SCEJ 49th Autumn Meeting
Sep. 22, 2017, Nagoya University

Analysis of segregation of additives in drying colloidal suspensions

微粒子分散液の乾燥における添加剤の偏析現象の解析

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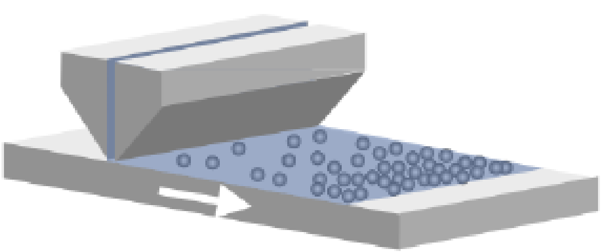
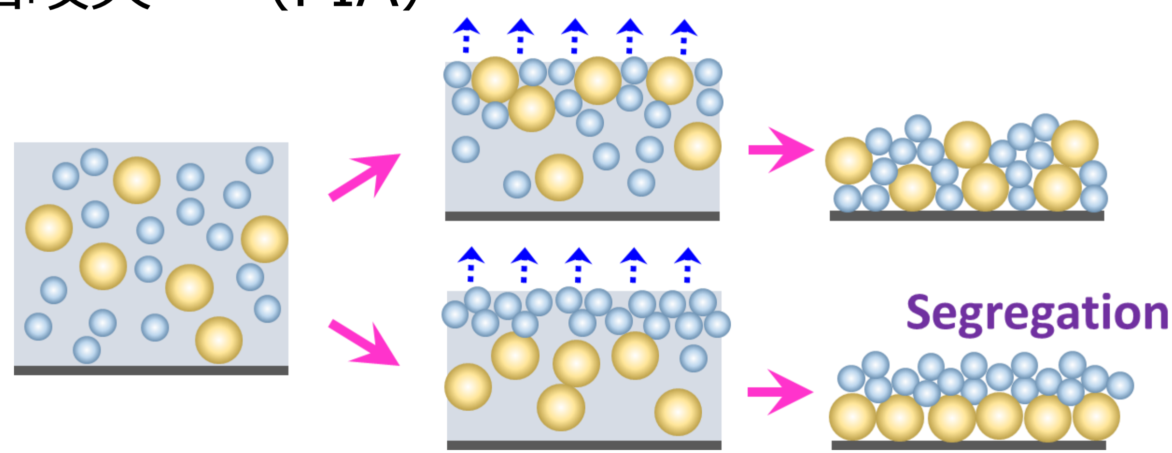
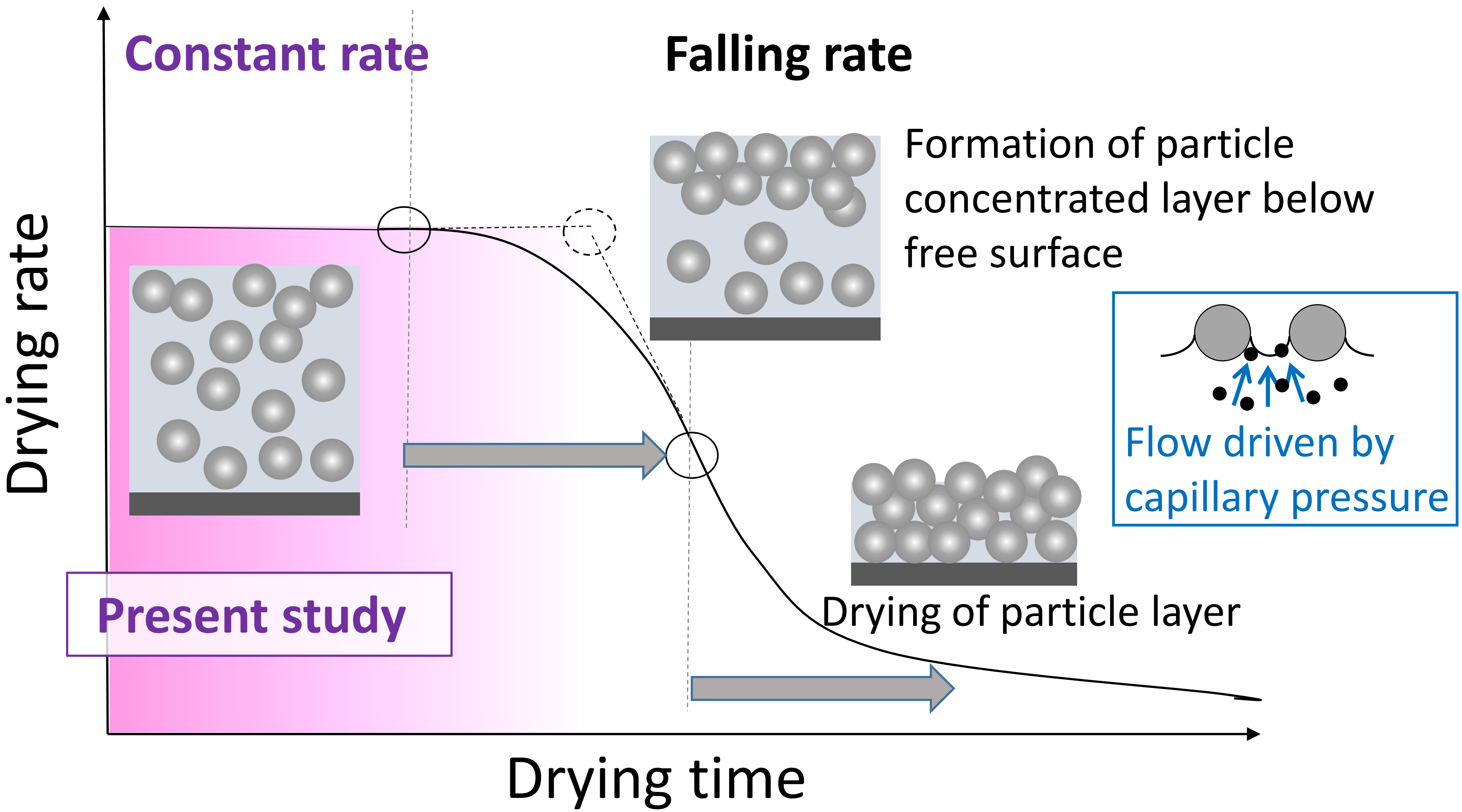


Coating, **Drying**



Drying Curve of Colloidal Suspensions

山口由岐夫,「ものづくりの化学工学」(2015).



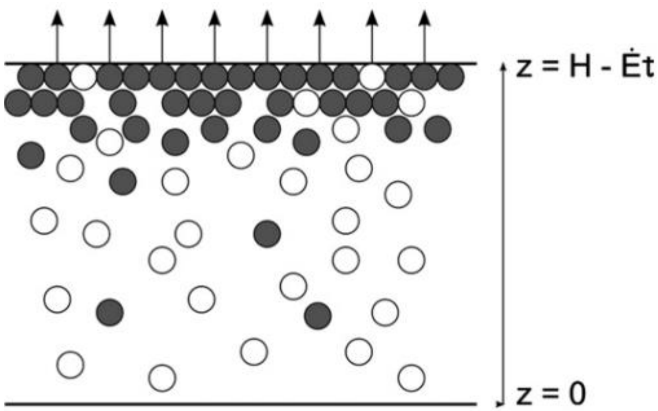
Previous Study (1)

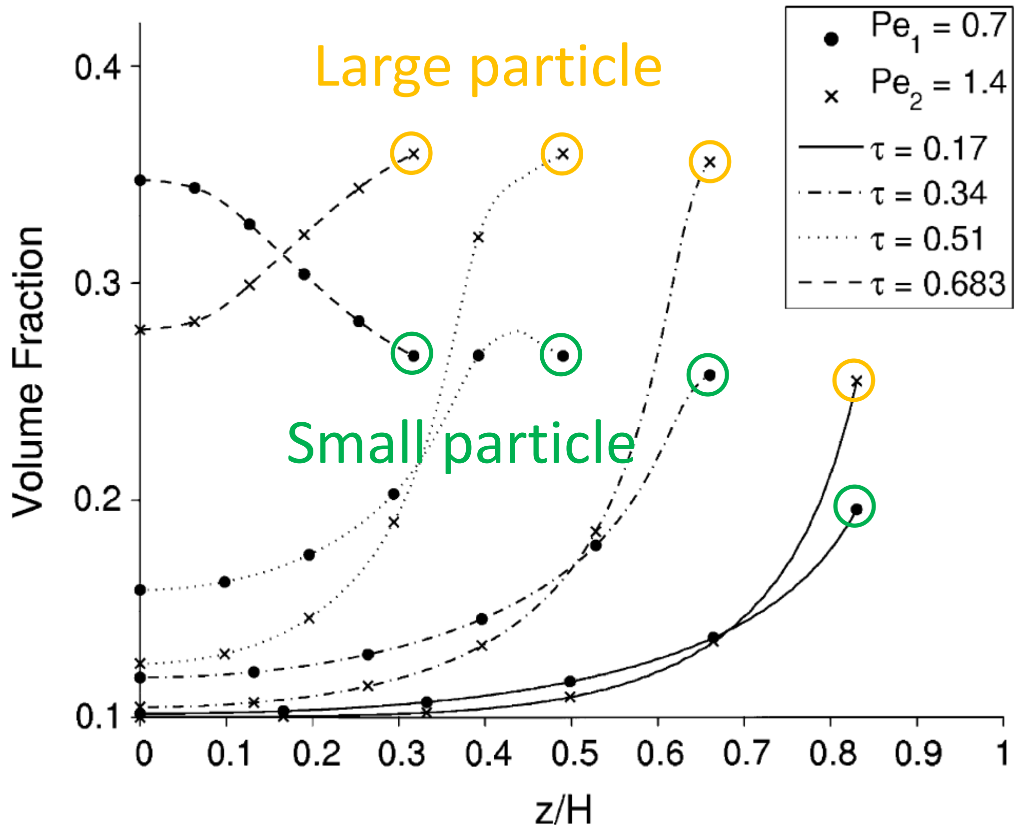
Trueman et al., J. Colloid Interface Sci. (2012).

