化学工学会第48回秋季大会
2016/09/06

二峰性微粒子分散液の乾燥下構造形成の直接数値計算

Direct numerical simulation of structure formation in drying bimodal colloidal suspensions

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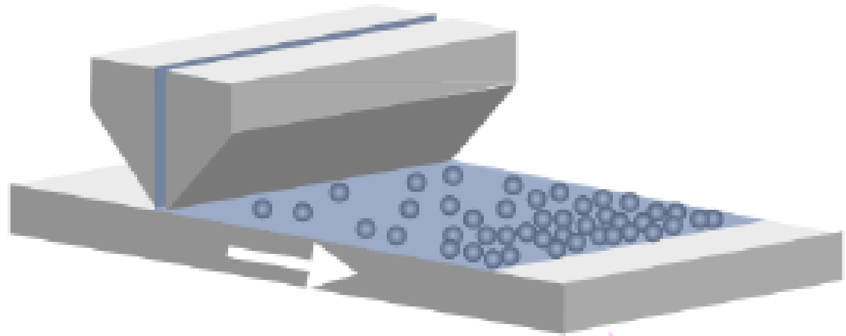
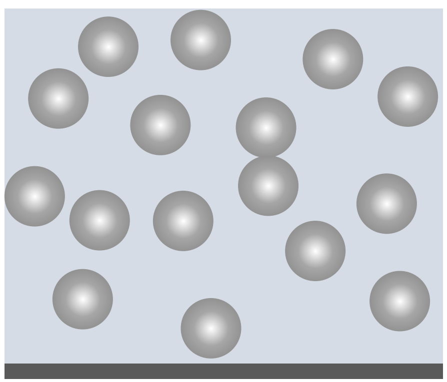
Particle film formation

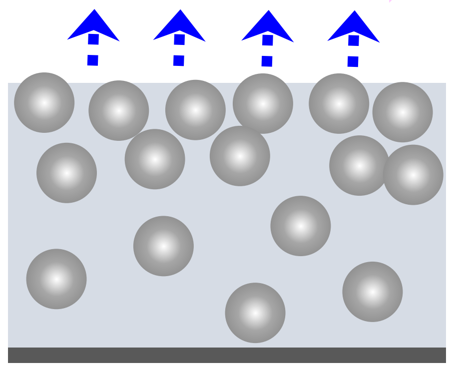


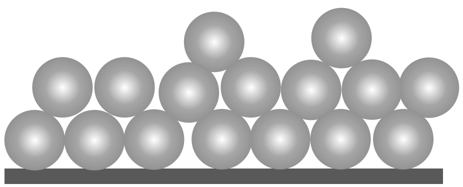
Colloidal suspensions

Coating, **Drying**

Functional thin films







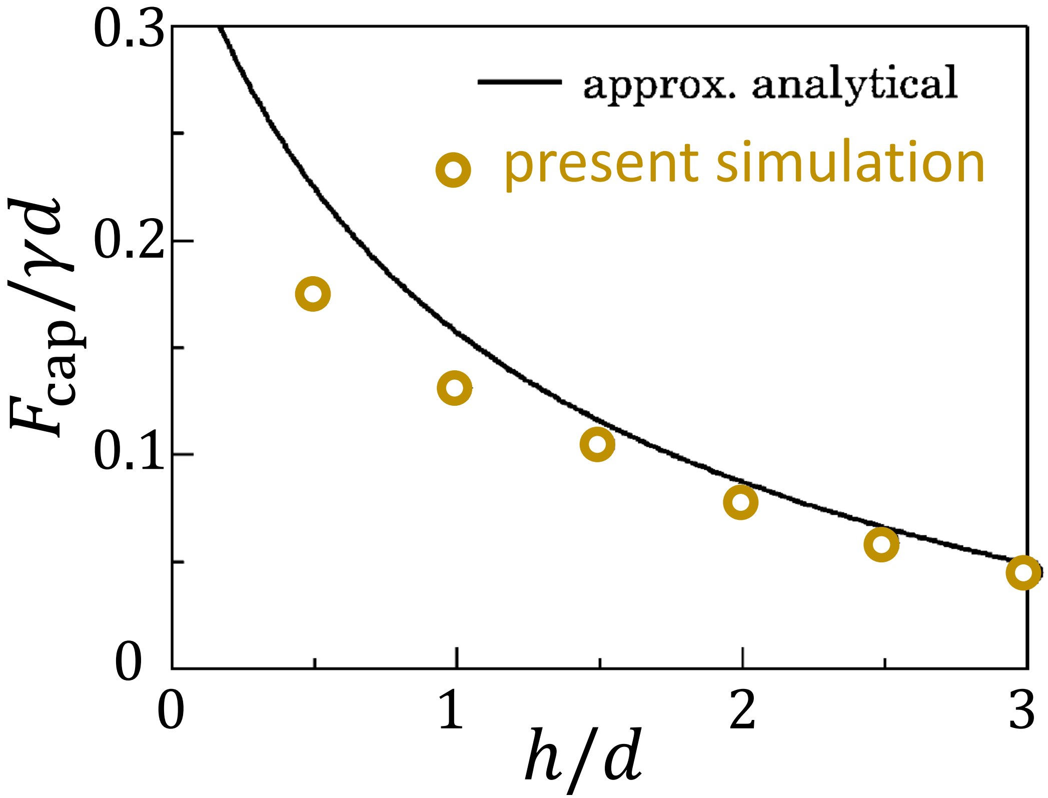
Particle configuration

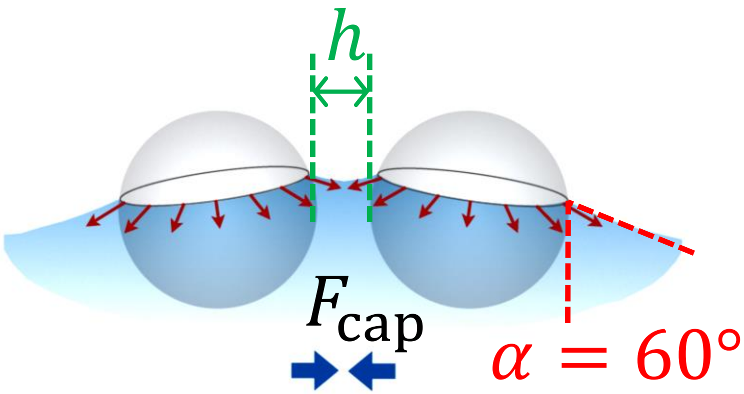
Physical properties of film

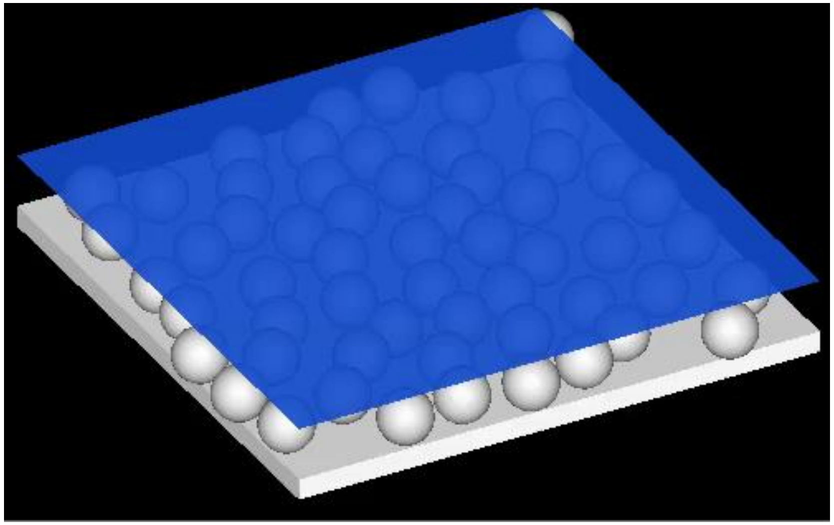
Mesoscale Modeling & **D**irect **N**umerical **S**imulation

