化学工学会第47回秋季大会
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吸着性溶質を含む微粒子分散液の乾燥･濃縮過程の直接数値計算

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Particle film formation

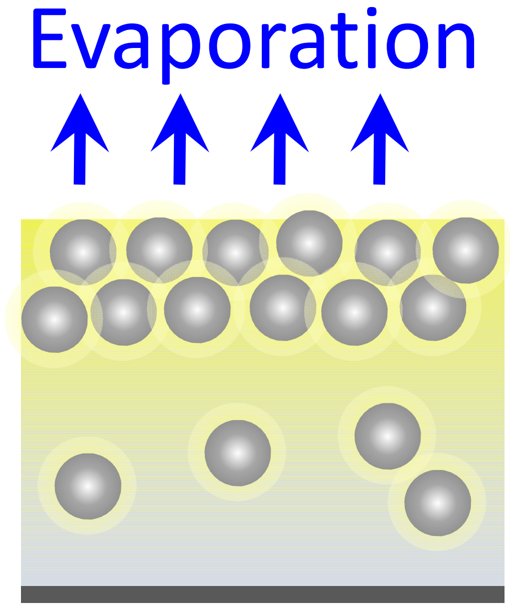
微粒子分散液 (Colloidal suspensions) → 塗布・乾燥 (Coating) (Drying) → 機能性薄膜 (Functional thin films)

溶質（高分子，界面活性剤など）の添加

(Addition of solutes)

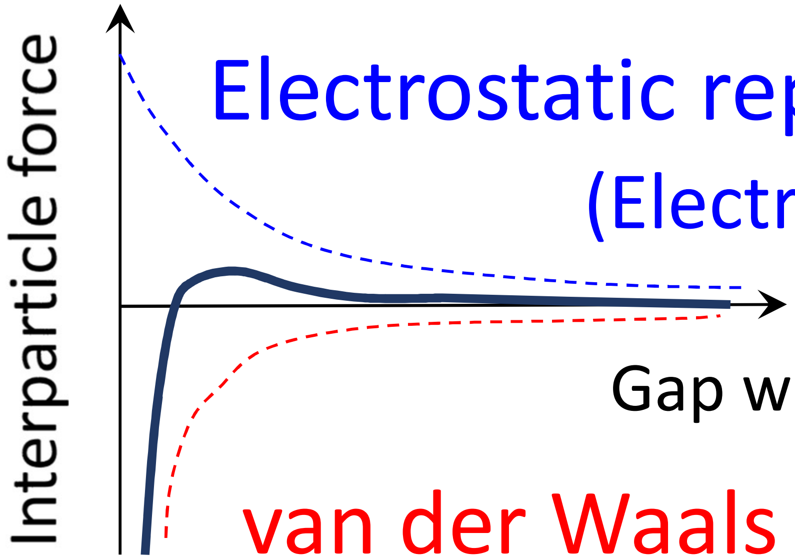
粒子構造の解明・制御

(Elucidation and control of particle configuration)



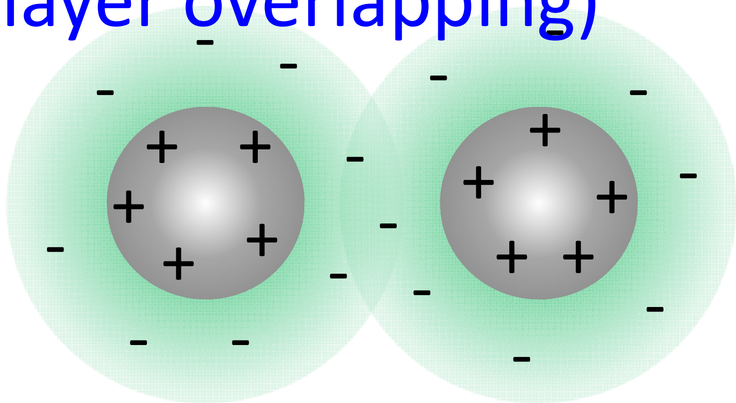
Interaction

DLVO Theory



Electrostatic repulsion

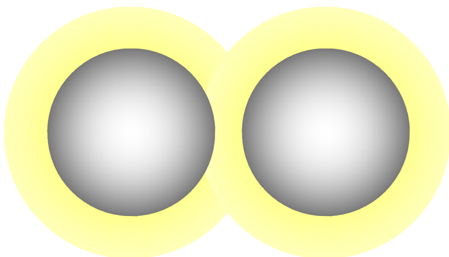
(Electrical double layer overlapping)



van der Waals attraction

Addition of adsorbing solutes

Adsorption layer overlapping

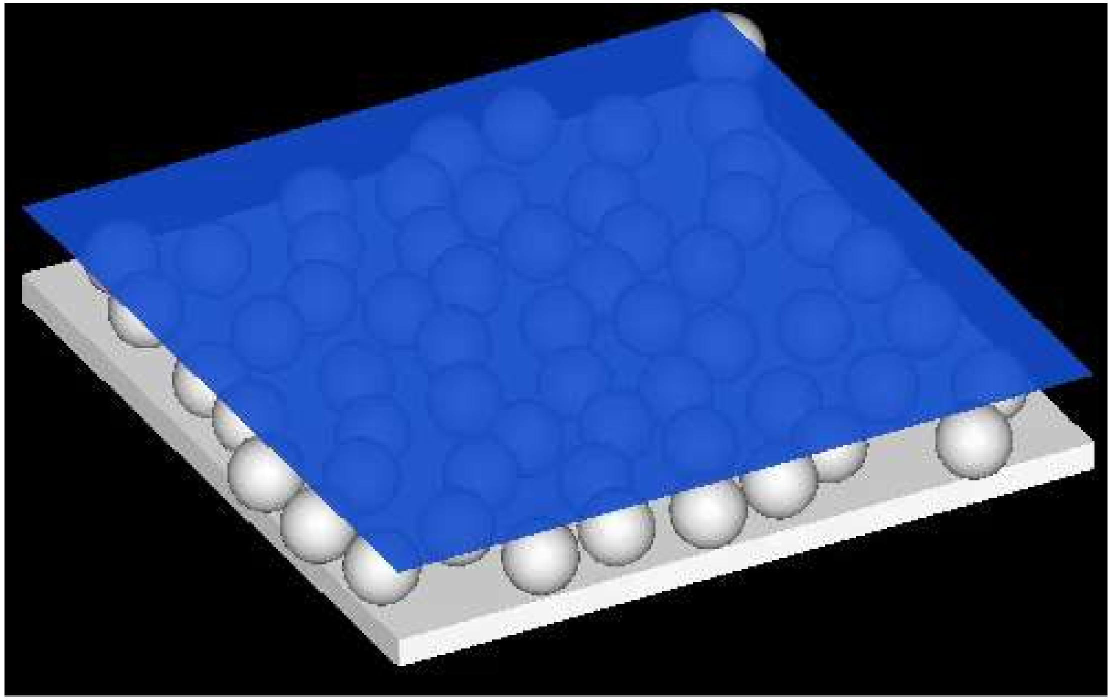


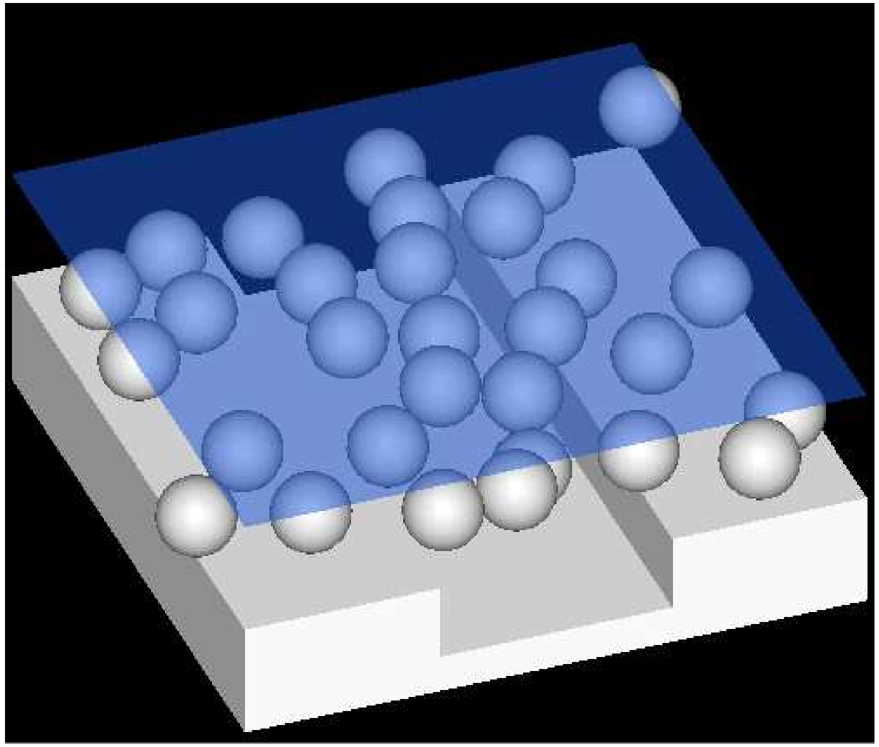
Purpose

メソスケールモデル構築（Mesoscale modeling）
直接数値計算（**D**irect **N**umerical **S**imulation）

- 粒子/流体運動（Particle/fluid motion）
- 自由界面移動（Free surface movement）
  [Previous work]
  M. Fujita et al., J. Comput. Phys. **281**, 421 (2015).
- 溶質吸着/移動（Transport of adsorbing solutes）

