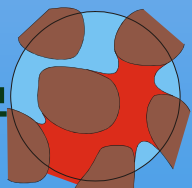


Diffusion effective: du microscopique au nanoscopique

M. Quintard

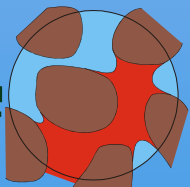
Institut de Mécanique des Fluides de Toulouse



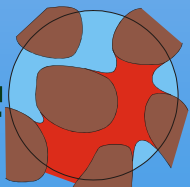
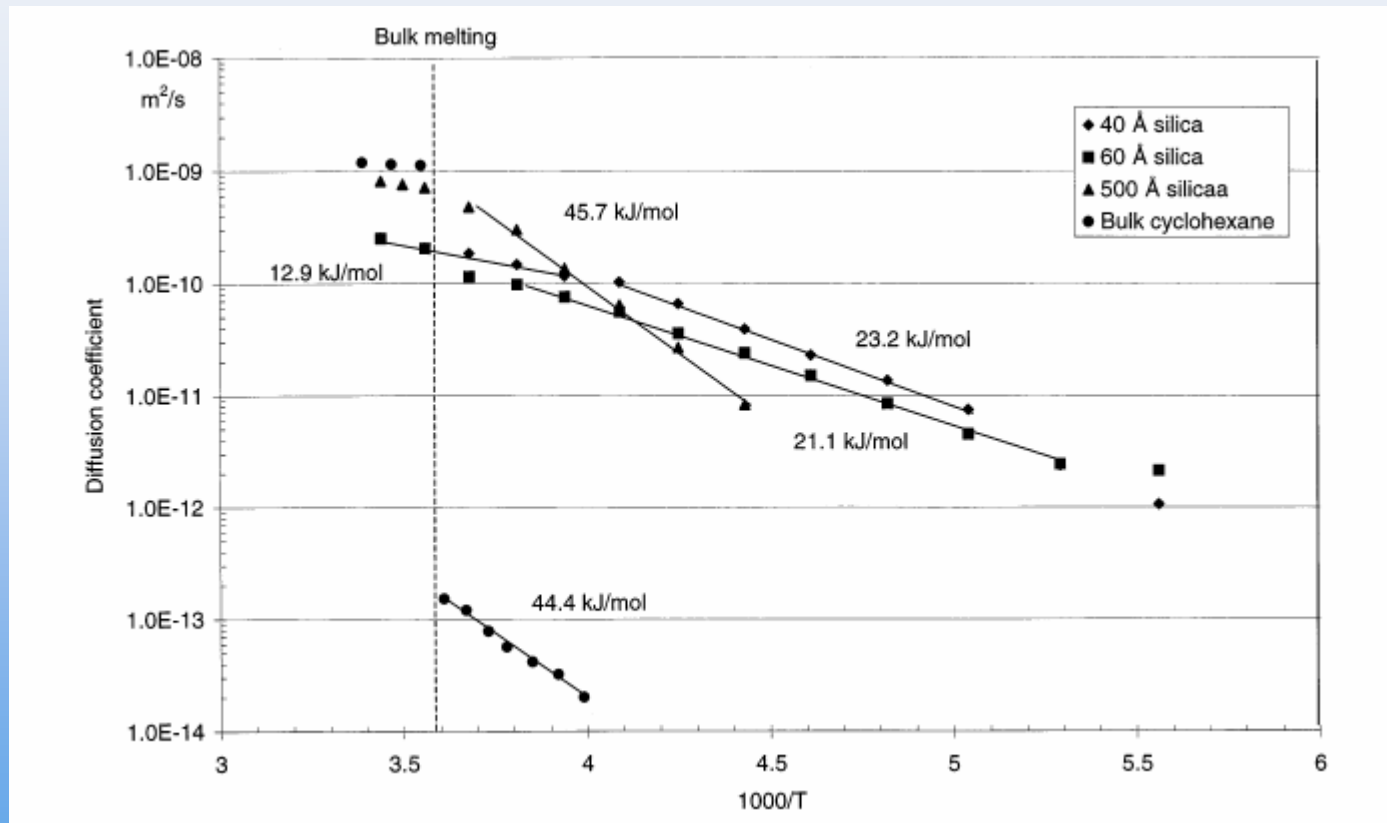
Introduction

- Introduction
- Changement d'échelle au sens de la MMC
- Corrections dans le cas sub-microscopique
- Approches mésoscopiques
- Dynamique Moléculaire
- Conclusion