Capillary force

Force induced by meniscus



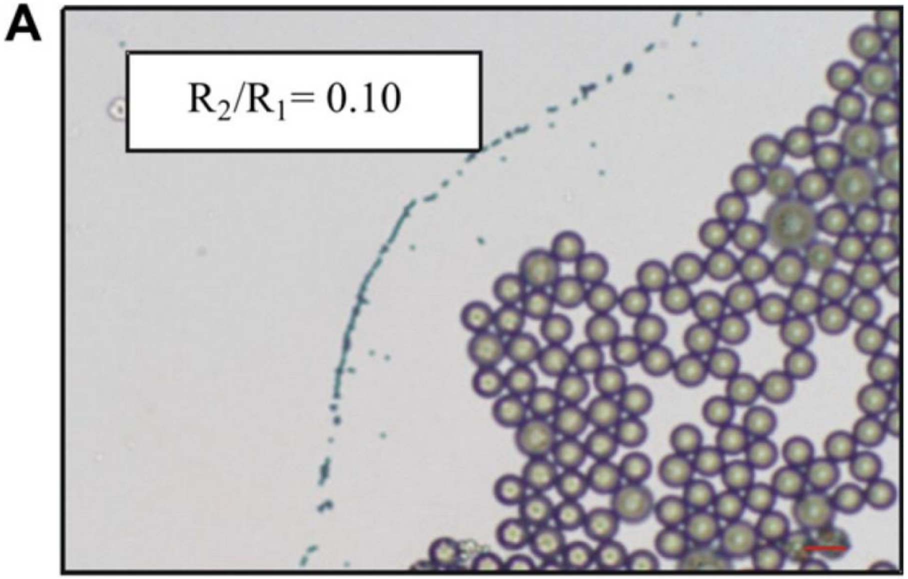


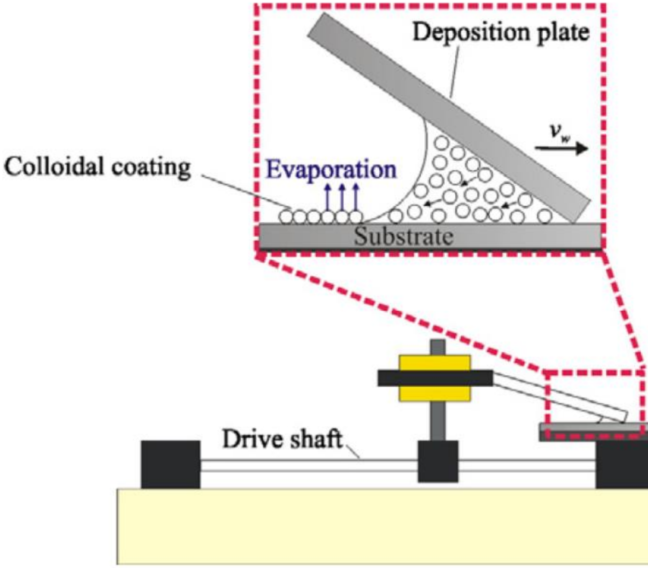


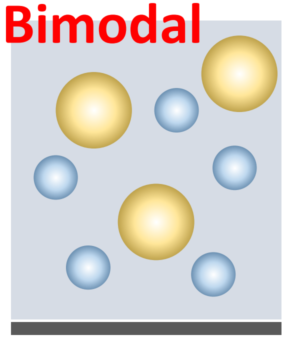
Fujita et al., Appl. Phys. Express (2013).

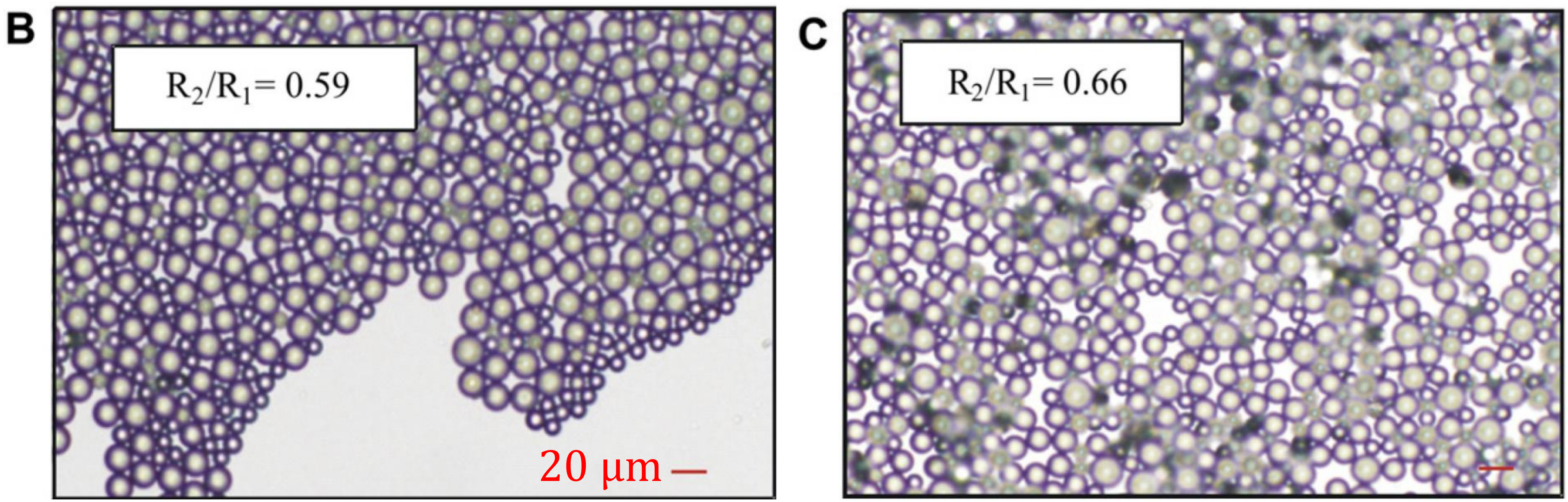
Fujita et al., J. Comput. Phys (2015).

Drying bimodal suspensions





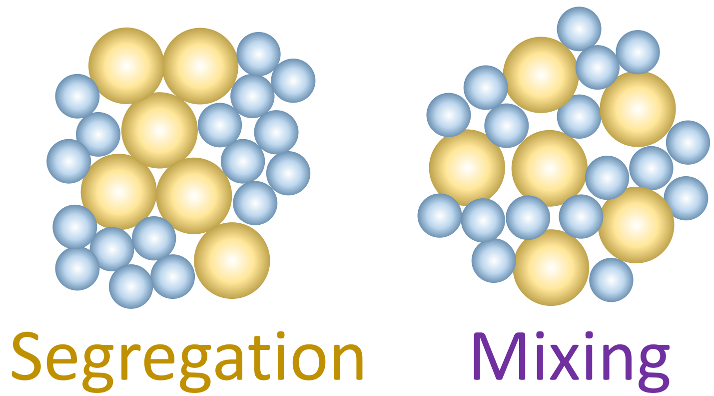


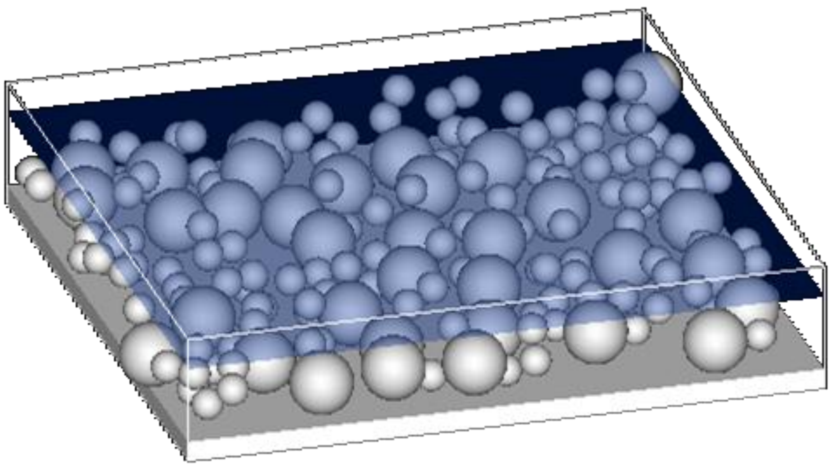


Jenkins et al., J. Colloid Interface Sci. (2012)

