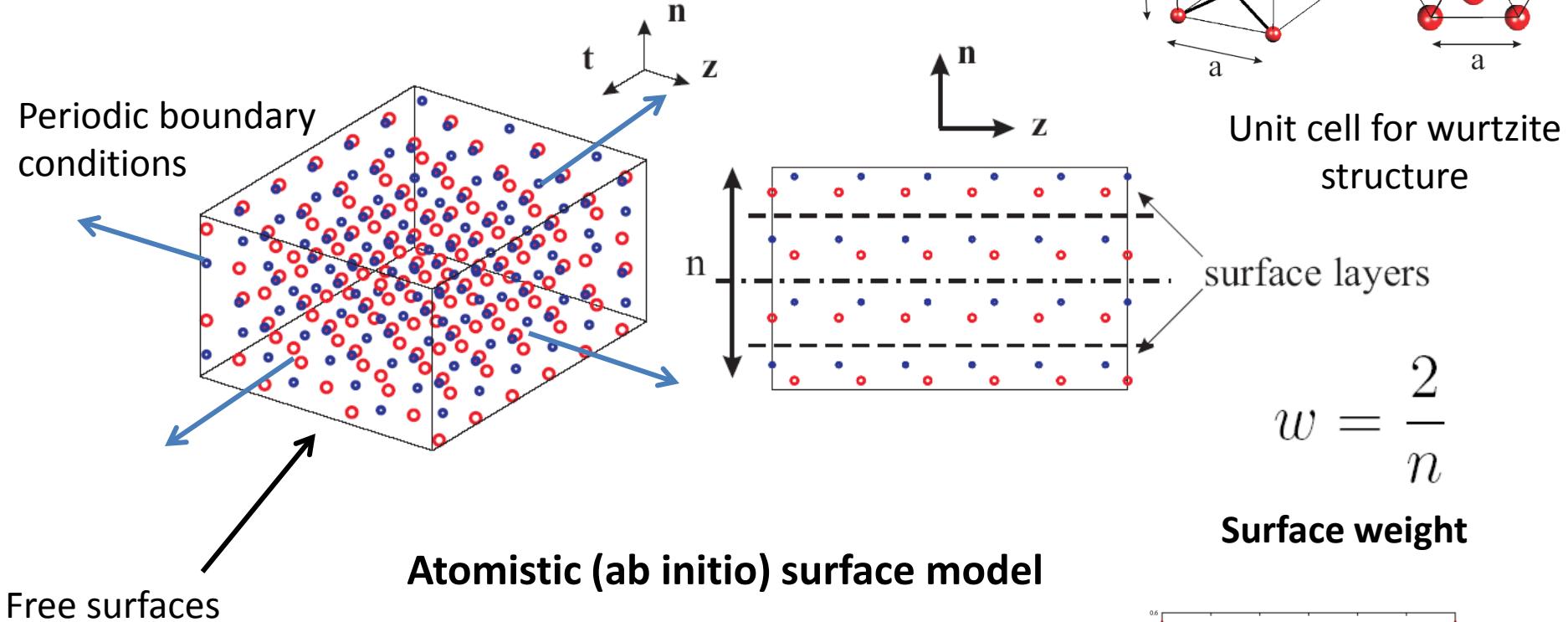
$$-\sum_{\alpha} \sum_i \frac{Z_{\alpha} e'^2}{d_{\alpha i}} + \sum_j \sum_{i>j} \frac{e'^2}{d_{ij}}$$

- (I) electrons kinetic energy
- (II) nuclei, *repulsion energy*
- (III) *attraction between electrons and nuclei potential energy*
- (IV) electrons repulsion potential energy.

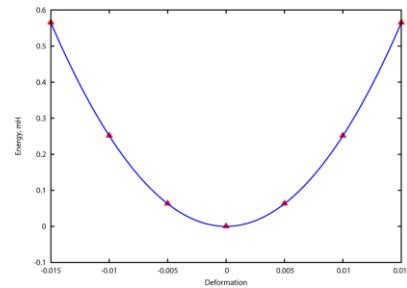
$$= (I) + (II) + (III) + (IV)$$

ab initio calculations performed using **DFT method** with extra large space integration grid,  
hybrid B3LYP functional

# Extracting surface coefficients



$$C_{ij}^{slab} = \frac{1}{S} \frac{\partial^2 E^{slab}}{\partial \varepsilon_i \partial \varepsilon_j}$$



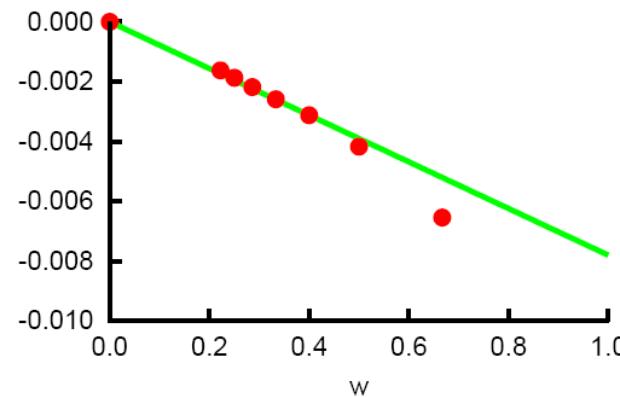
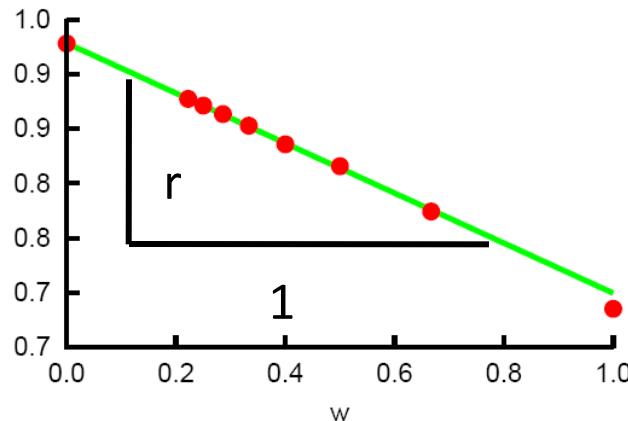
# Isolating the surface energy

$$E^{slab}(w) = wE^s + (1 - w)E^{slab}(w \rightarrow 0)$$

[Mitrushchenkov, Yvonnet et al., Nanotechnology, 2010]

$$C_{ij}^{slab}(w) = wC_{ij}^s + (1 - w)C_{ij}^{slab}(w \rightarrow 0)$$

$$C_{ij}(w) = w(C_{ij}^s - C_{ij}^{slab}(w \rightarrow 0)) + C_{ij}^{slab}(w \rightarrow 0)$$



$$C_{ij}^s = r + C_{ij}^{slab}(w \rightarrow 0)$$

$$\tau_i(w) = w\tau_i^s$$

# Extension to piezoelectricity

Balance equations

$$\sigma_{ij,j} = 0 \quad \text{in } \Omega,$$

$$P_{i,i} = 0 \quad \text{in } \Omega,$$

$$\sigma_{kj,i}^s S_{kj} + \sigma_{ij} n_j = 0 \quad \text{on } \Gamma,$$

$$P_{k,i} S_k + P_i n_i = 0 \quad \text{on } \Gamma,$$

Constitutive relations for bulk

$$\sigma_{ij} = C_{ijkl} \varepsilon_{kl}(\vec{u}) - e_{kij} E_k(\phi),$$

$$P_i = e_{ikl} \varepsilon_{kl}(\vec{u}) + \alpha_{ik} E_k(\phi),$$

Constitutive relations for surfaces

$$\sigma_{ij}^{(s)} = C_{ijkl}^{(s)} \varepsilon_{kl}^{(s)}(\vec{u}) - e_{kij}^{(s)} E_k^{(s)}(\phi) + \tau_{ij}^s,$$

$$P_i^{(s)} = e_{ikl}^{(s)} \varepsilon_{kl}^{(s)}(\vec{u}) + \alpha_{ik}^{(s)} E_k^{(s)}(\phi),$$

# Computation of surface piezoelectric coefficients by ab initio calculations

$$e_{ik}^s = \begin{bmatrix} 0 & 0 & 0 & 0 & e_{15}^s & 0 \\ 0 & 0 & 0 & e_{15}^s & 0 & 0 \\ e_{31}^s & e_{31}^s & e_{33}^s & 0 & 0 & 0 \end{bmatrix}$$

$$e_{ik}^{slab} = \frac{1}{S} \frac{\partial P^{slab}}{\partial \varepsilon_k}$$

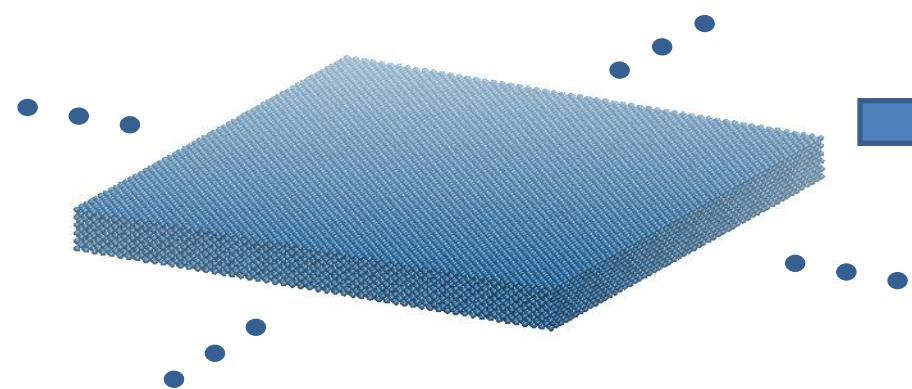
Ab initio calculations: Berry's phase approach

$$e_{ik}^{slab}(w) = w e_{ik}^{as} + (1 - w) e_{ik}^{slab}(w \rightarrow 0)$$

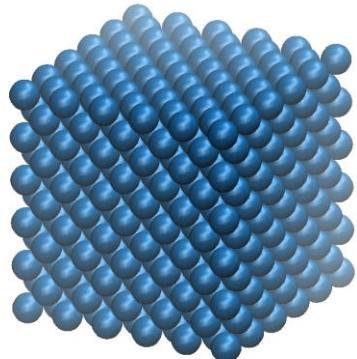
$$e_{ik}(w) = w(e_{ik}^{as} - e_{ik}^{slab}(w \rightarrow 0)) + e_{ik}^{slab}(w \rightarrow 0)$$

# Exemples numériques (contributions)

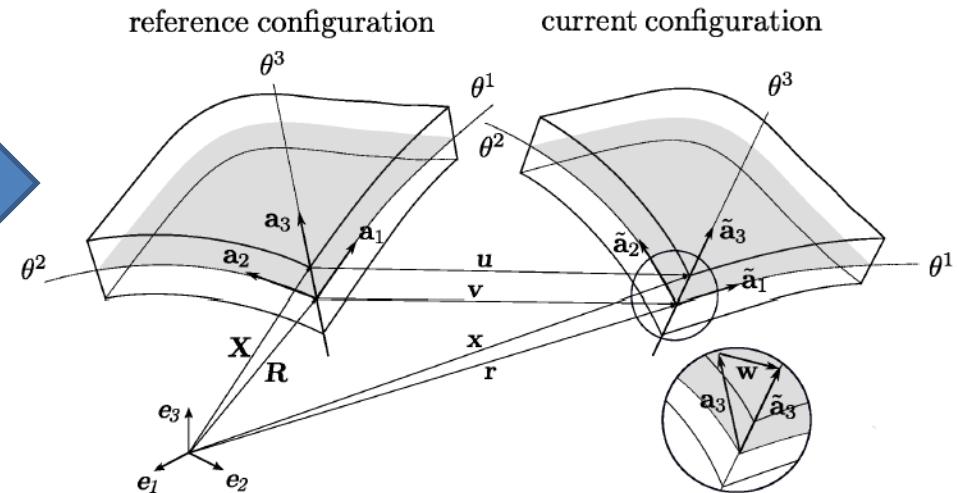
# Films minces : construction d'un modèle plaque identifié par calculs atomistiques



