6th Asian Coating Workshop (ACW2014)
May 8, 2014, Kobe

Simulation model of colloidal dispersions with solute transport and adsorption onto the particle surface

Rei Tatsumi, Osamu Koike, and Yukio Yamaguchi

Dept. Chem. Sys. Eng., The University of Tokyo

Solute Effects on Dispersions

Addition of solute
↓
Effects on dispersion stability

- Surfactants

  surface modification → change in adhesion

- Electrolytes

  electrical double layer overlap (DLVO theory)

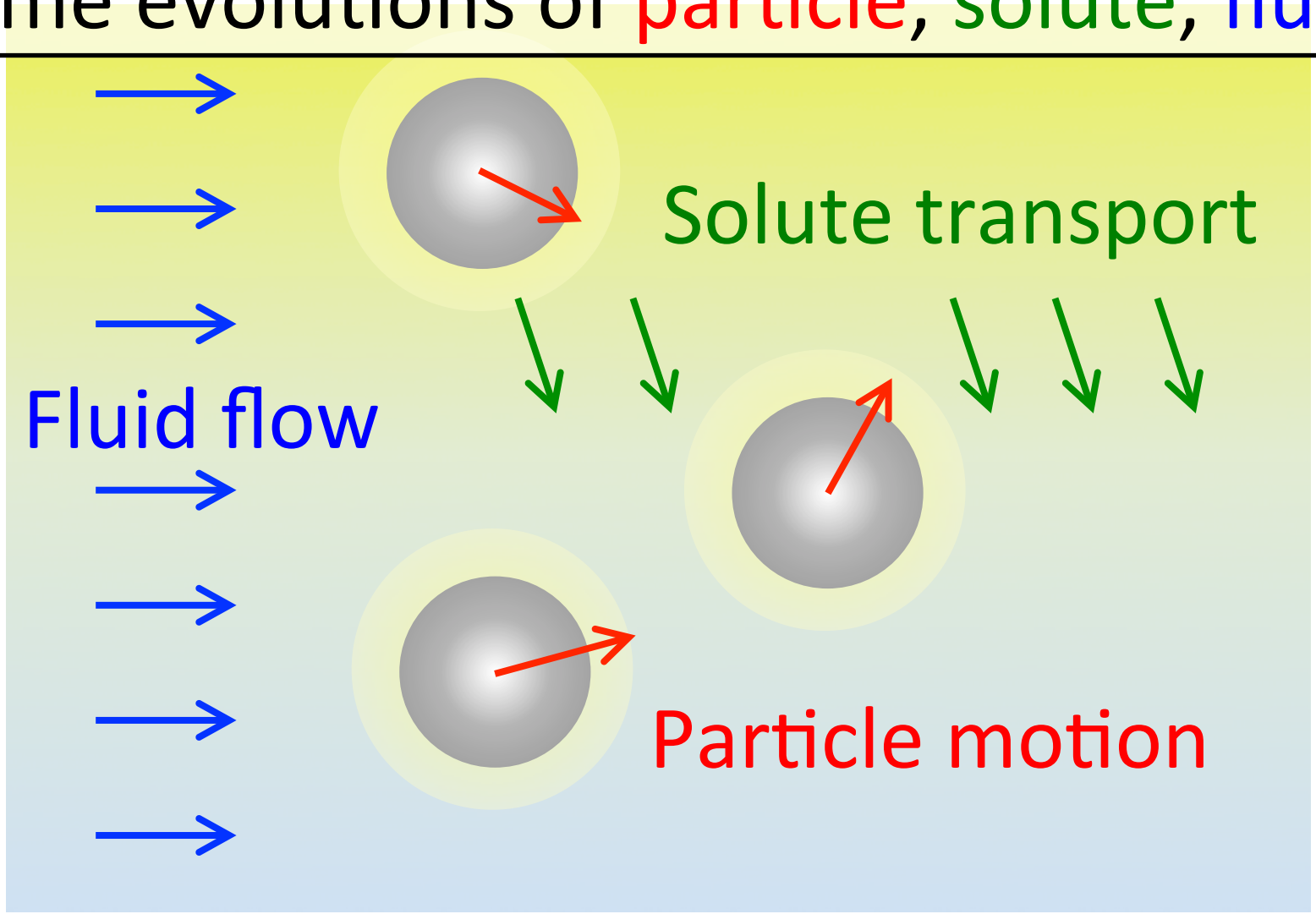
- Polymers

  adsorption layer overlap

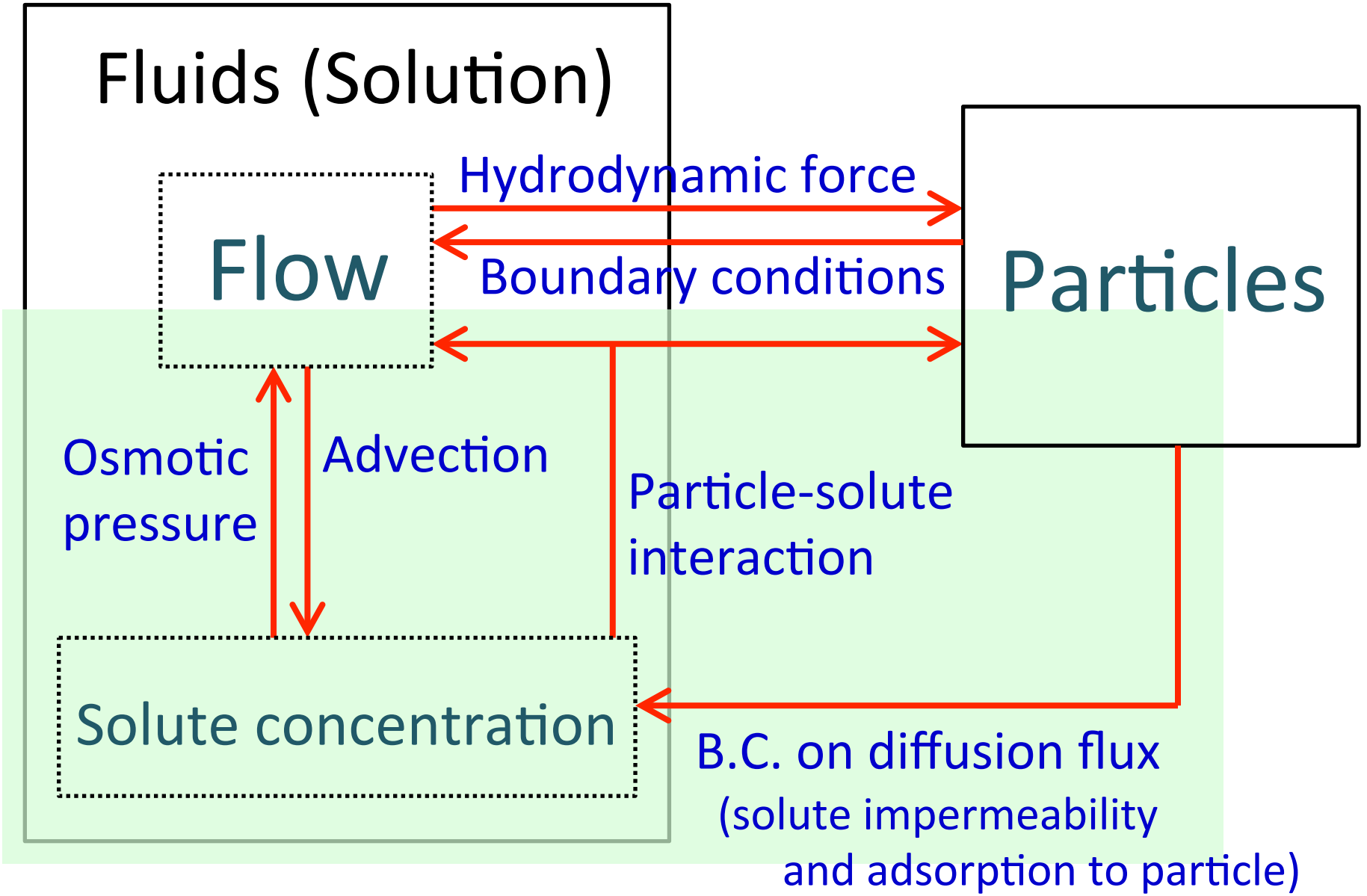
Modeling for numerical simulations

Modeling

Time evolutions of particle, solute, fluid



Coupling


Fluids (Solution)
Flow
Hydrodynamic force
Boundary conditions
Particles
Osmotic pressure
Advection
Particle-solute interaction
Solute concentration
B.C. on diffusion flux
(solute impermeability and adsorption to particle)

Equations

Concentration

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

Diffusion flux

B.C. on diffusion flux
- Impermeability
- Adsorption to particles

Flow

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

$$\rho\left(\frac{\partial \boldsymbol{v}}{\partial t} + \boldsymbol{v} \cdot \nabla \boldsymbol{v}\right) = -\nabla p + \eta \nabla^2 \boldsymbol{v} + \rho \Phi \boldsymbol{a} - c\nabla U_w - \nabla \pi$$

Constraint of particle velocities

Particle-solute interaction

Osmotic pressure

Total momentum conserved

Particles

$$M_i \frac{\mathrm{d}}{\mathrm{d}t}\boldsymbol{V}_i = \boldsymbol{F}_i^H + \boldsymbol{F}_i^S$$

$$\boldsymbol{I}_i \cdot \frac{\mathrm{d}}{\mathrm{d}t}\boldsymbol{\Omega}_i = \boldsymbol{N}_i^H$$