Objective

- Structure formation in drying bimodal colloidal suspensions
- Effects of particle wettability and interactions





- Mesoscale model
- **D**irect **N**umerical **S**imulation (DNS)

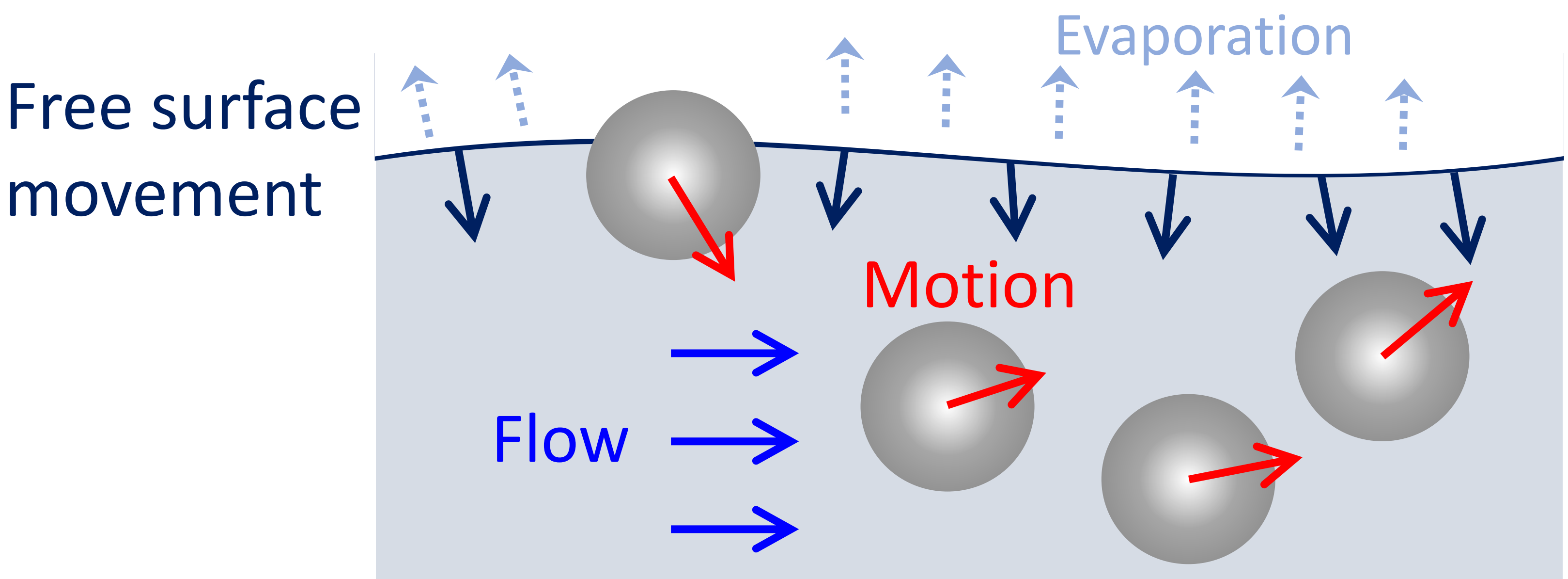
Model

Particles: Newton-Euler equations of motion

Fluid: Hydrodynamic equations

Free surface: Advection equation

Coupled



SNAP研究会 to get detailed information

Fluid motion

Mass conservation

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

Momentum conservation

Body force to constrain particle velocity

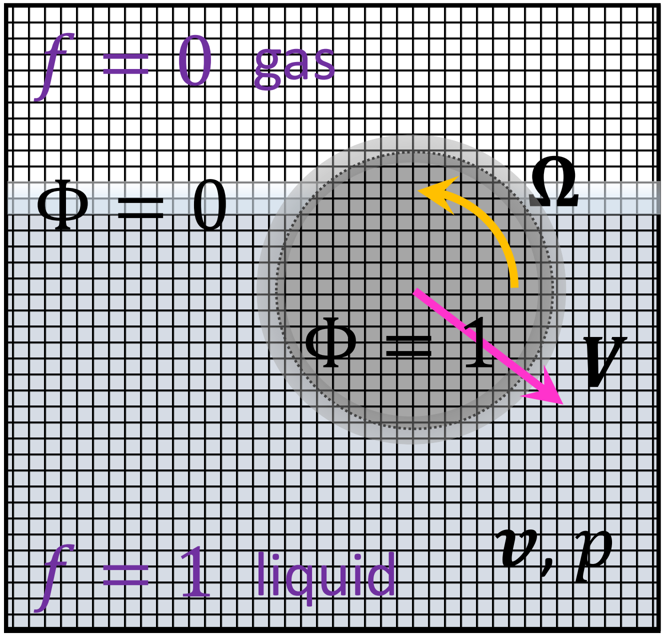
Random stress

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

Surface tension

Stress tensor

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



Direct Numerical Simulation

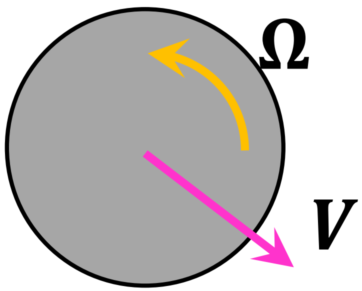
- Discretization
- Diffused boundary

Particle motion

Translation

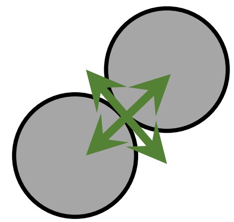
$$M_i \dot{\boldsymbol{V}}_i = \boldsymbol{F}_i^{\mathrm{contact}} + \boldsymbol{F}_i^{\mathrm{DLVO}} + \boldsymbol{F}_i^{\mathrm{H}} + \boldsymbol{F}_i^{\mathrm{buoyancy}}$$

$$\dot{\boldsymbol{R}}_i = \boldsymbol{V}_i$$



Rotation

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



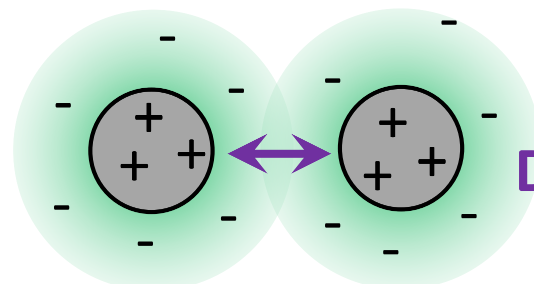
Contact force/torque

Hydrodynamic force/torque

(Momentum exchange with fluid)

$$\boldsymbol{F}_i^{\mathrm{H}} = -\int \rho \Phi_i \boldsymbol{a} \, \mathrm{d}\boldsymbol{r}$$

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



DLVO force

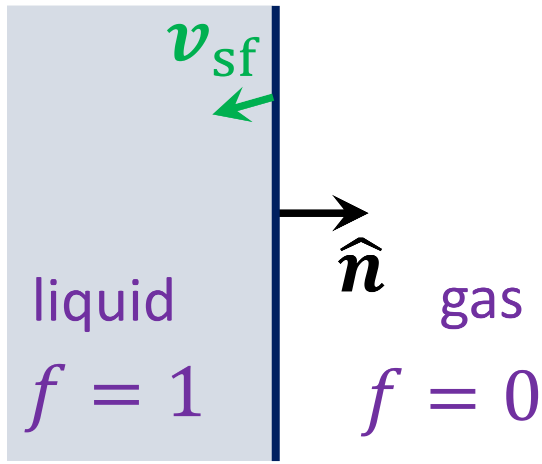
Electrical double layer repulsion

Van der Waals attraction

Free surface

Advection eq.