Modèle atomistique



VER



Modèle coque

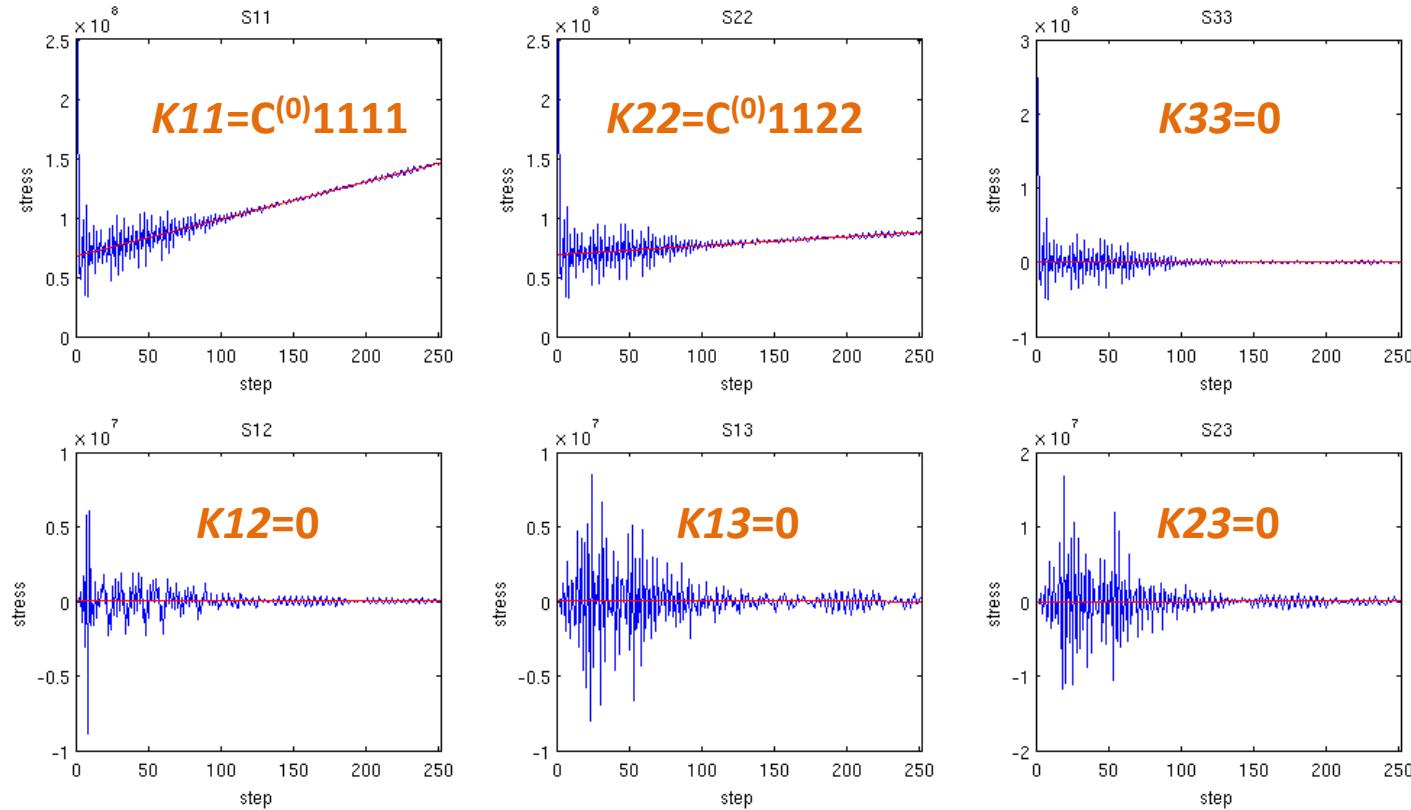
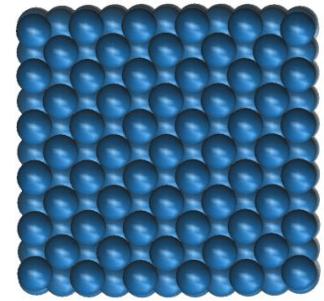
$$\mathbf{u}(\mathbf{X}) = \bar{\varepsilon} \mathbf{x} + \tilde{\mathbf{u}}(\mathbf{x})$$

$$\bar{\varepsilon}_{ij} = \bar{\varepsilon}_{ij}^0 + X_3 \bar{\varepsilon}_{\alpha\beta}^1 + X_3 \varepsilon_{33}^1$$

Conditions aux limites

# Bending Nanofilm

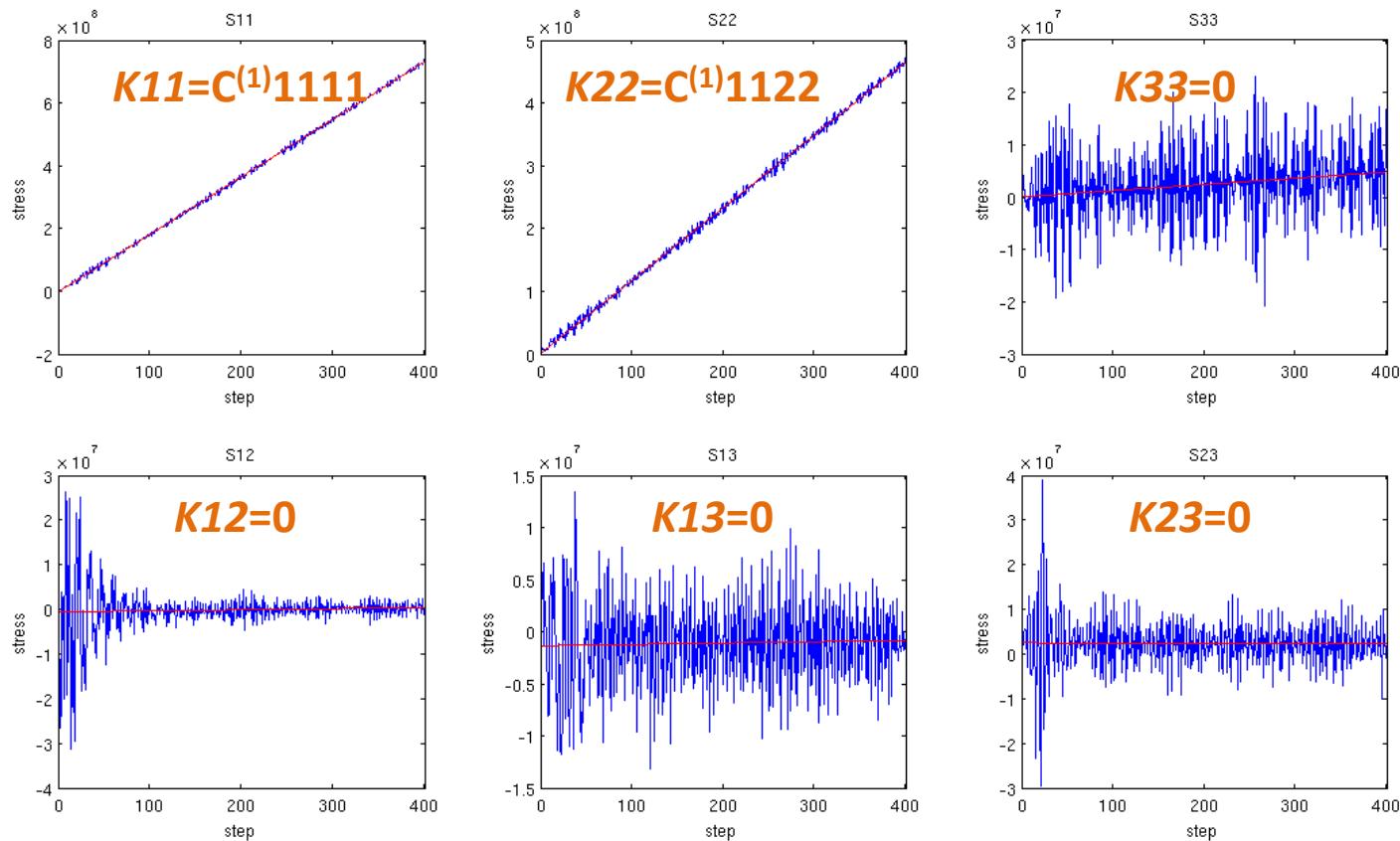
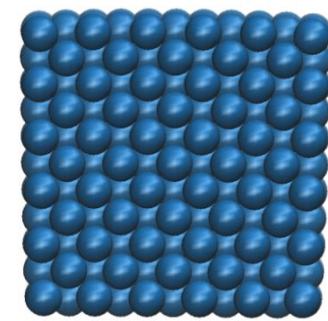
Stress evolution for the kinematics 11 at order 0 (tension)



Which gives  $C^{(0)}1111$ ,  $C^{(0)}1122$ ,  $C^{(0)}1133$ ,  $C^{(0)}1112$ ,  $C^{(0)}1113$ ,  $C^{(0)}1123$

# Bending Nanofilm

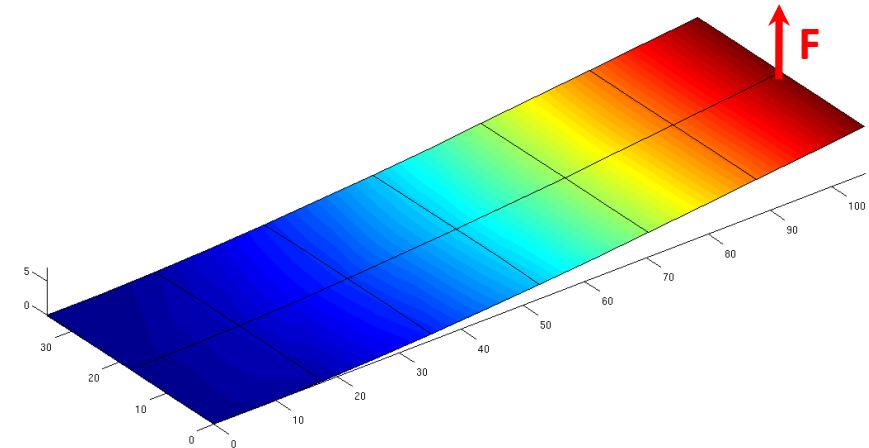
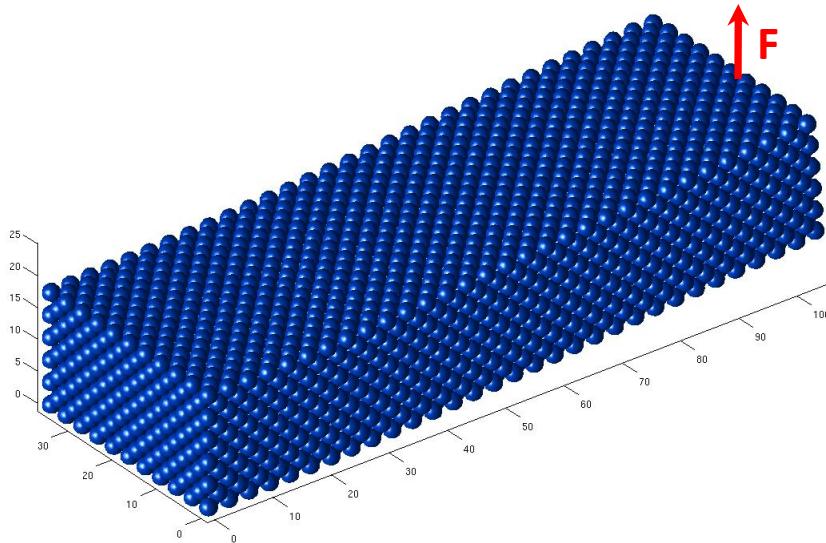
Stress evolution for the kinematics 11 at order 1 (bending)



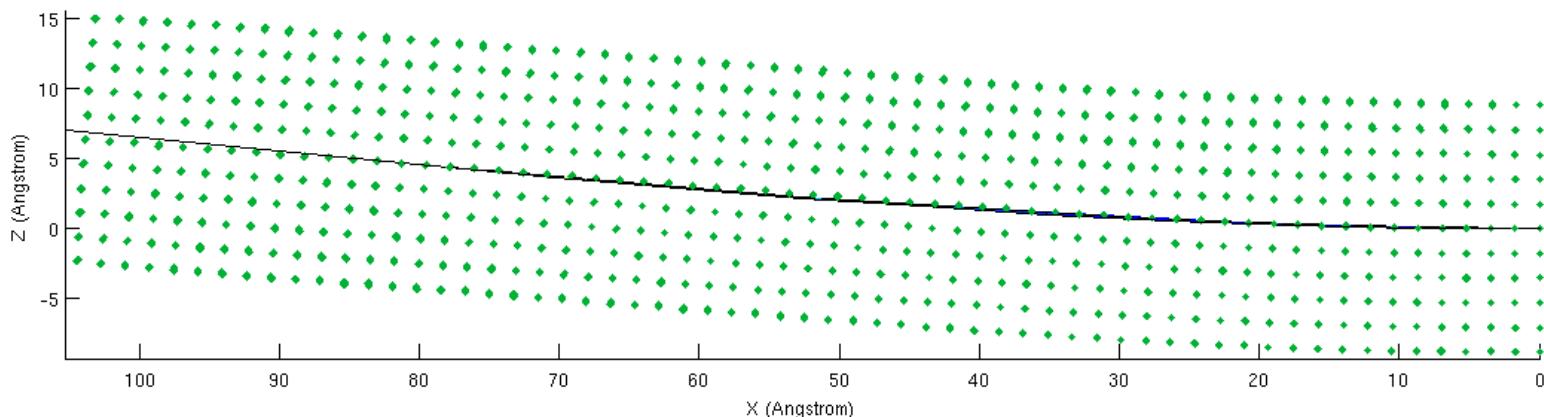
Which gives  $C^{(1)}1111$ ,  $C^{(1)}1122$ ,  $C^{(1)}1133$ ,  $C^{(1)}1112$ ,  $C^{(1)}1113$ ,  $C^{(1)}1123$

# Bending Nanofilm

Comparison between full MD model and homogenized shell



Side view of the two models 'overlapped' one on the other



# Statique moléculaire

## Potential models for nanostructure modeling

- **Modified Morse potential function**

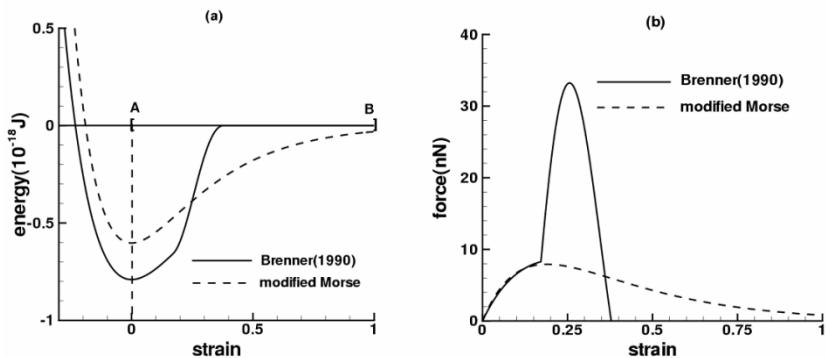
Both bond stretch, and bond angle variation are taken into account with a relatively simple formulation

$$E_{\text{intern}} = \sum_{(i,j) \in \Gamma_1} E_{\text{stretch}}(\mathbf{x}_i, \mathbf{x}_j) + \sum_{(i,j,k) \in \Gamma_2} E_{\text{angle}}(\mathbf{x}_i, \mathbf{x}_j, \mathbf{x}_k)$$