Previous work

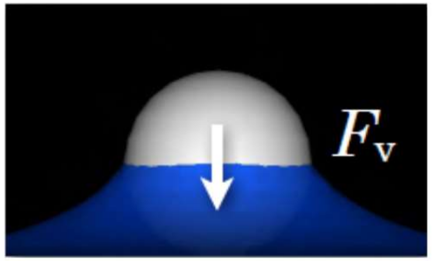




M. Fujita et al., J. Comput. Phys. **281**, 421 (2015).

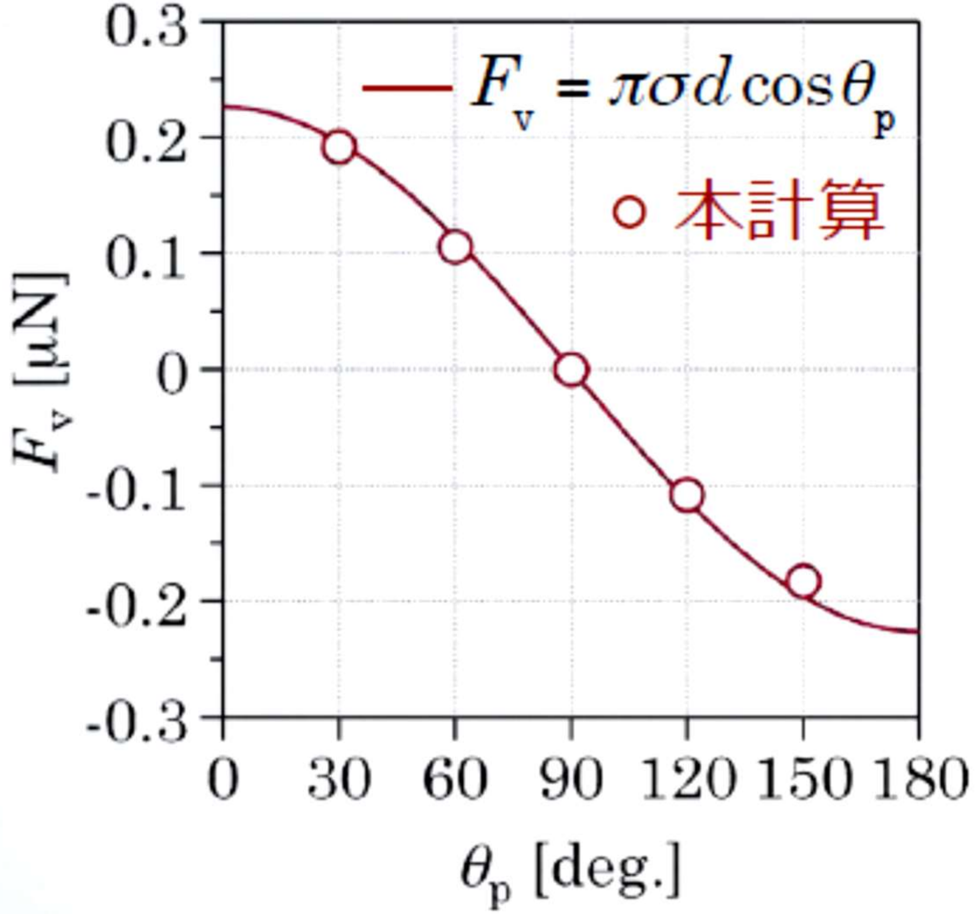
Previous work

縦毛管力 (Vertical capillary force)

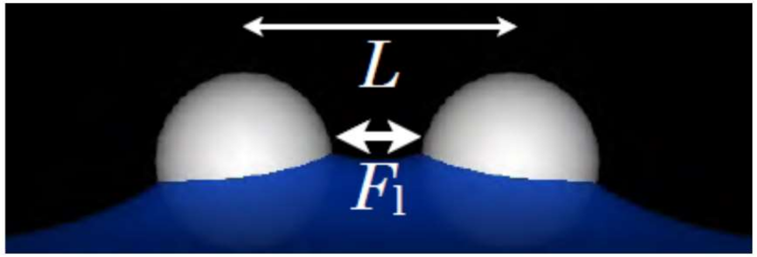


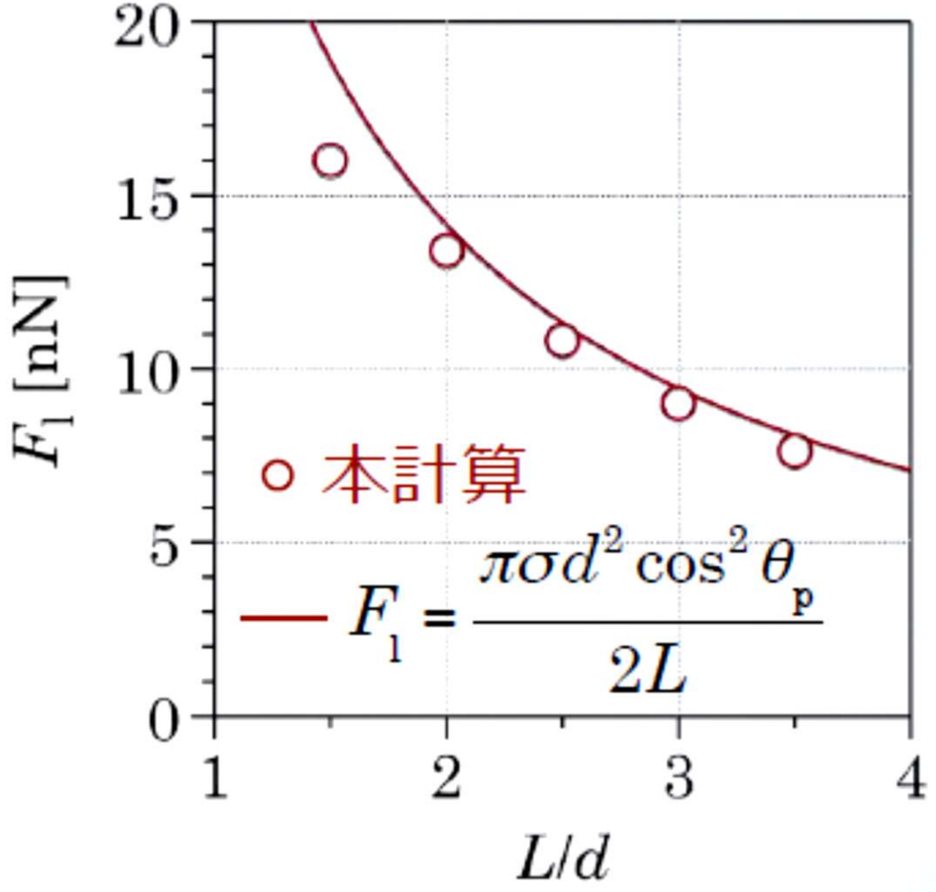
$d = 1\ \mu m$

$\sigma = 0.072\ N/m$



横毛管力 (Lateral capillary force)