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



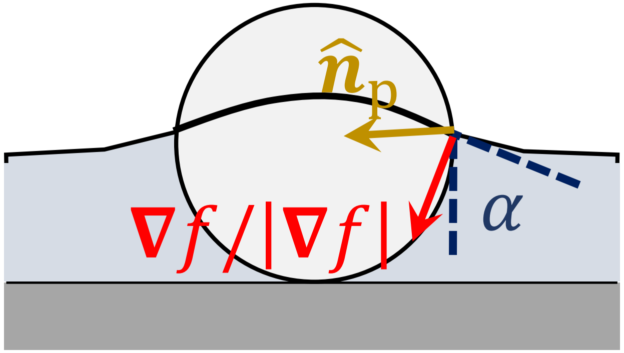
Evaporation mass flux on free surface

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

Velocity of free surface

$$\boldsymbol{v}_{\mathrm{sf}} = \boldsymbol{v} - (1 - \Phi) v_{\mathrm{e}} \hat{\boldsymbol{n}}$$

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



DNS: Level set method

Fujita et al., J. Comput. Phys. (2015).

Simulation conditions

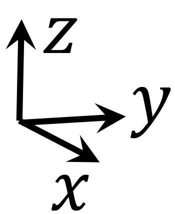
Particle diameter Large: $200\ \mathrm{nm}\ (d)$ Small: $100\ \mathrm{nm}\ (d/2)$

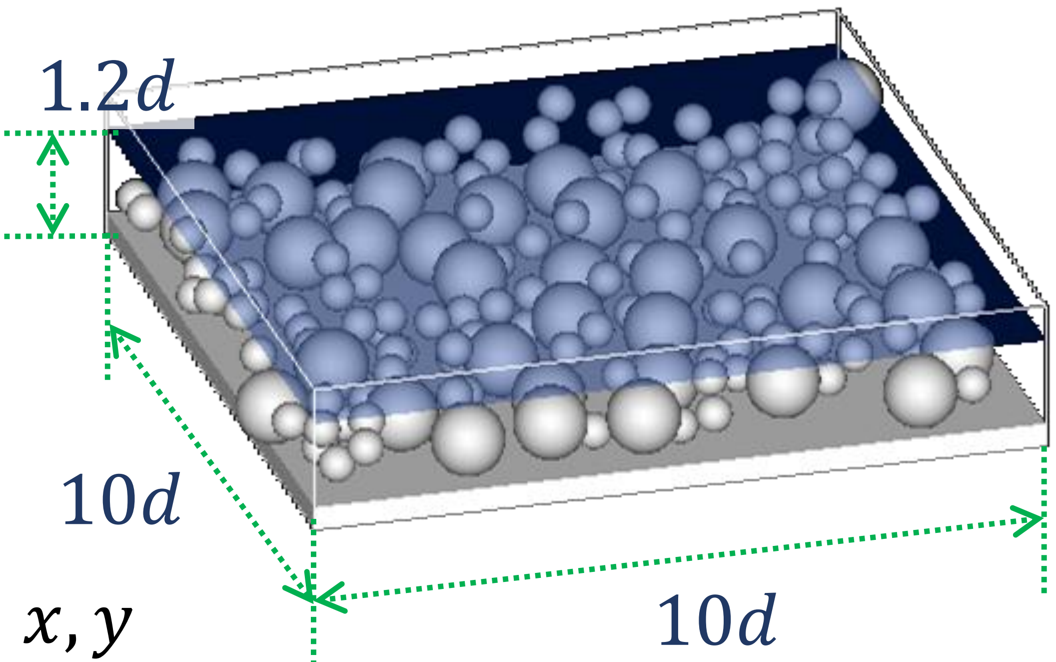
Final substrate coverage with particles L: 0.3 S: 0.3

Fluid: Water

Evaporation rate $2.0 \times 10^{-2}\ \mathrm{m/s}\ \ (v_\mathrm{e})$

Salt $1.0 \times 10^{-4}\ \mathrm{mol/L}$ Temperature $293\ \mathrm{K}$





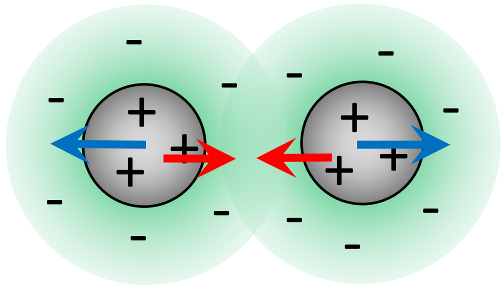
Periodic boundaries: x, y

Order estimation of force

DLVO force

Electrical double layer repulsion

$$F_{\mathrm{EDL}} \sim \frac{n_{\mathrm{salt}} k_{\mathrm{B}} T d}{\kappa} \sim 10^{-12}\ \mathrm{N}$$

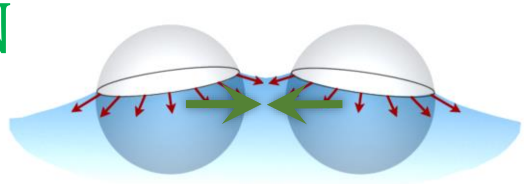


Van der Waals attraction

$$F_{\mathrm{vdW}} \sim \frac{A}{d} \sim 10^{-13}\ \mathrm{N}$$

Capillary force

$$F_{\mathrm{cap}} \sim \gamma d \sim 10^{-8}\ \mathrm{N}$$

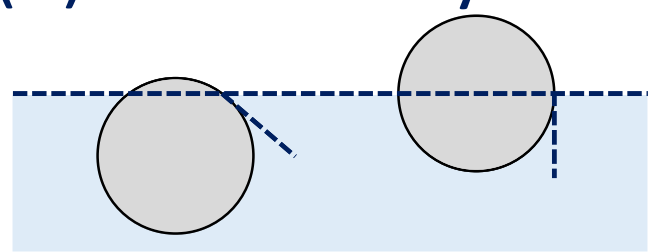


$$F_{\mathrm{cap}} \gg F_{\mathrm{EDL}} \sim F_{\mathrm{vdW}}$$

Simulation conditions

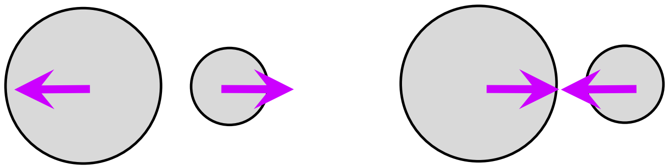
	Contact angle		Zeta potential $/\mathrm{mV}$	
	Large	Small	Large	Small
(a)	$30°$	$30°$	-50	-50
(b)	$90°$	$30°$	-50	-50
(c)	$30°$	$30°$	50	-50

(1) Wettability



(a) ⟷ (b)

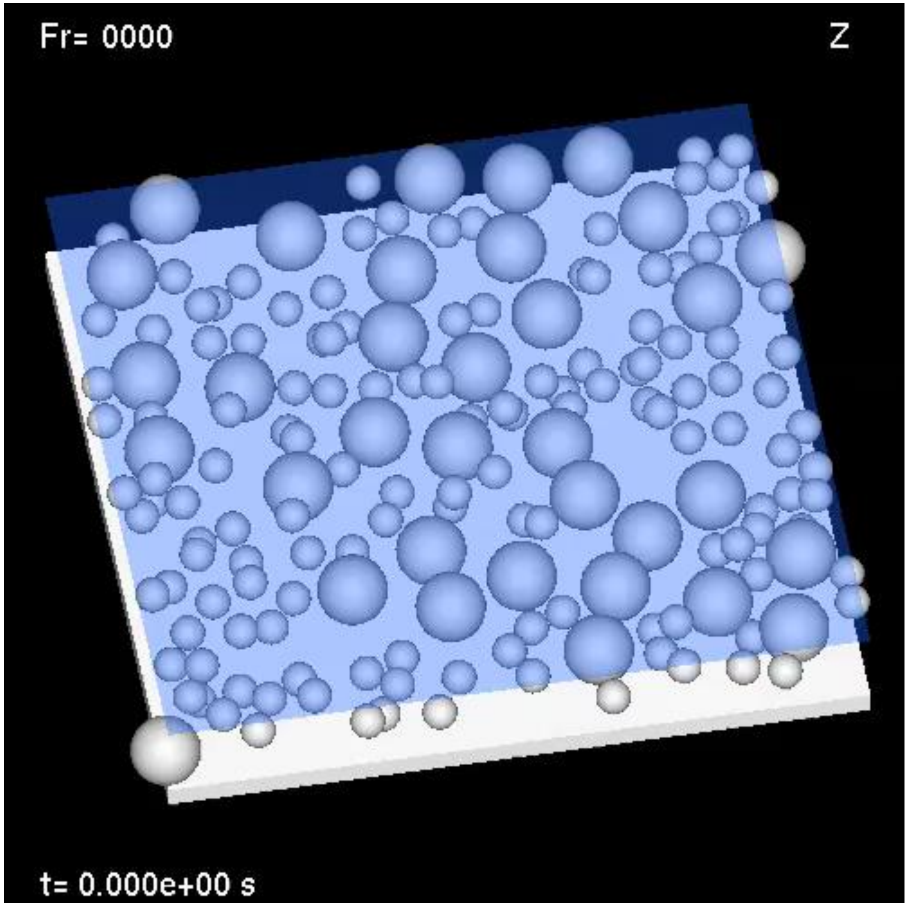
(2) Interaction: DLVO force



(a) ⟷ (c)