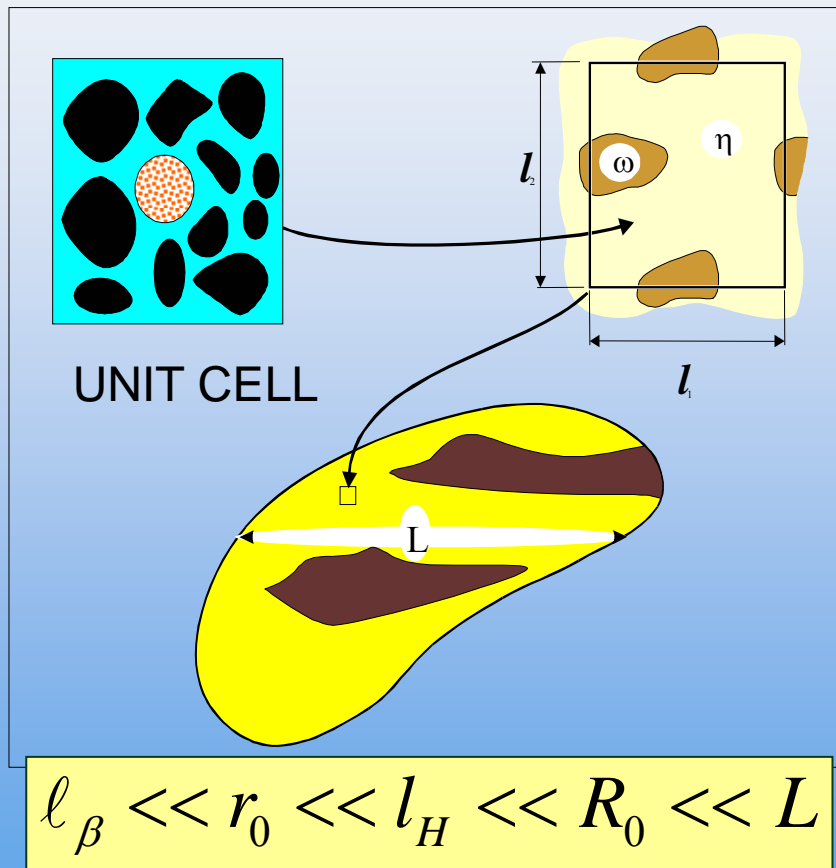
(Exemples tirés du pb. de diffusion)



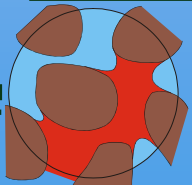
Diffusion de Cyclohexane (Aksnes et al., 1998)



Changement d'Echelle

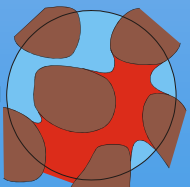


- physique à une échelle donnée (ex. Échelle du pore)
- description à une échelle supérieure? Grandeurs macroscopiques?
- Méthodes?



Changement d'Echelle: méthodes

- Heuristique
 - TPI
- Prop. Effectives? mesure, interprétation de simulations directes
- Homogénéisation, prise de moyenne, (« fermeture »)
 - Approche stochastique (« fermeture »)

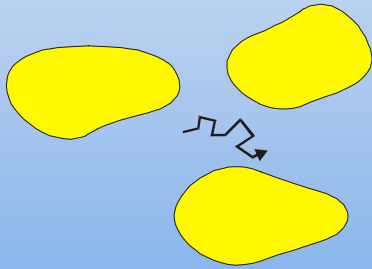


Hypothèse: échelle du pore → mécanique des milieux continus

● Libre parcours moyen: $\lambda = \frac{RT}{\sqrt{2}\pi d_{mol}^2 N_A P}$

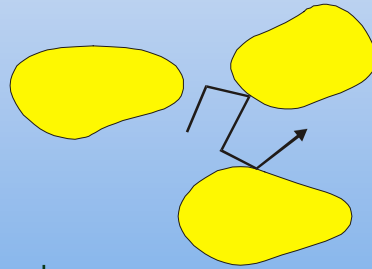
● Nombre de Knudsen:

$$K_n = \frac{\lambda}{d_{pore}}$$



$$Kn \ll 1$$

mécanique des milieux
continus



$$Kn \gg 1$$

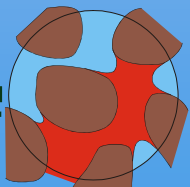
effet Klinkenberg,
Knudsen, ...

Exemple: O

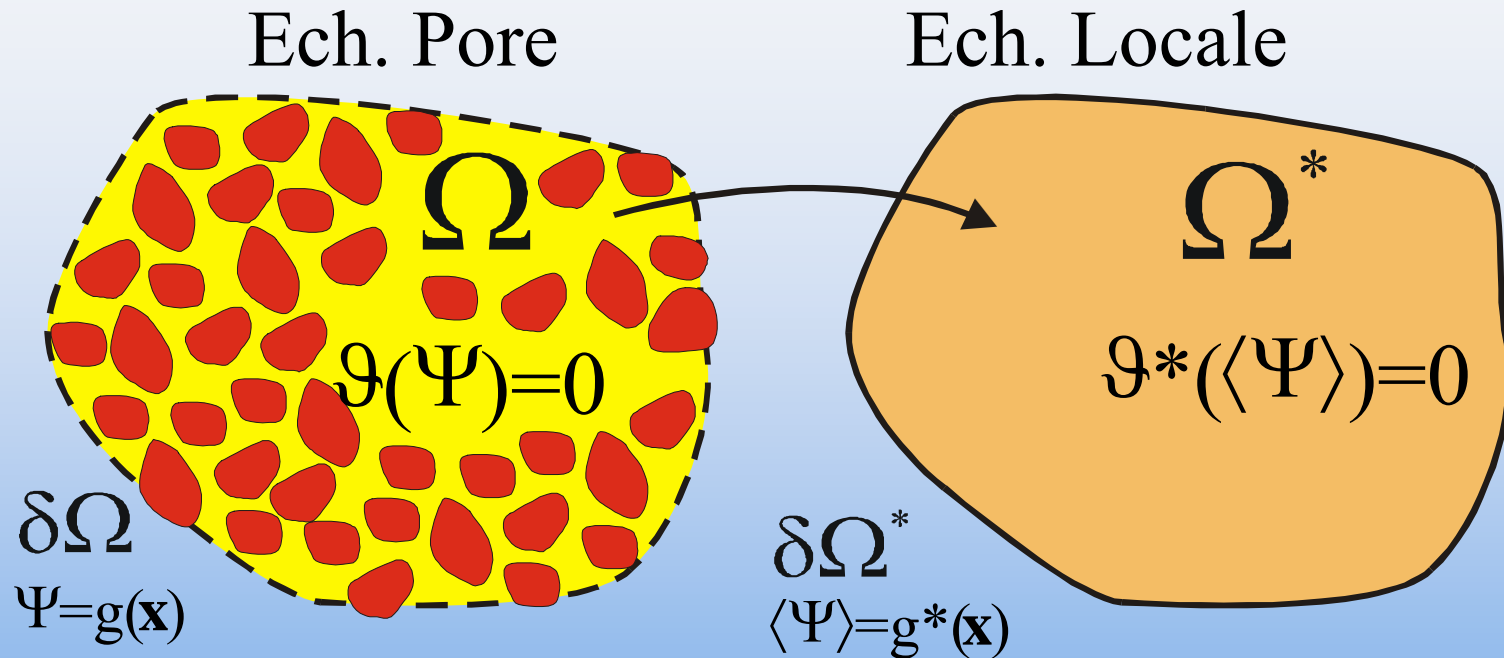
$$d_{mol} = 3.64 \times 10^{-10} \text{ m}$$