1D diffusion equation for particle concentration dist.

$$\frac{\partial \phi_1}{\partial t} + \nabla \cdot \phi_1 \mathbf{U}_1 = 0$$

$$\mathbf{U}_1 = -\frac{K(\phi_1, \phi_2)}{6\pi\eta R_1} \nabla \mu_1$$





Segregation of Larger particles to the top surface
← Diffusion rate: (Large particle) < (Small particle)

Previous Study (2)

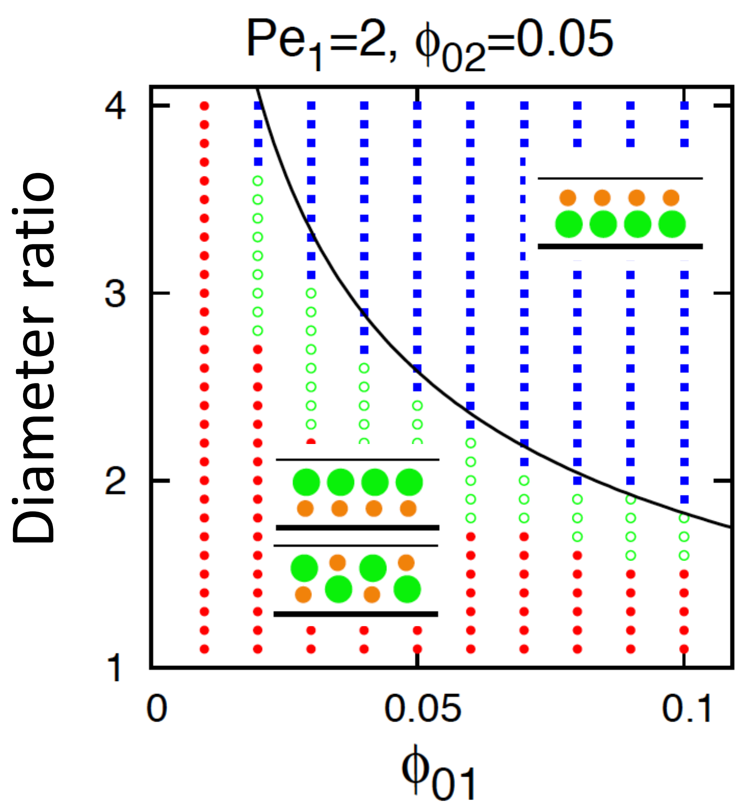
Zhou et al., PRL (2017).

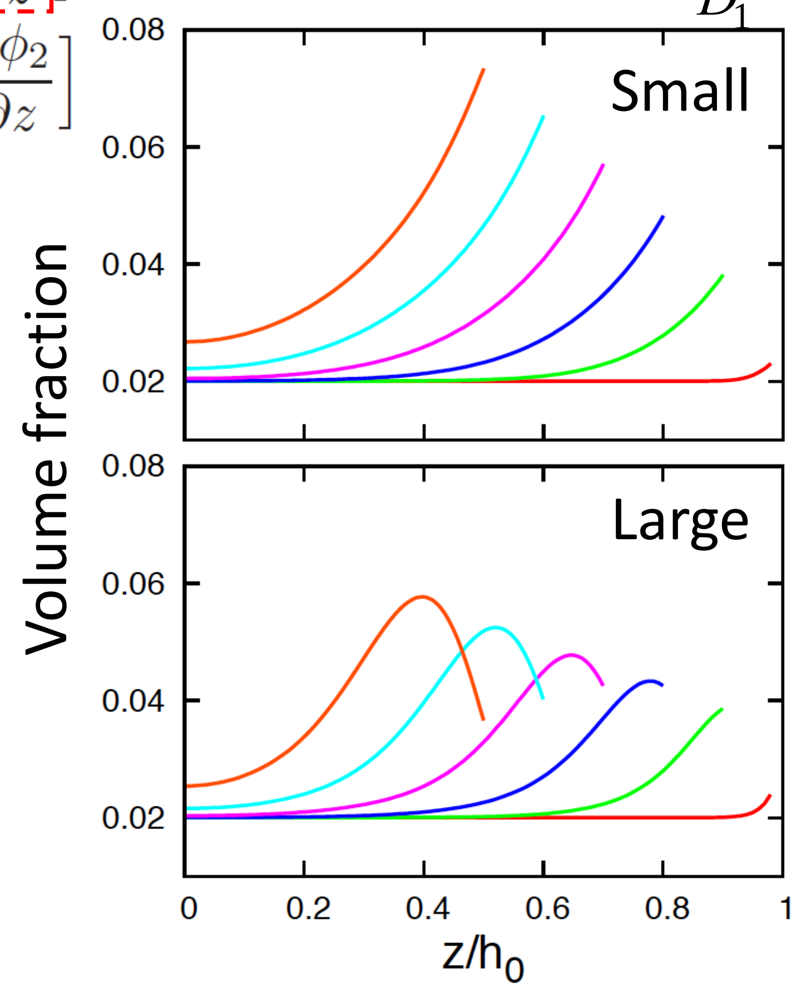
Cross-diffusion → Segregation of Smaller particles to the top surface

$$\frac{\partial \phi_1}{\partial t} = D_1 \frac{\partial}{\partial z}\left[(1+8\phi_1)\frac{\partial \phi_1}{\partial z} + \left(1+\frac{1}{\alpha}\right)^3 \phi_1 \frac{\partial \phi_2}{\partial z}\right]$$

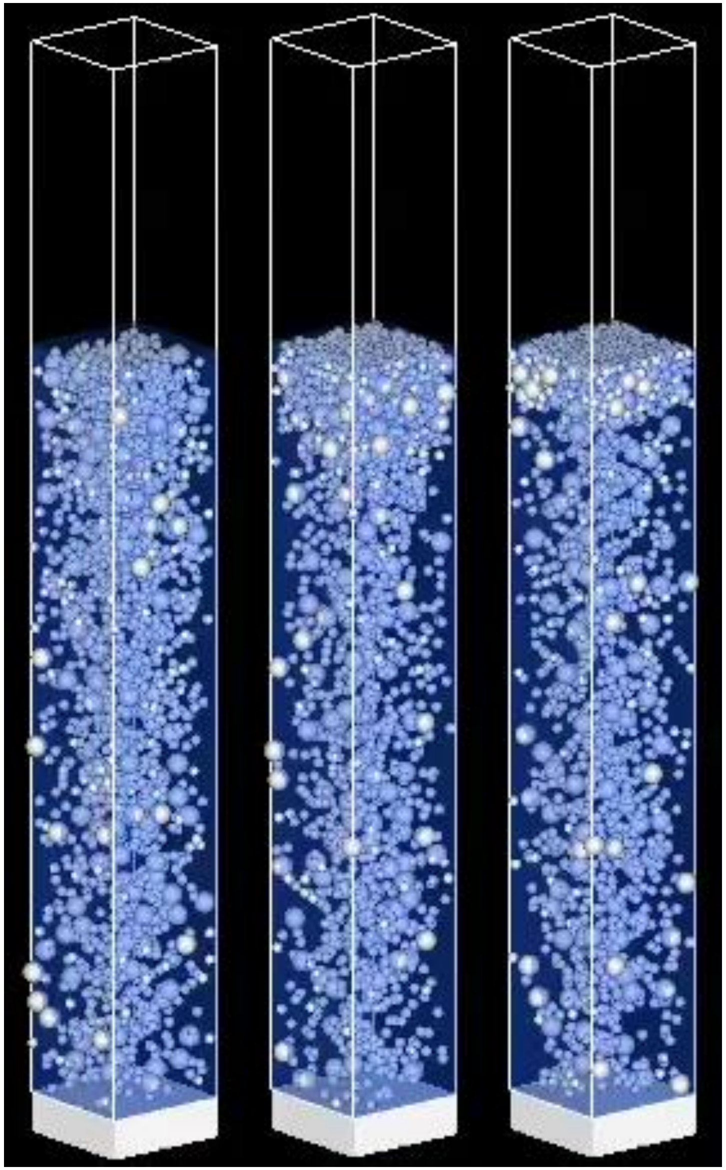
$$\frac{\partial \phi_2}{\partial t} = D_2 \frac{\partial}{\partial z}\left[(1+\alpha)^3 \phi_2 \frac{\partial \phi_1}{\partial z} + (1+8\phi_2)\frac{\partial \phi_2}{\partial z}\right]$$