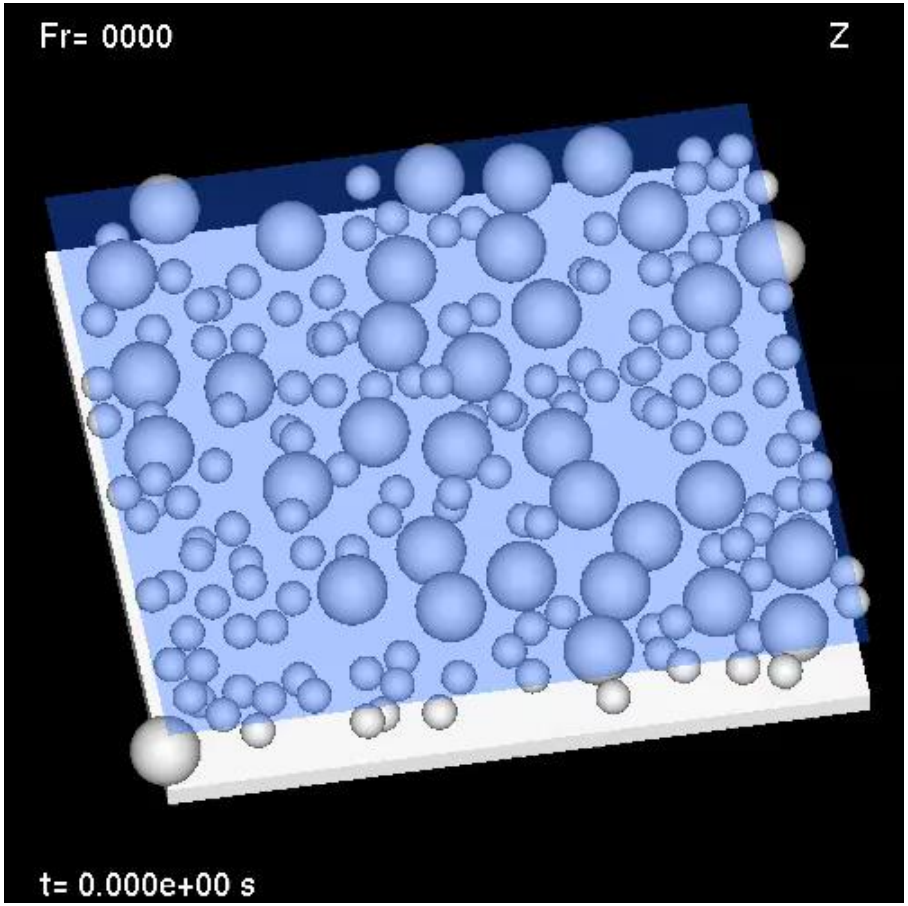
Result of (a)

Meniscus formation → Capillary force → Aggregation

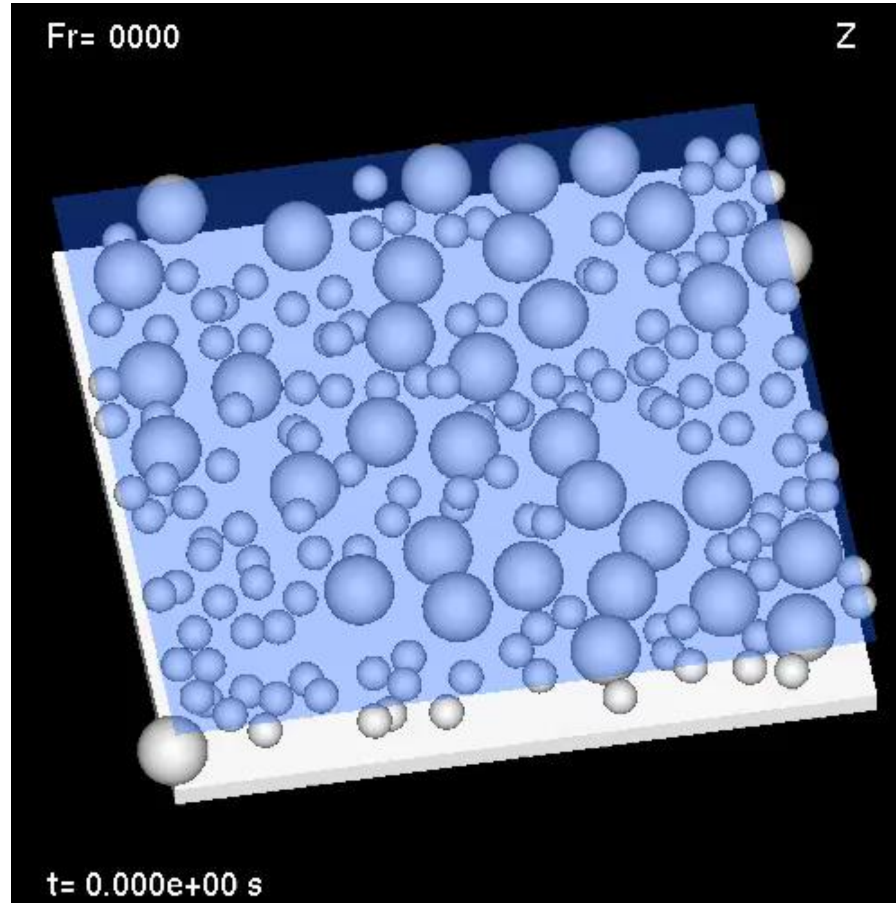


Segregation

(1) Wettability (Contact angle)

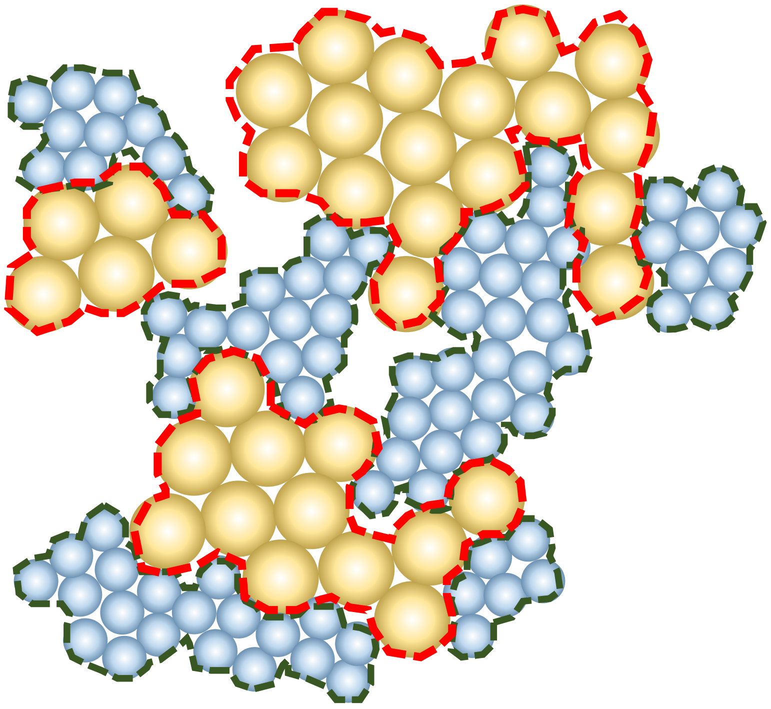


(a) L: 30° S: 30°



(b) L: 90° S: 30°

Nondimensional Boundary Length



$$\mathrm{NBL} = 1 - \frac{N_{\mathrm{average}}}{N_{\mathrm{max}}}$$

N: Coordination number

$N_{\mathrm{max}} = 6$
(Close packing in 2D)