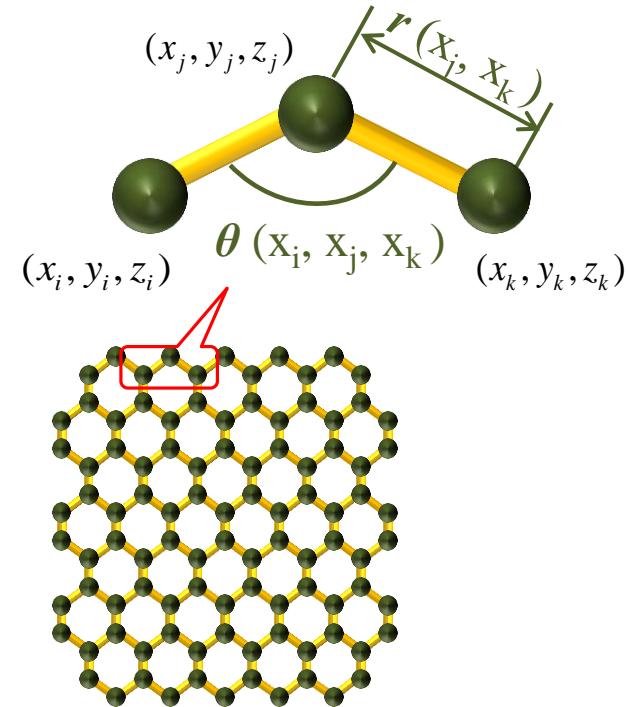
$$E_{\text{stretch}}(\mathbf{x}_i, \mathbf{x}_j) = D_e \left\{ \left[ 1 - e^{-\beta(r(\mathbf{x}_i, \mathbf{x}_j) - r_0)} \right]^2 - 1 \right\}$$

$$E_{\text{angle}}(\mathbf{x}_i, \mathbf{x}_j, \mathbf{x}_k) = \frac{1}{2} K_\theta [\cos \theta(\mathbf{x}_i, \mathbf{x}_j, \mathbf{x}_k) - \cos \theta_0]$$

- Comparison Modified Morse and Brenner potential



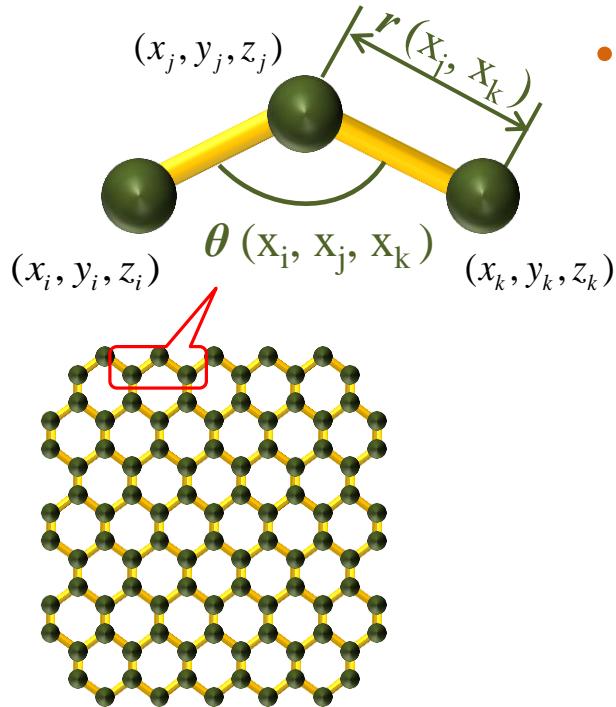
Comparison between Brenner and Modified Morse potential, Atomistic Simulations of Nanotube Fracture. T. Belytschko. 1. , S.P. Xiao. 2. , G.C. Schatz. 3 and R. Ruoff. Physical Review B Vol65, 2002



Modified Morse and Brenner  
are equivalent for strains  $\leq 15\%$

# Statique moléculaire

## Problem definition



**Γ1:** Set of adjacent atom triplets forming an angle

**Γ2:** Set of bonded atom pairs

- **Equilibrium configuration by energy minimization**

According to the Modified Morse potential formulation, both energy contributions by bond stretch and bond angle bending should be accounted for.

$$\frac{\partial}{\partial \mathbf{x}} \left( \sum_{(i,j) \in \Gamma_1} E_{\text{stretch}}(\mathbf{x}_i, \mathbf{x}_j) \right) + \frac{\partial}{\partial \mathbf{x}} \left( \sum_{(i,j,k) \in \Gamma_2} E_{\text{angle}}(\mathbf{x}_i, \mathbf{x}_j, \mathbf{x}_k) \right) - \lambda \mathbf{F} = \mathbf{0}$$

## Interatomic forces

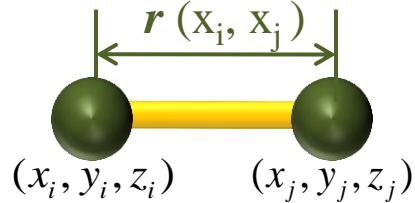
With  $\mathbf{x} = (\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)^T$  atomic position coordinates

$\mathbf{F} = (\mathbf{F}_1, \mathbf{F}_2, \dots, \mathbf{F}_N)^T$  external loads

# Statique moléculaire

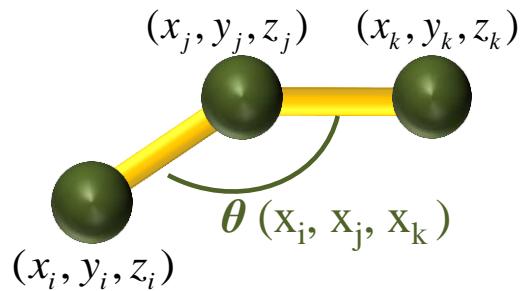
Equilibrium equation incorporates two problems to be considered independently:

- Forces due to bond stretch:



$$\left\{ \begin{array}{l} \mathbf{F}_{si}(\mathbf{x}_i, \mathbf{x}_j) = \frac{\partial}{\partial \mathbf{x}_i} E_{\text{stretch}}(\mathbf{x}_i, \mathbf{x}_j) \\ E_{\text{stretch}}(\mathbf{x}_i, \mathbf{x}_j) = D_e \left\{ 1 - e^{-\beta(r(\mathbf{x}_i, \mathbf{x}_j) - r_0)} \right\}^2 - 1 \\ r(\mathbf{x}_i, \mathbf{x}_j) = \sqrt{(\mathbf{x}_i - \mathbf{x}_j)^2} \end{array} \right.$$

- Forces due to bond angle variation:



$$\left\{ \begin{array}{l} \mathbf{F}_{ai}(\mathbf{x}_i, \mathbf{x}_j, \mathbf{x}_k) = \frac{\partial}{\partial \mathbf{x}_i} E_{\text{angle}}(\mathbf{x}_i, \mathbf{x}_j, \mathbf{x}_k) \\ E_{\text{angle}}(\mathbf{x}_i, \mathbf{x}_j, \mathbf{x}_k) = \frac{1}{2} K_\theta [\cos \theta(\mathbf{x}_i, \mathbf{x}_j, \mathbf{x}_k) - \cos \theta_0] \\ \cos \theta(\mathbf{x}_i, \mathbf{x}_j, \mathbf{x}_k) = \frac{(\mathbf{x}_i - \mathbf{x}_j)(\mathbf{x}_k - \mathbf{x}_j)}{\sqrt{(\mathbf{x}_i - \mathbf{x}_j)^2} \sqrt{(\mathbf{x}_k - \mathbf{x}_j)^2}} \end{array} \right.$$

Both to be reformulated for application of the ANM method

# Statique moléculaire

## Formulation of interatomic forces

- Forces applied on the atom  $i$  and due to the stretching effect of the bond  $ij$  can be formulated as follows:

$$\mathbf{F}_{si} = 2D_e \beta \frac{\mathbf{x}_i - \mathbf{x}_j}{\sqrt{(\mathbf{x}_i - \mathbf{x}_j)^2}} e^{-\beta(r(\mathbf{x}_i, \mathbf{x}_j) - r_0)} \left[ 1 - e^{-\beta(r(\mathbf{x}_i, \mathbf{x}_j) - r_0)} \right]$$

- In order to apply the ANM method, this equation should be transformed in **quadratic** form and all intermediate variables introduced are to be expanded into series to order " $n$ :

$$\begin{cases} \mathbf{F}_{si} = 2D_e \beta \cdot A \cdot B \\ B = \alpha(1 - \alpha) \\ -\beta\alpha \cdot dr = d\alpha \\ r \cdot A = \mathbf{u} \\ r^2 = \mathbf{u}^2 \\ \mathbf{u} = \mathbf{x}_i - \mathbf{x}_j \end{cases}$$



$$\begin{cases} A(a) = A_0 + aA_1 + \dots + a^n A_n \\ B(a) = B_0 + aB_1 + \dots + a^n B_n \\ \alpha(a) = \alpha_0 + a\alpha_1 + \dots + a^n \alpha_n \\ r(a) = r_0 + ar_1 + \dots + a^n r_n \\ \mathbf{u}(a) = \mathbf{u}_0 + a\mathbf{u}_1 + \dots + a^n \mathbf{u}_n \end{cases}$$

Linearization  
of  
the problem

Where "A, B,  $\alpha$ ,  $r$ ,  $\mathbf{u}$ " are  
intermediate variables

Asymptotic Expansion of all variables  
to order " $n$ "

# Statique moléculaire

## Formulation of interatomic forces

- By identification of all terms at the same order with respect to “ $a$ ”, we obtain:

For order 1

$$\begin{cases} (\mathbf{F}_{si})_1 = 2D_e\beta \cdot (A_0B_1 + A_1B_0) \\ B_1 = \alpha_1 - 2\alpha_1\alpha_0 \\ A_1 = \frac{1}{r_0}(\mathbf{u}_1 - A_0\mathbf{r}_1) \\ \alpha_1 = -\beta\alpha_0 r_1 \\ r_1 = \frac{1}{r_0}\mathbf{u}_1\mathbf{u}_0 \end{cases}$$

For order  $k$  ( $k>1$ )

$$\begin{cases} (\mathbf{F}_{si})_k = 2D_e\beta \cdot (A_0B_k + A_kB_0) + 2D_e\beta \cdot \sum_{i=1}^{k-1} A_iB_{k-i} \\ B_k = \alpha_k - 2\alpha_k\alpha_0 - \sum_{i=1}^{k-1} \alpha_i\alpha_{k-i} \\ A_k = \frac{1}{r_0}(\mathbf{u}_k - A_0\mathbf{r}_k) - \frac{1}{r_0} \sum_{i=1}^{k-1} r_i A_{k-i} \\ \alpha_k = -\beta\alpha_0 r_k - \frac{\beta}{k} \sum_{i=1}^{k-1} (k-i)\alpha_i r_{k-i} \\ r_k = \frac{1}{r_0}\mathbf{u}_k\mathbf{u}_0 + \frac{1}{2r_0} \sum_{i=1}^{k-1} \mathbf{u}_i\mathbf{u}_{k-i} \end{cases}$$

$\mathbf{F}_{si}^{\text{nl}}_k$        $\mathbf{B}^{\text{nl}}_k$        $\mathbf{A}^{\text{nl}}_k$        $\boldsymbol{\alpha}^{\text{nl}}_k$        $\mathbf{r}^{\text{nl}}_k$

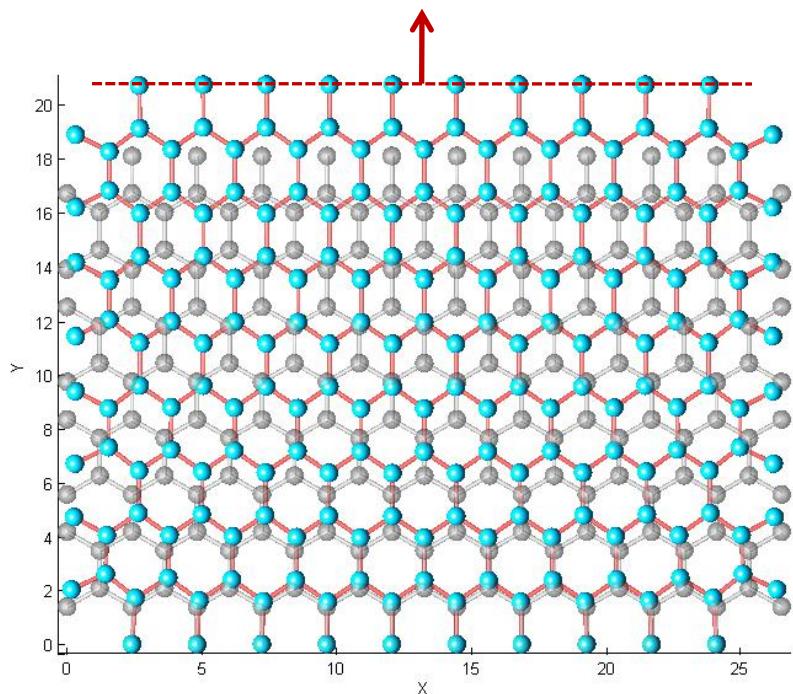
# Applications

Three examples:

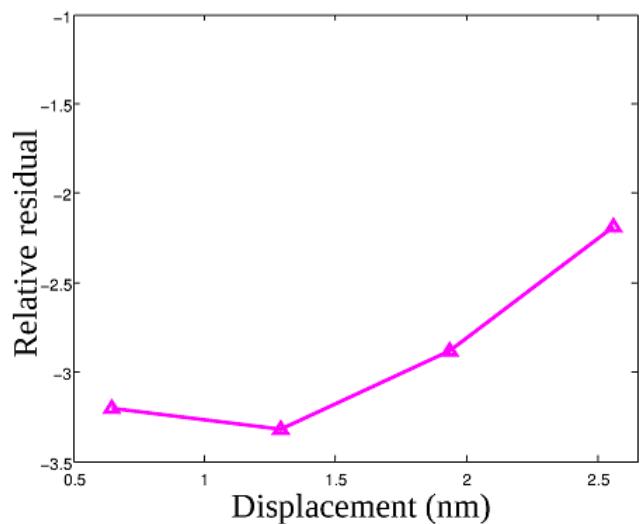
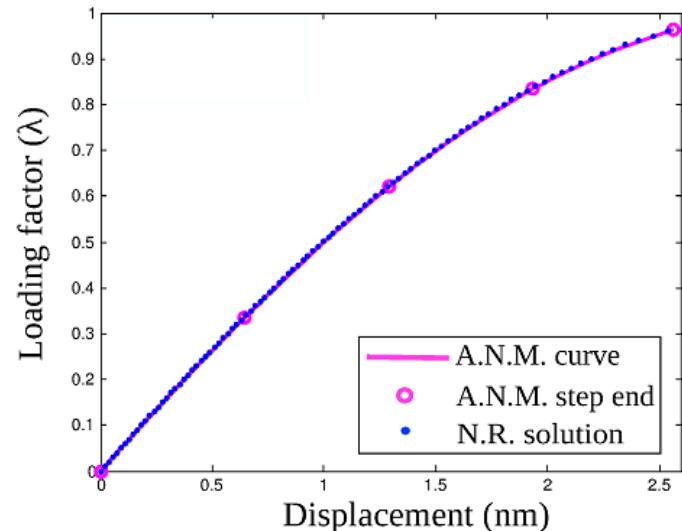
- Tension of a graphene monolayer
- Local deformation of a nanotube (3D)
- Buckling of a nanotube subjected to compression (3D)

# Applications

## Tension of a graphene layer

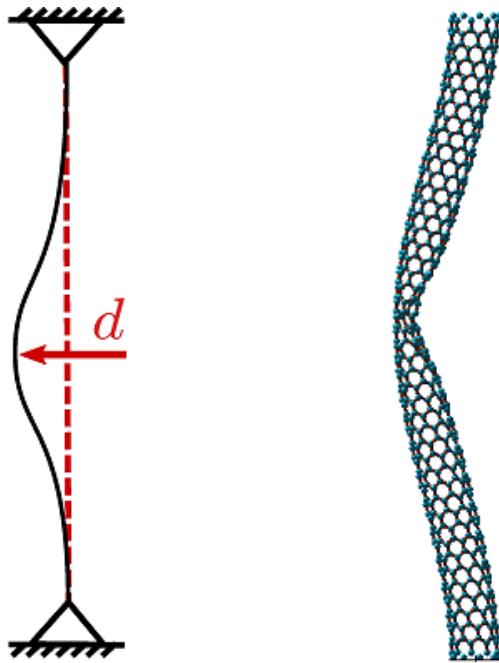


	N.R.	A.N.M.
Number of step	98	4
Number of tangent matrix inversion	196	4
Computation time	70s	5.6s

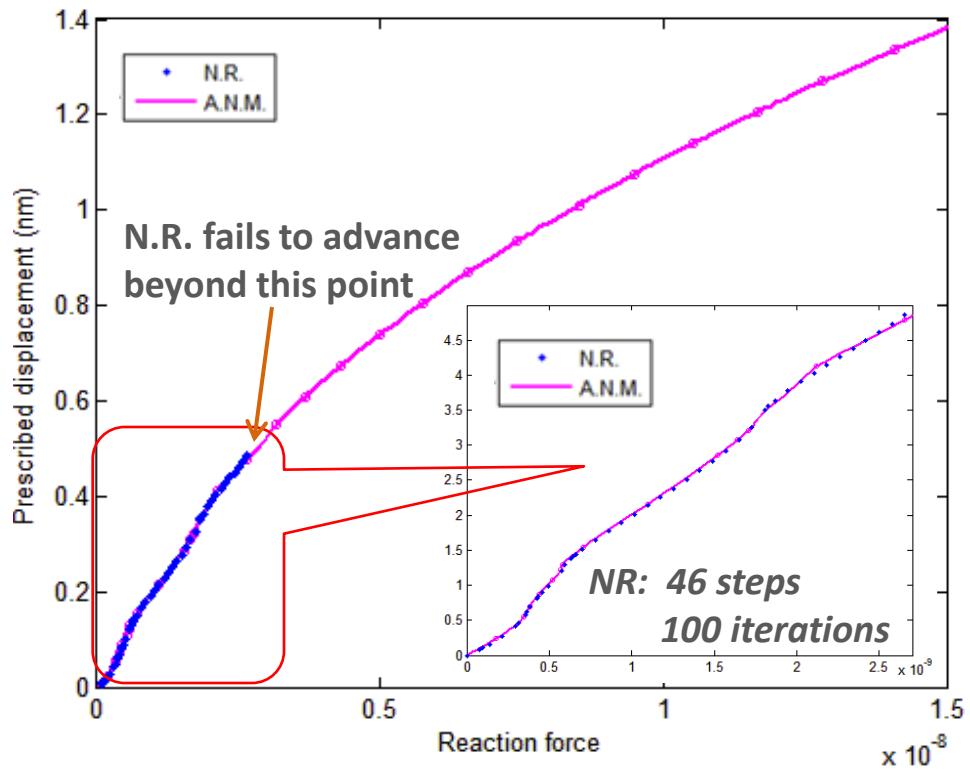


# Applications

## Radial compression of a nanotube



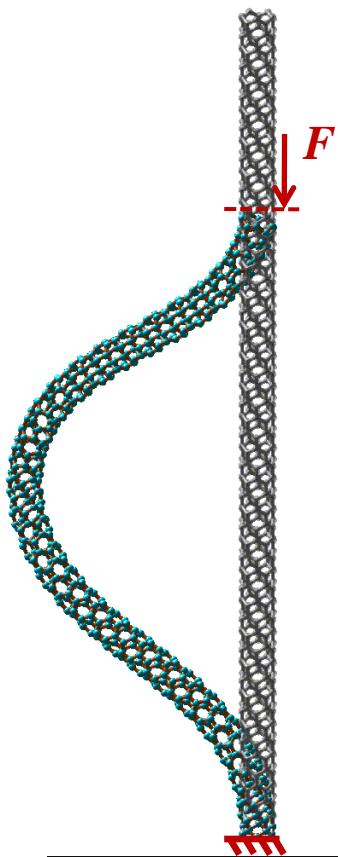
Buckling of a (18,0) Zig-zag nanotube.  
 $d = 1.39\text{e-}2 \text{ nm}$  (radial displacement)  
 $N$  (series order) = 10  
 $\delta = 1\text{e-}4$



	N.R.	A.N.M.
Number of step	--	29
Number of tangent matrix inversion	--	29

# Applications

## Buckling of a nanotube



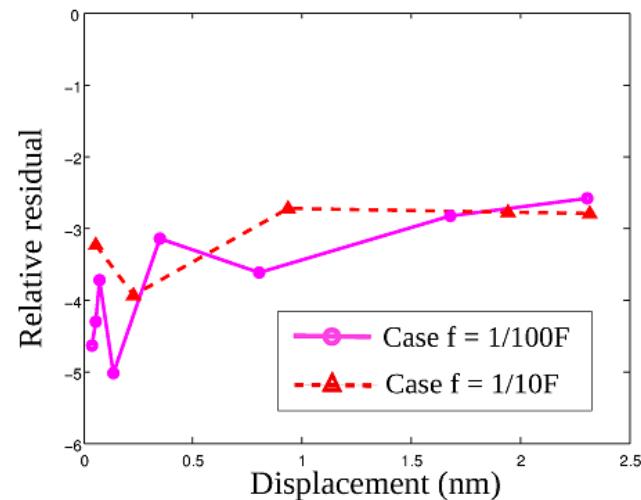
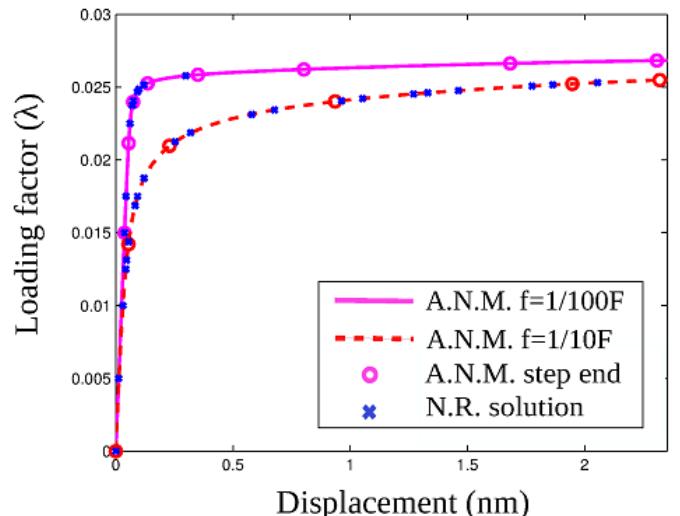
Buckling of a (10,0)  
Zig-zag nanotube.

Compression force:  
 $\mathbf{F} = 7.9 \times 10^{-8} \text{ N}$

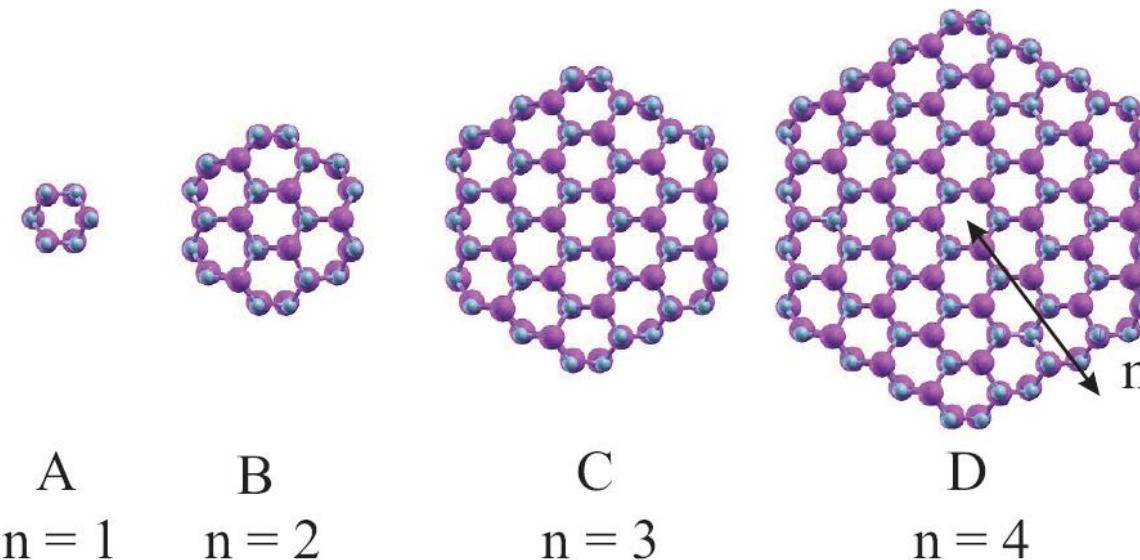
Disturbance force:  
 $f_1 = 1/10 \cdot \mathbf{F}$   
 $f_2 = 1/100 \cdot \mathbf{F}$

$N$  (series order) = 20  
 $\delta = 10^{-5}$

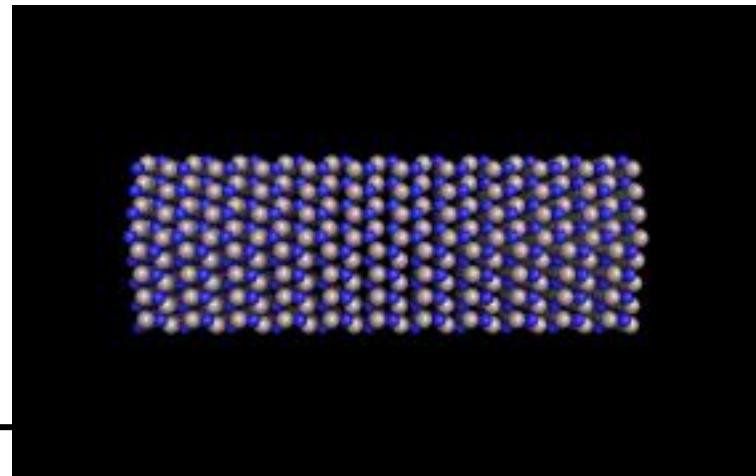
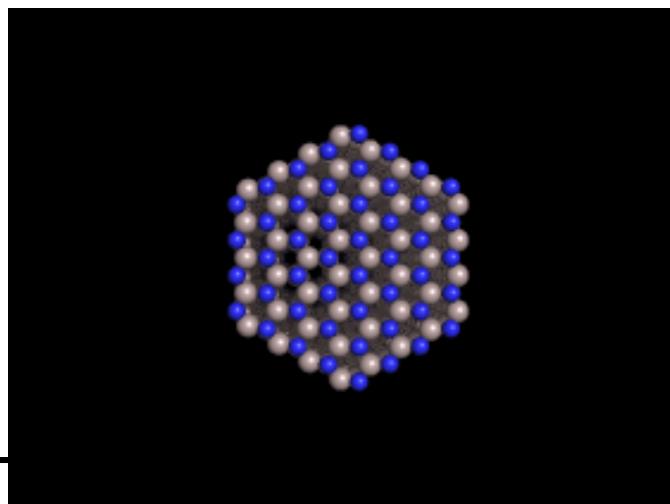
	N.R.	A.N.M.
Number of step	20	5
Number of tangent matrix inversion	50	5
Computation time	4min 7s	39s