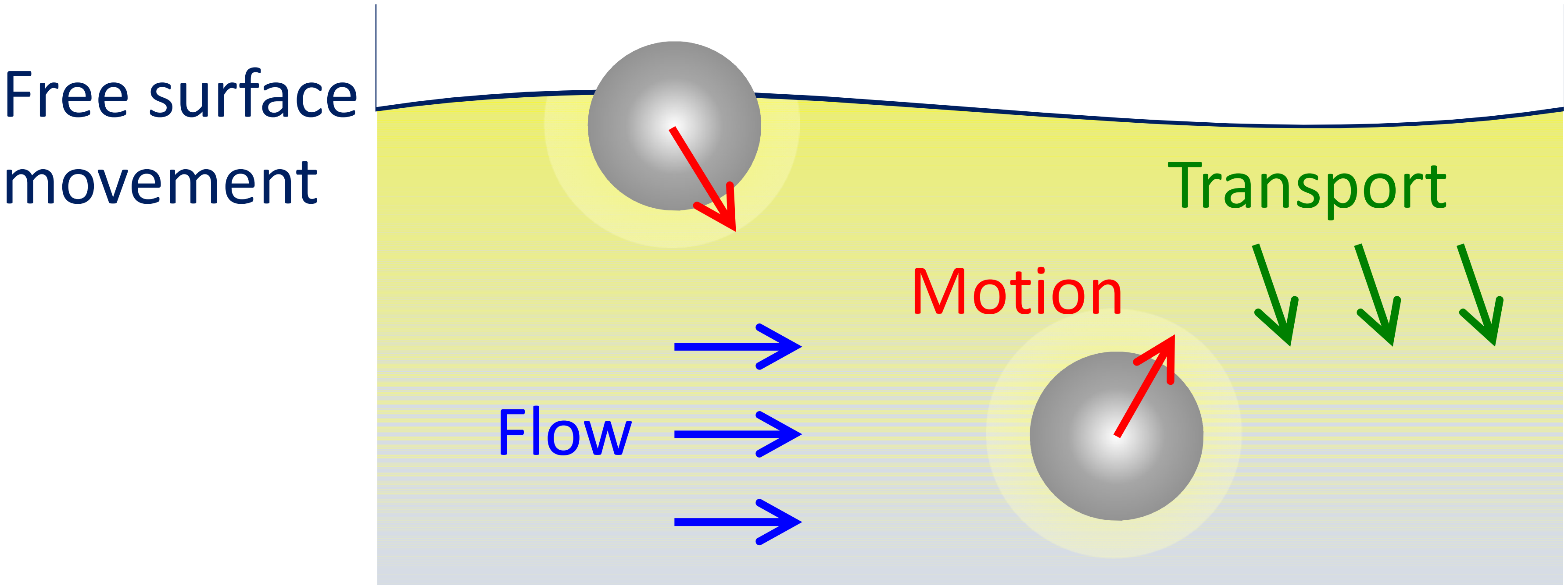


M. Fujita et al., J. Comput. Phys. **281**, 421 (2015).

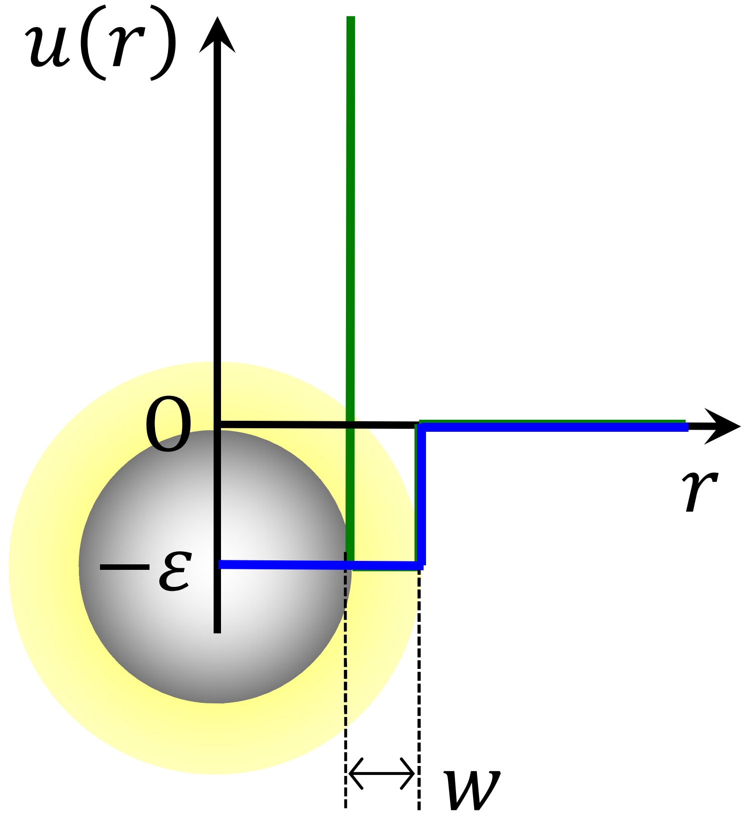
Model

Coupled

- 粒子：　Newton-Euler 運動方程式
- 流体：　流体方程式
- 自由界面：　移流方程式
- 溶質：　移流拡散方程式



Particle-solute interaction



井戸型ポテンシャル
(Square-well potential)

$$u(r) = \begin{cases} \infty & r < a \\ -\varepsilon & a \le r < a + w \\ 0 & r \ge a + w \end{cases}$$

吸着エネルギー: $\beta\varepsilon = \varepsilon / k_{\mathrm{B}}T$
(Adsorption energy)

吸着層厚み: $\lambda = w/a$
(Adsorption layer thickness)

吸着ポテンシャル
(Adsorption potential)

$$u^{\mathrm{ad}}(r) = \begin{cases} -\varepsilon & r < a + w \\ 0 & r \ge a + w \end{cases}$$

$$U^{\mathrm{ad}}(\boldsymbol{r}) = \sum_i u^{\mathrm{ad}}(|\boldsymbol{r} - \boldsymbol{R}_i|)$$

Indicator functions

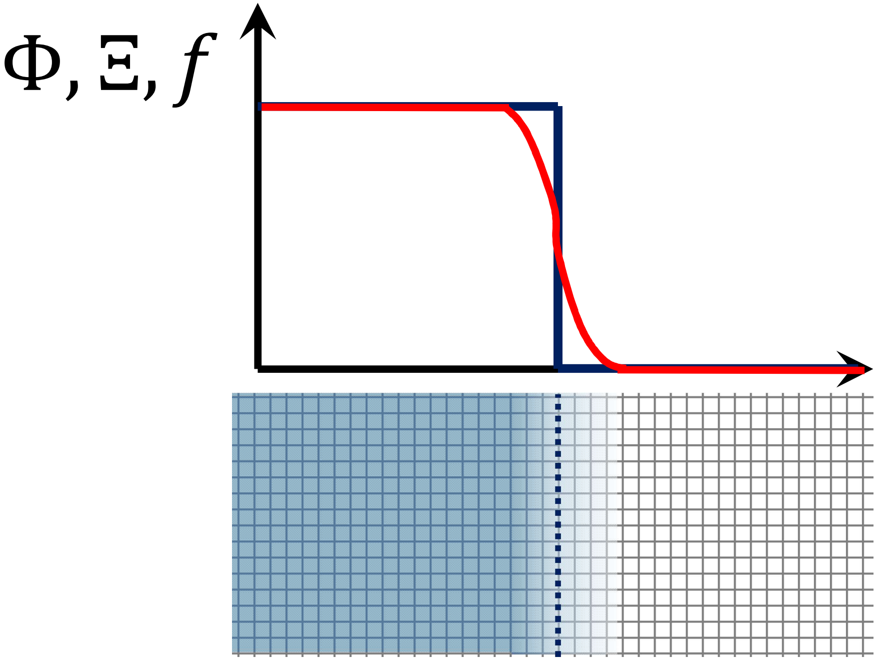
Particle $\Phi \in [0,1]$

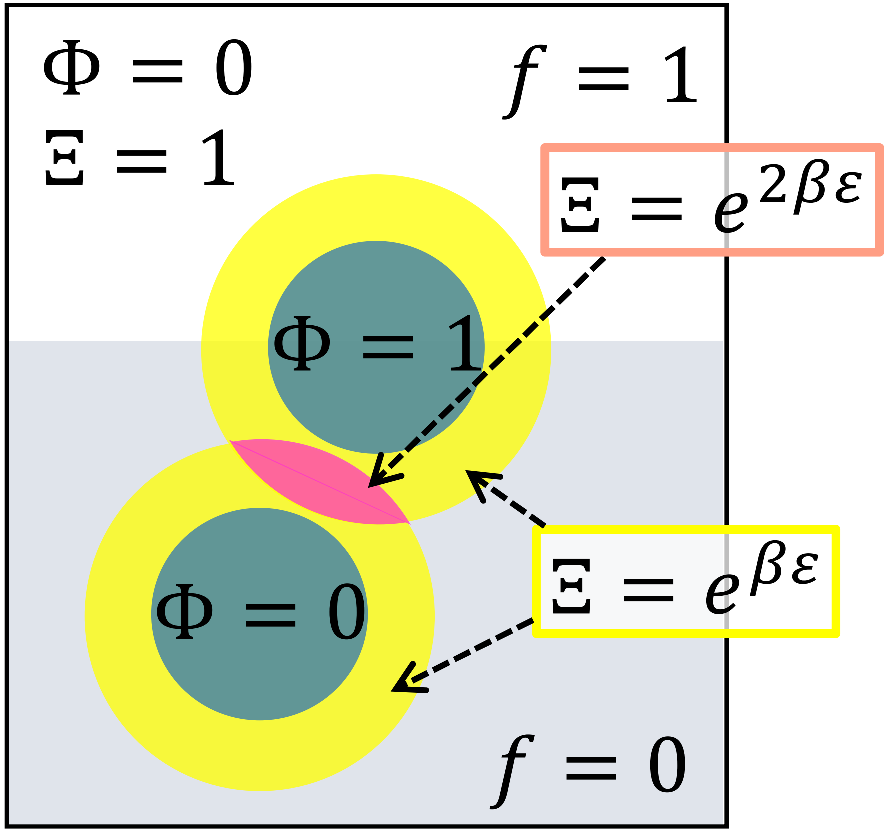
Liquid $f \in [0,1]$

Adsorption $\Xi = e^{-\beta U^{\mathrm{ad}}}$

$= e^{n\beta\varepsilon}$

Overlapping number : n





For DNS:

step function

→ continuous function

Solute transport

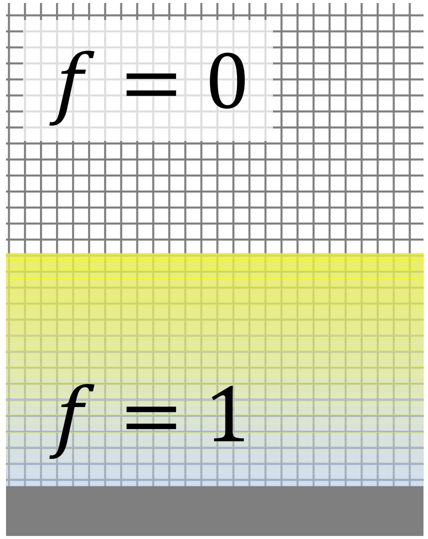
$$\frac{\partial c}{\partial t} + \nabla \cdot (c\boldsymbol{v}) = -\nabla \cdot (\boldsymbol{J} + \boldsymbol{\zeta})$$

Fluctuations

$$\boldsymbol{J} = -f(1-\Phi)\Xi D \nabla c^*$$

Liquid Gas

$$c = (1-\Phi)\Xi[fc^* + (1-f)kc^*]$$
$$= (1-\Phi)\Xi[f(1-k)+k]c^*$$



分配係数(Partition coefficient) : k

気相への溶質非透過条件(impermeability) : $k = 0$

For DNS : $0 < k \ll 1$

Free surface movement

Mass conservation

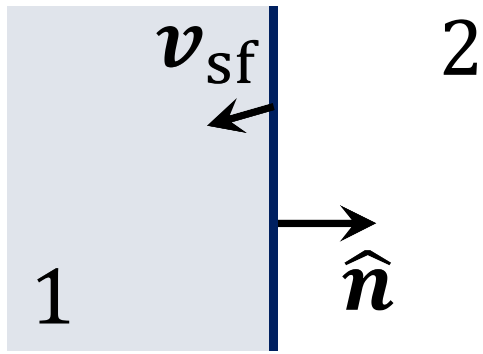
$$[\rho(\boldsymbol{v} - \boldsymbol{v}_{\mathrm{sf}}) \cdot \hat{\boldsymbol{n}}] = 0$$

$$\rho(\boldsymbol{v} - \boldsymbol{v}_{\mathrm{sf}}) \cdot \hat{\boldsymbol{n}} = (1 - \Phi)\dot{\omega}$$

$$\boldsymbol{v}_{\mathrm{sf}} = \boldsymbol{v} - (1 - \Phi)\frac{\dot{\omega}}{\rho}\hat{\boldsymbol{n}}$$

$\dot{\omega}$: evaporation mass flow rate

$\boldsymbol{v}_{\mathrm{sf}}$: velocity of free surface



$$[Q] \equiv Q_2 - Q_1$$

on free surface

Free surface movement

$$\frac{\partial f}{\partial t} + \left[\boldsymbol{v} - (1 - \Phi)\frac{\dot{\omega}}{\rho}\hat{\boldsymbol{n}}\right] \cdot \boldsymbol{\nabla} f = 0$$

For DNS: level set method

Fluid flow

Mass conservation $[\boldsymbol{v} \cdot \hat{\boldsymbol{n}}] = (1 - \Phi)\dot{\omega}[1/\rho]$

$$\nabla \cdot \boldsymbol{v} = (1 - \Phi)\dot{\omega}|\nabla(1/\rho)|$$

Momentum conservation

Fluctuations

$$\rho\left(\frac{\partial \boldsymbol{v}}{\partial t} + \boldsymbol{v} \cdot \nabla \boldsymbol{v}\right) = \nabla \cdot (\boldsymbol{\sigma} + \boldsymbol{s}) + \rho \boldsymbol{g} + \gamma\kappa\nabla f - c\nabla U^{\mathrm{ad}} + \rho\Phi\boldsymbol{a}$$

Surface tension ($\gamma\kappa\nabla f$) | Particle-solute interaction ($c\nabla U^{\mathrm{ad}}$) | Particle velocity forcing ($\rho\Phi\boldsymbol{a}$)

$$\boldsymbol{\sigma} = -(p + \pi)\boldsymbol{I} + \eta[\nabla\boldsymbol{v} + (\nabla\boldsymbol{v})^T] - \tfrac{2}{3}\eta(\nabla \cdot \boldsymbol{v})\boldsymbol{I}$$

Osmotic pressure $\pi = k_B T(\Xi - 1)c^*$

Particles' motion

[Translation] $M_i \dot{\boldsymbol{V}}_i = \boldsymbol{F}_i^{\mathrm{C}} + \boldsymbol{F}_i^{\mathrm{H}} + \boldsymbol{F}_i^{\mathrm{S}}$ $\quad \dot{\boldsymbol{R}}_i = \boldsymbol{V}_i$

[Rotation] $\boldsymbol{I}_i \cdot \dot{\boldsymbol{\Omega}}_i = \boldsymbol{N}_i^{\mathrm{C}} + \boldsymbol{N}_i^{\mathrm{H}}$

Hydrodynamic force/torque

$$\boldsymbol{F}_i^{\mathrm{H}} = -\int \left[\rho \Phi \boldsymbol{a} - \Phi\left(\rho_{\mathrm{p}} - \rho\right)\boldsymbol{g}\right] \mathrm{d}\boldsymbol{r}$$

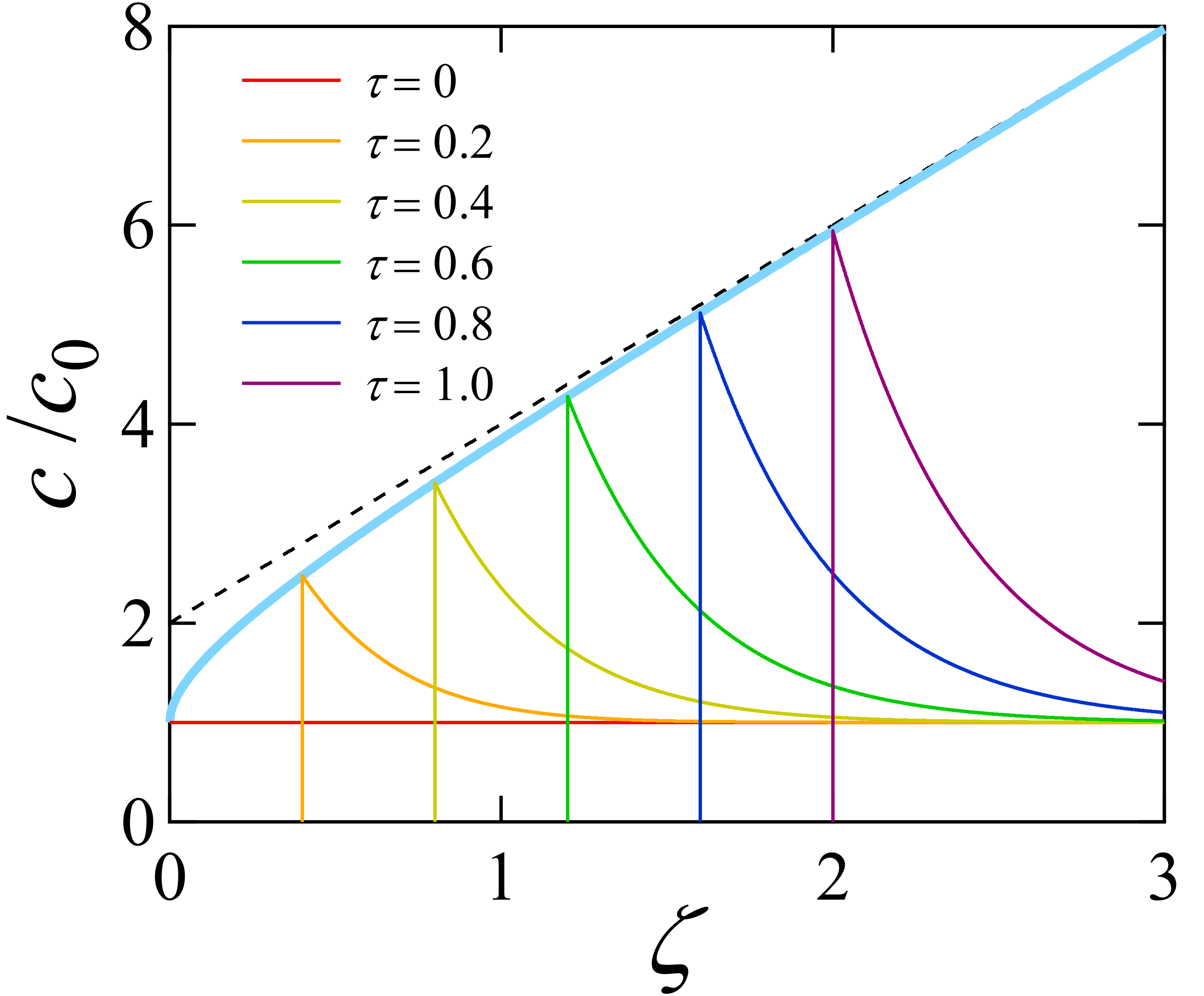
$$\boldsymbol{N}_i^{\mathrm{H}} = -\int (\boldsymbol{r} - \boldsymbol{R}_i) \times \rho \Phi \boldsymbol{a} \, \mathrm{d}\boldsymbol{r}$$