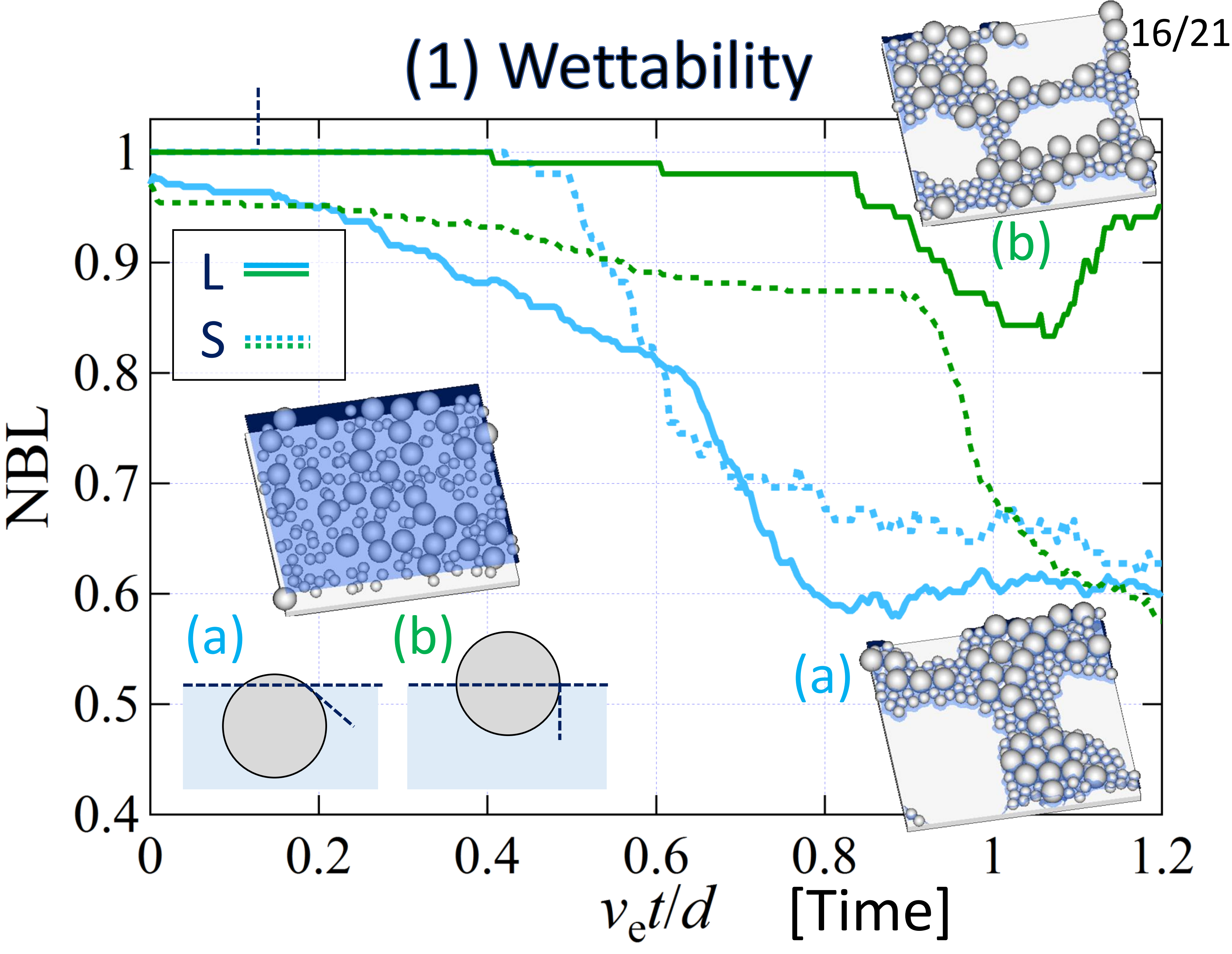
$$0 \leq \mathrm{NBL} \leq 1$$

Close-packed Dispersed

NBL for L-L / S-S coordination → Packing domain size

Segregation Mixing

(1) Wettability



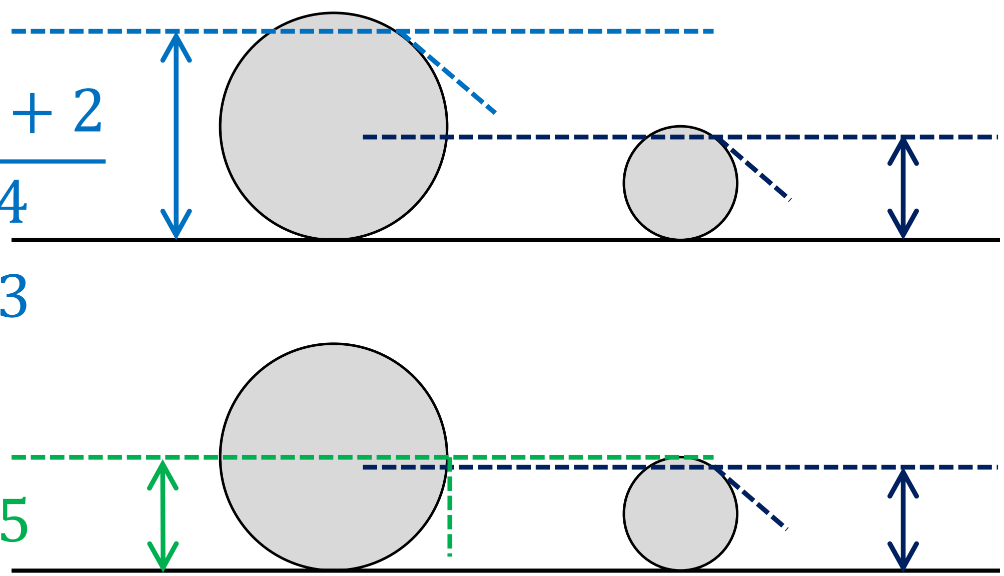
(1) Wettability

Meniscus formation $\rightarrow$ Capillary force $\rightarrow$ Aggregation

Meniscus is formed around a large (small) particle when liquid layer thickness is smaller than h_{L} (h_{S}).

(a)

$$\frac{h_{\mathrm{L}}}{d} = \frac{\sqrt{3}+2}{4} \approx 0.93 \qquad \frac{h_{\mathrm{S}}}{d} = \frac{\sqrt{3}+2}{8} \approx 0.47$$