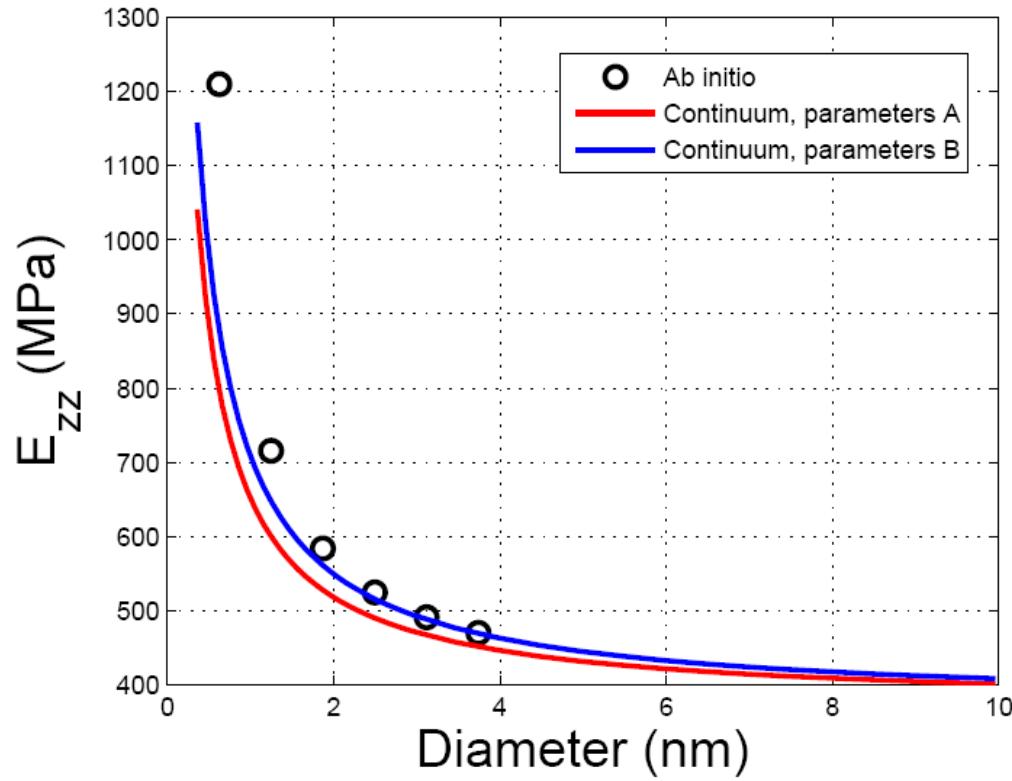
# Modélisation continue de nanofils ioniques : confrontations avec modèle ab initio complet



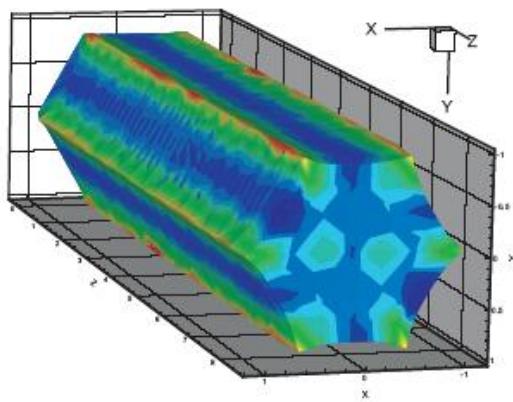
Ab initio computations on cells up to  $n = 7$  (588 atoms) :  $d = 3.1 \text{ nm}$



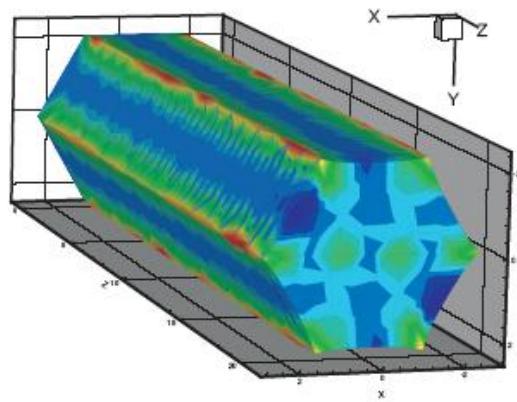
# Results : Young's modulus



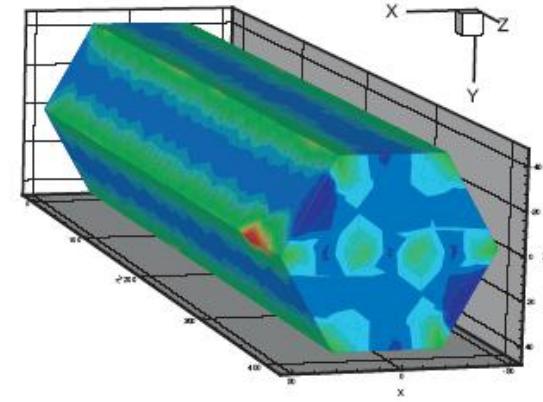
# Results: residual axial and radial strains



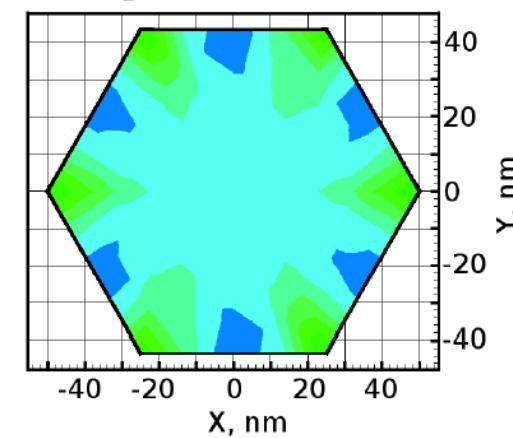
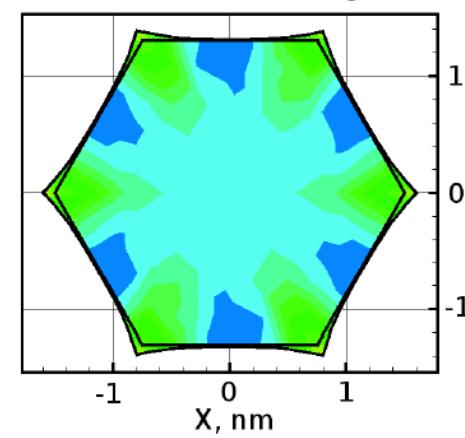
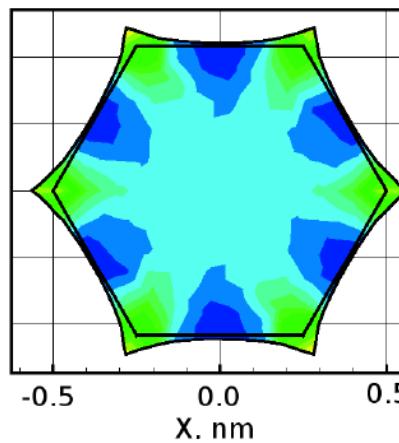
$d = 1 \text{ nm}$



$d = 3 \text{ nm}$

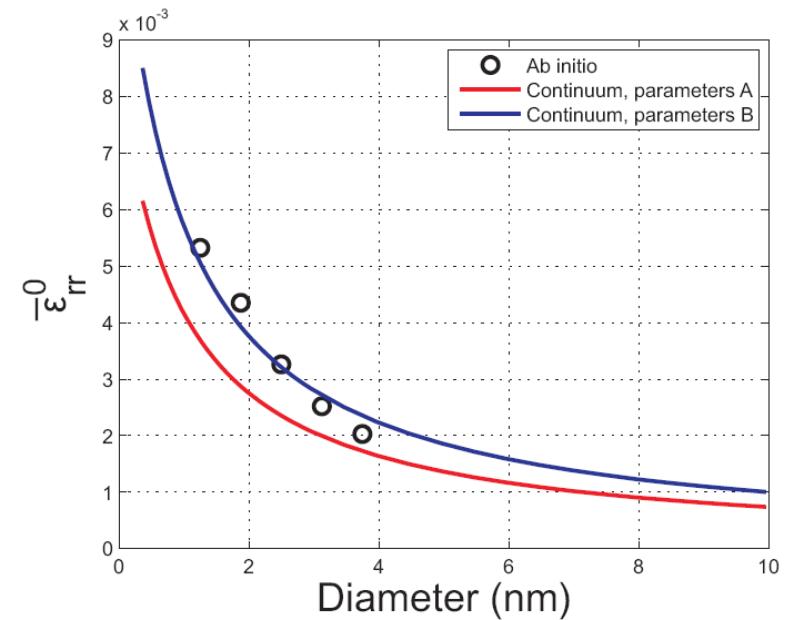
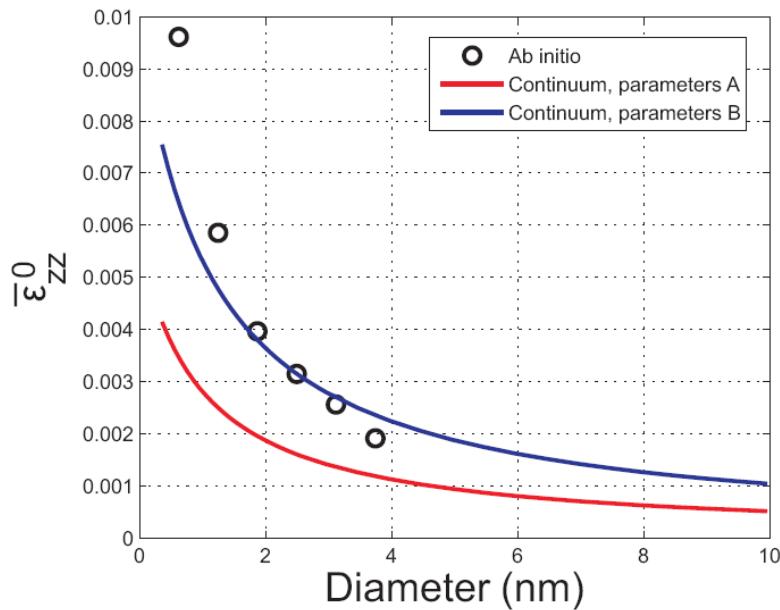


$d = 100 \text{ nm}$



**Size-dependent deformations due to surface residual stress**

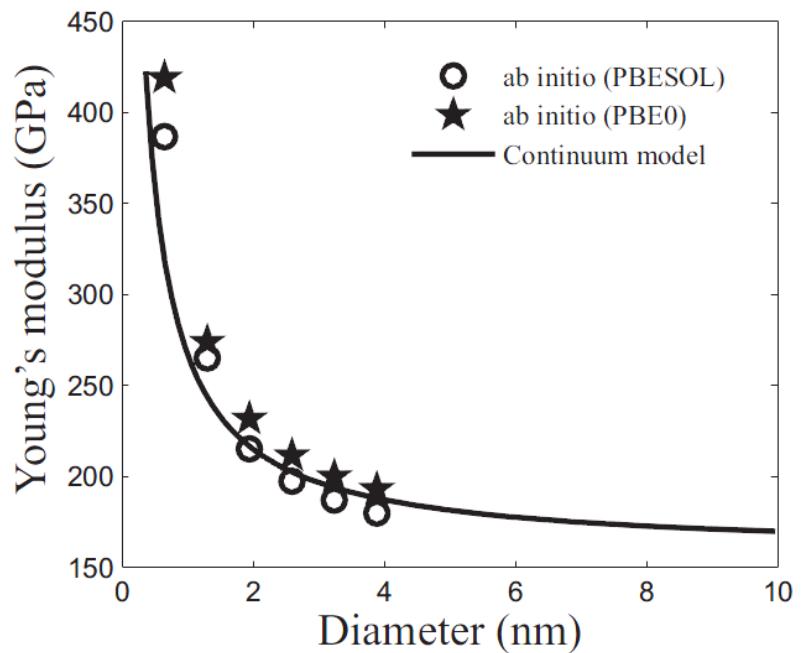
# Results: residual axial and radial strains



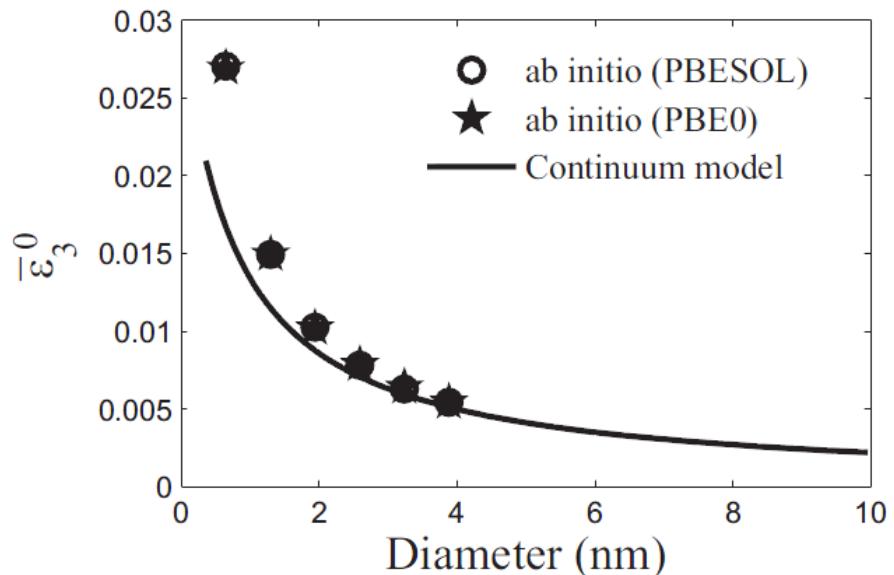
Surface elastic parameters (N/m).