Diameter ratio 4 $\mathrm{Pe}_1 = \frac{v_e h_0}{D_1} = 5$



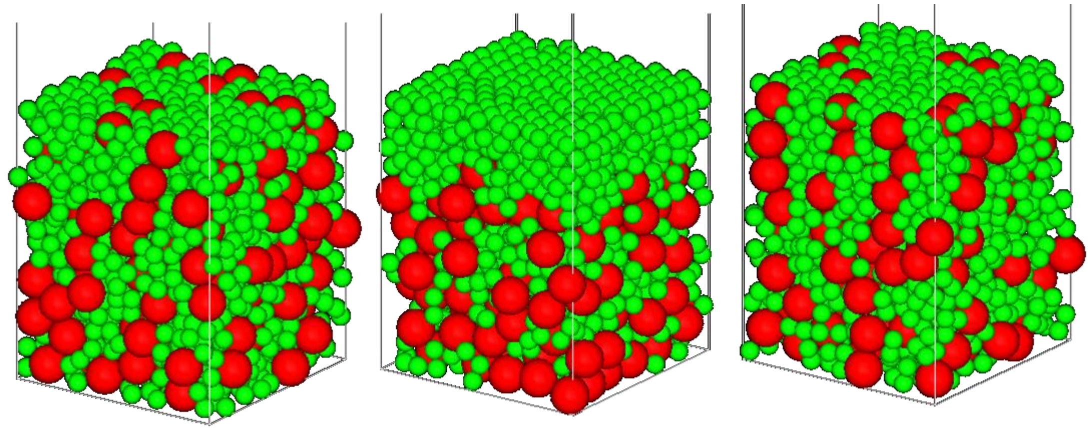


Previous Study (3)



Pe = 0.3　　5　　100

Tatsumi et al., SCEJ 82th Annual Meeting (2017).



Pe = 0.3　　5　　100

Diameter ratio: 2

Particle drying Péclet number

$$\mathrm{Pe} = \frac{(\text{Evaporation rate})}{(\text{Diffusion rate})} = \frac{v_{\mathrm{e}} d}{D}$$

Objective

- Investigation of the segregation of additives in the constant drying rate period

- Analysis using a simple model

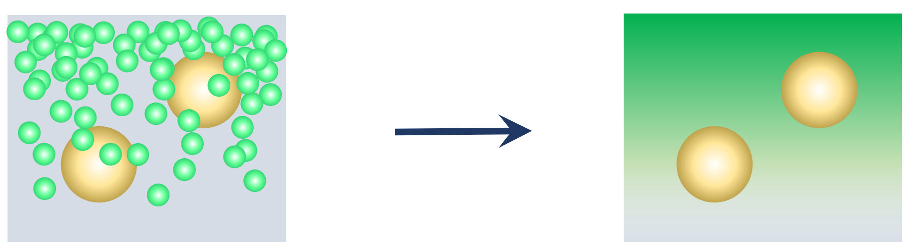
· Particles: Equation of motion (Langevin eq.)

← Force induced by particle-solute interaction

· Solute concentration dist. : 1D advection-diffusion eq.

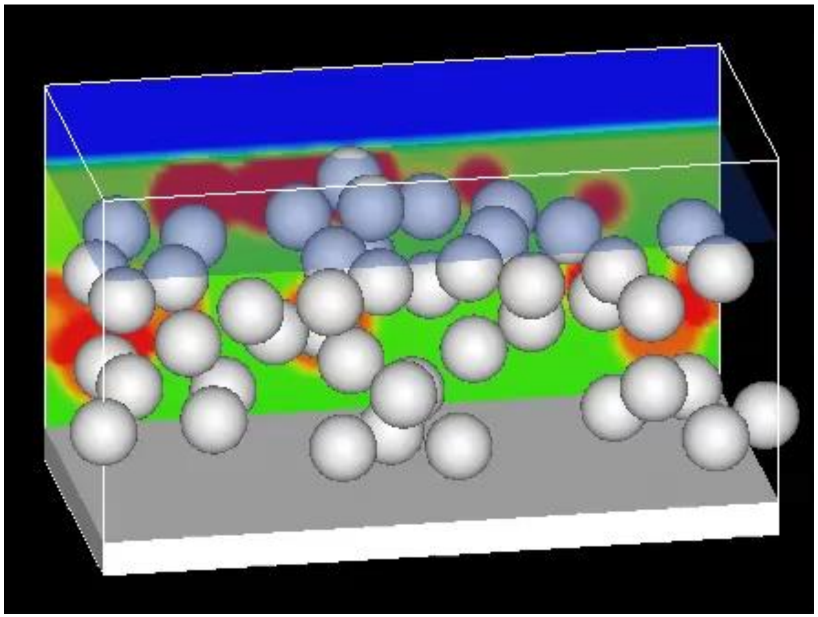
(Approximated by the analytical solution without particles)

· Free surface moving at constant rate



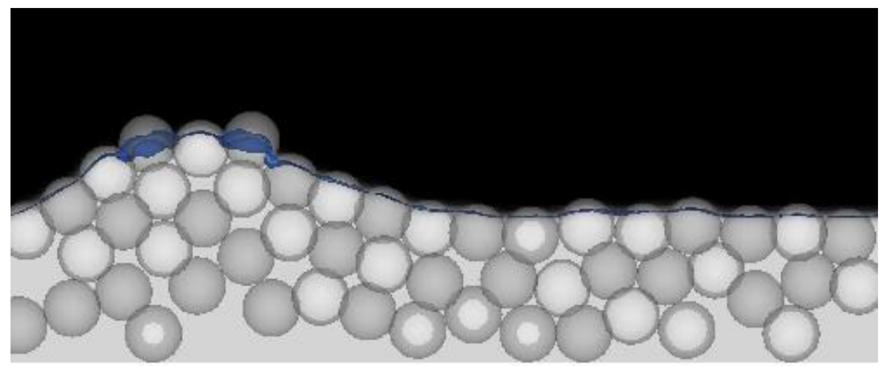
For Your Information

Detailed model



Consideration of coupled motion

Particle ⟷ { Fluid flow, Free surface, Solute distribution }



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Equation of Particles' Brownian Motion

Langevin equation

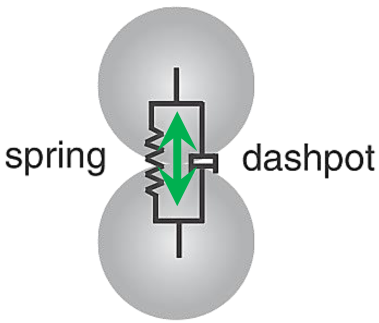
$$M_i \dot{\boldsymbol{V}}_i = -\xi \boldsymbol{V}_i + \boldsymbol{F}_i^{\mathrm{R}} + \boldsymbol{F}_i^{\mathrm{cnt}} + \boldsymbol{F}_i^{\mathrm{cpl}} + \boldsymbol{F}_i^{\mathrm{slt}}$$

Drag force: $-\xi \boldsymbol{V}_i$ Stokes' law: $\xi = 3\pi\eta d$

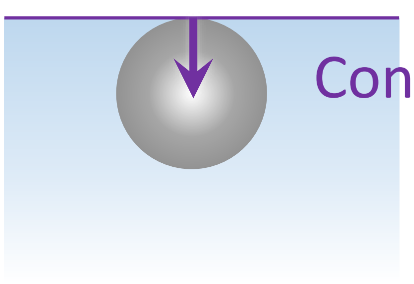
Random force: $F_{i\alpha}^{\mathrm{R}}(t) \sim N(0, 2\xi k_{\mathrm{B}} T)$ Stochastic variables obeying the Gaussian dist.

→ **Brownian Diffusion**: $D_{\mathrm{p}} = \dfrac{k_{\mathrm{B}} T}{3\pi\eta d}$ Diffusion coefficient in infinite dilution

Contact force: $\boldsymbol{F}_i^{\mathrm{cnt}}$



Vertical capillary force: $\boldsymbol{F}_i^{\mathrm{cpl}}$

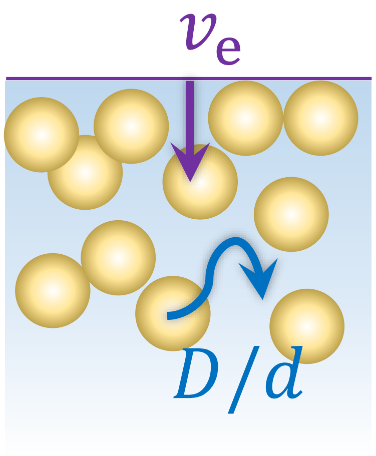


Contact angle $\alpha = 0$

Particle-solute interaction force: $\boldsymbol{F}_i^{\mathrm{slt}}$ ← Solute concentration dist.