$$\lambda = \frac{8.3145 \times 300}{\sqrt{2} \times \pi \times (3.64 \times 10^{-10})^2 \times 6.02 \times 10^{23} \times 10^5}$$

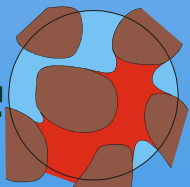
$$\lambda = 0.69 \times 10^{-7} \text{ m}$$



Changement d'Echelle: approche milieu continu



- **Objectif:** *obtenir les équations macroscopiques, les propriétés effectives, et les conditions aux limites macroscopiques*



Changement d'Echelle: « algorithme », prise de moyenne spatiale

$$\psi = \langle \psi \rangle + \tilde{\psi}$$

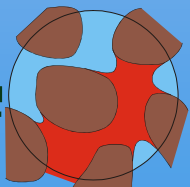
Équations couplées

$$\begin{cases} \mathcal{G}(\langle \psi \rangle, \tilde{\psi}) = 0 & \text{équations à l'échelle du pore} \\ \langle \mathcal{G}(\langle \psi \rangle, \tilde{\psi}) \rangle = 0 & \text{équations moyennées} \end{cases}$$

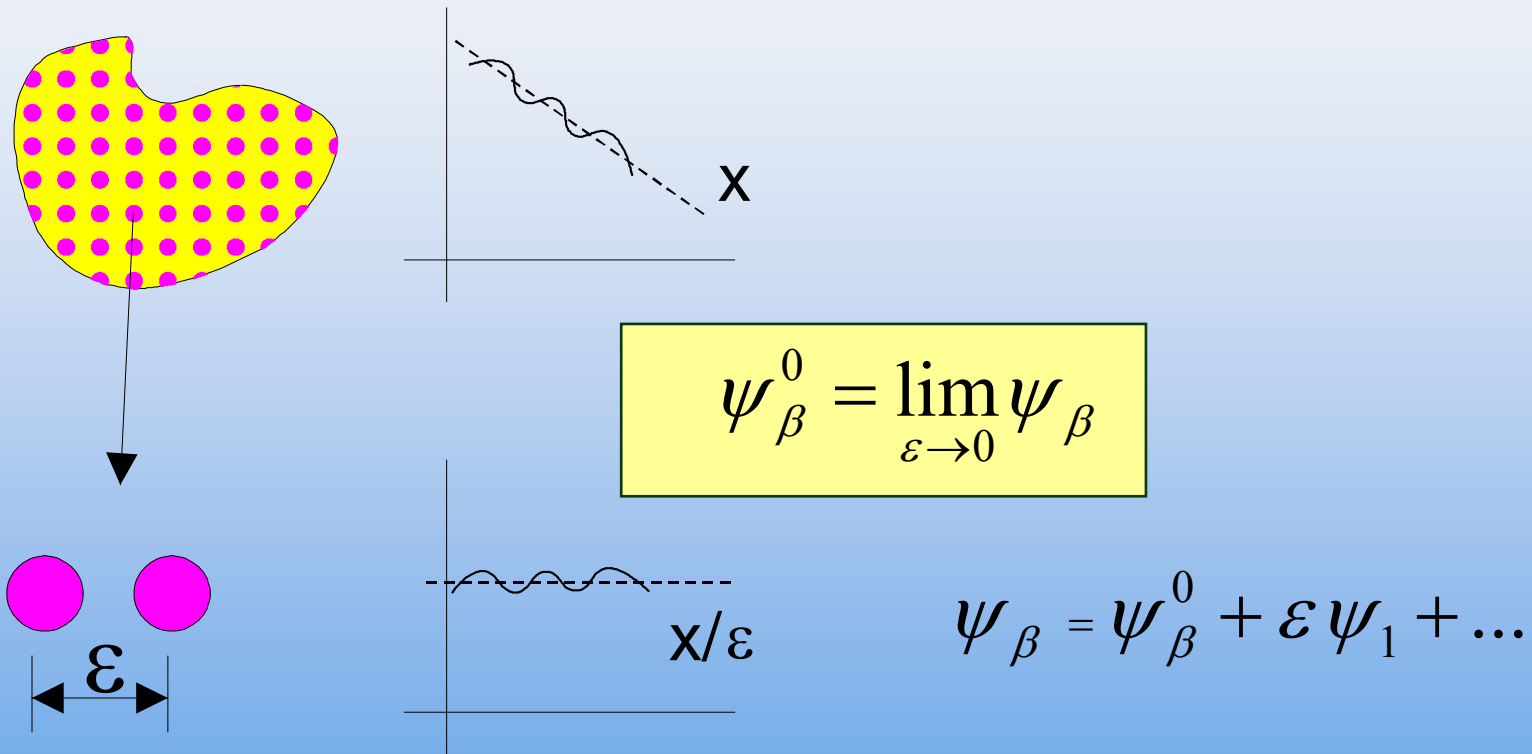
● **solution approchée, si** $\ell_\beta \ll r_0 \ll L$

$$\tilde{\psi} = f(\langle \psi \rangle) \quad (\text{fermeture}) \quad \Rightarrow \quad \text{propriétés effectives}$$

$$\langle \mathcal{G}(\langle \psi \rangle, f(\langle \psi \rangle)) \rangle = 0 \quad \text{équations macroscopiques}$$

