化学工学会第81年会
2016/03/15

乾燥による粒子系構造形成における溶質吸着の影響

Solute adsorption effects on structure formation of colloidal particles during drying

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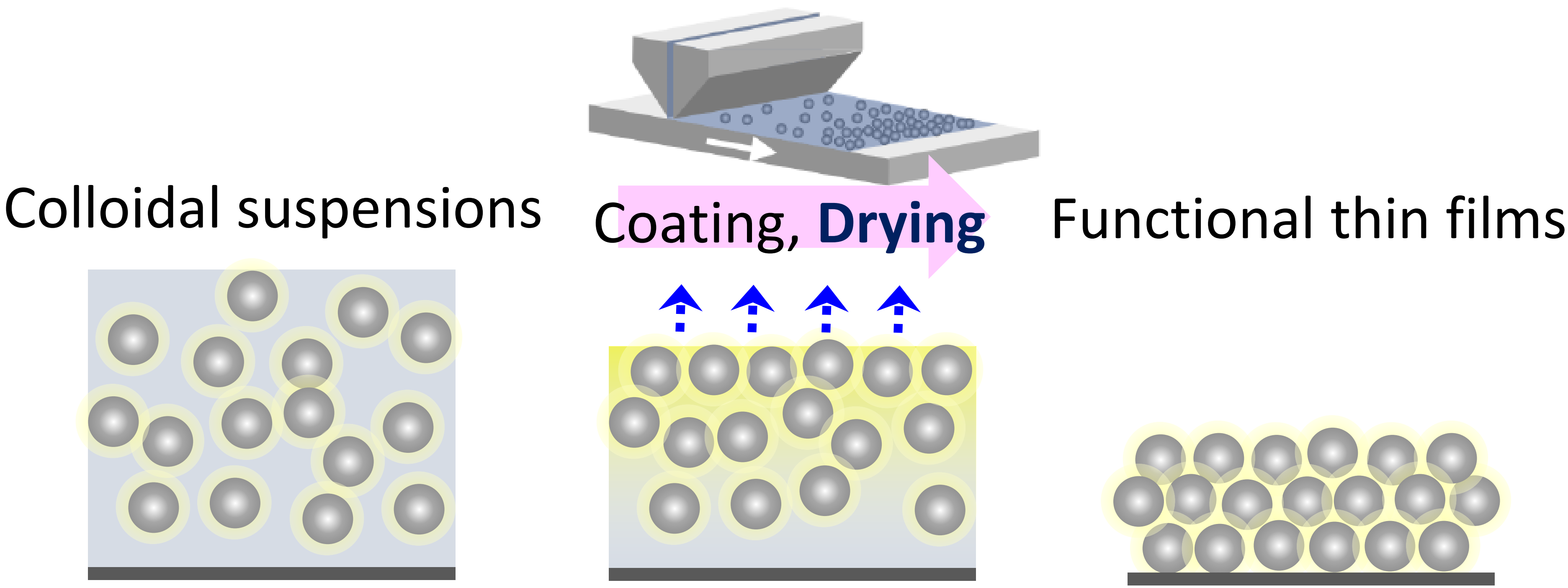
Particle film formation



Addition of solutes

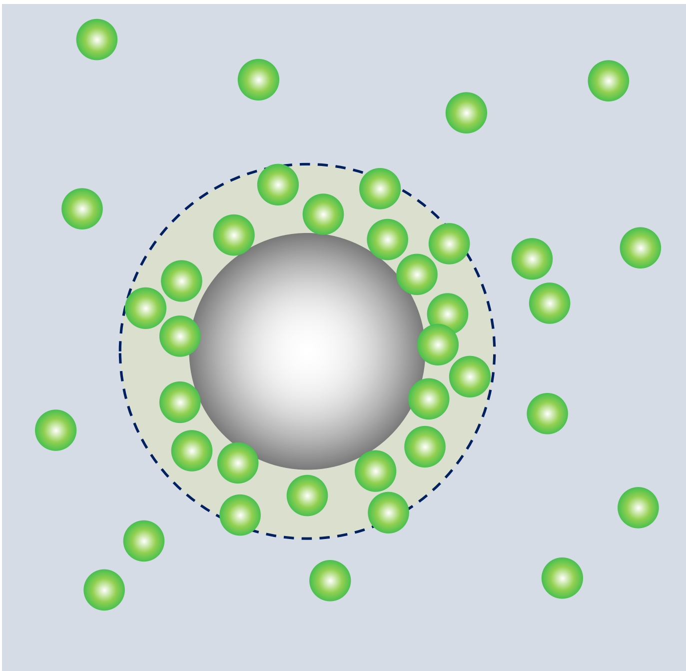
- Dispersant
- Binder

Particle configuration

Physical properties of film

Mesoscale Modeling & **D**irect **N**umerical **S**imulation

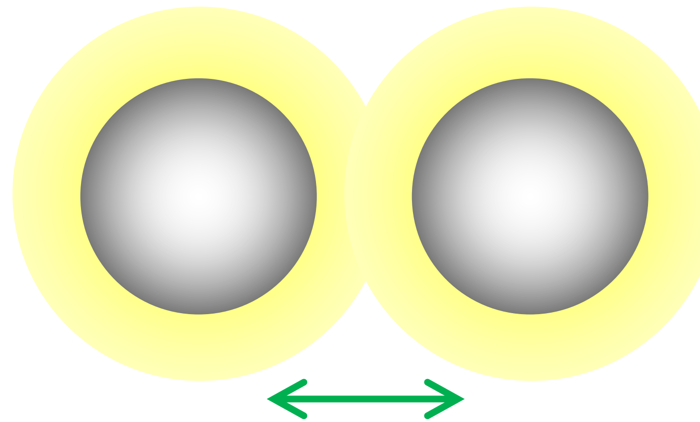
Adsorption of solutes



Physical adsorption

(Reversible adsorption)

Adsorption layer overlapping



Interparticle force

Model

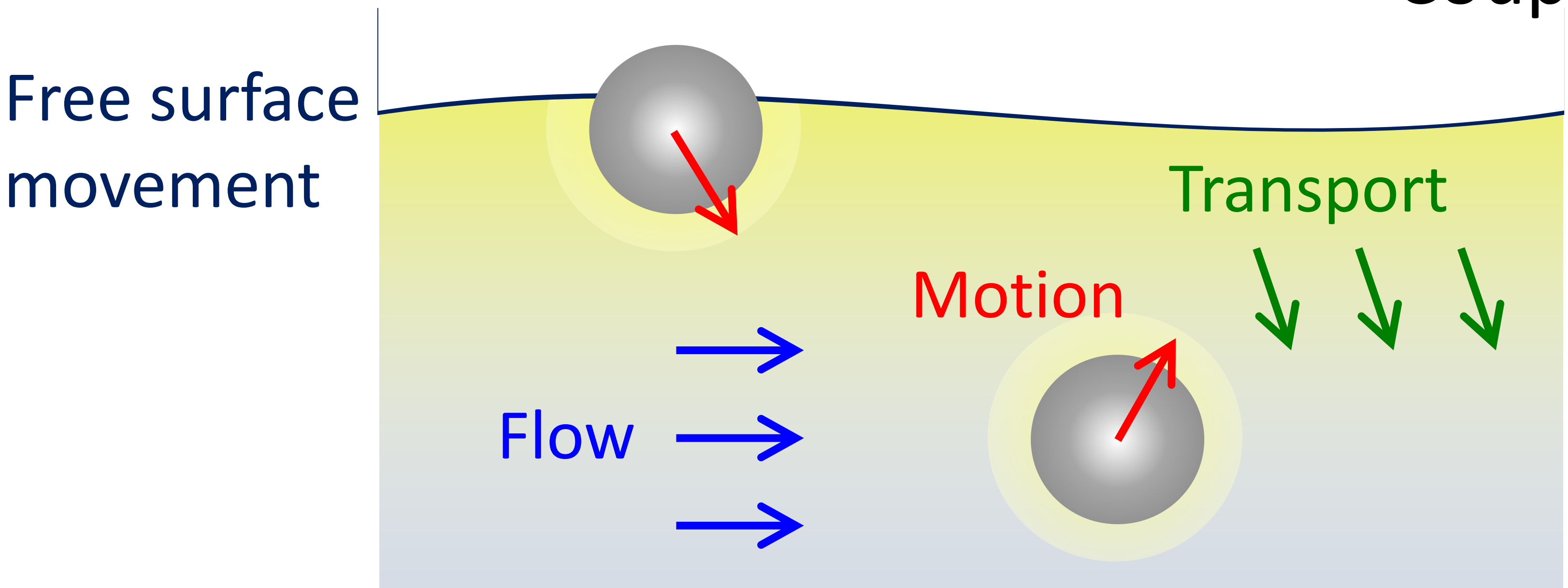
Particles: Newton-Euler equations of motion