Particle-solute interaction

$$\boldsymbol{F}_i^{\mathrm{S}} = \int c \boldsymbol{\nabla} U^{\mathrm{ad}} \, \mathrm{d}\boldsymbol{r}$$

Momentum exchange:
particle ↔ fluid

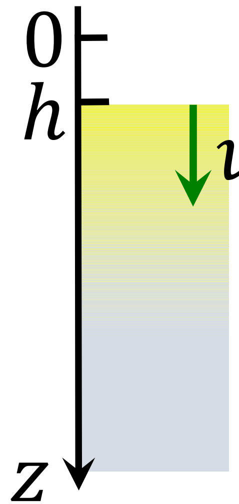
Concentration distribution



解析解

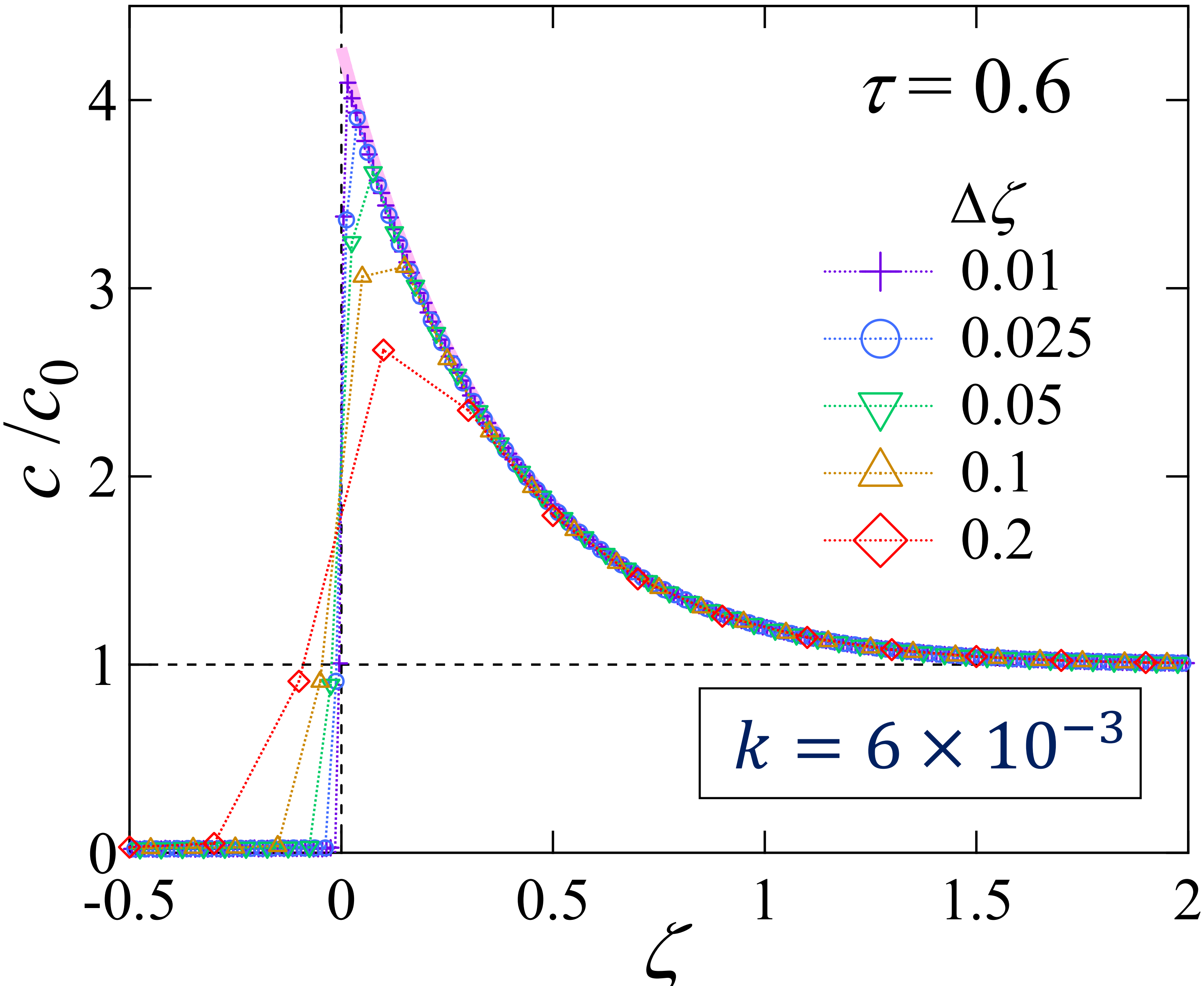
$$\zeta = \frac{v_\mathrm{e}}{2D} z$$

$$\tau = \frac{v_\mathrm{e}^2}{4D} t$$



$$h(t) = v_\mathrm{e} t$$