Hydrodynamic force/torque

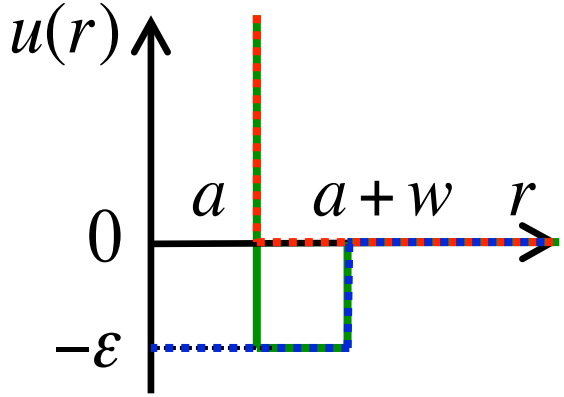
$$\boldsymbol{F}_i^H = -\int \rho \Phi \boldsymbol{a} \mathrm{d}\boldsymbol{r} \qquad \boldsymbol{N}_i^H = -\int (\boldsymbol{r} - \boldsymbol{R}_i) \times \rho \Phi \boldsymbol{a} \mathrm{d}\boldsymbol{r}$$

Particle-solute interaction

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

Model of Adsorption

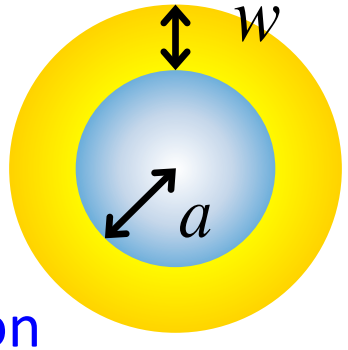
Particle-solute interaction: Square-well potential



$$u(r) = u_{ex}(r) + u_w(r)$$

Hard-core repulsion

Attraction → Adsorption



$$u_{ex}(r) = \begin{cases} \infty & r < a \\ 0 & r \geq a \end{cases} \qquad u_w(r) = \begin{cases} -\varepsilon & 0 \leq r < a + w \\ 0 & r \geq a + w \end{cases}$$

Adsorption energy: $\beta\varepsilon = \varepsilon / RT$

Thickness of adsorption layer: w

Equation (Concentration)

Concentration

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

Osmotic pressure

$$\pi = RT(\Xi - 1)c^*$$

Diffusion flux

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

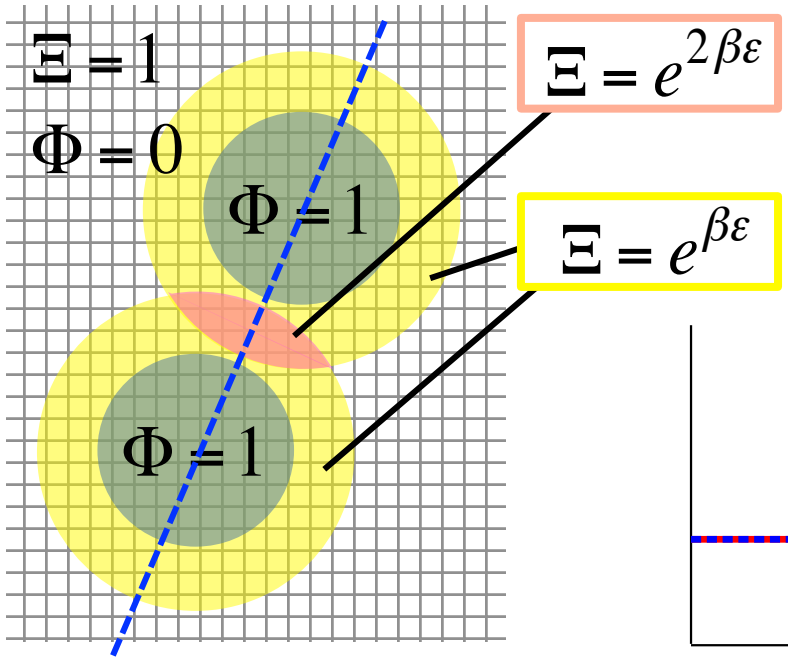
Impermeability & Adsorption to particles