Fluid: Hydrodynamic equations

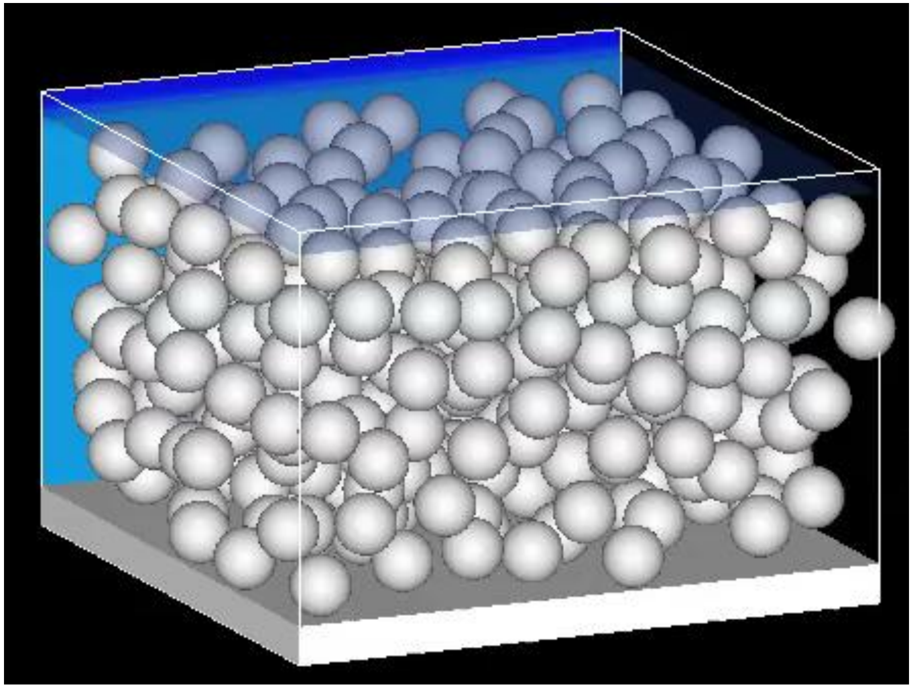
Free surface: Advection equation

Solute: Advection-diffusion equation

Coupled



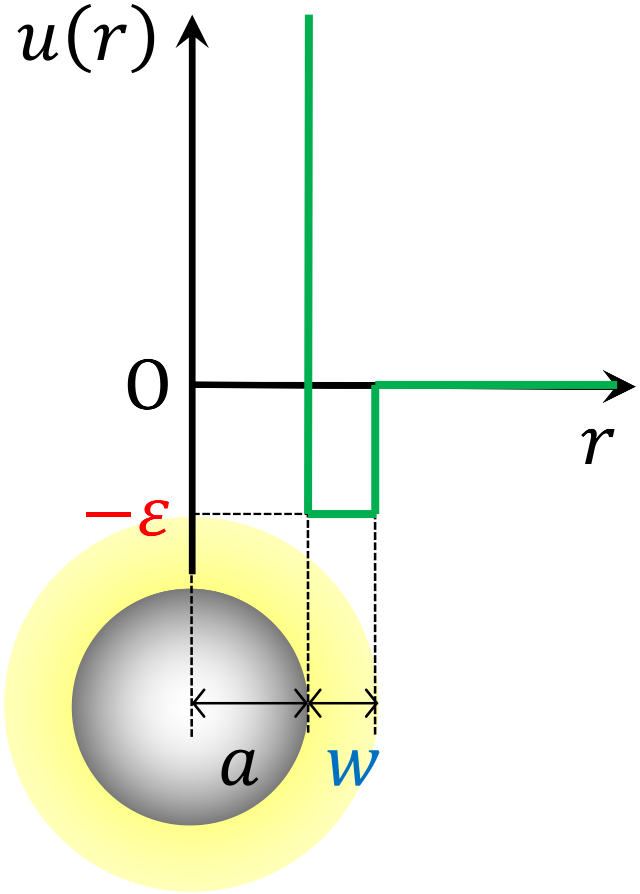
Objective



Drying → Recession of free surface

- Arrangement of particles
- Distribution of solute

Particle-solute adsorption interaction



Square-well potential
（井戸型ポテンシャル）

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

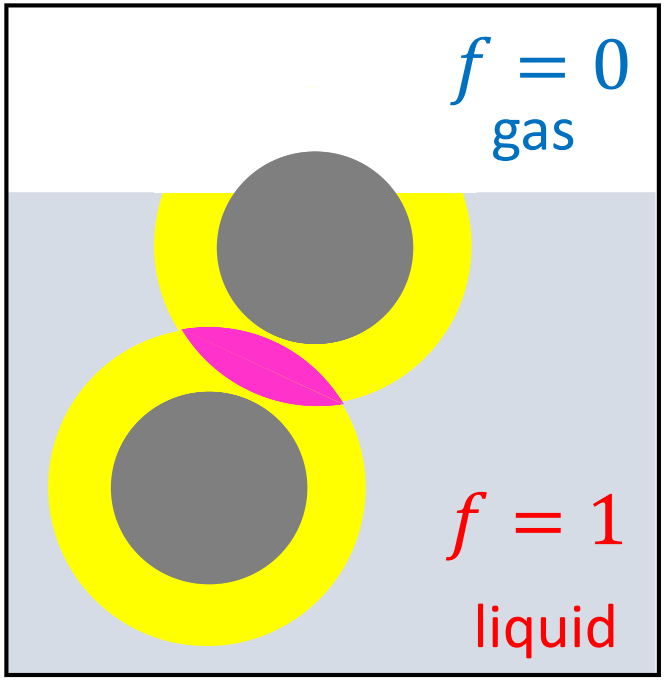
Adsorption energy: ε

Adsorption layer thickness: w

Physical adsorption (Reversible): $\varepsilon \sim RT$

Solute transport

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



Diffusion flux

$$\boldsymbol{J} = -cD\nabla\mu$$

Chemical potential

$$\mu = RT\ln\frac{c}{c^0} + f\sum_i u_i + (1-f)\Delta\mu_{\mathrm{g}}$$

Particle-solute interaction

Excess chemical potential in gas

$\Delta\mu_{\mathrm{g}}/RT \gg 1 \rightarrow$ Impermeability to gas

Fluid/Particle motion

Fluid

$$\nabla \cdot \boldsymbol{v} = 0$$

Body force to constrain particle velocity

Surface tension

$$\rho\left(\frac{\partial \boldsymbol{v}}{\partial t} + \boldsymbol{v}\cdot\nabla\boldsymbol{v}\right) = \nabla\cdot\boldsymbol{\sigma} + \gamma\kappa\nabla f - c\sum_i \nabla u_i + \rho\Phi\boldsymbol{a}$$

Particle-solute interaction

Stress tensor $\boldsymbol{\sigma} = -(p + RTc)\boldsymbol{I} + \eta[\nabla\boldsymbol{v} + (\nabla\boldsymbol{v})^T]$

Momentum exchange

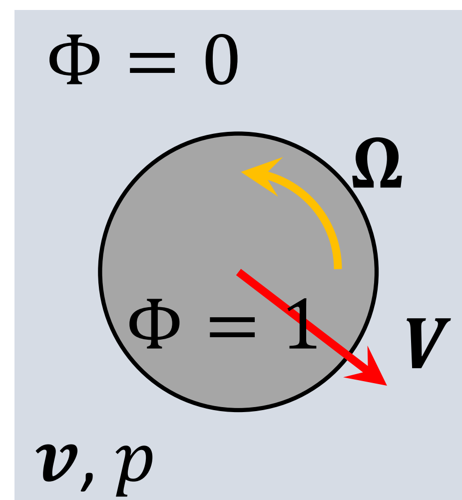
Particle

$$M_i\dot{\boldsymbol{V}}_i = \boldsymbol{F}_i^{\mathrm{C}} + \boldsymbol{F}_i^{\mathrm{S}} + \boldsymbol{F}_i^{\mathrm{H}} \qquad \dot{\boldsymbol{R}}_i = \boldsymbol{V}_i$$