Validation

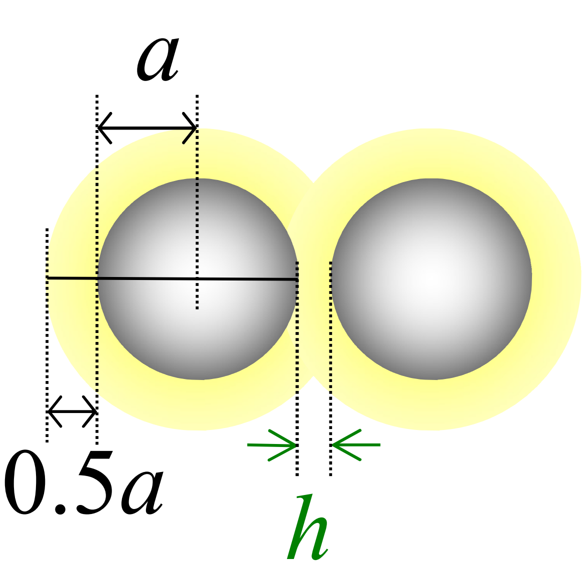


$$\zeta = \frac{v_e}{2D} z$$

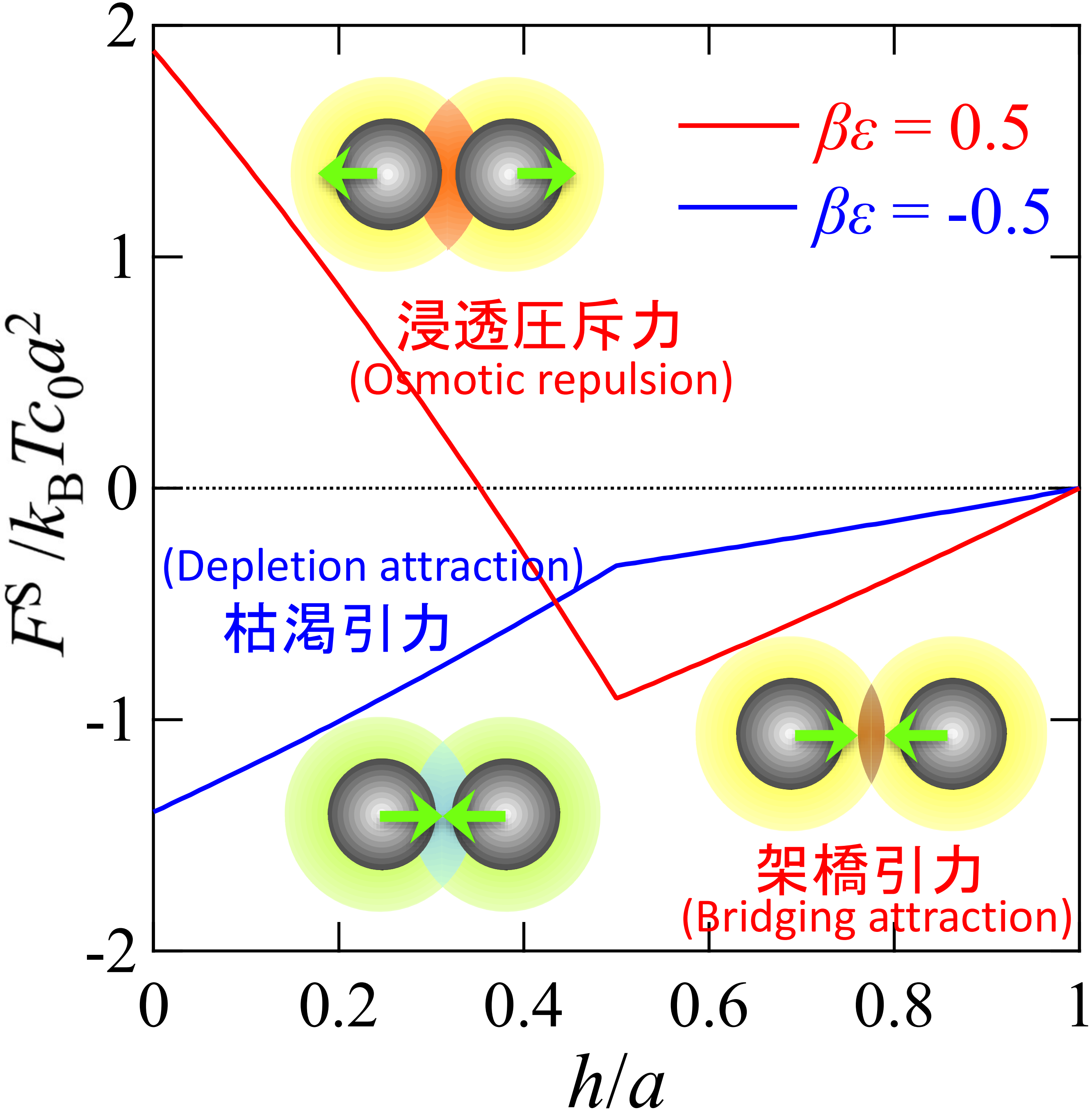
$$\tau = \frac{v_e^2}{4D} t$$

Interpaticle force

解析解



粒子表面間距離
(Gap width)



Simulation conditions

粒子半径 (Particle radius)
$a = 50\ \mathrm{nm}$

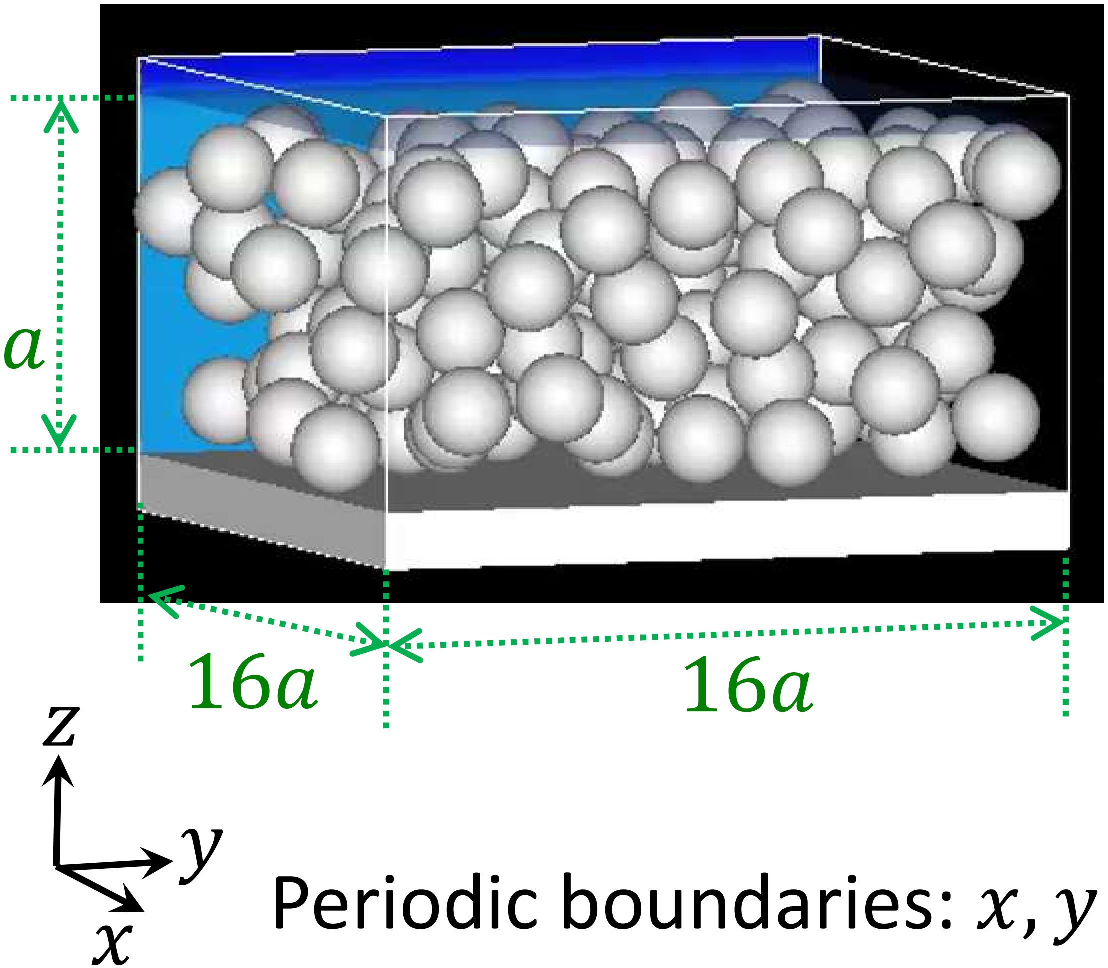
動粘性係数 (Dynamic viscosity)
$\nu = 5.0 \times 10^{-6}\ \mathrm{m^2/s}$