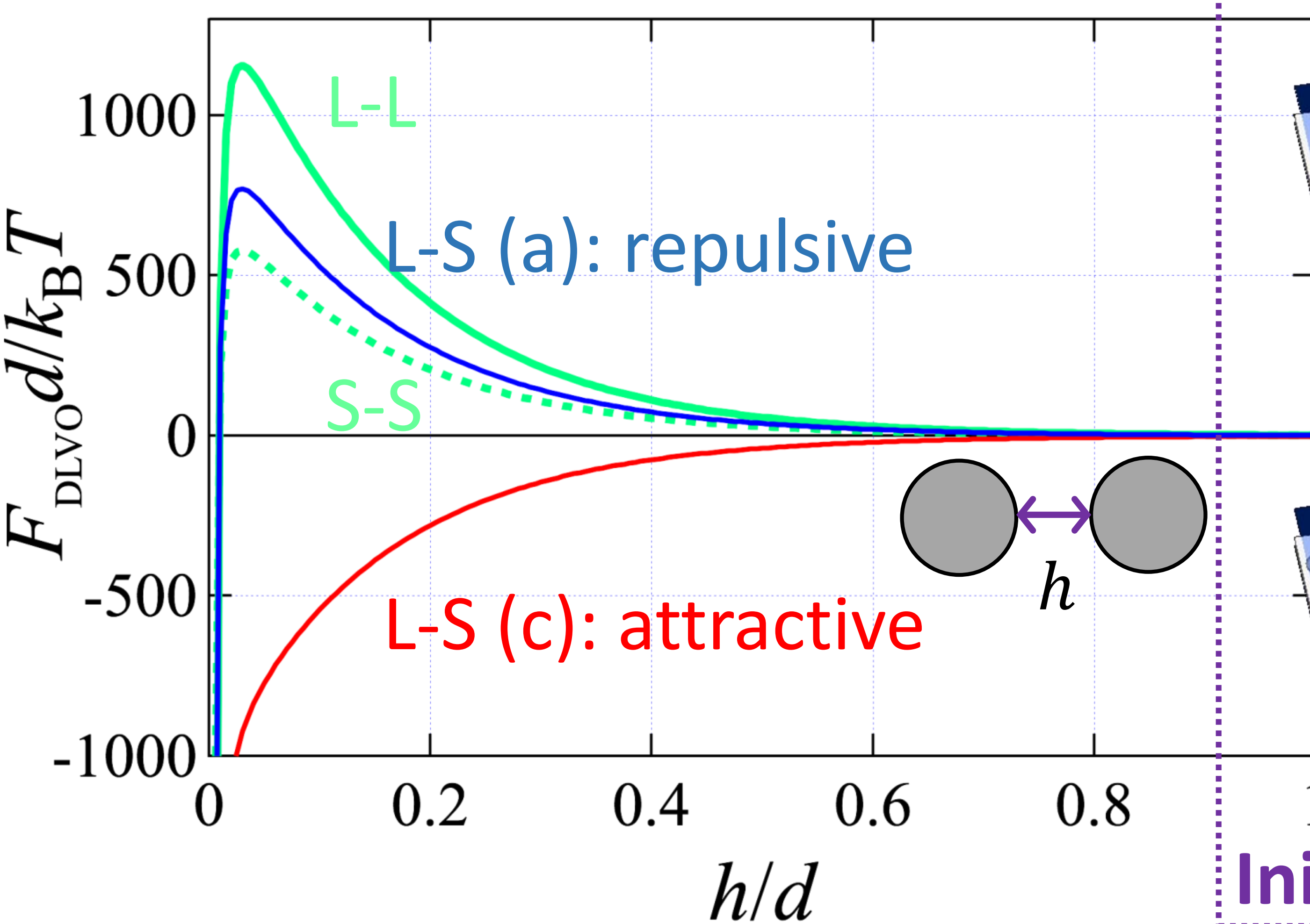


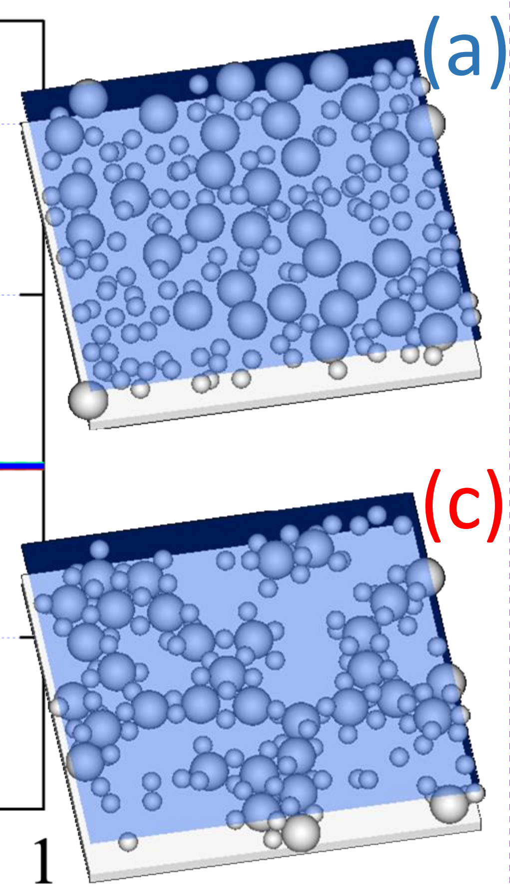
(b)

$$\frac{h_{\mathrm{L}}}{d} = 0.5 \qquad \frac{h_{\mathrm{S}}}{d} \approx 0.47$$

(2) Interaction (DLVO force)

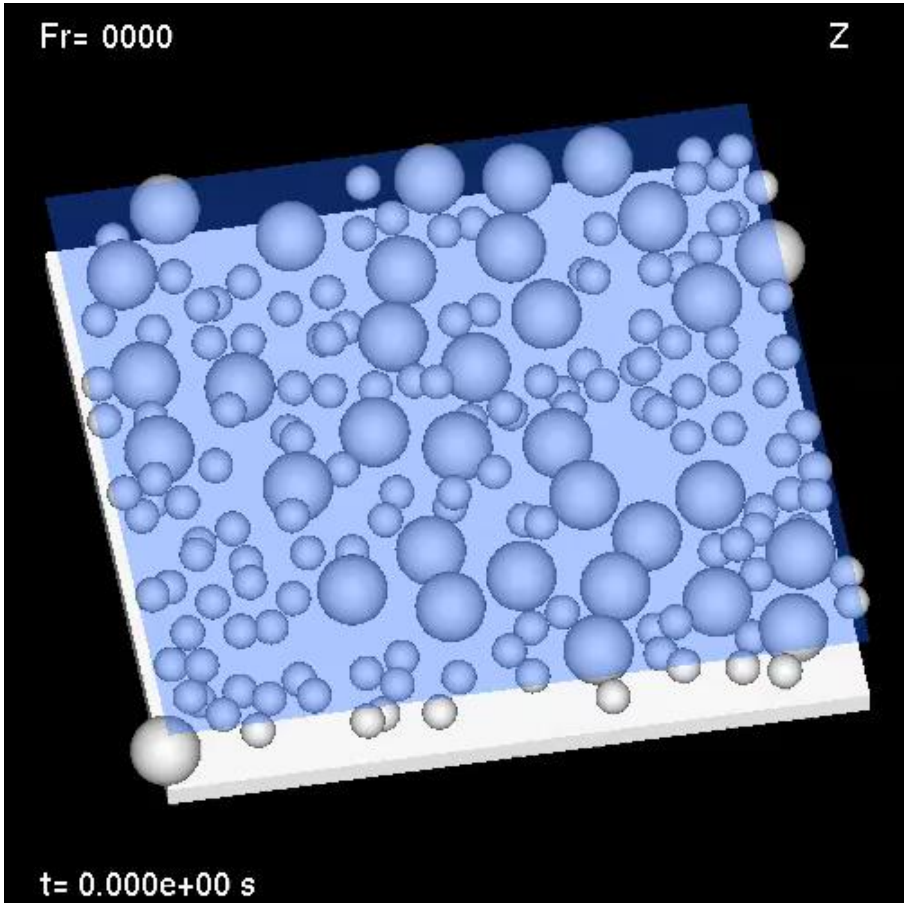
Zeta potential (a) L: -50 mV, S: -50 mV
(c) L: 50 mV, S: -50 mV