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

$$\boldsymbol{F}_i^{\mathrm{S}} = \int c\nabla u_i \mathrm{d}\boldsymbol{r} \qquad \boldsymbol{F}_i^{\mathrm{H}} = -\int \rho\Phi\boldsymbol{a}\mathrm{d}\boldsymbol{r}$$

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



Free surface

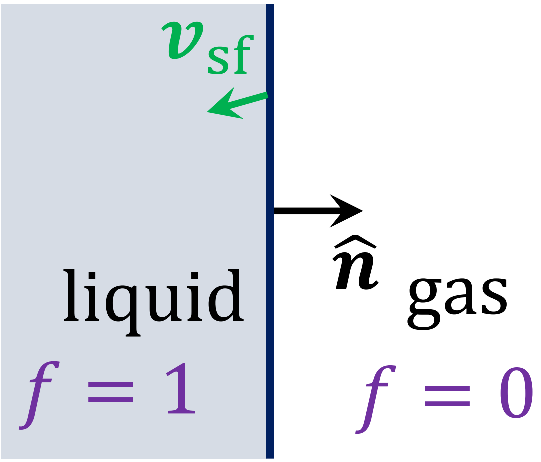
$$\frac{\partial f}{\partial t} + \boldsymbol{v}_{\mathrm{sf}} \cdot \boldsymbol{\nabla} f = 0$$

Evaporation mass flux on free surface

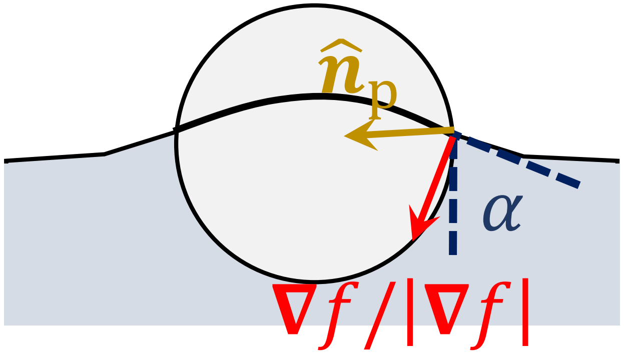
$$\rho(\boldsymbol{v} - \boldsymbol{v}_{\mathrm{sf}}) \cdot \hat{\boldsymbol{n}} = (1 - \Phi)\dot{\omega}$$

Velocity of free surface

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



Contact angle $\quad \dfrac{\boldsymbol{\nabla} f}{|\boldsymbol{\nabla} f|} \cdot \hat{\boldsymbol{n}}_{\mathrm{p}} = \cos\alpha$



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

Simulation conditions

Particle diameter
$d = 100\ \mathrm{nm}$

Contact angle
$\alpha = 45°$

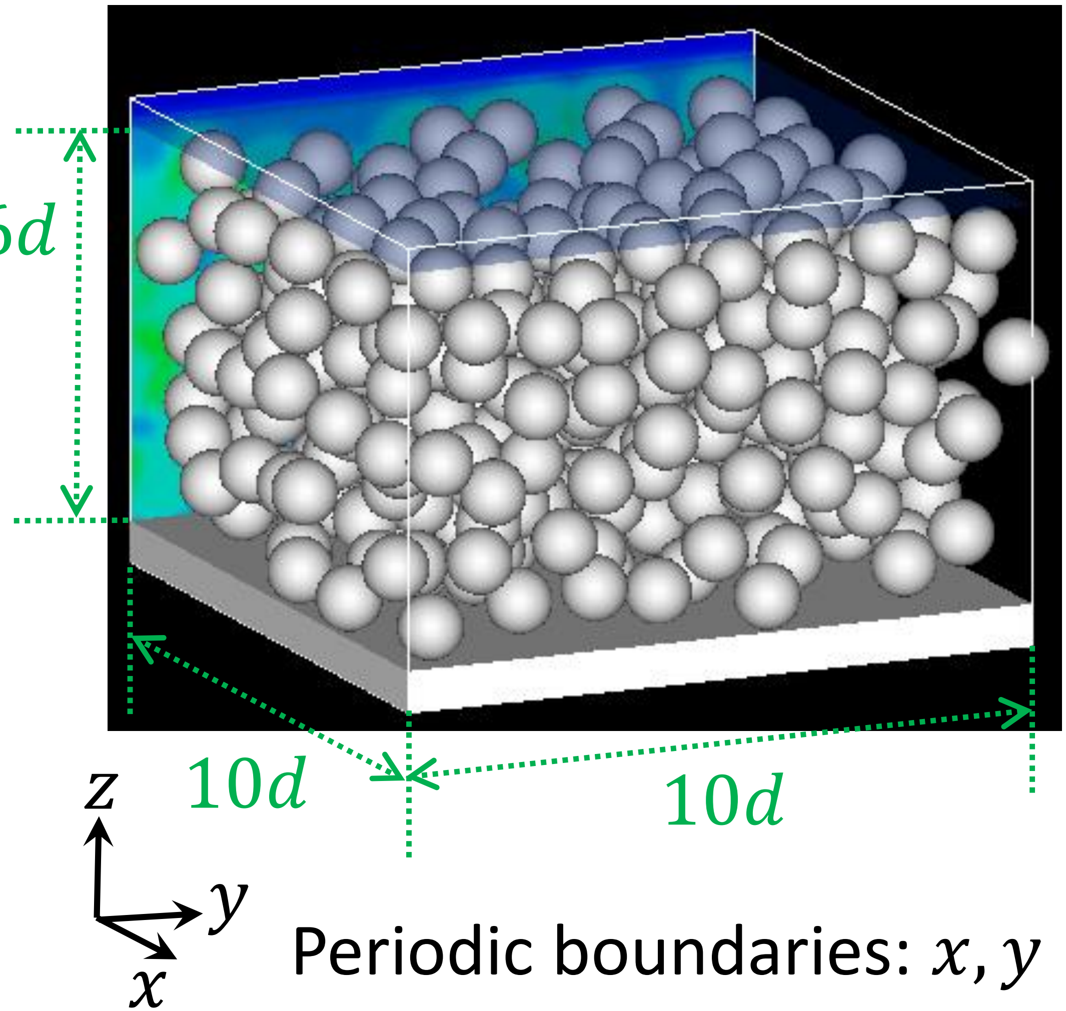
Kinematic viscosity
$\nu = 5.0 \times 10^{-6}\ \mathrm{m^2/s}$

Surface tension
$\gamma = 2.0 \times 10^{-2}\ \mathrm{N/m}$

Evaporation rate
$v_\mathrm{e} = 1.0 \times 10^{-2}\ \mathrm{m/s}$

Solute concentration
$c_0 = 5.0 \times 10^{-3}\ \mathrm{mol/L}$

Initial volume fraction
$\phi_0 = 30\ \mathrm{vol.\%}$ (3 particle layers)



Periodic boundaries: x, y

Diffusion of particle/solute

Péclet number

$$\mathrm{Pe}_\alpha = \frac{v_\mathrm{e} d}{D_\alpha}$$

Diffusion coefficient

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

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

$$\frac{\mathrm{Pe}_\mathrm{prt}}{\mathrm{Pe}_\mathrm{slt}} = \frac{D_\mathrm{slt}}{D_\mathrm{prt}} \gg 1$$

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

(Non-Brownian particle)

Simulation conditions

	Adsorption	w/d	ε/RT	$\mathbf{Pe}_{\mathbf{slt}}$	$D_{\mathrm{slt}}/[\mathrm{m}^2/\mathrm{s}]$
(a)	**No**	0	0	$\mathbf{0.02}$	5.0×10^{-8}
(b)	**Yes**	0.25	0.5	$\mathbf{0.02}$	5.0×10^{-8}
(c)	**Yes**	0.25	0.5	$\mathbf{0.4}$	2.5×10^{-9}

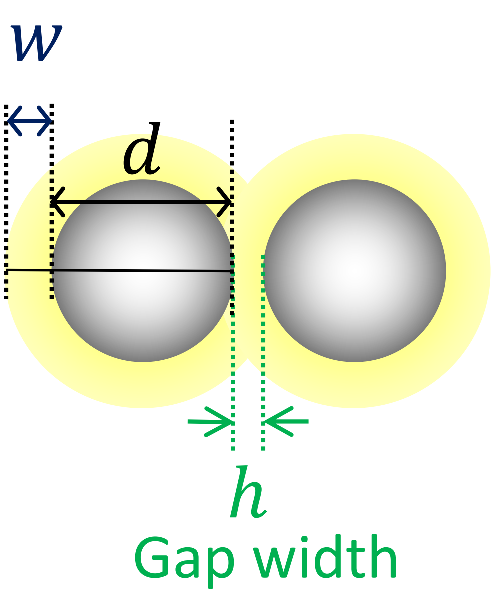
Effects of
- (1) Solute adsorption (a) ↔ (b)
- (2) Solute Péclet number (b) ↔ (c)