Drying Péclet Numbers

$$\mathrm{Pe} = \frac{(\text{Evaporation rate})}{(\text{Diffusion rate})} = \frac{v_\mathrm{e}}{D/d} = \frac{v_\mathrm{e} d}{D}$$



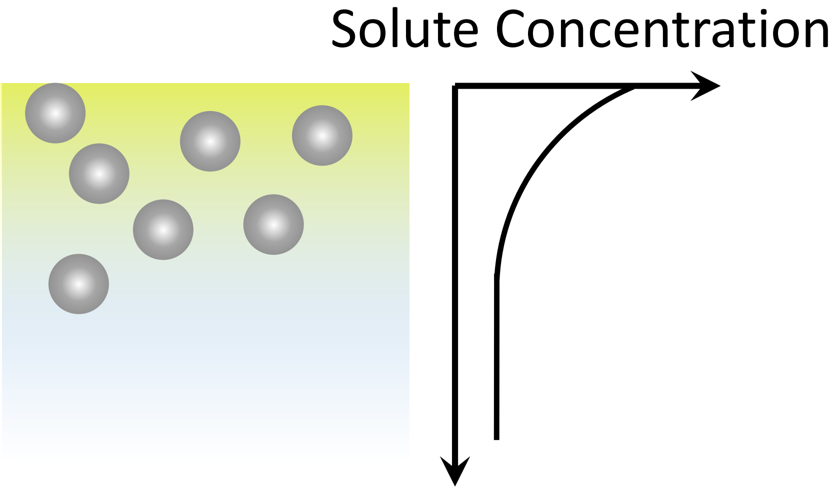
characteristic length = particle diameter d

Particle

$$\mathrm{Pe_p} = \frac{v_\mathrm{e} d}{D_\mathrm{p}}$$

Solute

$$\mathrm{Pe_s} = \frac{v_\mathrm{e} d}{D_\mathrm{s}}$$

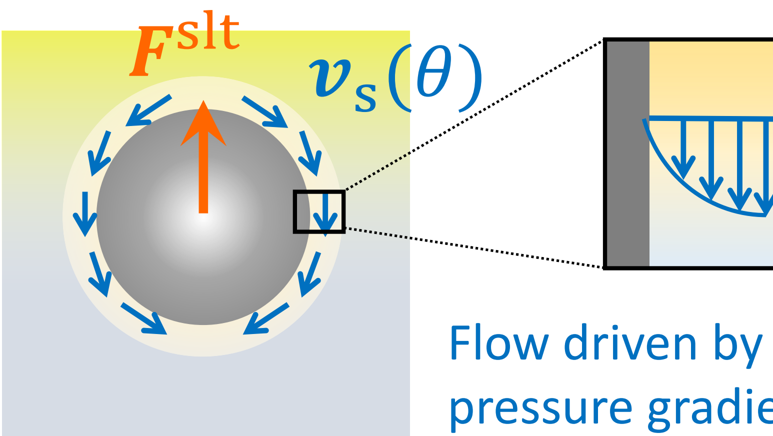


$\boldsymbol{F}_i^{\mathrm{slt}}$: Force induced by “Solute concentration gradient field”

→ Diffusiophoresis (拡散泳動)

Force Induced by Concentration Gradient

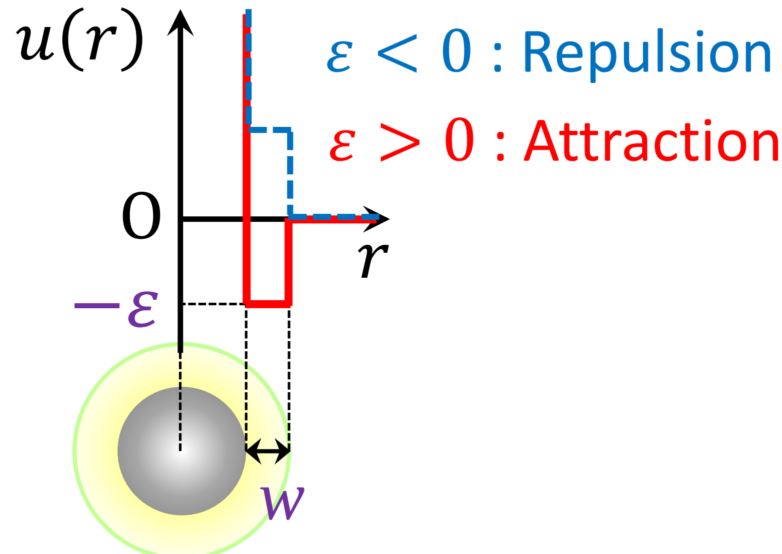
Slip boundary model $(w/d \ll 1)$



Flow driven by osmotic pressure gradient

Anderson & Prieve, Sep. Purif. Meth. (1986)

Particle-solute interaction



$$\boldsymbol{F}^{\mathrm{slt}} = -3\pi\eta d\langle \boldsymbol{v}_{\mathrm{s}} \rangle = \Gamma k_{\mathrm{B}} T \frac{\boldsymbol{K}}{c_0}$$

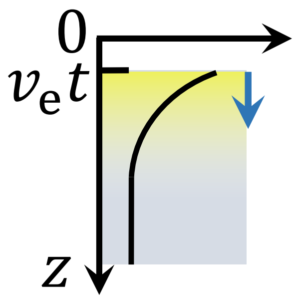
Interaction parameter

$$\Gamma = \frac{3}{2}\pi\left(e^{\beta\varepsilon} - 1\right)c_0 w^2 d$$

Solute concentration gradient $\boldsymbol{K}$

← Analytical solution of the concentration dist. without particles

Solute Concentration Distribution



$$c = c(z,t) = c_0 f(\zeta,\tau)$$

$$\zeta = (z - v_\mathrm{e}t)/l_\mathrm{c}$$

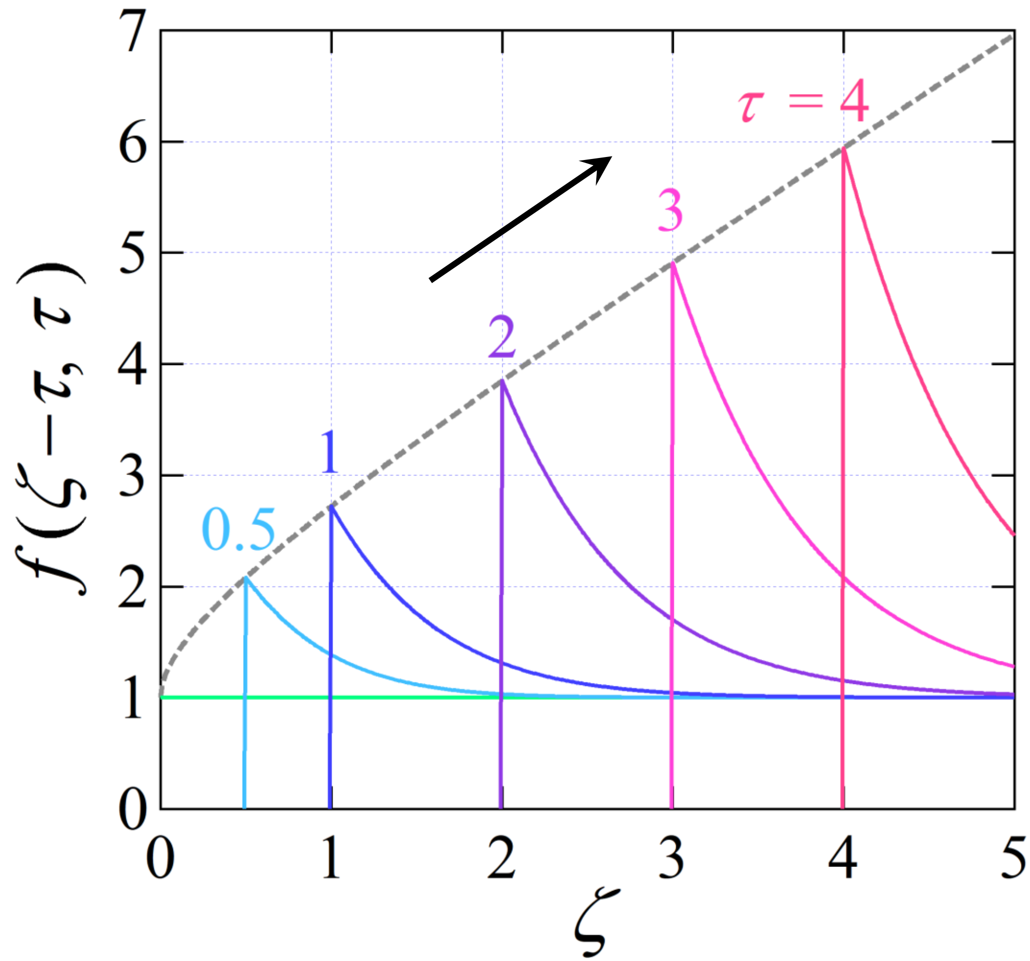
$$\tau = v_\mathrm{e}t/l_\mathrm{c}$$

Length scale of concentration change $l_\mathrm{c} = D_\mathrm{s}/v_\mathrm{e}$

1D advection-diffusion eq.