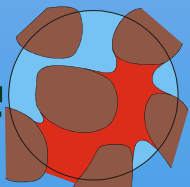


Autres méthodes: Homogénéisation



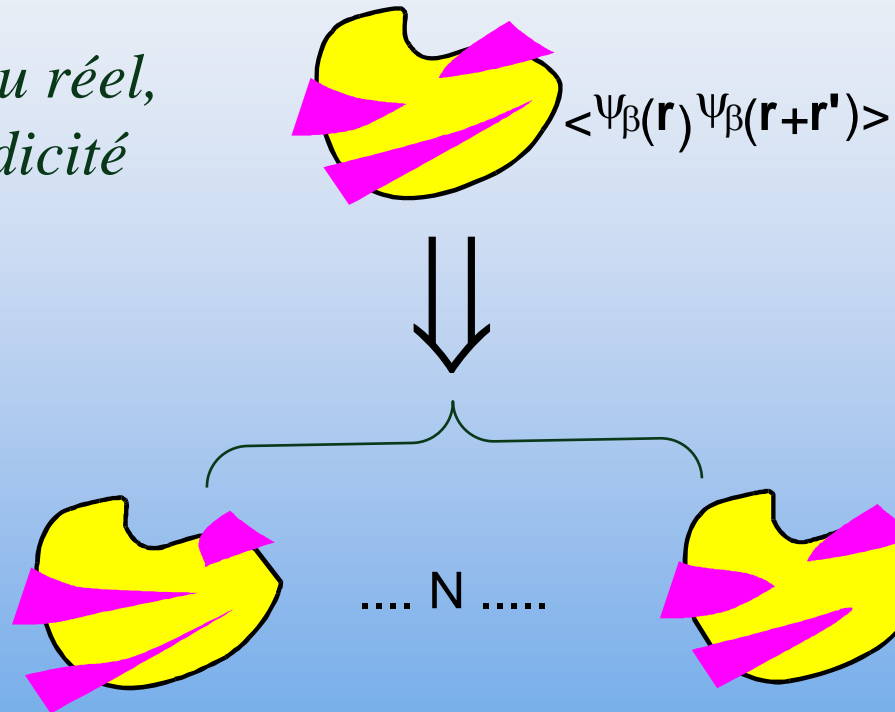
REFERENCES:

Bensoussan et al. (1978), Sanchez-Palencia (1980), ...



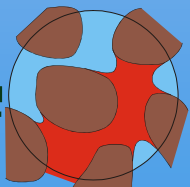
Autres Méthodes: Approche Stochastique

*milieu réel,
ergodicité*



REFERENCES:

Matheron (1965), Dagan (1989), ...



Structure générale d'une équation de transport macroscopique

● échelle du pore

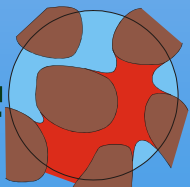
$$\frac{\partial \rho_\beta \omega_\beta}{\partial t} + \nabla \cdot (\rho_\beta \omega_\beta \mathbf{v}_\beta) = \nabla \cdot (\rho_\beta D_\beta \nabla \omega_\beta) - \underbrace{r_\beta}_{\text{réaction homogène}}$$

$$\text{B.C. 1} \quad \mathbf{n}_{\beta\sigma} \cdot (\rho_\beta \omega_\beta (\mathbf{v}_\beta - \mathbf{w}_{\beta\sigma}) - \rho_\beta D_\beta \nabla \omega_\beta) = \underbrace{f(\omega_\beta)}_{\text{réaction hétérogène}} \quad \text{sur } A_{\beta\sigma}$$

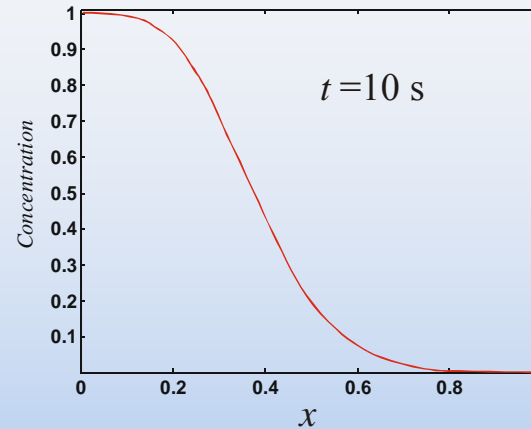
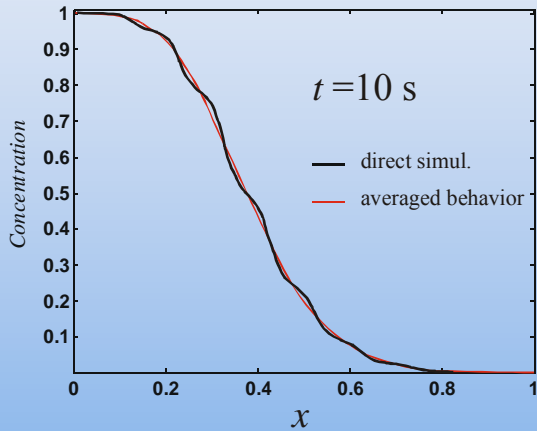
● échelle macroscopique

$$\frac{\partial \langle \rho_\beta \omega_\beta \rangle}{\partial t} + \nabla \cdot \langle \rho_\beta \omega_\beta \mathbf{v}_\beta \rangle = \nabla \cdot (\langle \rho_\beta D_\beta \nabla \omega_\beta \rangle) - \langle r_\beta \rangle - K_{\beta\sigma}$$