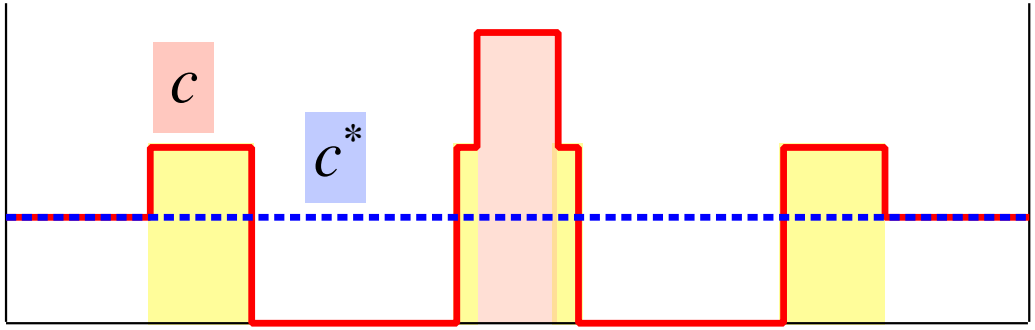
$$\Xi = \exp(-U_w / RT)$$

$$U_w = \sum_k u_w\left(\left|\boldsymbol{r} - \boldsymbol{R}_k\right|\right)$$

$$c = (1-\Phi)\Xi c^*$$

Virtual concentration

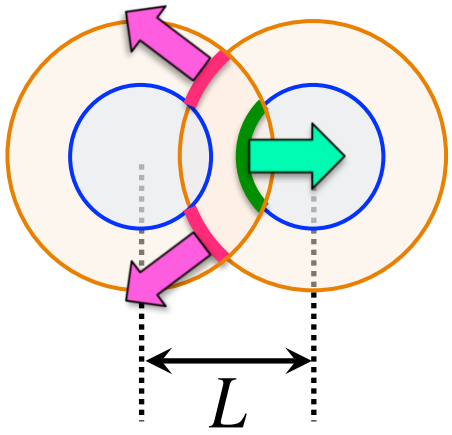


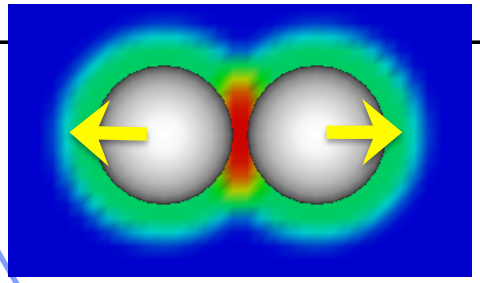


Interparticle Force

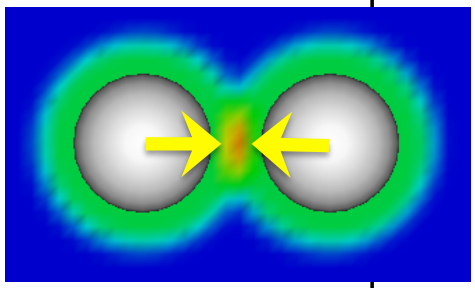
Positive adsorption

$\beta\varepsilon > 0$





Osmotic pressure
(Repulsion)