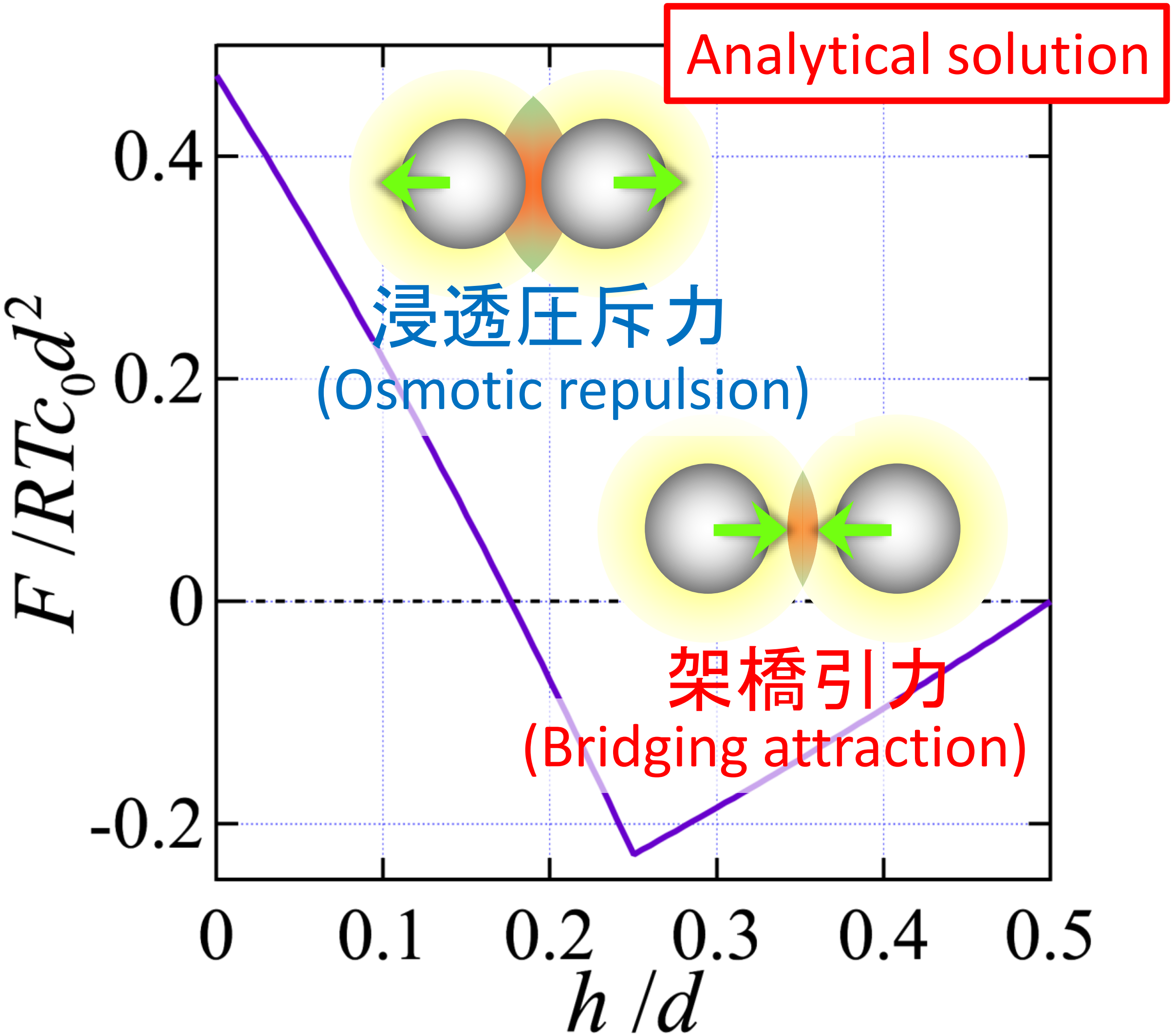
Interpaticle force

(Equilibrium solute distribution)

(1) Solute adsorption → Interparticle force

$$\varepsilon/RT = 0.5$$
$$w/d = 0.25$$

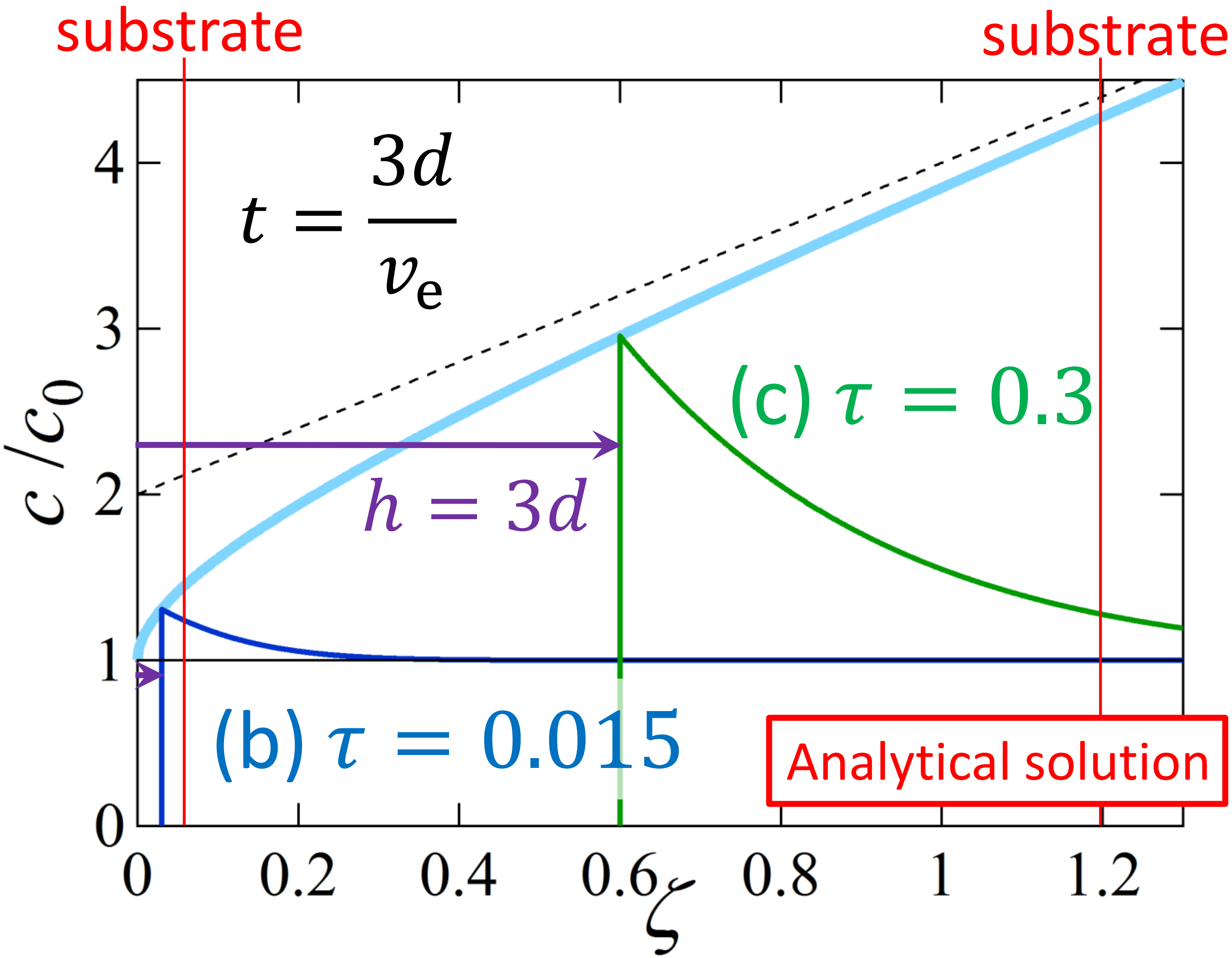


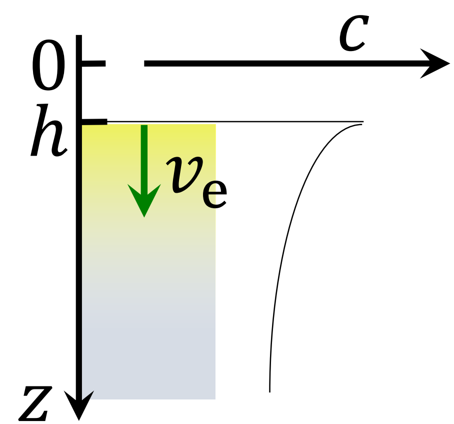


Solute distribution during drying

(without particles)