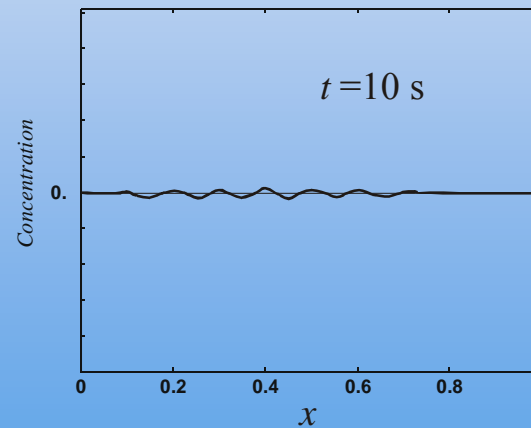
avec $K_{\beta\sigma} = \frac{1}{V} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \cdot (\rho_\beta \omega_\beta (\mathbf{v}_\beta - \mathbf{w}_{\beta\sigma}) - \rho_\beta D_\beta \nabla \omega_\beta) dA$



Exemple: diffusion, convection



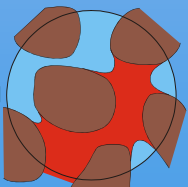
$$\langle c_{A\beta} \rangle^\beta$$



déviation

$$\tilde{c}_{A\beta} = \mathbf{b}_\beta \cdot \nabla \langle c_{A\beta} \rangle^\beta + \dots$$

$$c_{A\beta} = \langle c_{A\beta} \rangle^\beta + \tilde{c}_{A\beta}$$



Diffusion (cont.)

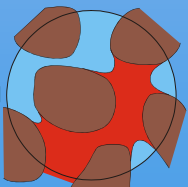
- **Problème à l'échelle du pore (cas du traceur)**

$$\frac{\partial c_\beta}{\partial t} = \nabla \cdot (D_\beta \nabla c_\beta) \quad C.L.1 \quad \mathbf{n}_{\beta\sigma} \cdot D_\beta \nabla c_\beta = 0 \quad \text{sur } A_{\beta\sigma}$$

- **Déviation:** $c_\beta = \langle c_\beta \rangle^\beta + \tilde{c}_\beta$

- **Equation moyenne**

$$\frac{\partial \varepsilon_\beta \langle c_\beta \rangle^\beta}{\partial t} = \nabla \cdot \left(\varepsilon_\beta D_\beta \nabla \langle c_\beta \rangle^\beta + \underbrace{\frac{D_\beta}{V} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \tilde{c}_\beta dA}_{\text{tortuosité}} \right)$$



Diffusion (cont.)

- **Fermeture**

$$\tilde{c}_\beta = \mathbf{b}_\beta \cdot \nabla \langle c_\beta \rangle^\beta + \dots$$

- **Problème local
(cellule périodique
représentative)**

$$0 = \nabla^2 \mathbf{b}_\beta$$

$$\text{C.L.1} \quad \mathbf{n}_{\beta\sigma} \cdot \nabla \mathbf{b}_\beta = -\mathbf{n}_{\beta\sigma} \quad \text{sur } A_{\beta\sigma}$$

$$\mathbf{b}_\beta(\mathbf{r}) = \mathbf{b}_\beta(\mathbf{r} + \mathbf{l}_i)$$

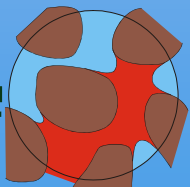
$$\langle \mathbf{b}_\beta \rangle = 0$$