Parameters A (obtained from slab calculations)	Parameters B (optimized)
$C_{33}^s = 78.0$	$C_{33}^s = 93.59$
$C_{11}^s = 114.1$	$C_{11}^s = 114.1$
$C_{13}^s = 22.3$	$C_{13}^s = 22.3$
$C_{55}^s = 44.0$	$C_{55}^s = 44.0$
$\tau_1^s = -2.33$	$\tau_1^s = -3.33$
$\tau_1^s = -0.873$	$\tau_1^s = -1.533$

## Results for ZnO nanowires

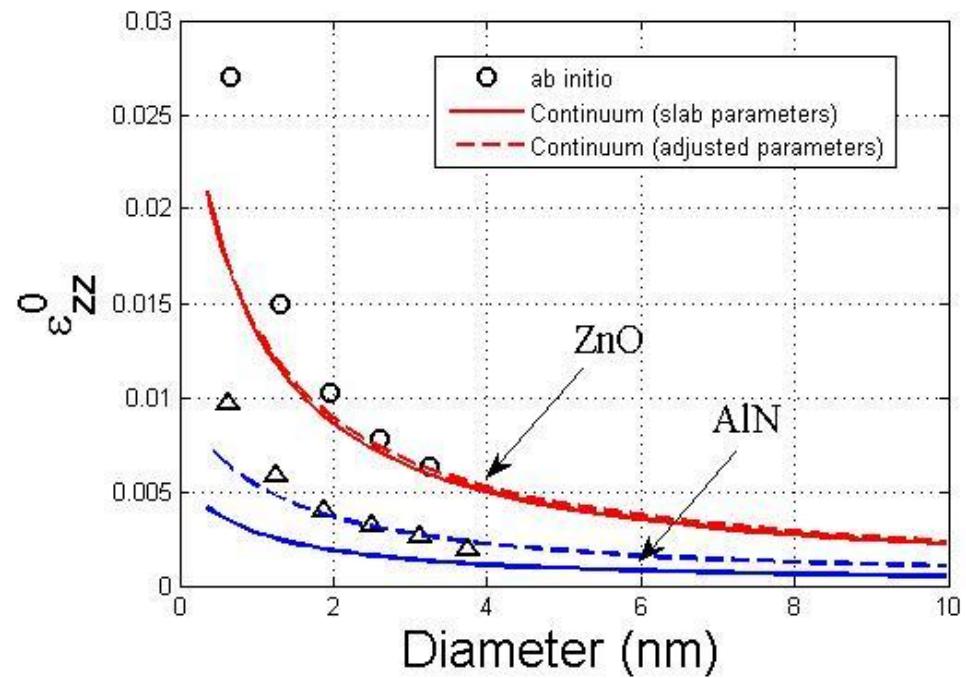
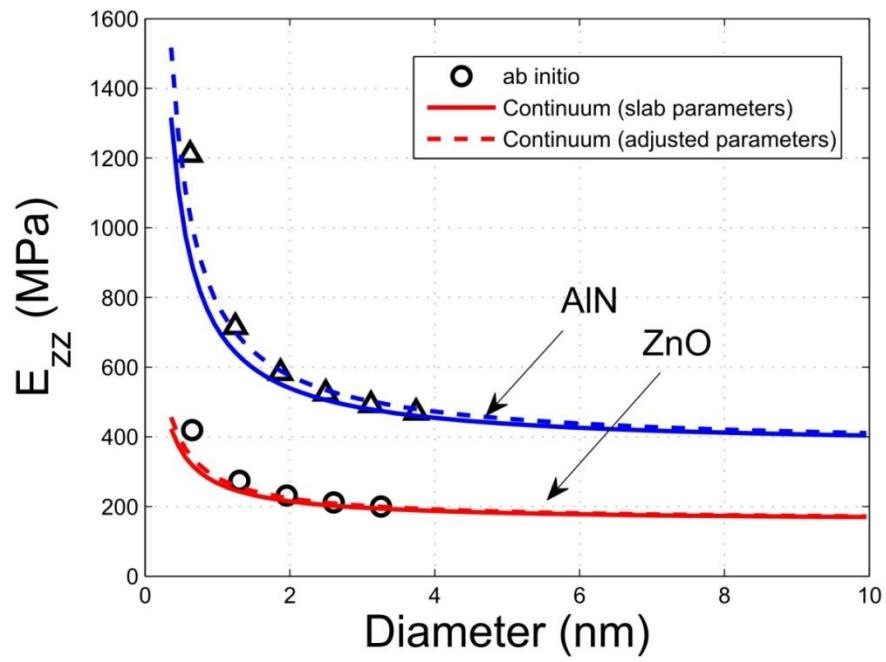


Young's modulus

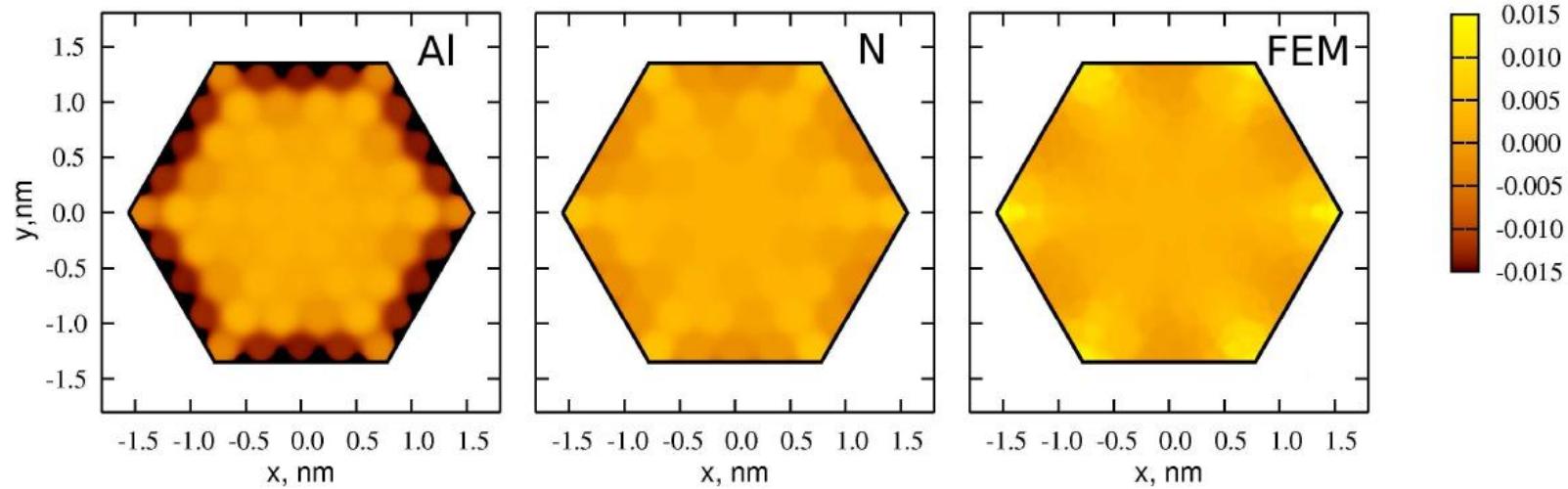
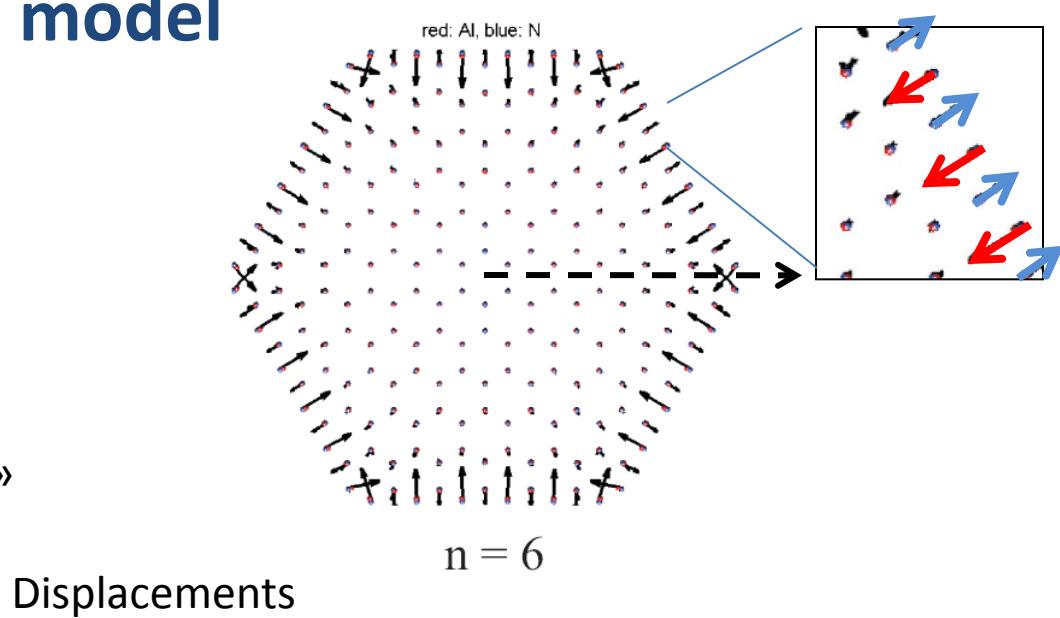
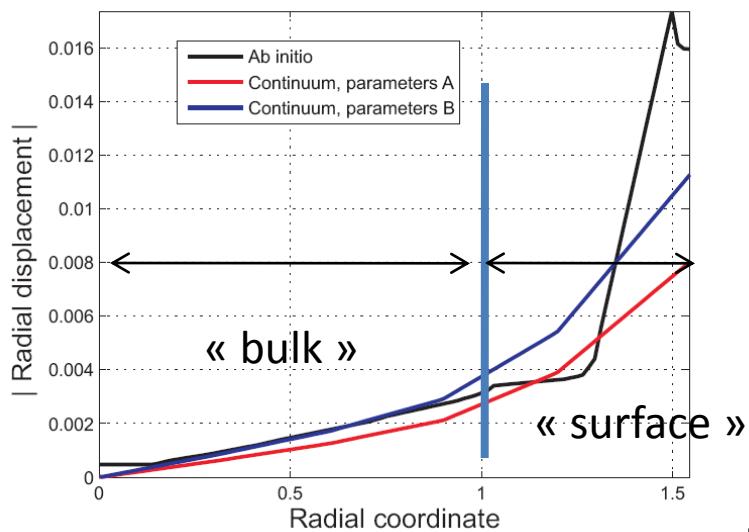