$$\frac{\partial f}{\partial \tau} = \frac{\partial f}{\partial \zeta} + \frac{\partial^2 f}{\partial \zeta^2}$$

- $f(\zeta,0) = 1$ Initial condition
- $\partial_\zeta f(0,\tau) = -f(0,\tau)$
  Free surface
- $\partial_\zeta f(\infty,\tau) = 0$
  Substrate position $\gg l_\mathrm{c}$



Concentration Gradient

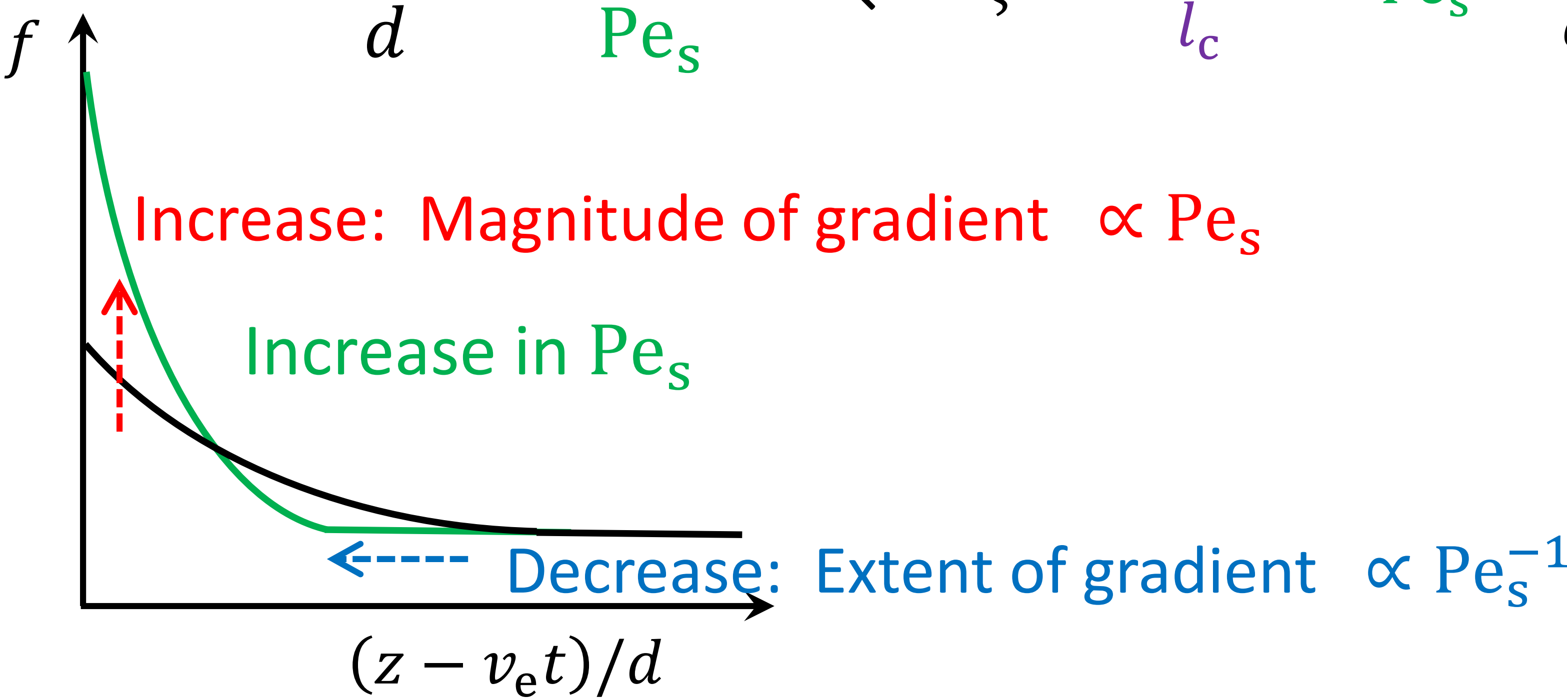
Magnitude of gradient

$$\frac{|\boldsymbol{K}|}{c_0} = \frac{\partial f}{\partial z} = \frac{1}{l_\mathrm{c}}\frac{\partial f}{\partial \zeta} = \frac{\mathrm{Pe_s}}{d}\frac{\partial f}{\partial \zeta}$$

z = Center of the particle

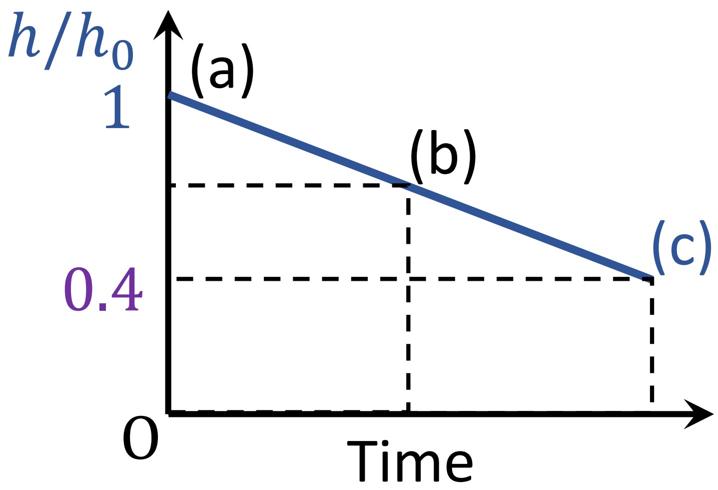
Coordinate transform in $f(\zeta)$

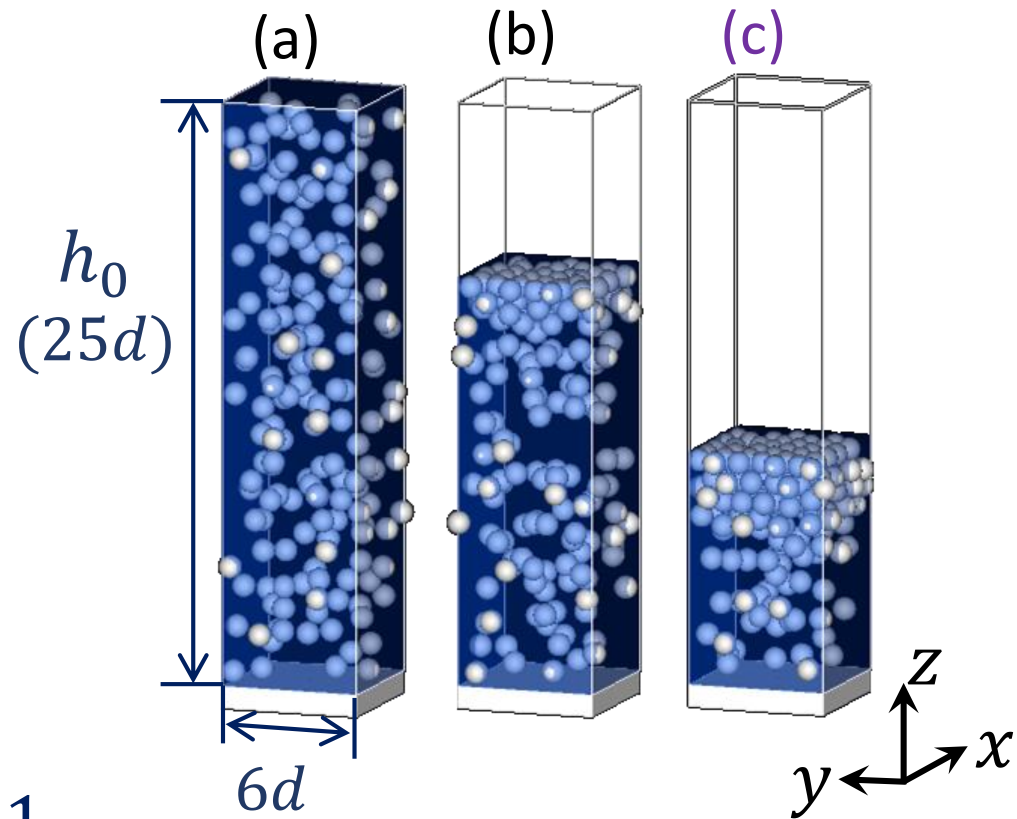
$$\frac{z - v_\mathrm{e} t}{d} = \frac{\zeta}{\mathrm{Pe_s}} \quad \leftarrow \quad \zeta = \frac{z - v_\mathrm{e} t}{l_\mathrm{c}} = \mathrm{Pe_s}\frac{z - v_\mathrm{e} t}{d}$$