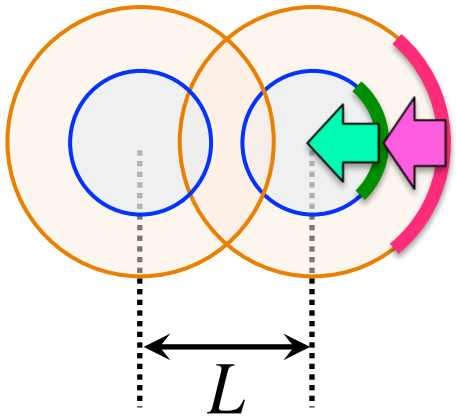


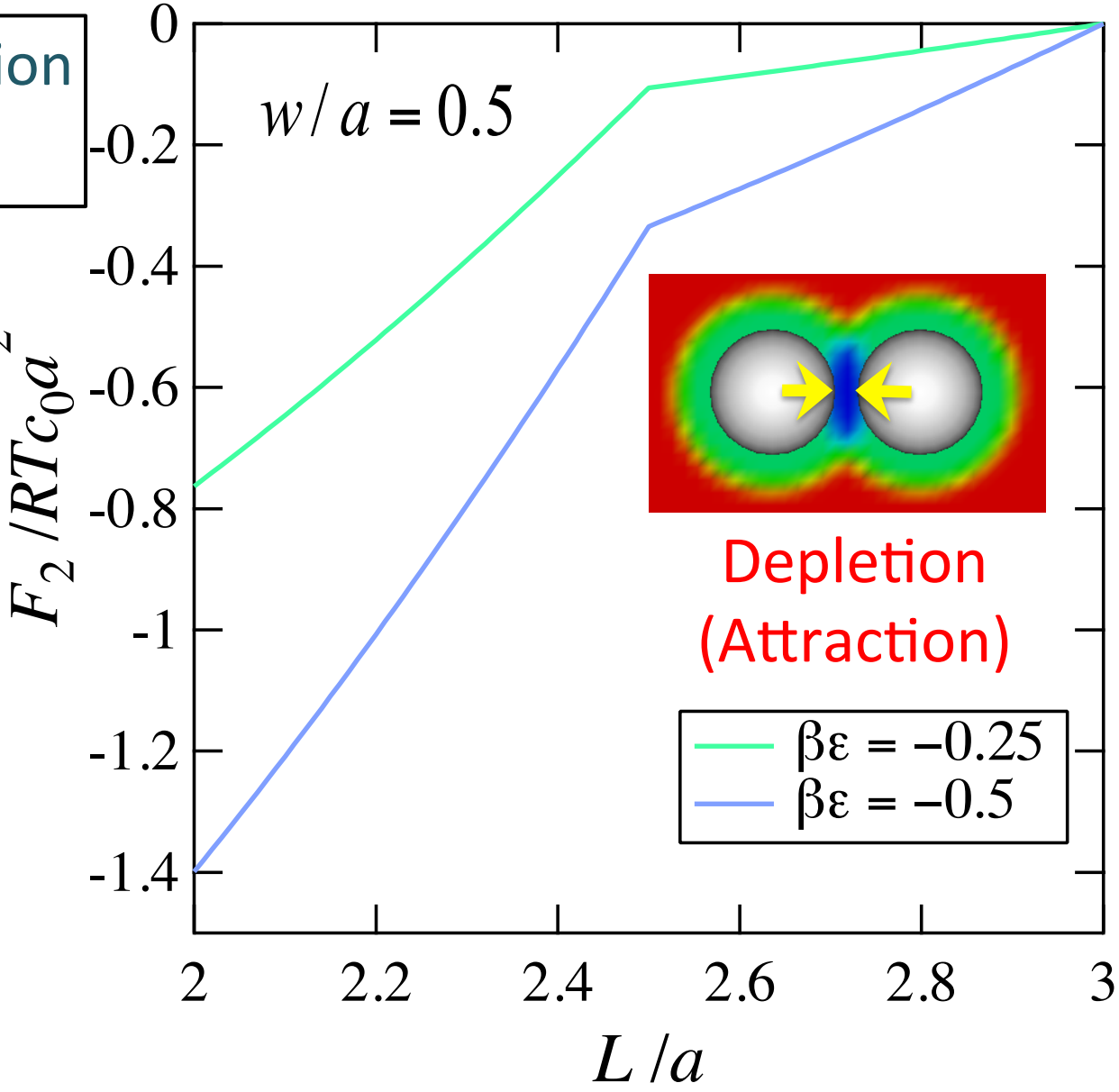
Bridging
(Attraction)

Interparticle Force

Negative adsorption

$\beta\varepsilon < 0$





Diffusiophoresis

particle diameter

$d = 100\ \mathrm{nm}$

system size

$7d \times 4d \times 4d$

(x: fixed; y, z: periodic)