表面張力 (Surface tension)
$\gamma = 2.0 \times 10^{-2}\ \mathrm{N/m}$

接触角 (Contact angle)
$\alpha = 45°$

溶質濃度 (Solute concentration)
$c_0 = 5.0 \times 10^{-3}\ \mathrm{mol/L}$

初期体積分率 (Initial volume fraction)
$\phi_0 = 30\ \mathrm{vol.\%}$



Periodic boundaries: x, y

Diffusion

Diffusion coefficient

Particle $D_{\mathrm{prt}} = 10^{-12} \sim 10^{-11}\ \mathrm{m^2/s}$

Solute $D_{\mathrm{slt}} = 10^{-10} \sim 10^{-8}\ \mathrm{m^2/s}$

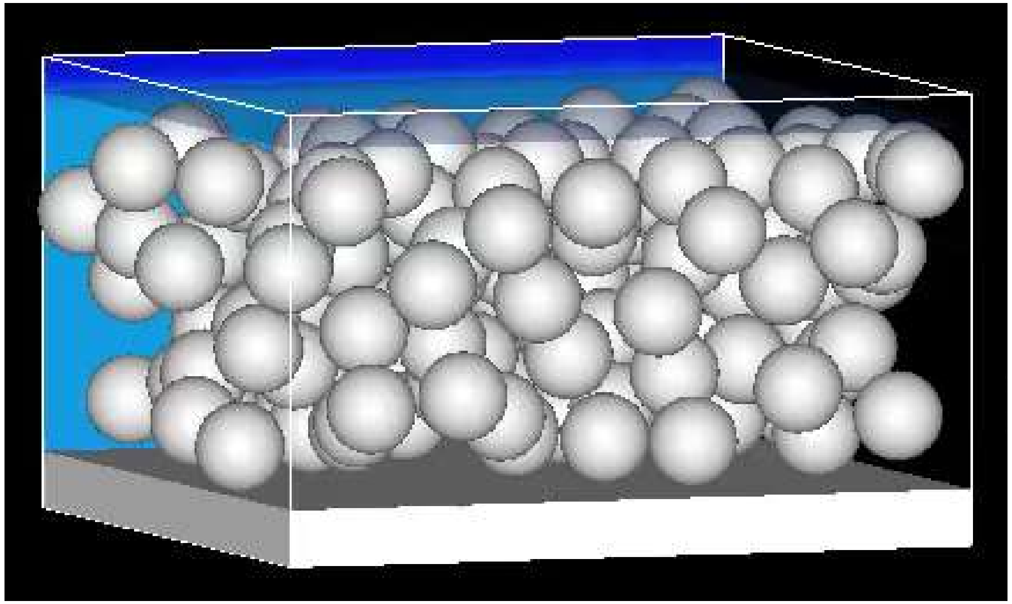
Péclet number

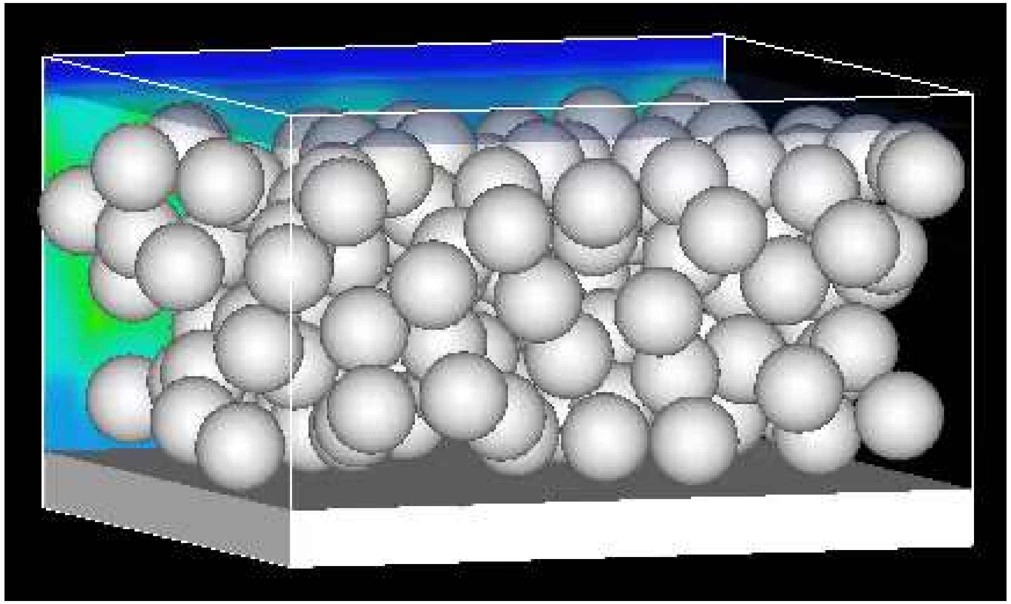
$$\mathrm{Pe} = \frac{a v_{\mathrm{e}}}{D} \qquad \frac{\mathrm{Pe}_{\mathrm{prt}}}{\mathrm{Pe}_{\mathrm{slt}}} = \frac{D_{\mathrm{slt}}}{D_{\mathrm{prt}}} \gg 1$$

Approximation: $\mathrm{Pe}_{\mathrm{prt}} = \infty$

Solute adsorption

$\mathrm{Pe_{slt}} = 0.01$

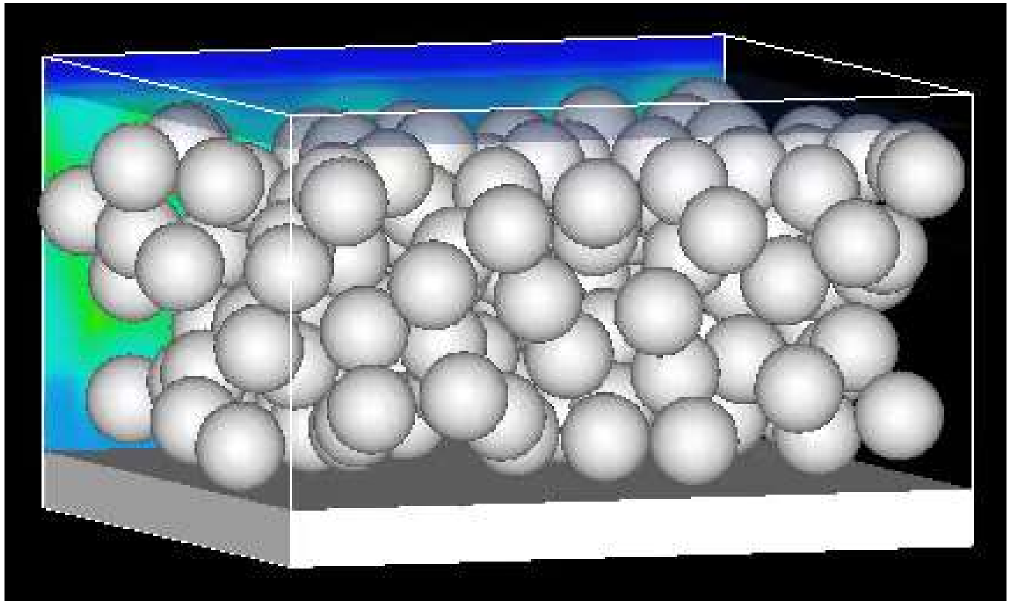




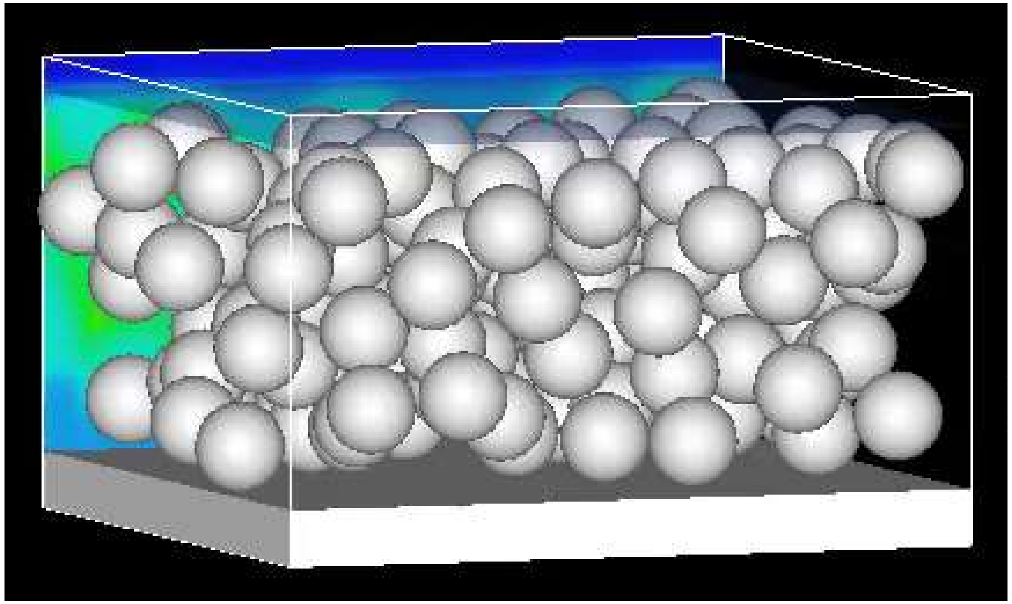
$\beta\varepsilon = 0$ $\beta\varepsilon = 0.5$