- **Equation
macroscopique**

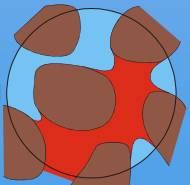
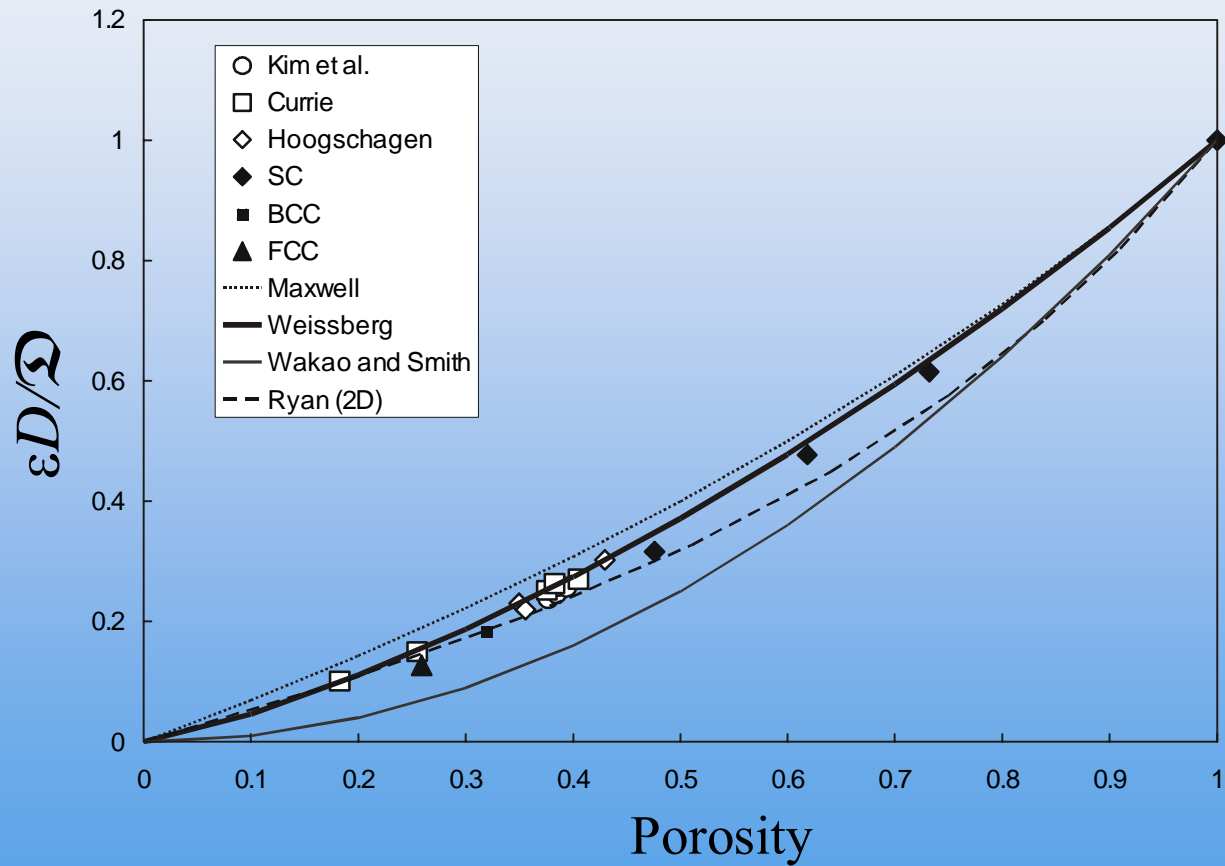
$$\frac{\partial \varepsilon_\beta \langle c_\beta \rangle^\beta}{\partial t} = \nabla \cdot \left(\varepsilon_\beta \mathbf{D}_\beta^* \cdot \nabla \langle c_\beta \rangle^\beta \right)$$

- **Tenseur de
diffusion effective**

$$\mathbf{D}_\beta^* = D_\beta \left(\mathbf{I} + \frac{1}{V_\beta} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \mathbf{b}_\beta dA \right)$$



Diffusion (cont.)



Correction dans le cas $Kn > 1$

● Dusty Gas Model (Mason et Malinauskas, 1983), heuristique

$$\mathbf{J}_A = -D_A \left[1 + \frac{D_{AS}}{D_A} + x_A \frac{(D_{AS} - D_{BS})}{D_{AB}} \right] \nabla n_A + x_A \frac{D_A}{D_{AB}} \mathbf{J} - x_A \frac{D_A}{D_{AK}} \left(\frac{nB_0}{\mu} \right) \nabla p + \frac{x_A}{kT} \frac{D_{AS}}{D_{AB}} \nabla p \quad \left(\text{avec } \frac{1}{D_A} = \frac{1}{D_{AK}} + \frac{1}{D_{AB}} \right)$$

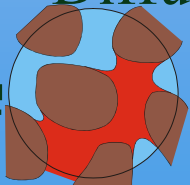
•Knudsen

•Diffusion en volume

•Diffusion de surface

•Effets visqueux

Paramètres ajustables!



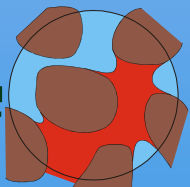
Correction dans le cas $Kn > 1$

- Altevogt et al., 2003: condition de glissement (cas binaire)

$$\mathbf{v}_\beta \cdot \mathbf{t}_{\beta\sigma} = v_{slip} = \frac{D_{AB} \mathbf{t}_{\beta\sigma} \cdot \nabla \omega_{A\beta}}{\omega_{A\beta} + \alpha}$$

→ fermeture, équ. macro.,...

$$\begin{aligned} & \underbrace{\left(\varepsilon_\beta + a_v \frac{k}{(1 + K \langle \rho_{A\beta} \rangle^\beta)^2} \right)}_{\text{Retardation}} \frac{\partial \langle \rho_{A\beta} \rangle^\beta}{\partial t} \\ & = \underbrace{-\nabla \cdot \left(\langle \mathbf{v}_\beta \rangle \cdot \left(\mathbf{I} \langle \rho_{A\beta} \rangle^\beta - \mathbf{R}_\beta \right) \right)}_{\text{Advection and slip coupling}} \\ & + \underbrace{\nabla \cdot \left[\mathbf{D}_{\text{eff}} \rho_\beta \cdot \nabla \langle \omega_{A\beta} \rangle^\beta \right]}_{\text{Diffusion}} + \underbrace{\nabla \cdot \left[\mathbf{D}_\beta \cdot \nabla \langle \omega_{A\beta} \rangle^\beta \right]}_{\text{Mechanical dispersion}} \end{aligned}$$