- adsorption

layer thickness

$w = 0.25d$

energy

$\beta\varepsilon = 0.5$

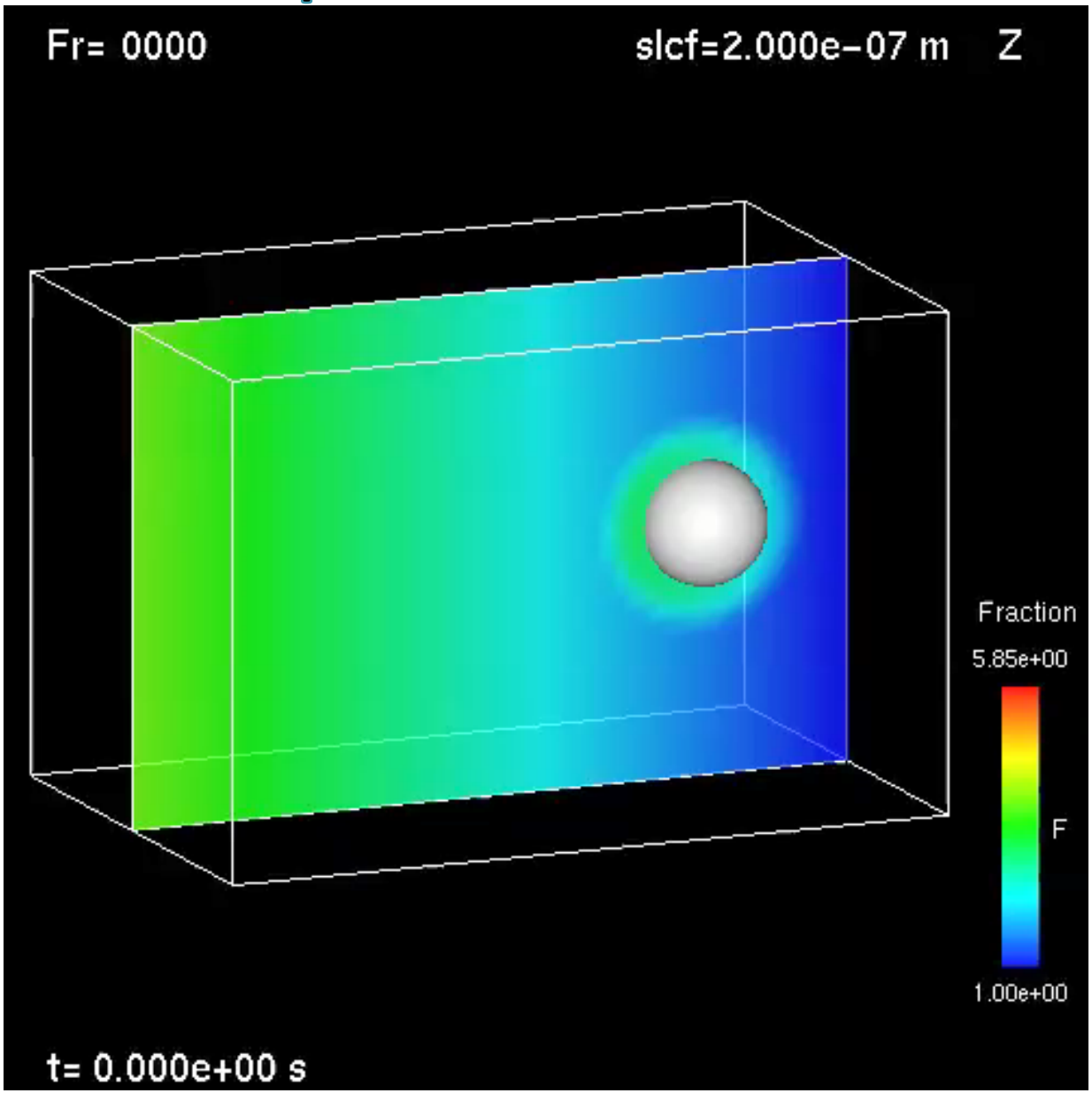
- concentration

average

$1\ \mathrm{mol/L}$

gradient

$2 \times 10^{9}\ \mathrm{mol\ m^{-4}}$



Aggregation by Adsorption

particle diameter

$d = 100\ \mathrm{nm}$

system size

$5d \times 5d \times 3d$

(periodic)