Simulation Conditions

Film height $h(t) = h_0 - v_e t$





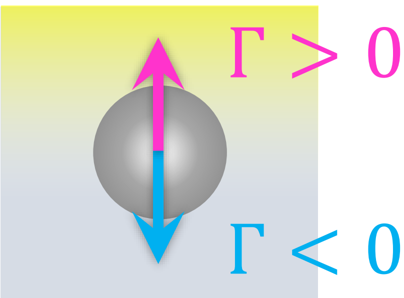
Periodic boundaries: x, y

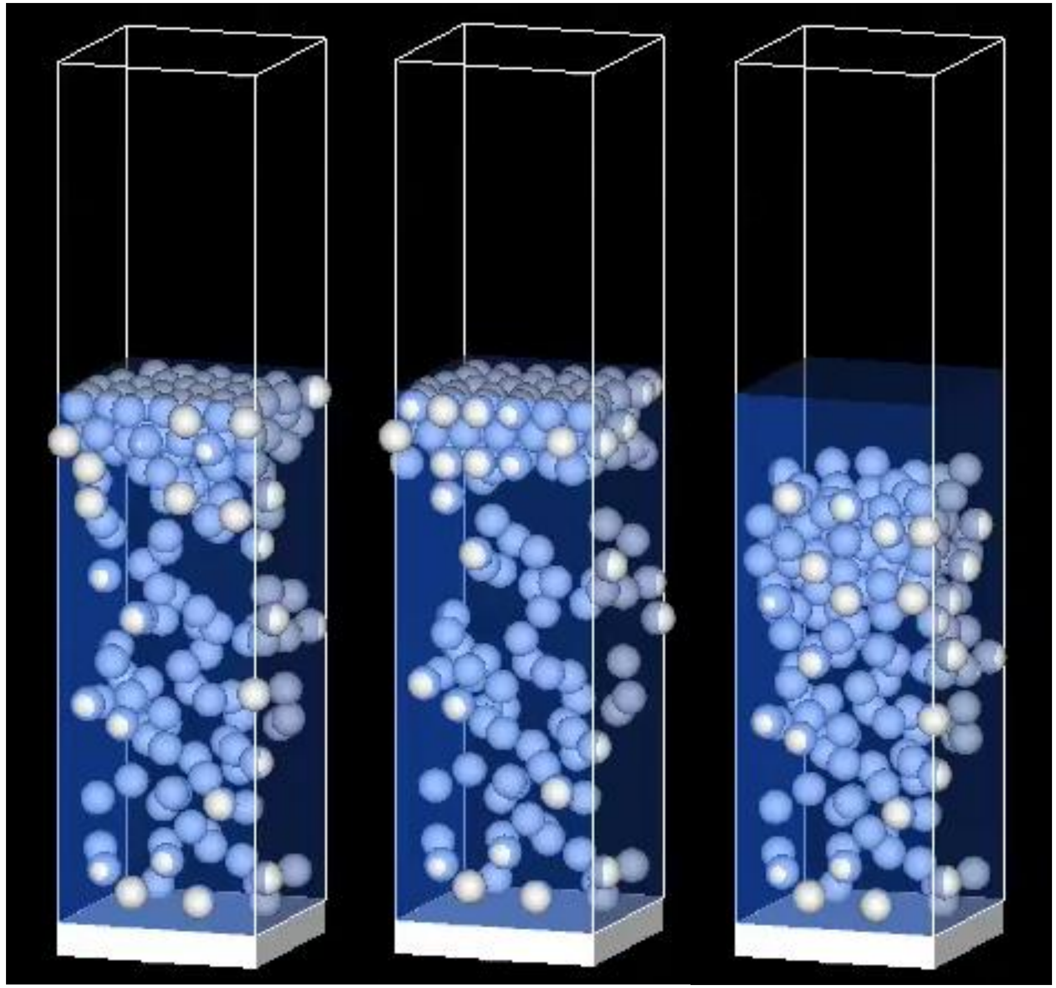
- Particle diameter d
- Initial volume fraction 0.1
- Particle Péclet number $\mathrm{Pe_p} = 20$