Ordering by interparticle force

Solute Péclet number

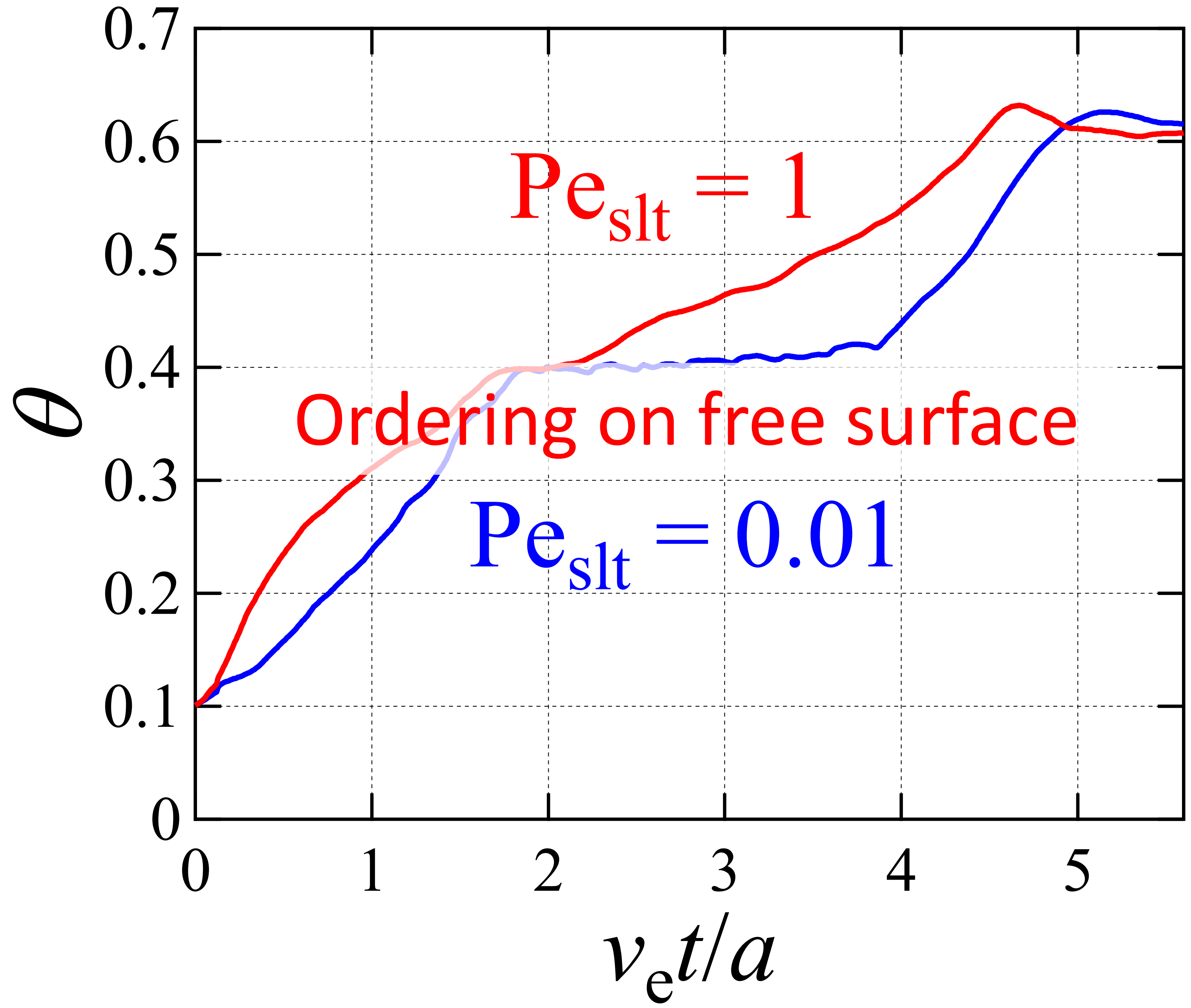


$\mathrm{Pe_{slt}} = 0.01$

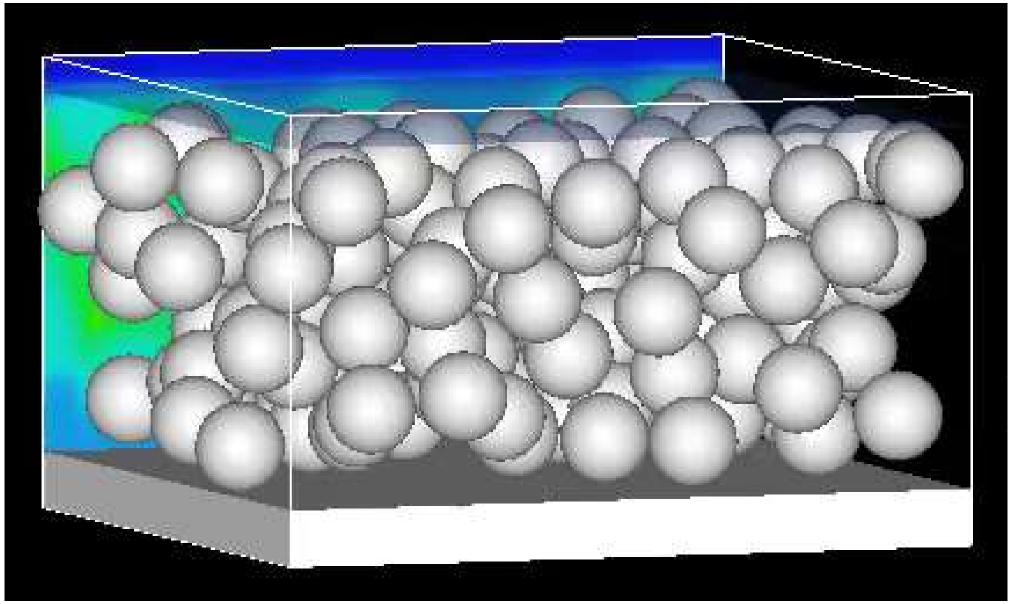


$\mathrm{Pe_{slt}} = 1$

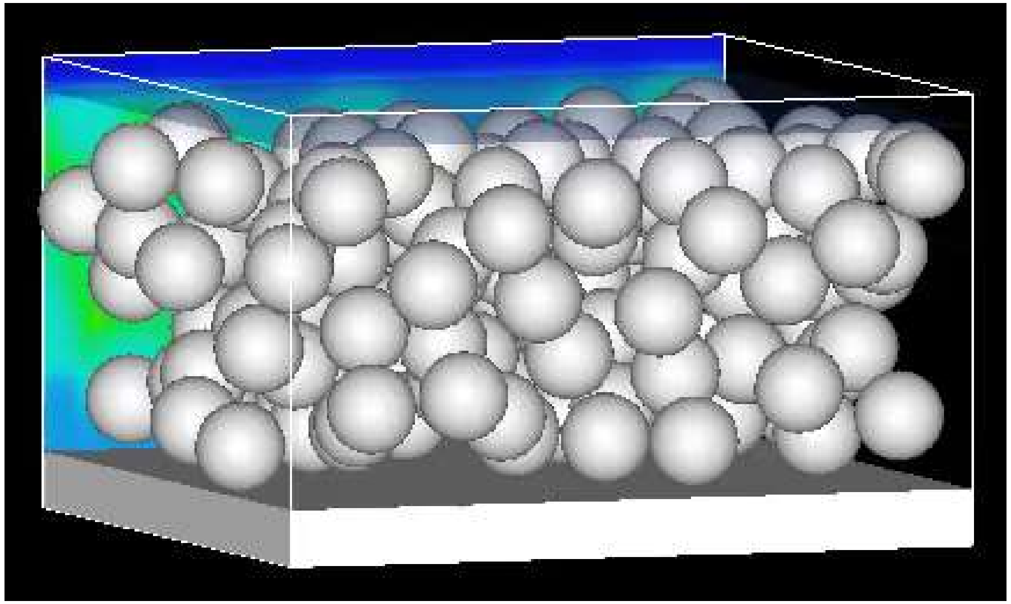
Coverage


0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
θ
0
1
2
3
4
5
$v_e t/a$
$Pe_{slt} = 1$
Ordering on free surface
$Pe_{slt} = 0.01$

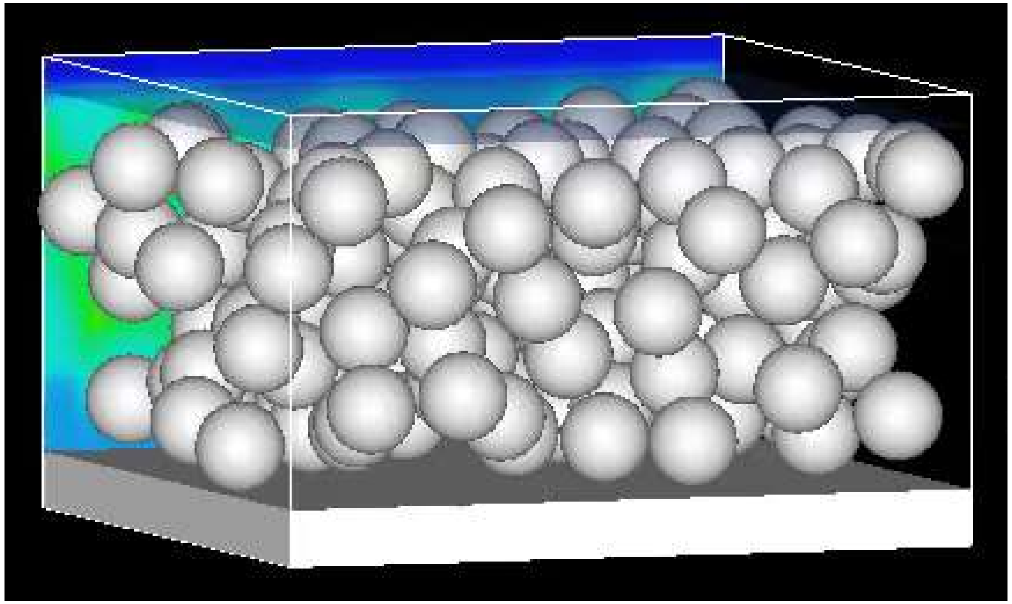
Solute Péclet number



$Pe_{slt} = 0.1$



$Pe_{slt} = 0.01$



$Pe_{slt} = 1$

Summary

メソスケールモデル構築（Mesoscale modeling）

・粒子/流体運動（particle/fluid motion）

・自由界面移動（free surface movement）

・溶質吸着/移動（transport of adsorptive solutes）

数値計算結果（Numerical results）

・溶質吸着　→　粒子整列に影響

・Péclet数（溶質濃縮層の発達）に依存

Particle ordering depends on solute Péclet number.