- adsorption

layer thickness

$w = 0.25d$

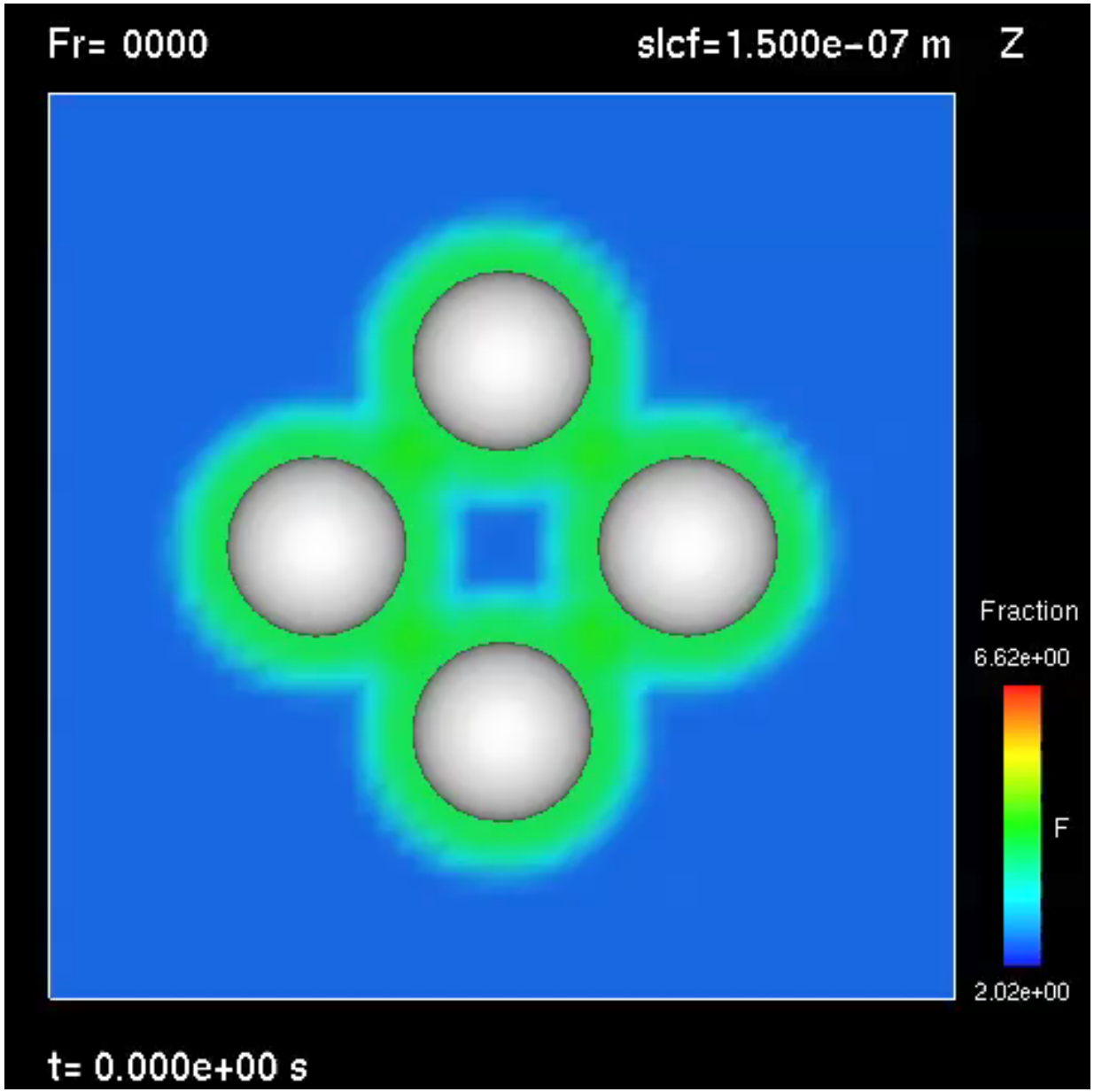
energy

$\beta\varepsilon = 0.5$

- concentration

average

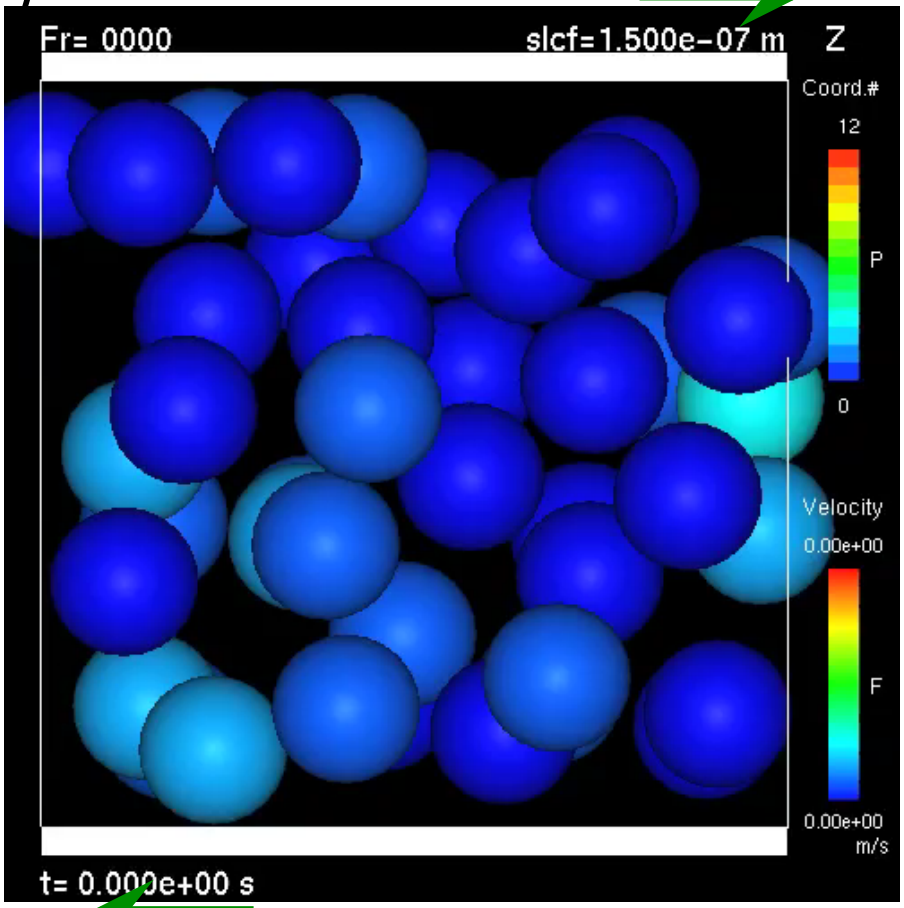
$0.1\ \mathrm{mol/L}$



Shear Flow

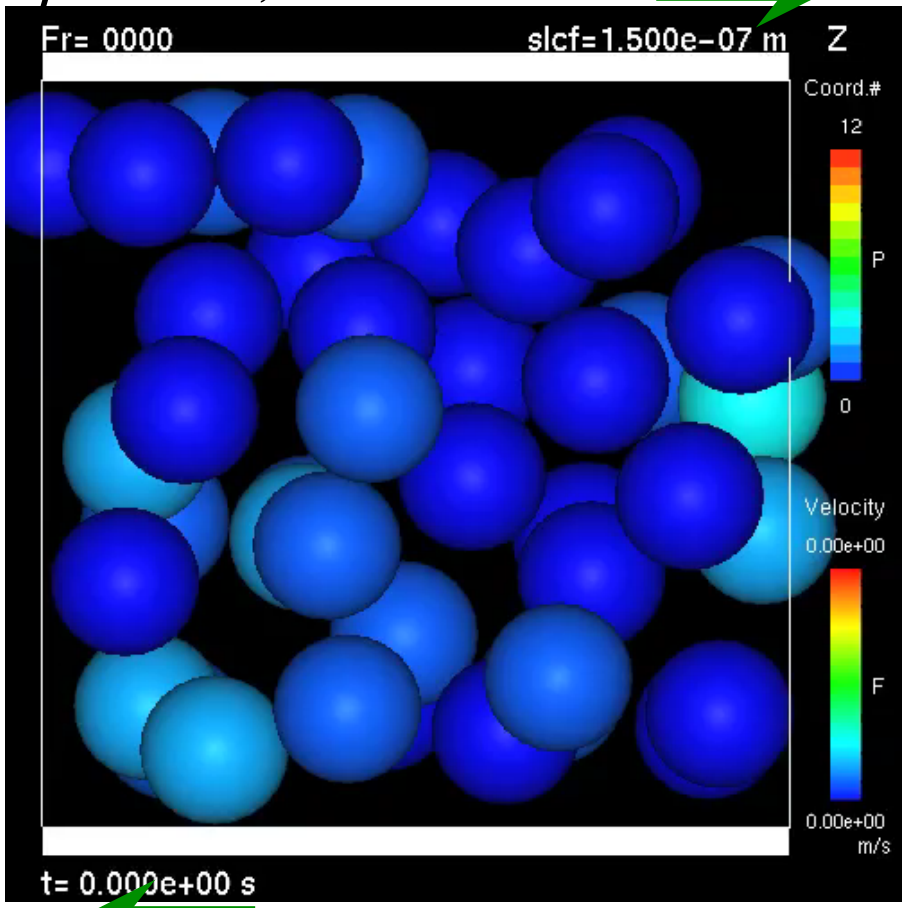
Particle diameter: $d = 100\ \mathrm{nm}$ System size: $5d \times 5d \times 3d$

$\beta\varepsilon = 0$ 1.6 m/s



No adsorption

$\beta\varepsilon = 0.5,\ w/d = 0.25$



Adsorption

Summery

Simulation model of colloidal dispersions with solute transport and adsorption onto the particle is constructed.

- Solute transport