(1) Interaction parameter $\Gamma = -100 \sim 100$, $\mathrm{Pe_s} = 0.2$

(2) Solute Péclet number $\mathrm{Pe_s} = 0.1 \sim 10$, $\Gamma = -100$

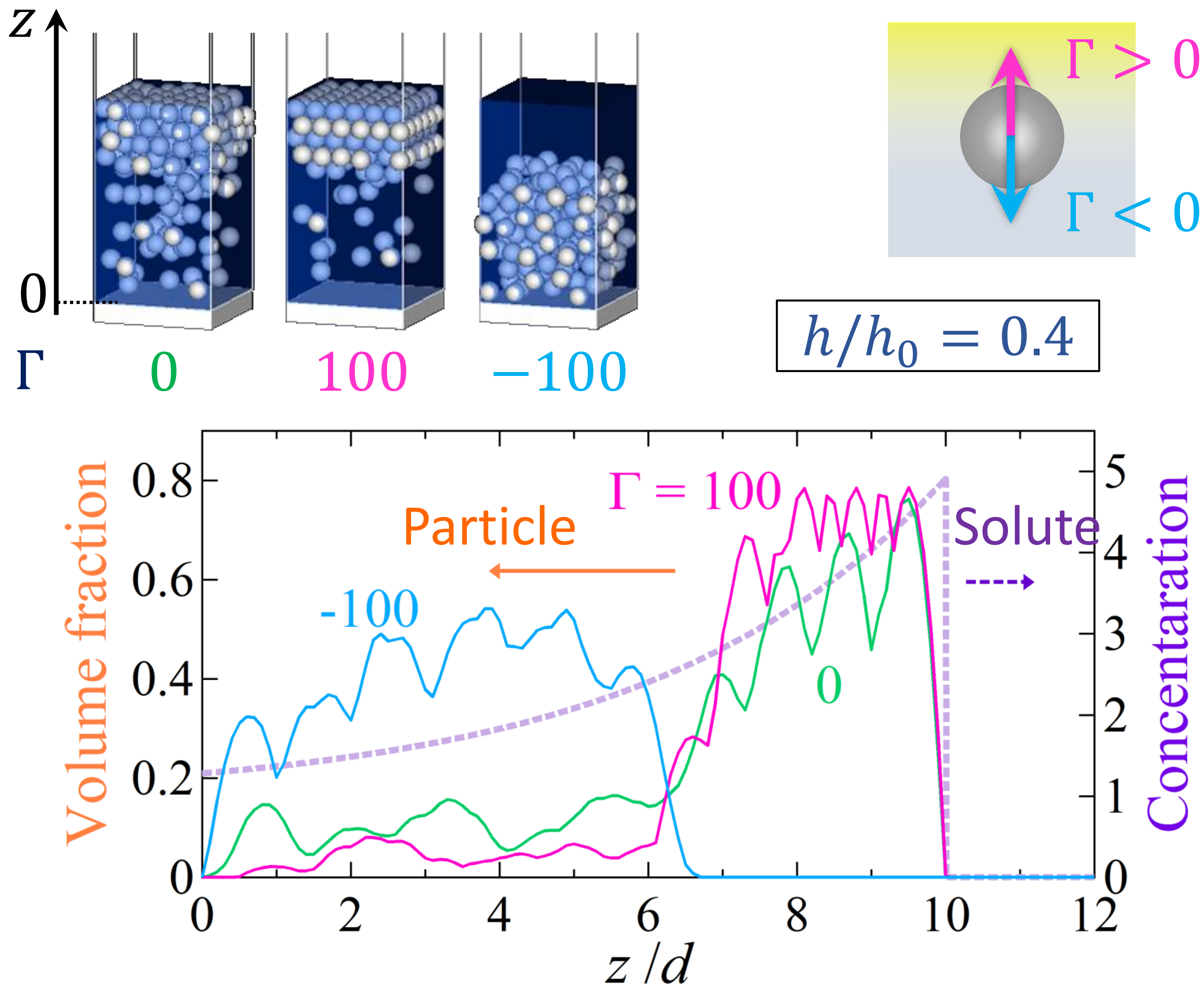
Effects of Particle-Solute Interaction





Γ	0	100	-100
Particle-solute interaction	-	Attractive	Repulsive

Particle/Solute Distribution

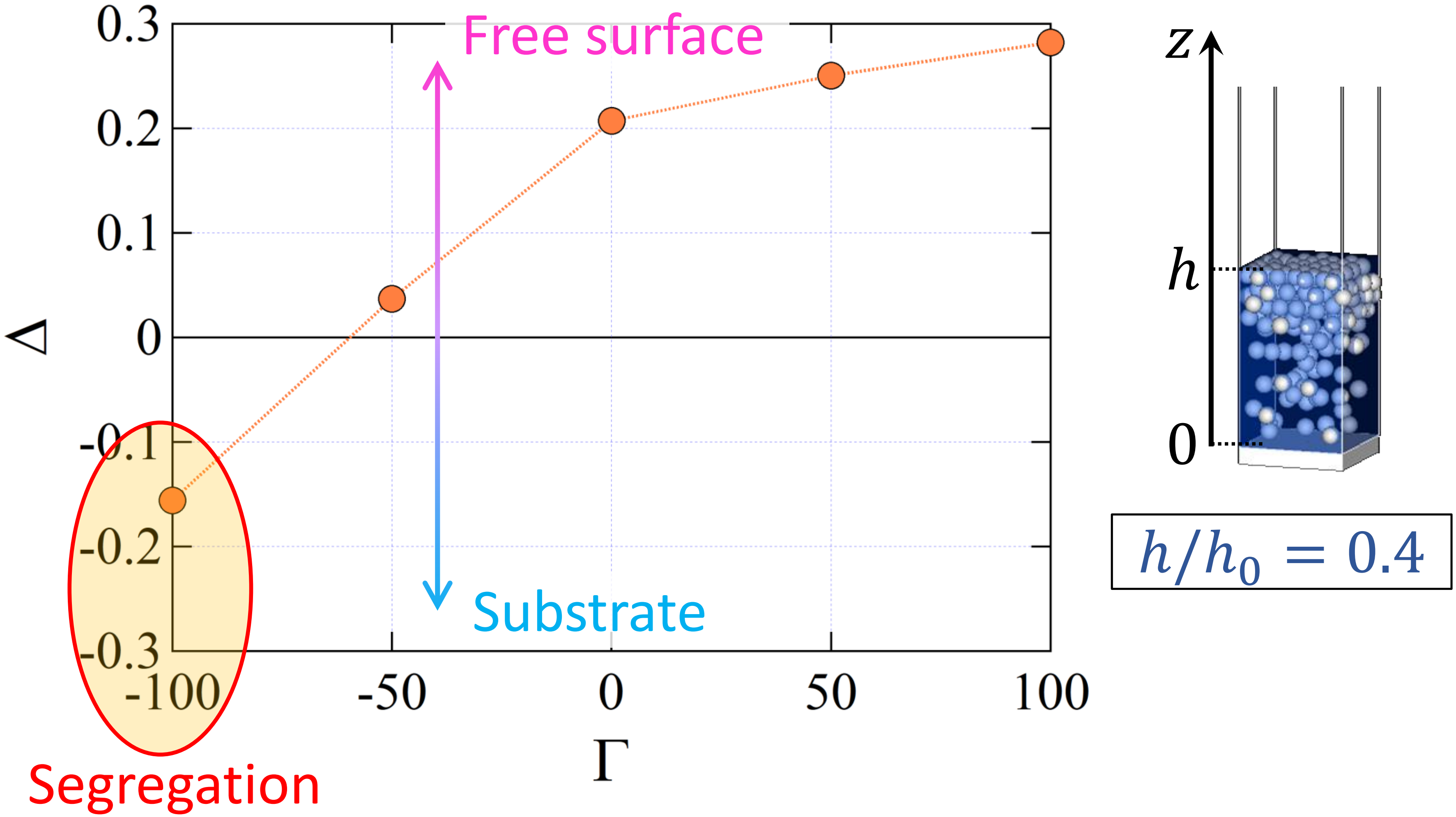


Bias of the Particle Distribution

Deviation from the uniform distribution

$$\Delta \equiv \frac{\langle z \rangle}{h} - \frac{1}{2}$$

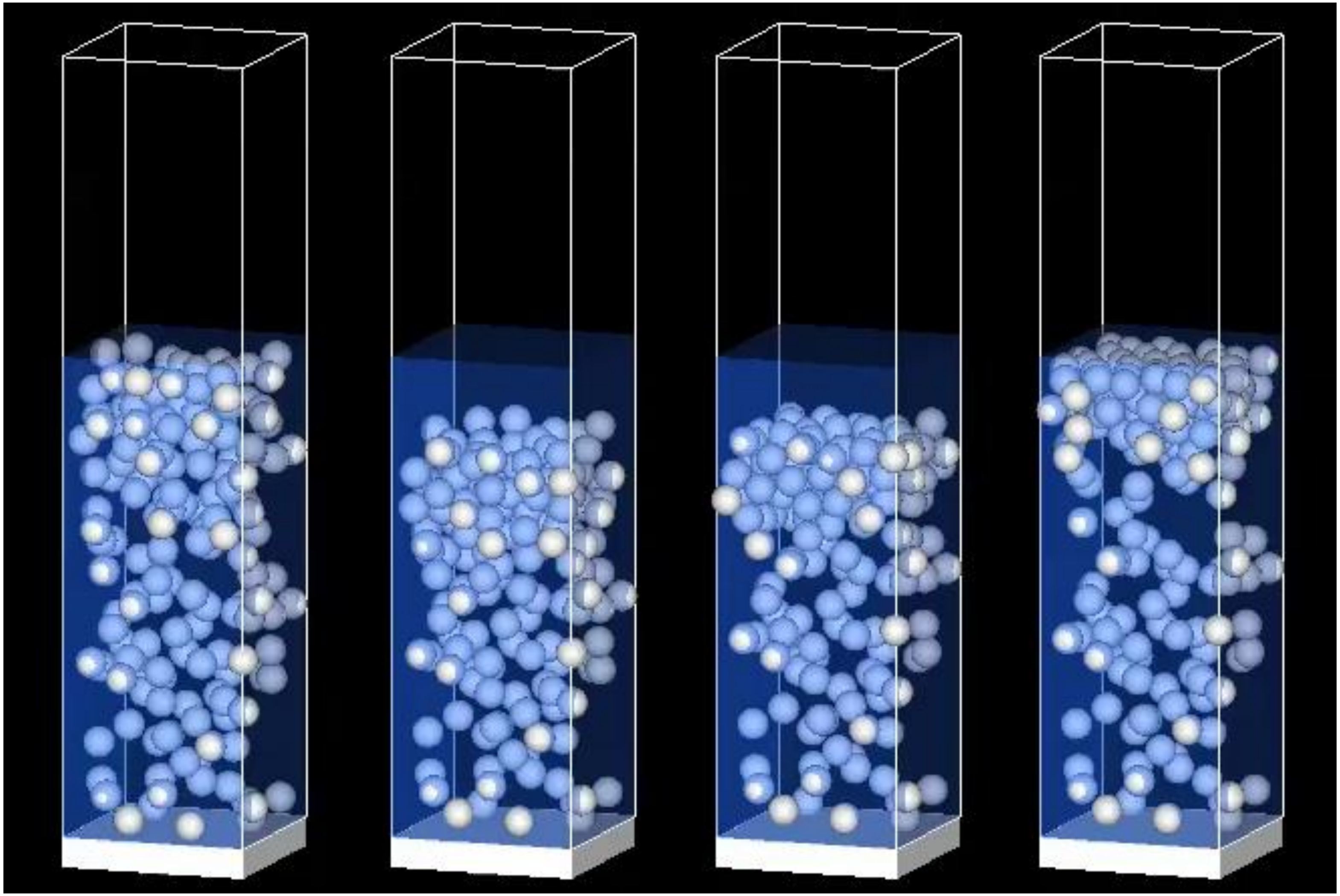
Average z-coordinate of particles $\langle z \rangle$



Solute Péclet Number → Segregation

(Diffusivity of solute)