(2) High solute Péclet number → Concentration gradient





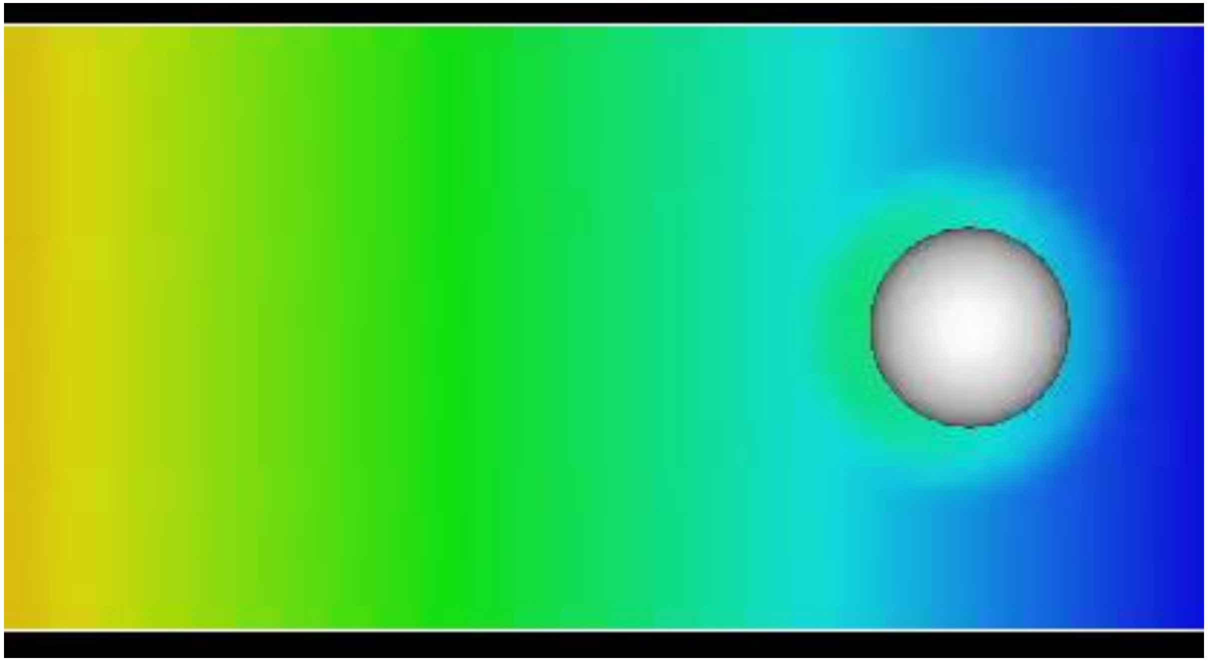
$$h(t) = v_e t$$

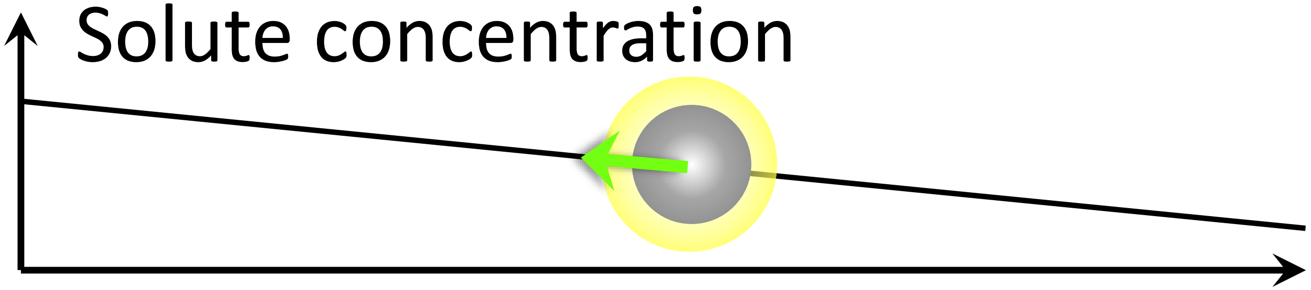
$$\tau = \frac{v_e^2}{4D} t$$

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

Diffusiophoresis（拡散泳動）

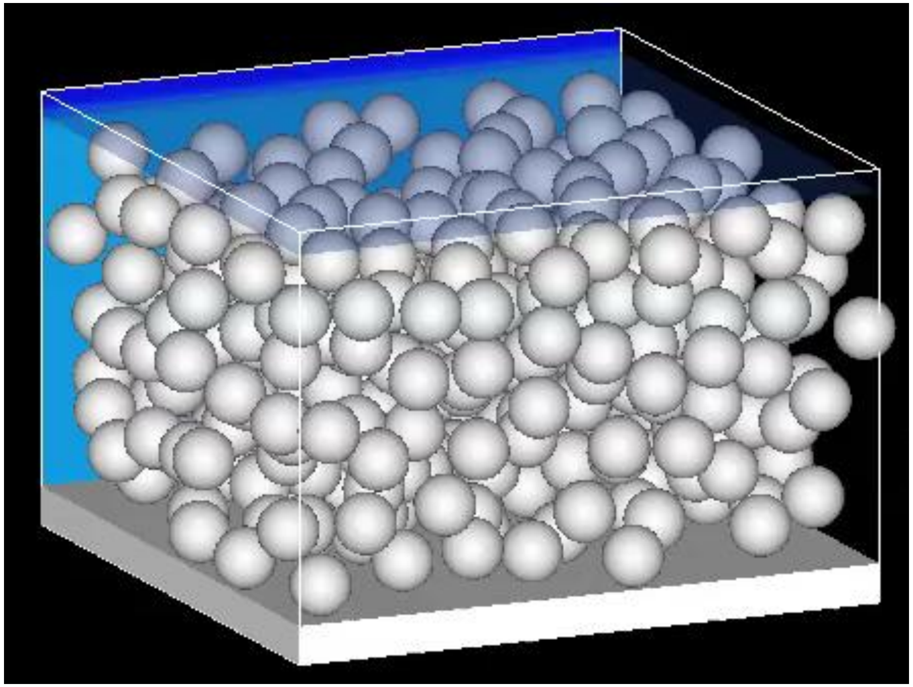
(2) High solute Péclet number →
Concentration gradient → Diffusiophoresis