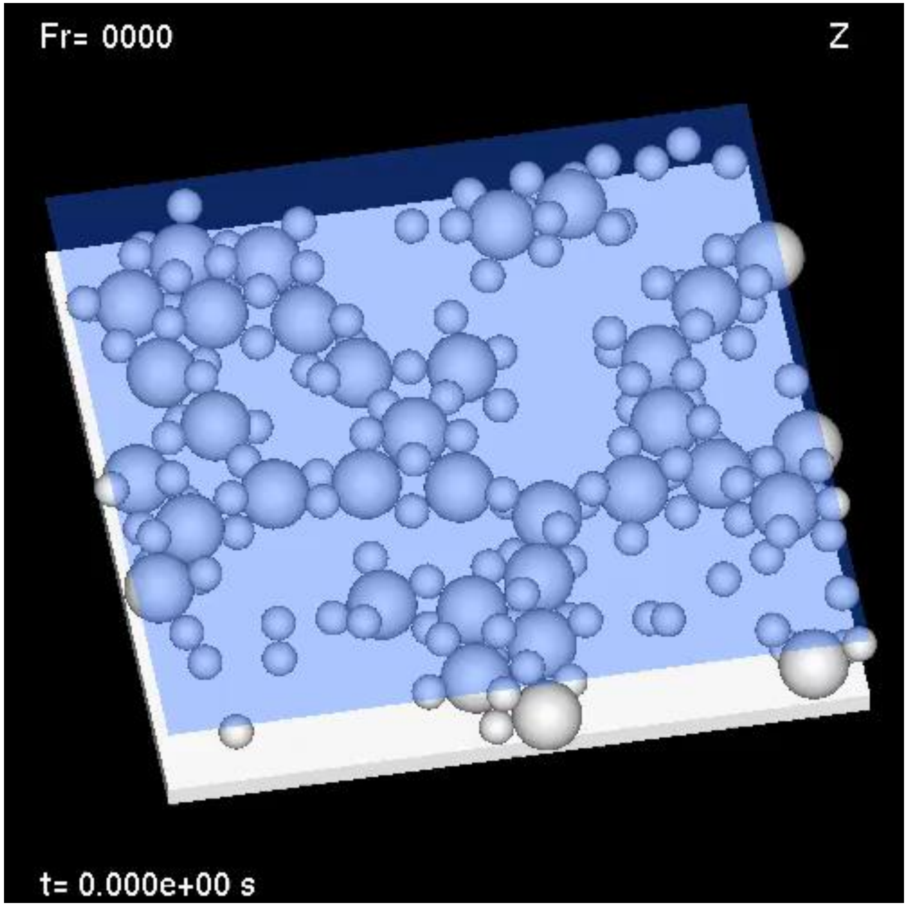




Initial structure

(2) Interaction

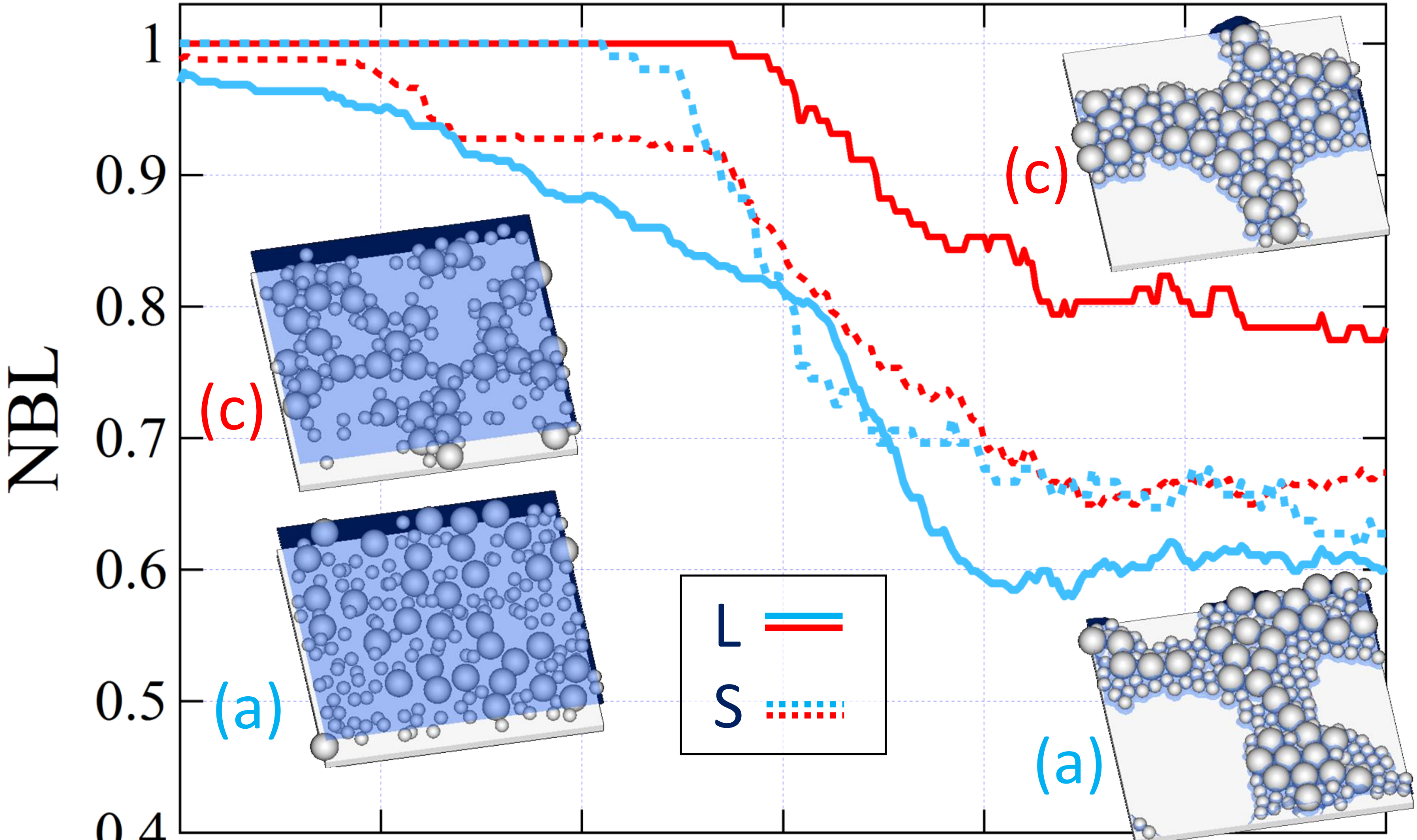




(a) L: $-50\ \mathrm{mV}$
S: $-50\ \mathrm{mV}$

(c) L: $50\ \mathrm{mV}$
S: $-50\ \mathrm{mV}$

(2) Interaction

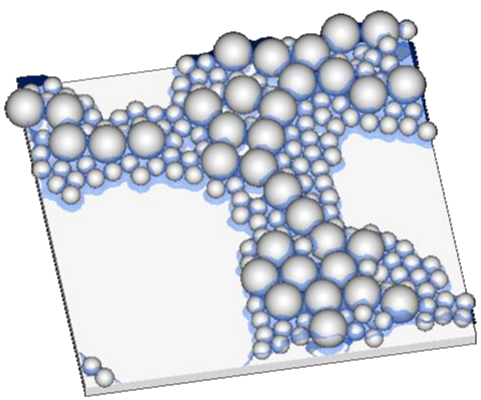


$v_e t/d$ [Time]

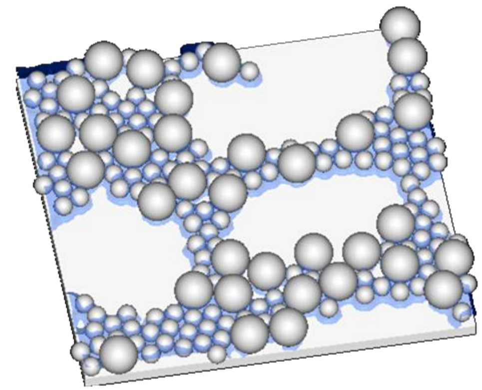
Summary

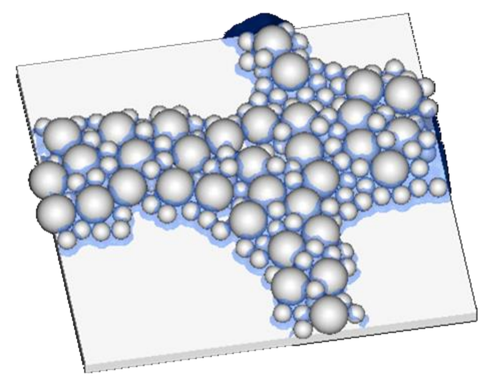
structure formation in drying bimodal colloidal suspensions

Decrease in wettability of L particles



Segregation





L-S attractive interaction

Mixing