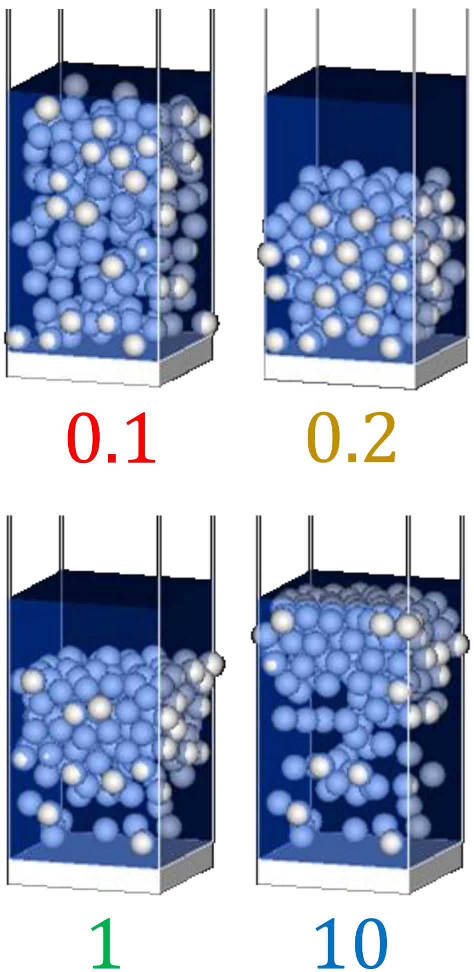
$\Gamma = -100$

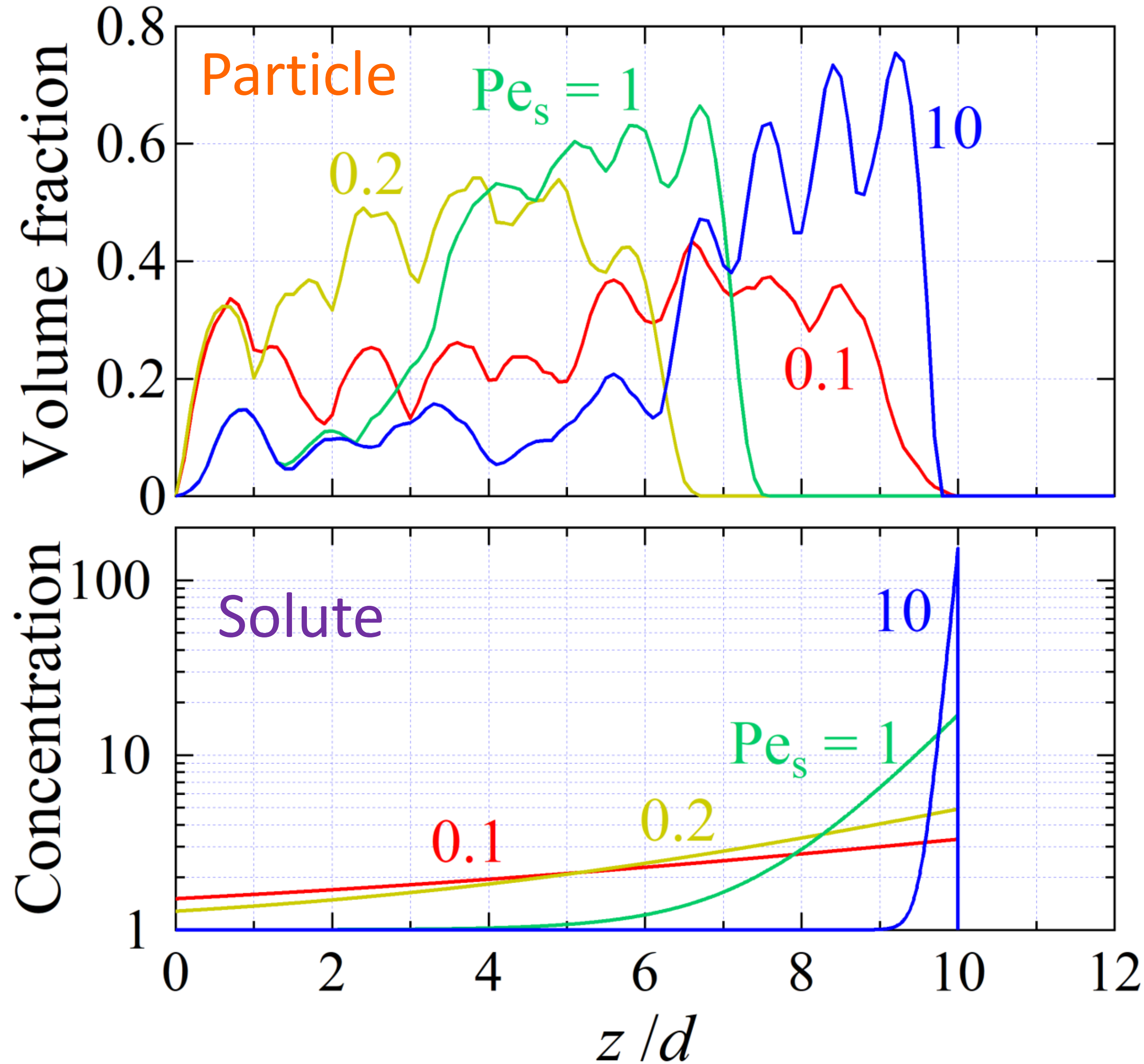


$\mathrm{Pe_s} = 0.1$ 0.2 1 10

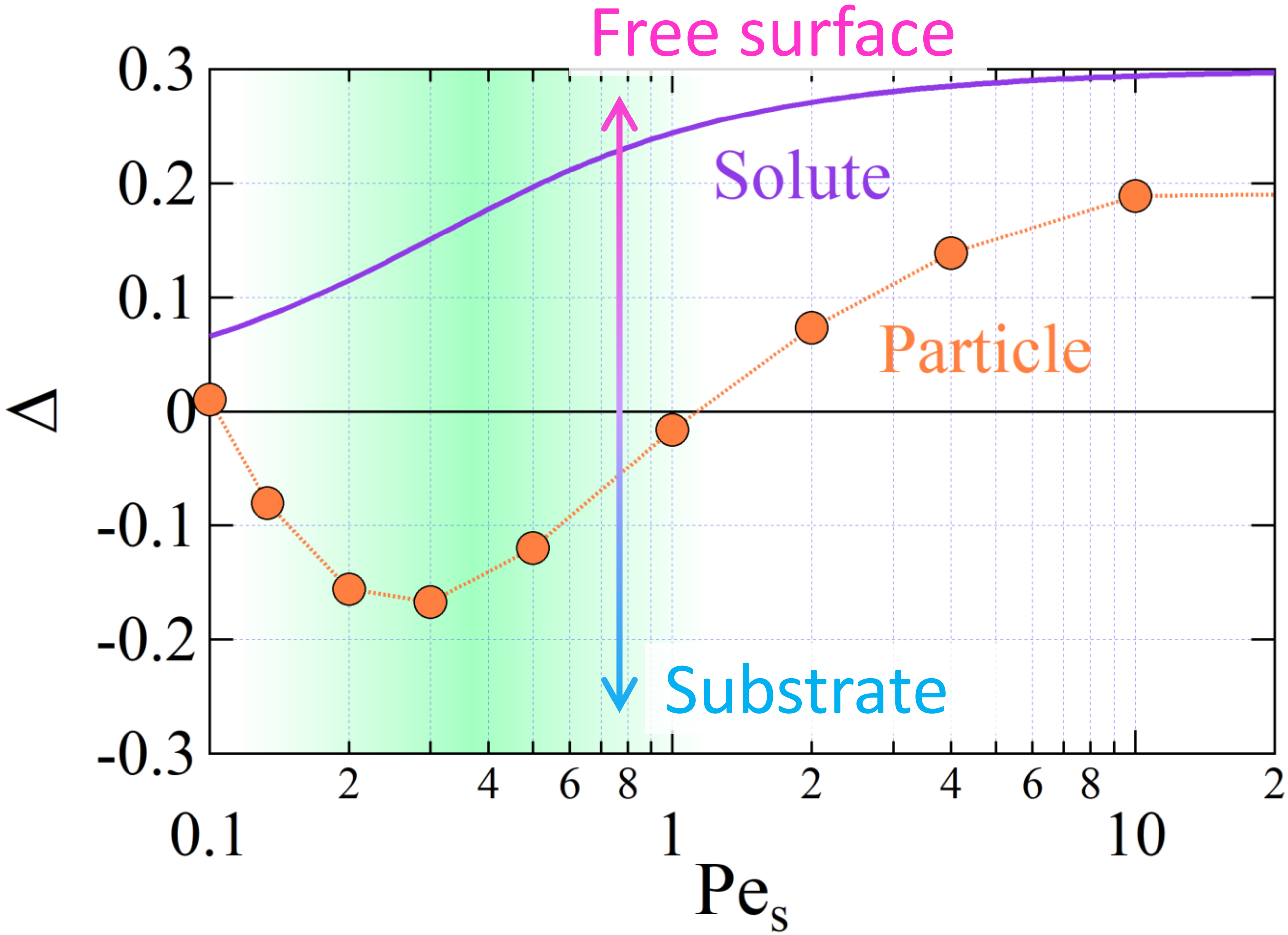
Particle/Solute Distribution

$h/h_0 = 0.4$

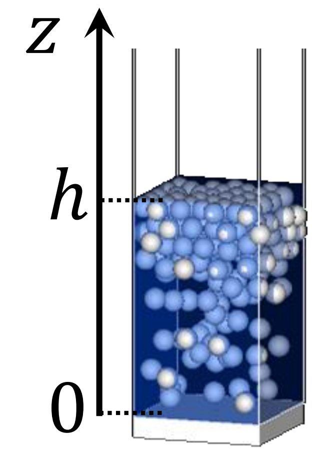




Bias of the Particle/Solute Distribution



$$\Delta \equiv \frac{\langle z \rangle}{h} - \frac{1}{2}$$



$h/h_0 = 0.4$

Trade-off

Concentration gradient Magnitude $\propto \mathrm{Pe_s}$ Small ↔ Large

Extent $\propto \mathrm{Pe_s^{-1}}$ Large ↔ Small

Summery

- "Solute concentration gradient field" is generated by drying and exerts force on the particles. (Diffusiophoresis)

  - Attractive particle-solute interaction
  → Migration of particles toward the free surface

  - Repulsive particle-solute interaction
  → Migration of particles toward the substrate
  → Segregation

- Segregation is maximized at $\mathrm{Pe_s} \sim 0.3$.

  ← Trade-off relation about solute concentration gradient:
  Magnitude $\propto \mathrm{Pe_s}$, Extent $\propto \mathrm{Pe_s^{-1}}$