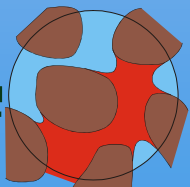
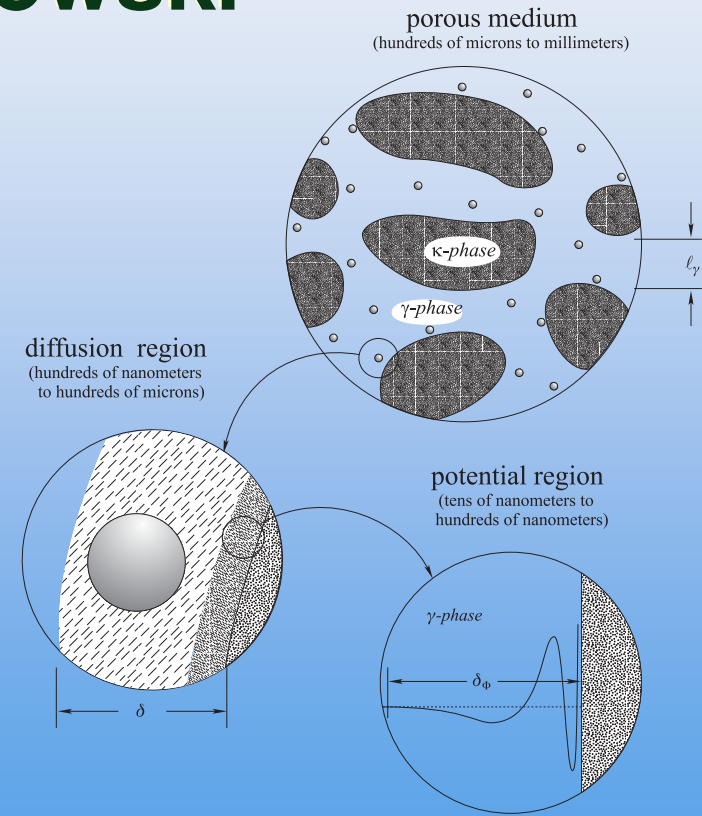
Modèles mésoscopiques: exemple adsorption près d'une paroi

● Équations de Smoluchowski

$$\underbrace{\frac{\partial c_A}{\partial t}}_{\text{accumulation}} + \underbrace{\nabla \cdot (c_A \mathbf{v}_0)}_{\text{convection}} = \underbrace{\nabla \cdot (\mathbf{D}_0 \cdot \nabla c_A)}_{\text{diffusion}} + \underbrace{\nabla \cdot \left[\left(\frac{\mathbf{D}_0}{kT} \cdot \nabla \Phi_A \right) c_A \right]}_{\text{interaction force}}, \text{ in the } \gamma\text{-phase}$$

$$\text{B.C. } D_\gamma \frac{\partial c_{A\gamma}}{\partial \eta} = k_1 c_{A\gamma} - k_{-1} c_{As}$$

voir Wood et al., 2004



Approche discrète: Dynamique moléculaire

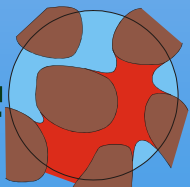
27/01/2005

Voir par ex.: Allen, M. P., and D. J. Tildesley. 1987.
Computer Simulation of Liquids. Clarendon Press, Oxford.

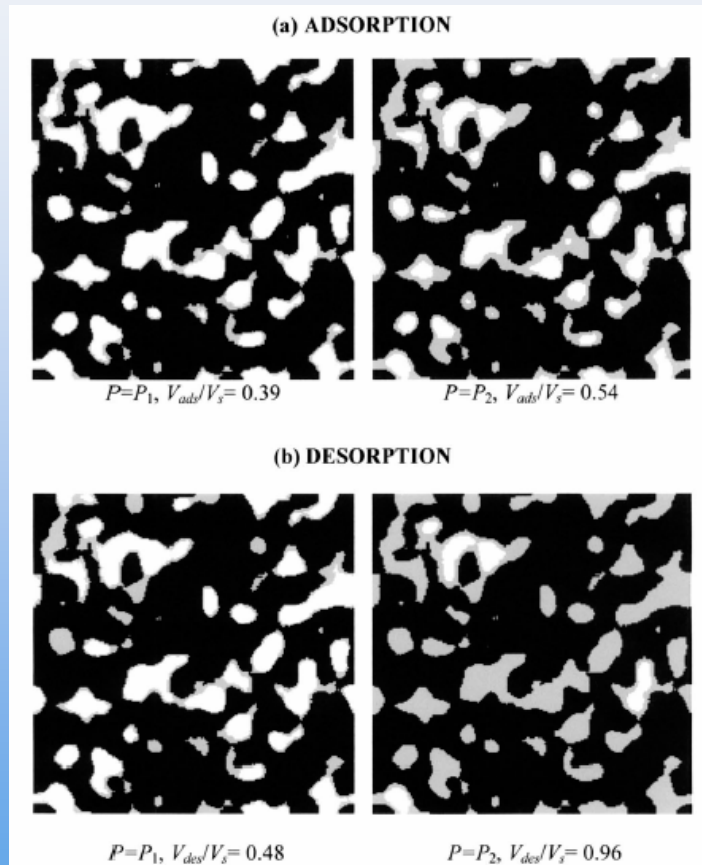
- **Principe: mouvements élémentaires, interactions**

$$\ddot{\mathbf{r}}_i = -\frac{1}{m} \sum_{j \neq i} \nabla_i \Phi_{ij} + \Gamma - \lambda(t) \dot{\mathbf{r}}_i$$

- **En pratique: simplifications**
 - Périodicité
 - Dynamique plus simple (parois, molécules-atomes,...)
 - Géométrie (milieu poreux, parois rugueuses,...)
 - Algorithmes
- **Problème: interprétation (équations, propriétés effectives)**