Axial free dilatation

# Size effects: comparison between AlN and ZnO materials

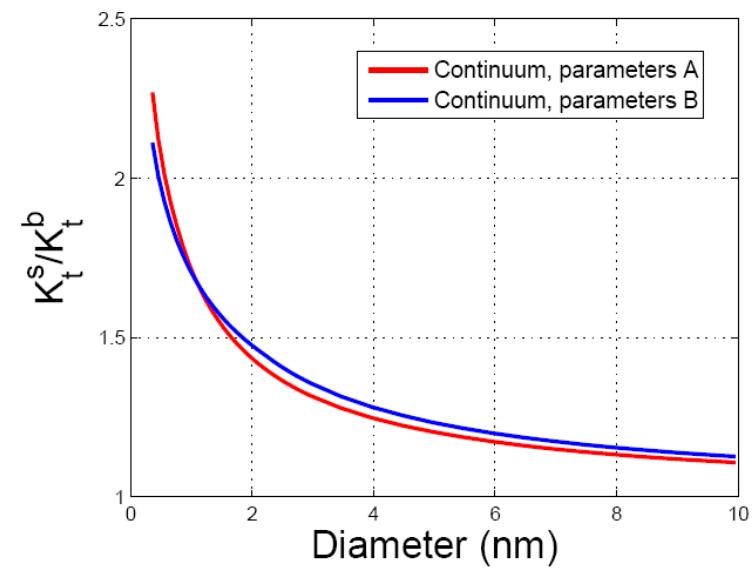
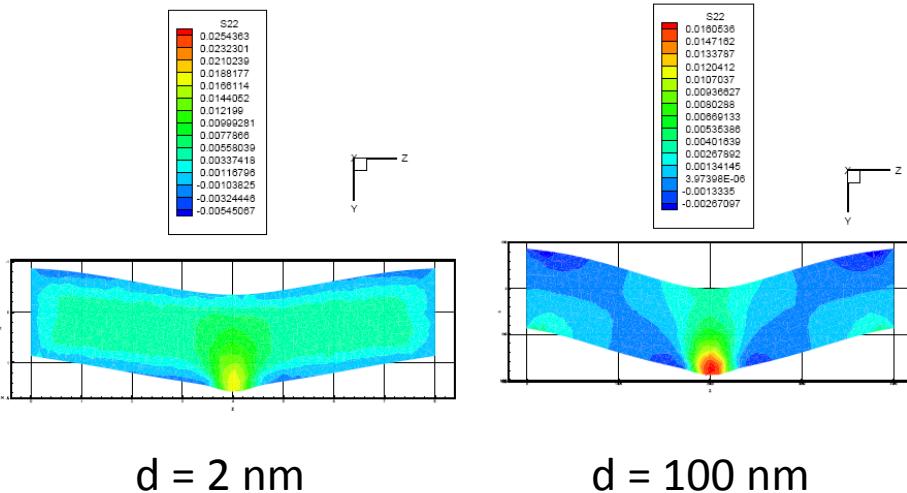
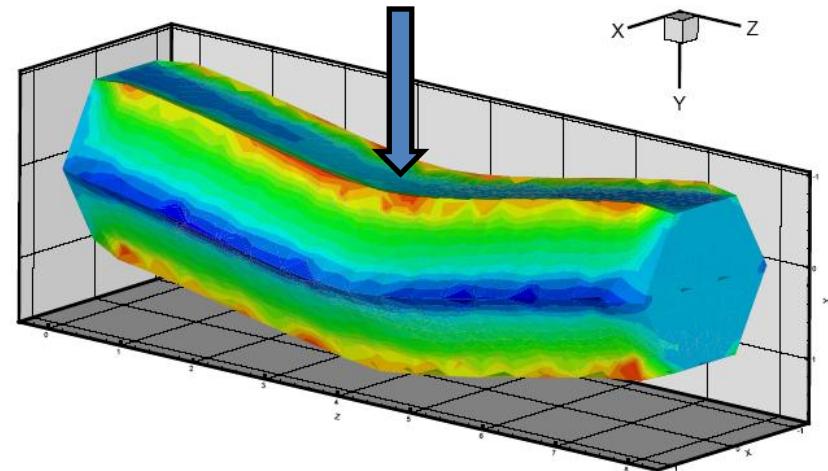
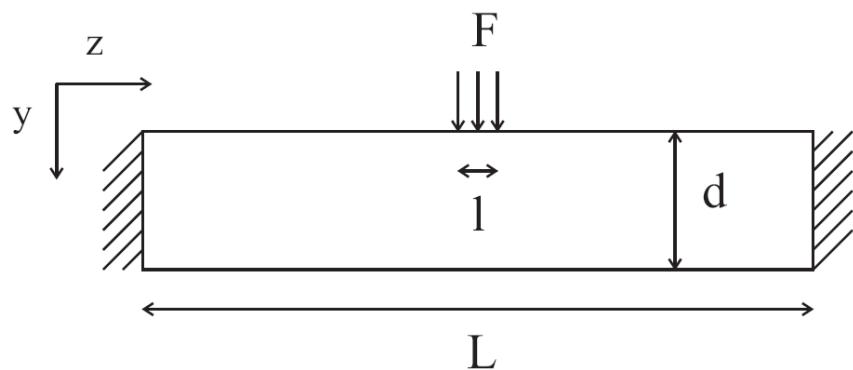


# Local fields: comparisons FEM-continuum/ab initio model



Radial strains

# Application: size-dependent effects in bending analysis of a nanowire

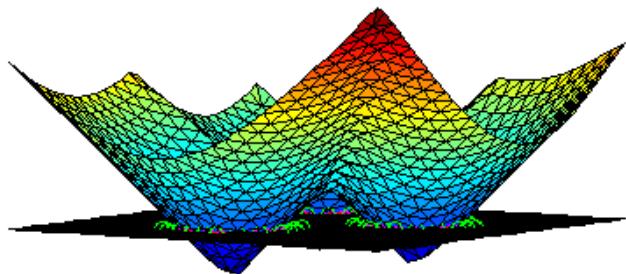


# Avoiding surface meshes in complex nanostructures with many free surfaces: a combined XFEM/level-set approach

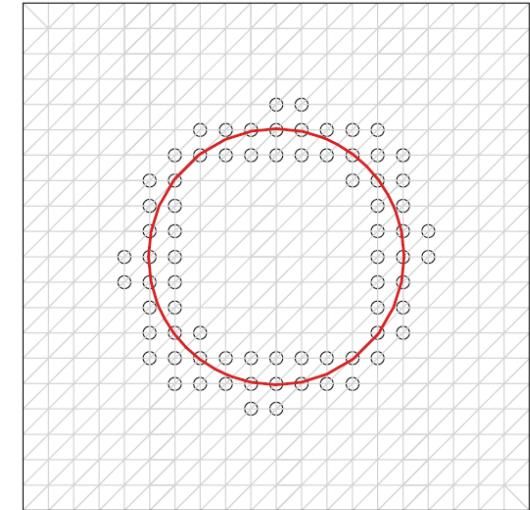
Enriched FEM approximation

$$\mathbf{u}^h(\mathbf{x}) = \sum_{i=1}^n N_i(\mathbf{x}) \mathbf{u}_i + \sum_{j=1}^m N_j(\mathbf{x}) \psi(\mathbf{x}) \mathbf{a}_j$$

Discontinuous enrichment  
based on the level-set  
function

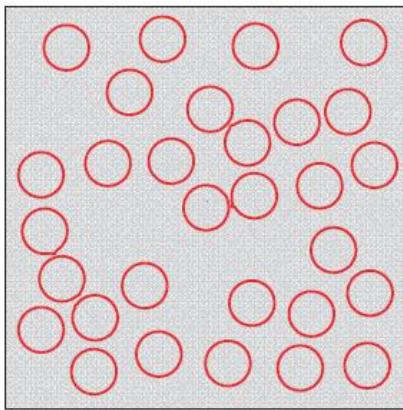
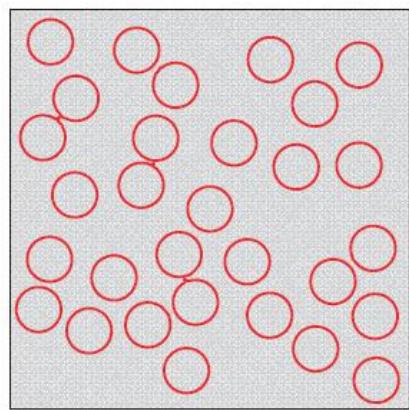
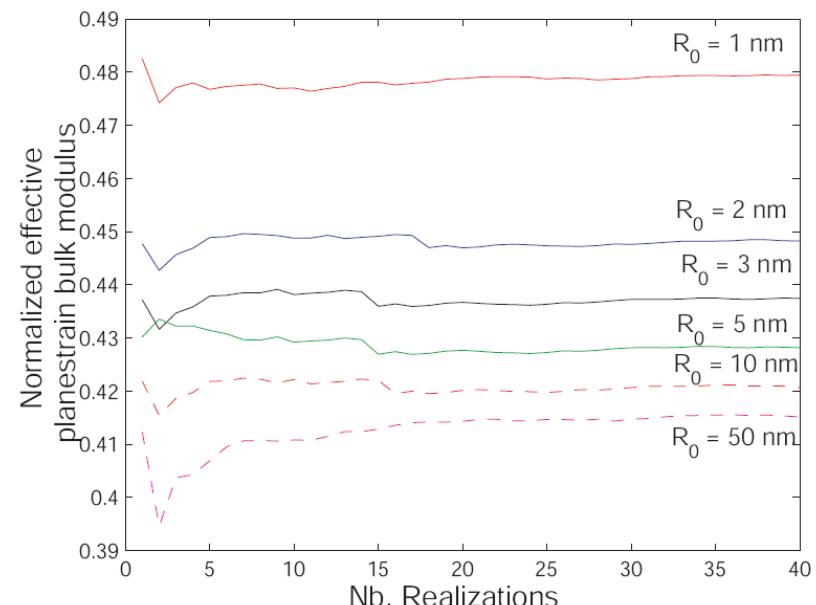
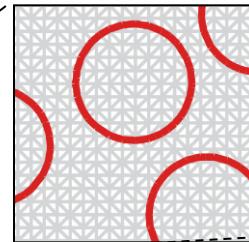
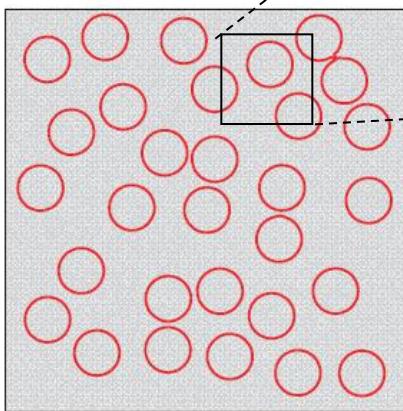
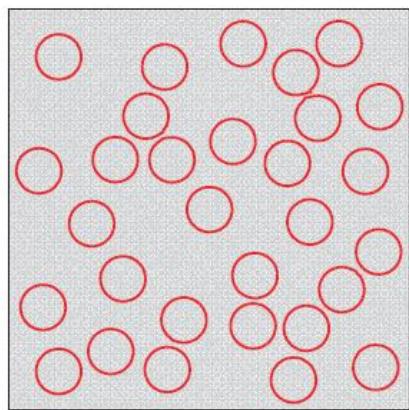


Level-set function



$$\mathbf{n}(\mathbf{x}) = \frac{\nabla \tilde{\phi}(\mathbf{x})}{\|\nabla \tilde{\phi}(\mathbf{x})\|},$$

# Statistical computations on stochastic RVEs with size effects : nano pores

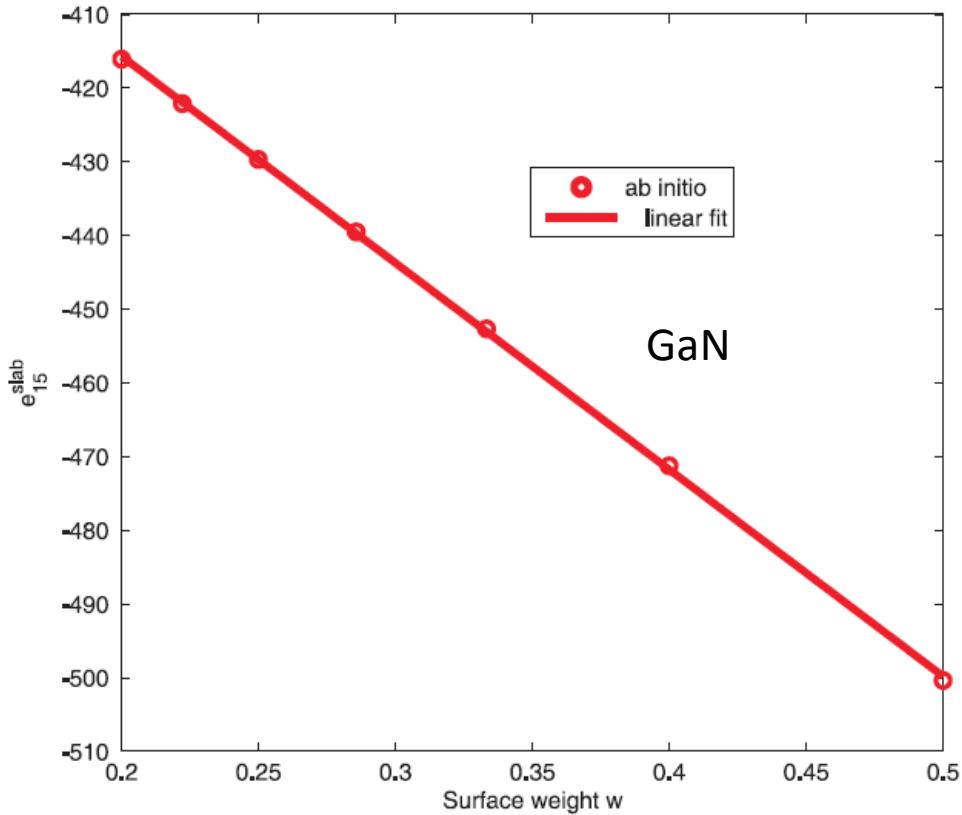


Size effects in randomly distributed nanostructures

Level-set description of the interfaces

[JY et al. Comput. Mech. 2008]

# Computation of surface piezoelectric coefficients by ab initio calculations



ZnO

Method	$e_{33}^s$	$e_{31}^s$	$e_{15}^s$
PBESOL	0.6277	-0.1952	-0.1731
PBE0	0.5966	-0.1992	-0.1768