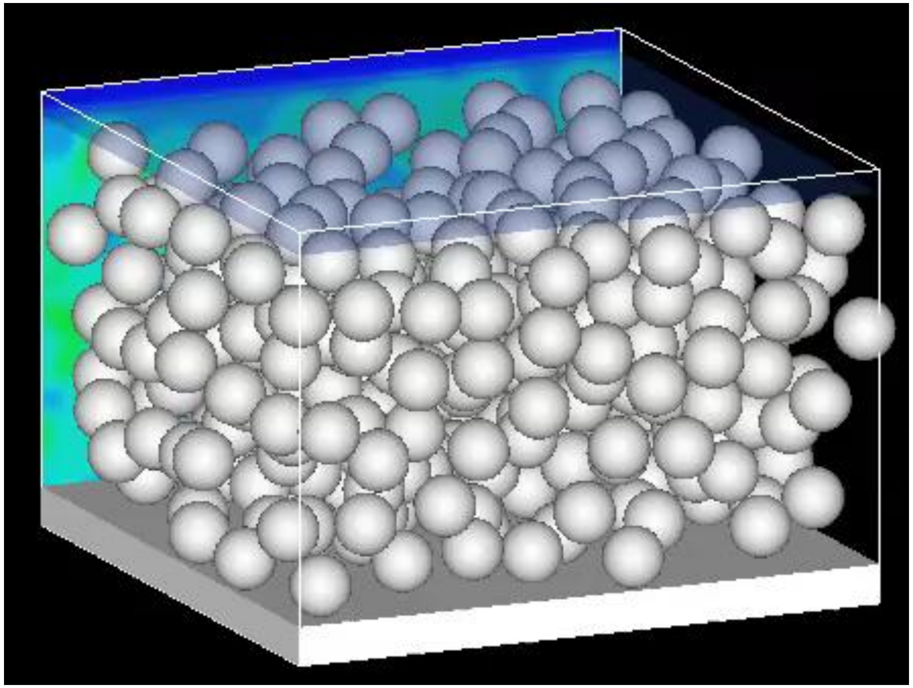




Solute adsorption

(1) Solute adsorption → Interparticle force





(a) $\varepsilon/RT = 0$

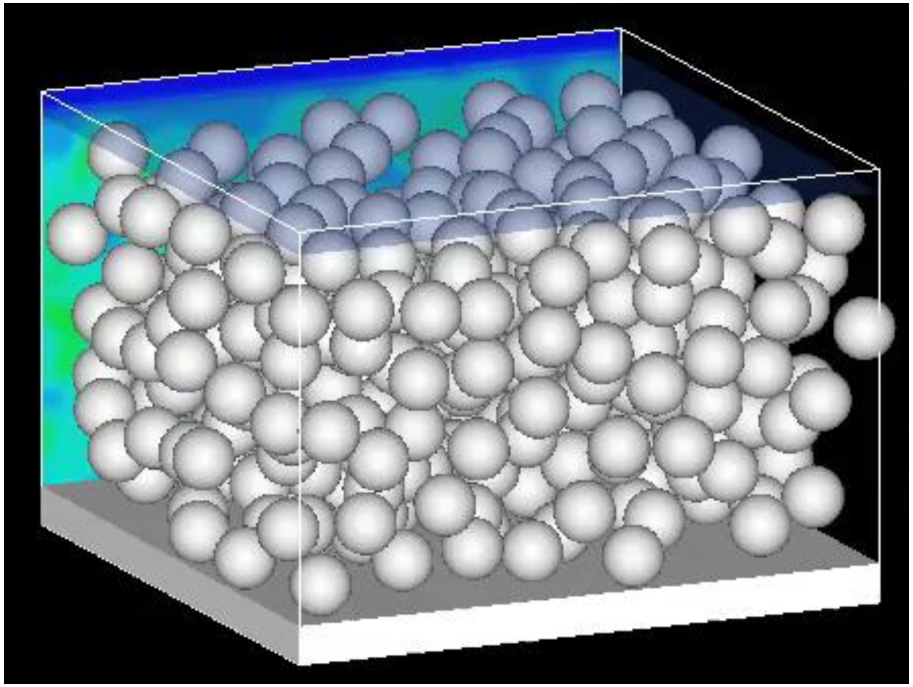
Non-adsorptive

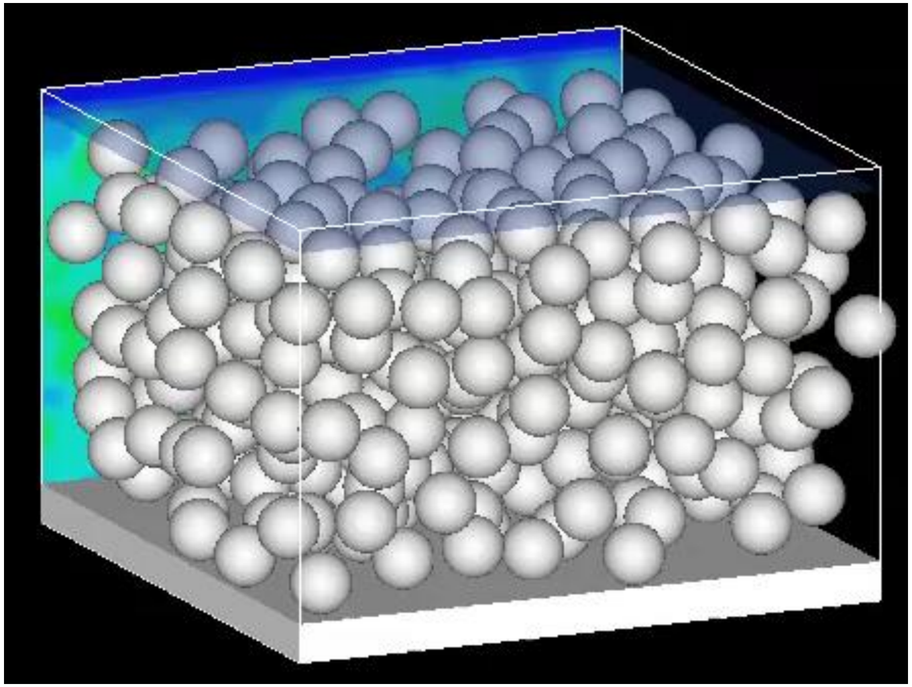
(b) $\varepsilon/RT = 0.5$

Adsorptive

Solute Péclet number

(2) Concentration gradient → Diffusiophoresis





(b) $\mathrm{Pe}_{\mathrm{slt}} = 0.02$

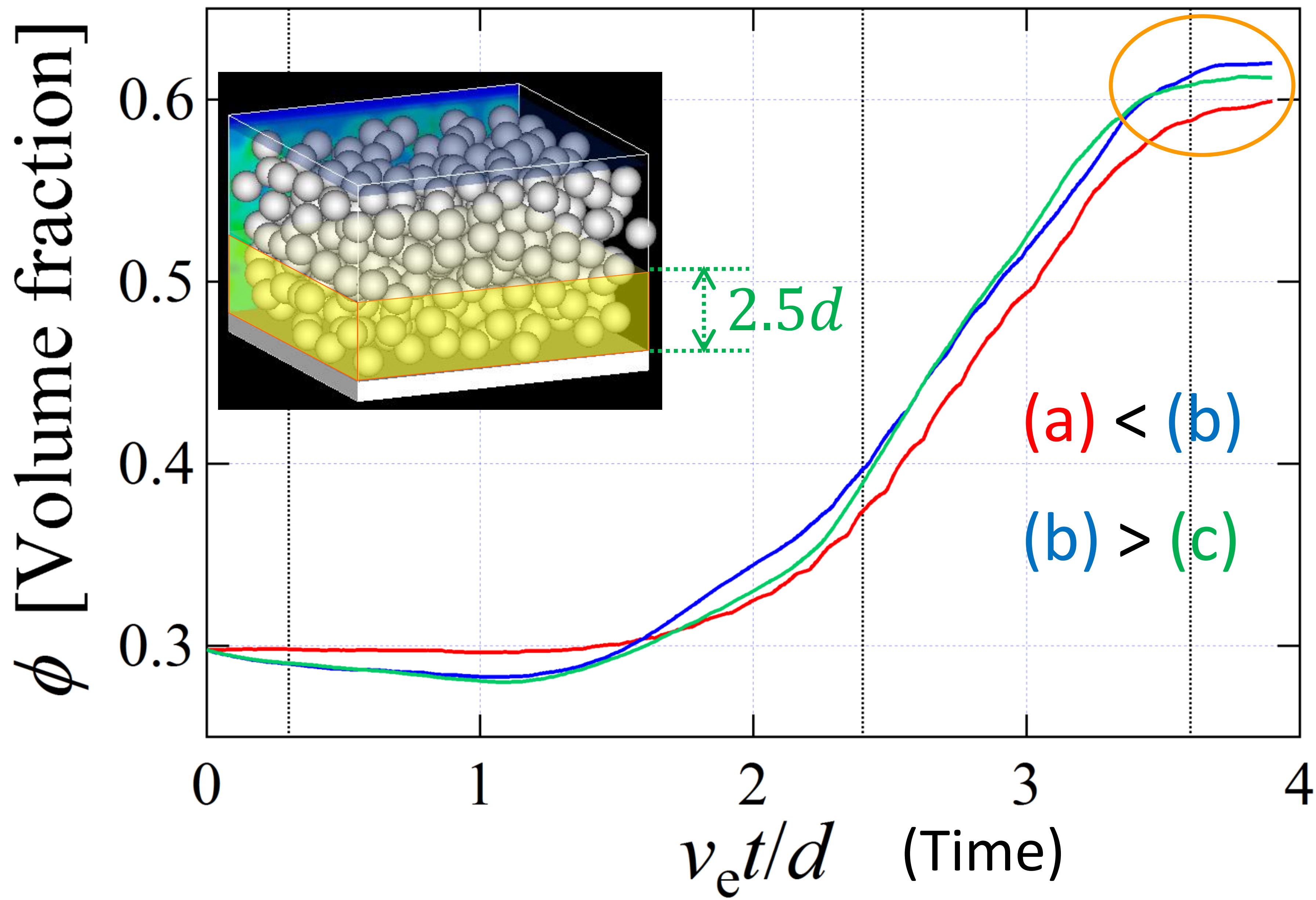
(c) $\mathrm{Pe}_{\mathrm{slt}} = 0.4$

Concentration gradient below free surface:

Shallow

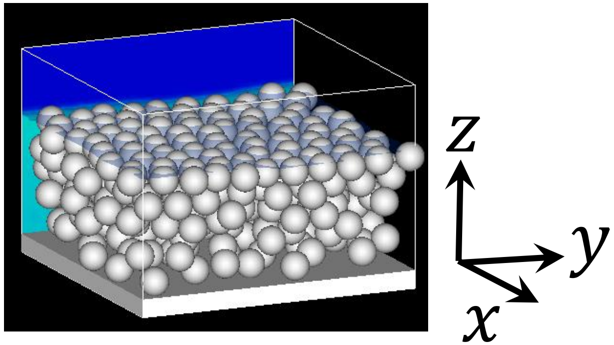
Steep

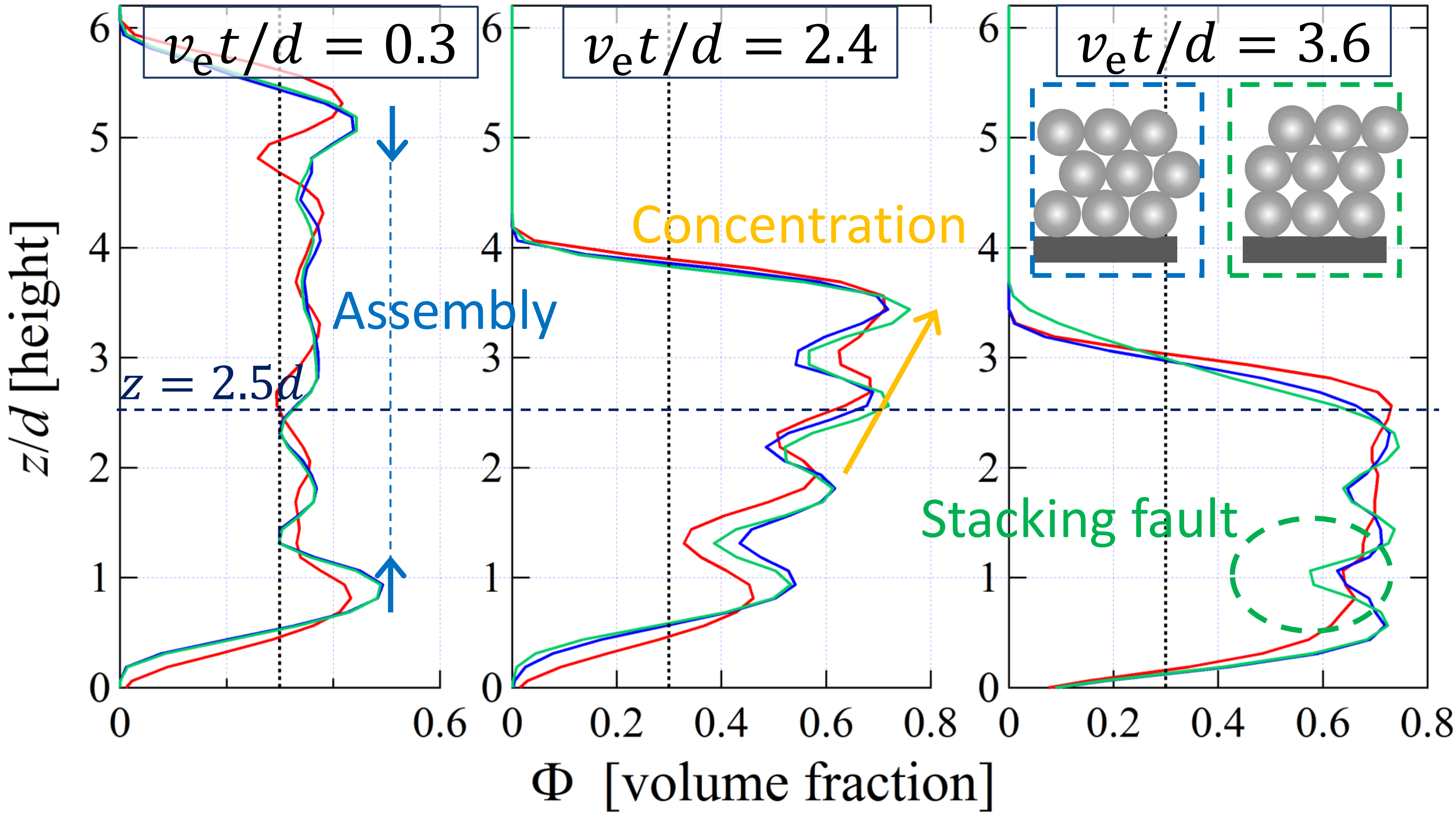
Volume fraction (Packing efficiency)



Particle distribution

Structural order
(a) < (b)
(b) > (c)