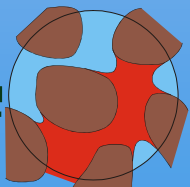
Exemple: diffusion, sorption, désorption



$\langle D_{Kn} \rangle$ ($\text{cm}^2 \text{ s}^{-1}$)	$D_{Kn,z}$ ($\text{cm}^2 \text{ s}^{-1}$)	$D_{Kn,exp}$ ($\text{cm}^2 \text{ s}^{-1}$)
7.7×10^{-3}	8.0×10^{-3}	8.2×10^{-3}

Assemblages aléatoire de sphères, porosité: 0.42

Kainourgiakis et al., 2002



Exemple: effet de rugosité

Malek et Coppens, 2001

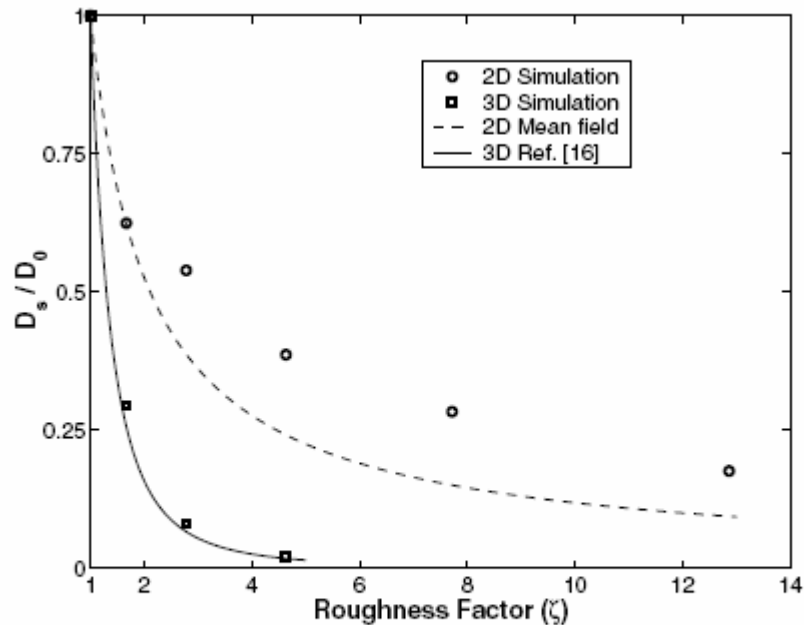
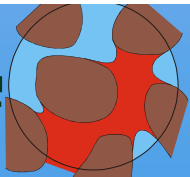
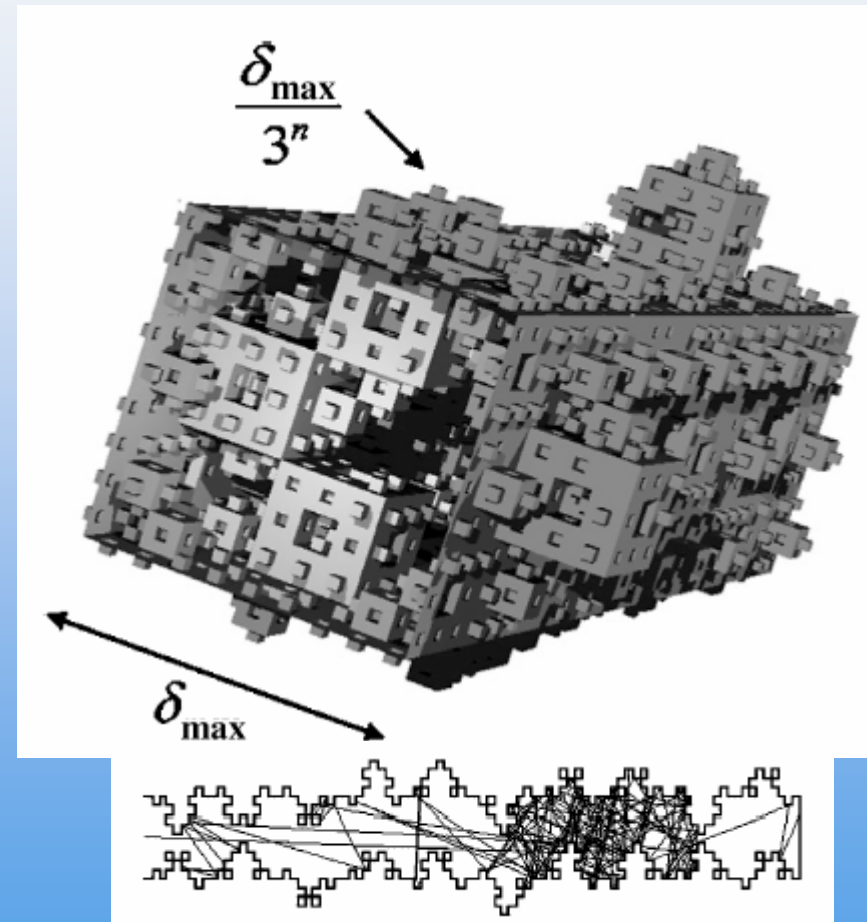


FIG. 4. Self-diffusion vs roughness factor. Symbols are Monte Carlo simulation results; lines correspond to analytical calculations in 2D (dashed line) and 3D (solid line).



Conclusions

- **Modélisation: de l'approche milieux continus à la DM**
- **Limitations?**
- **Interprétation**
- **Perspectives: multiconstituant, couplage thermique, ...**