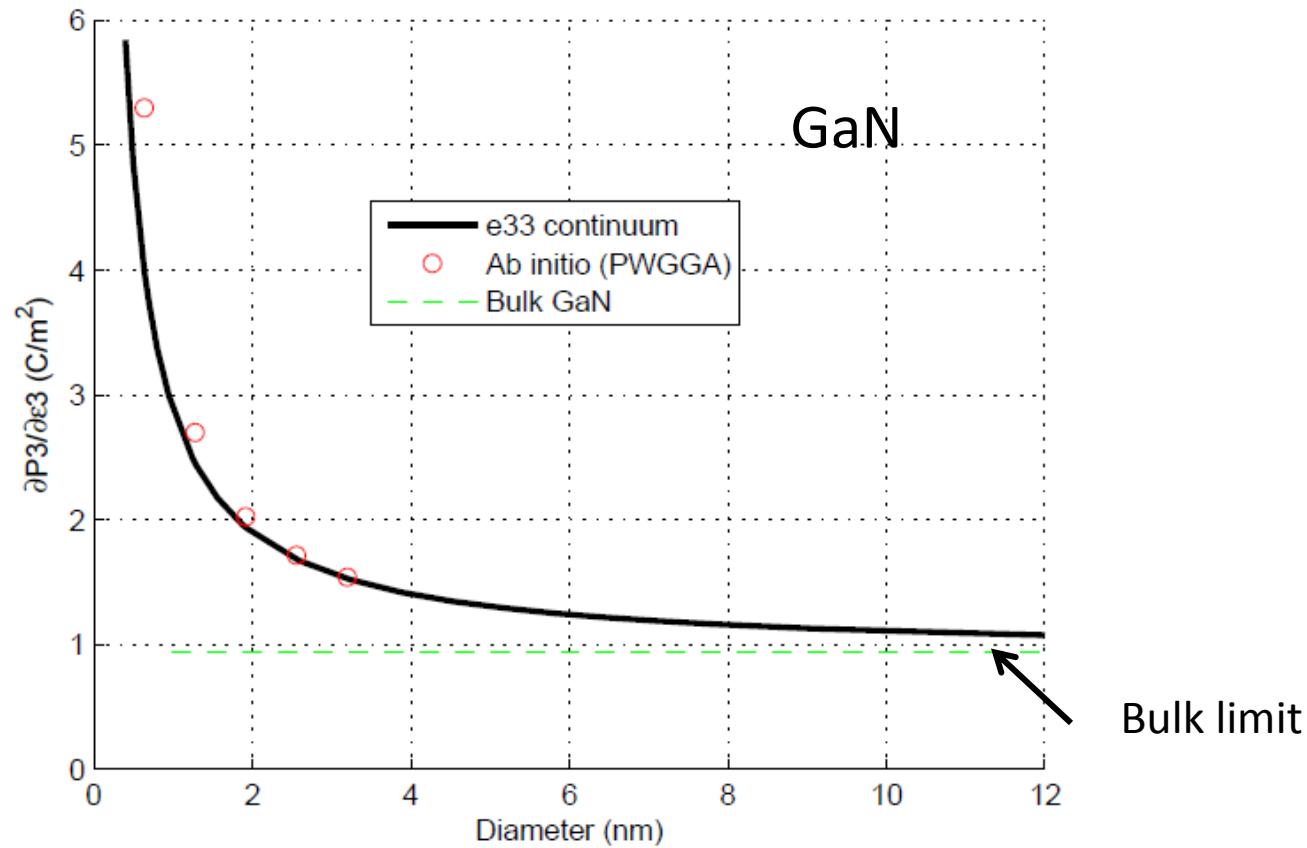
AlN

Method	$e_{33}^s$	$e_{31}^s$	$e_{15}^s$
PBESOL	0.4084	-0.1533	-0.1664
PBE0	0.4019	-0.1744	-0.1725
PWGGA	0.3746	-0.1428	-0.1529

GaN

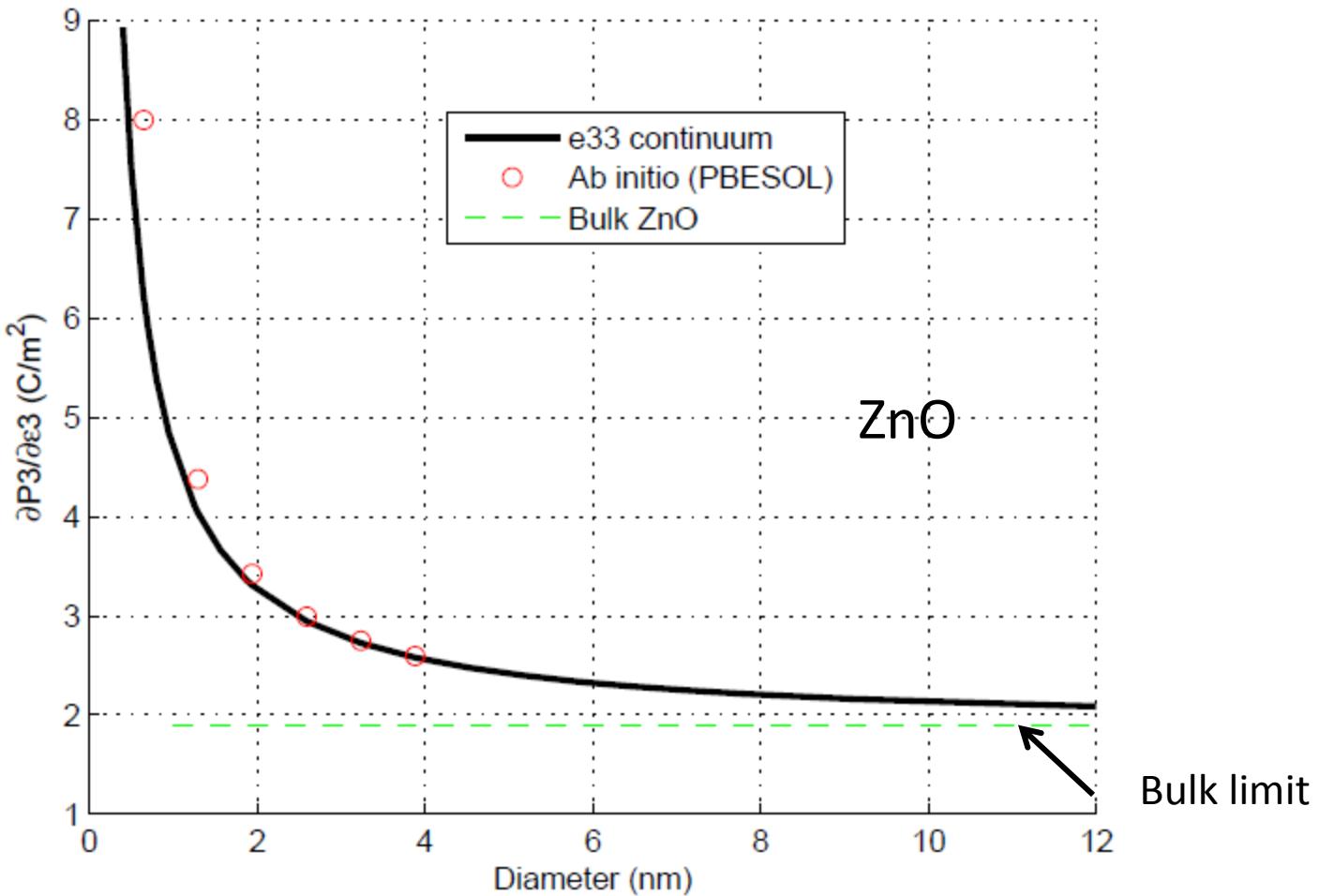
Method	$e_{33}^s$	$e_{31}^s$	$e_{15}^s$
PBESOL	0.4084	-0.1533	-0.1664
PBE0	0.4019	-0.1744	-0.1725
PWGGA	0.3746	-0.1428	-0.1529
Expt. <sup>19</sup>	-0.32	0.29	

# Comparison with FEM multiscale continuum model

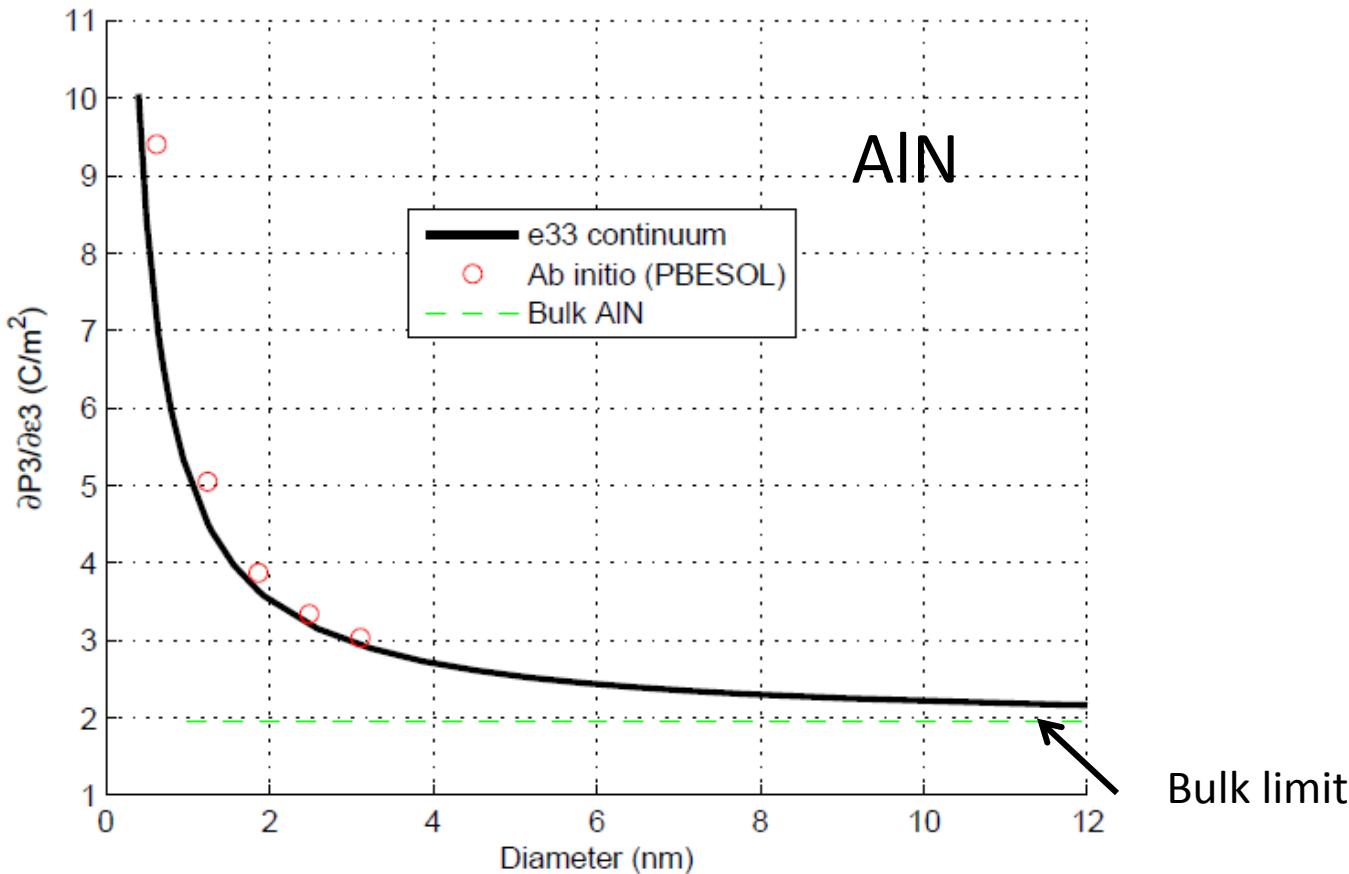


Efficient and accurate method: does not require computing the full models of nanowires (only small surface models)

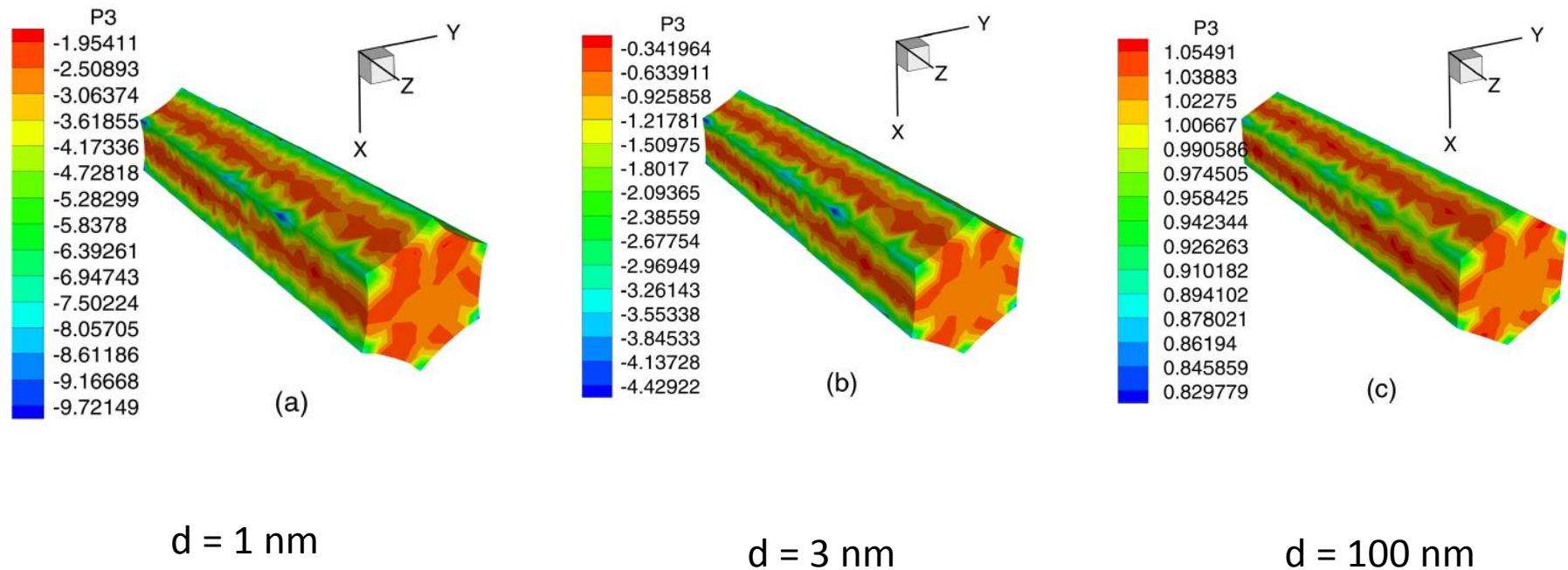
# Comparison with FEM multiscale continuum model



# Comparison with FEM multiscale continuum model



# FEM continuum model: polarization field and local strains due to surface effects



[M.T Hoang, JY, S. Mitrushchenkov, G. Chambaud, J. Appl. Phys. 2013]

Merci pour votre attention !