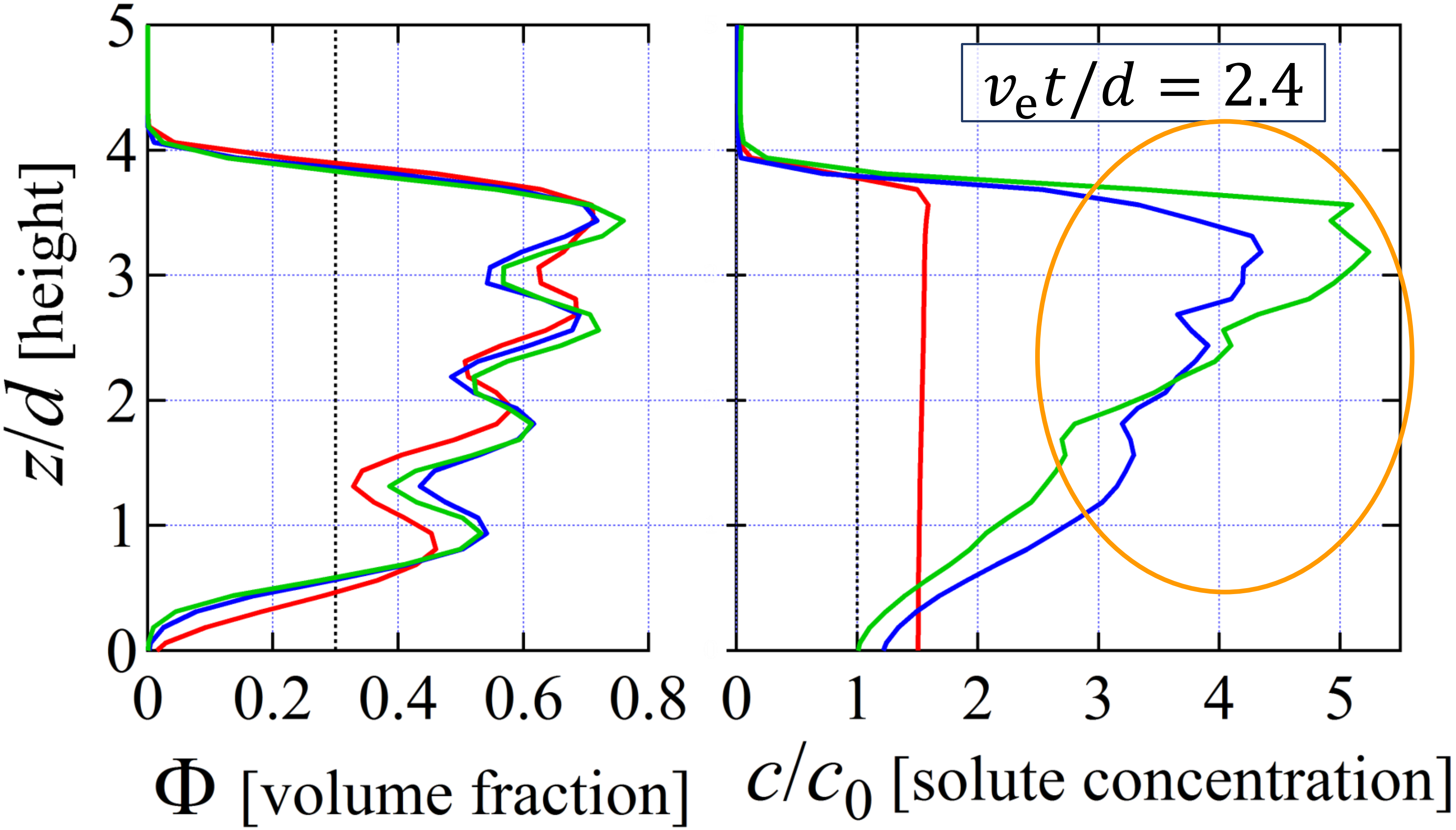




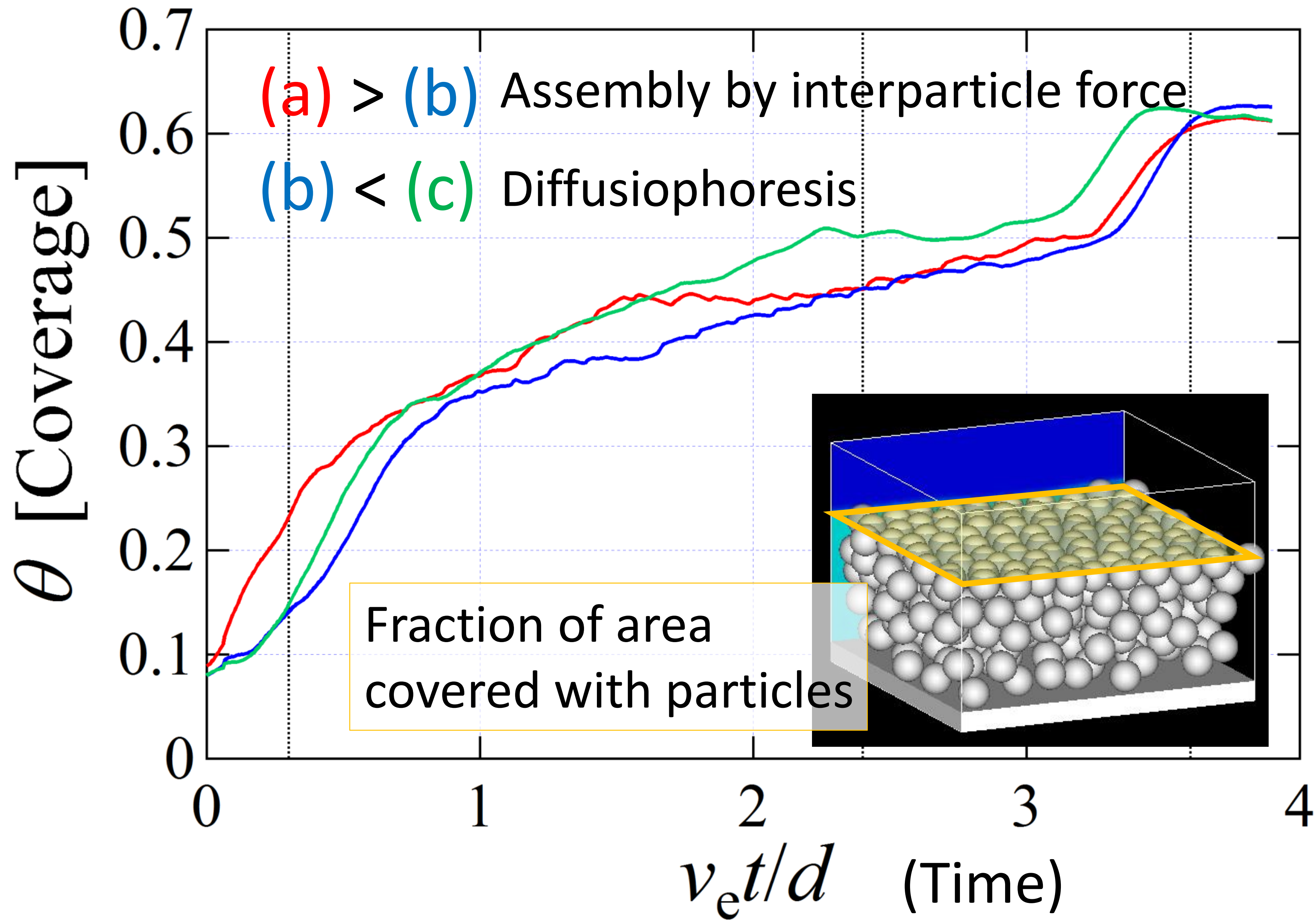
Solute distribution

(a) < (b) Attraction by particles

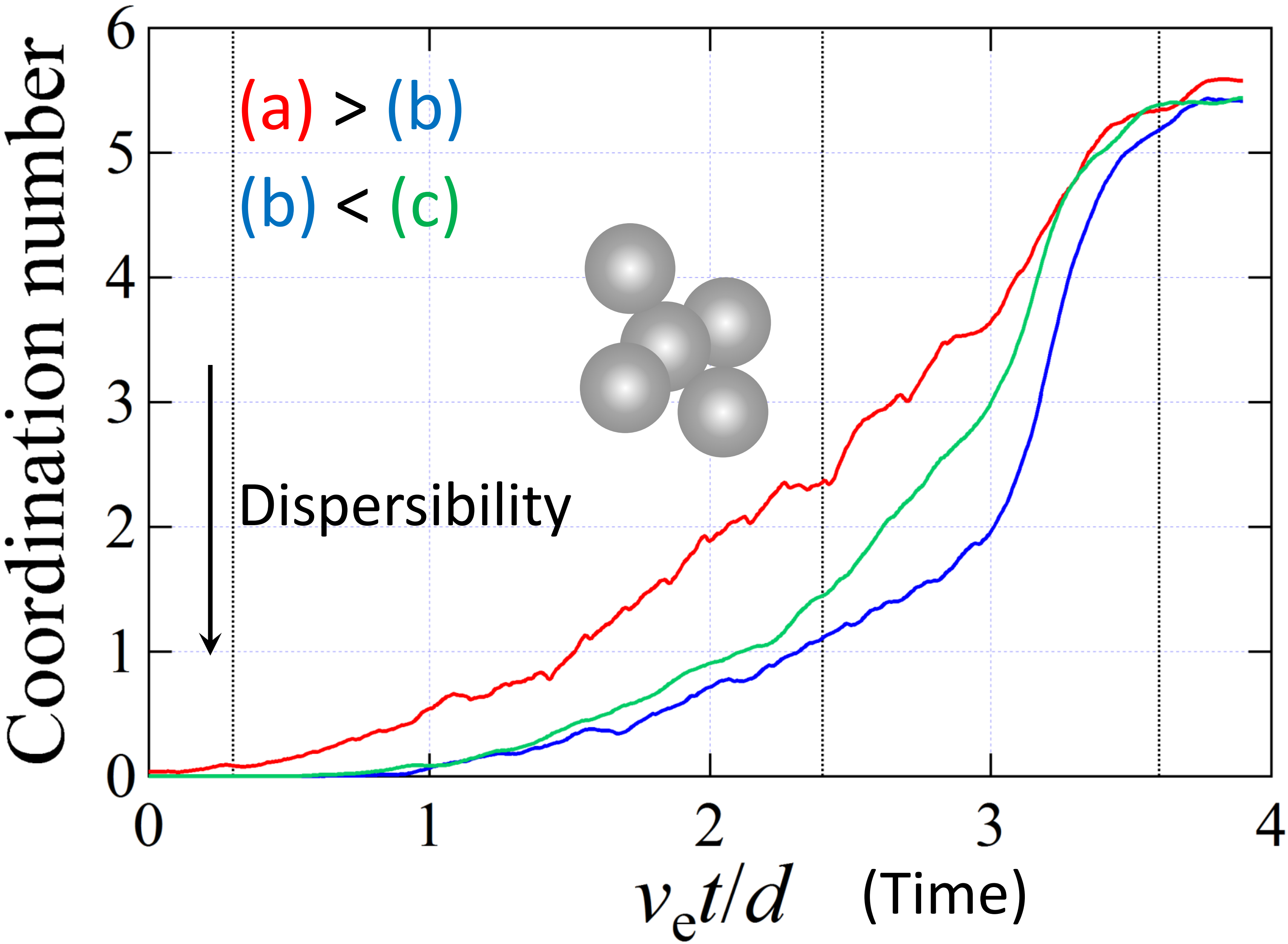
(b) < (c) Low diffusivity of solute



Particle migration to free surface



Coordination number



Summary

Solute adsorption effects on structure formation of colloidal particles during drying

- Solute adsorption → Interparticle force

  Particle ordering

- High solute Péclet number →

  Concentration gradient → Diffusiophoresis

  Increase in particle migration to free surface

  → Decrease in packing efficiency