  B. C. on diffusion flux ← Virtual concentration

  (solute impermeability and adsorption to particle)

- Solute adsorption onto the particle

  Particle-solute interaction (Square-well potential)

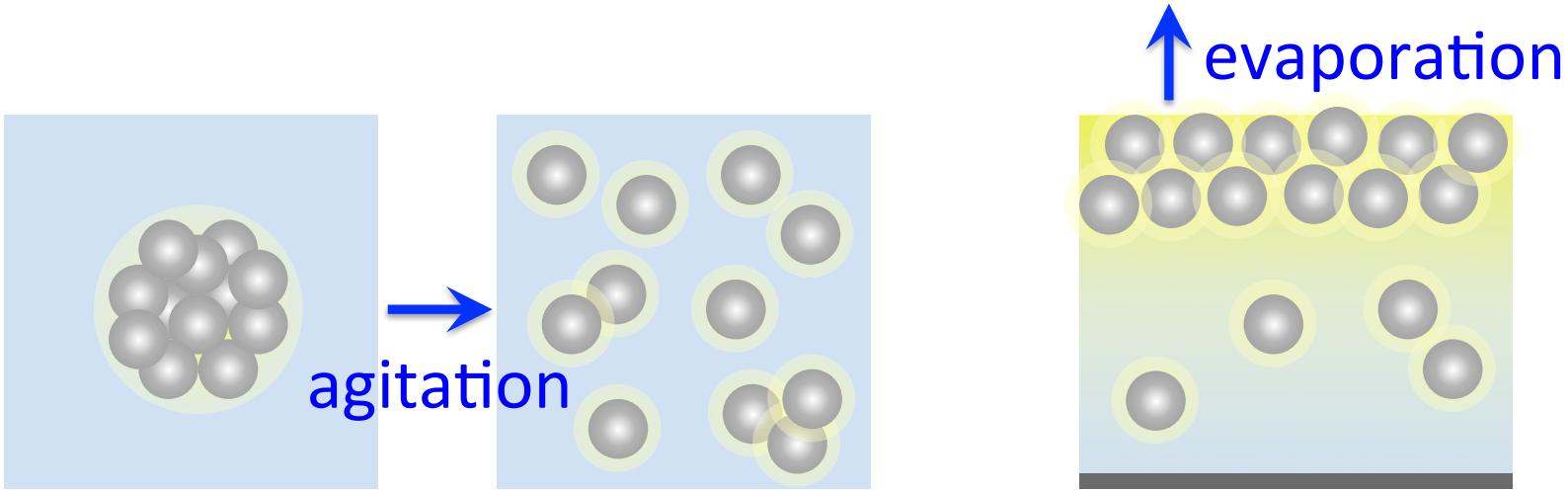
→ interactions among particles

Attractive force: Bridging force, Depletion force

Repulsive force: Osmotic pressure

Outlook for Application

- Breakup process of particle aggregates with polymer additives
- Drying and concentration process of particle-polymer dispersions



Diffusiophoresis

particle diameter:
$d = 100\ \mathrm{nm}$

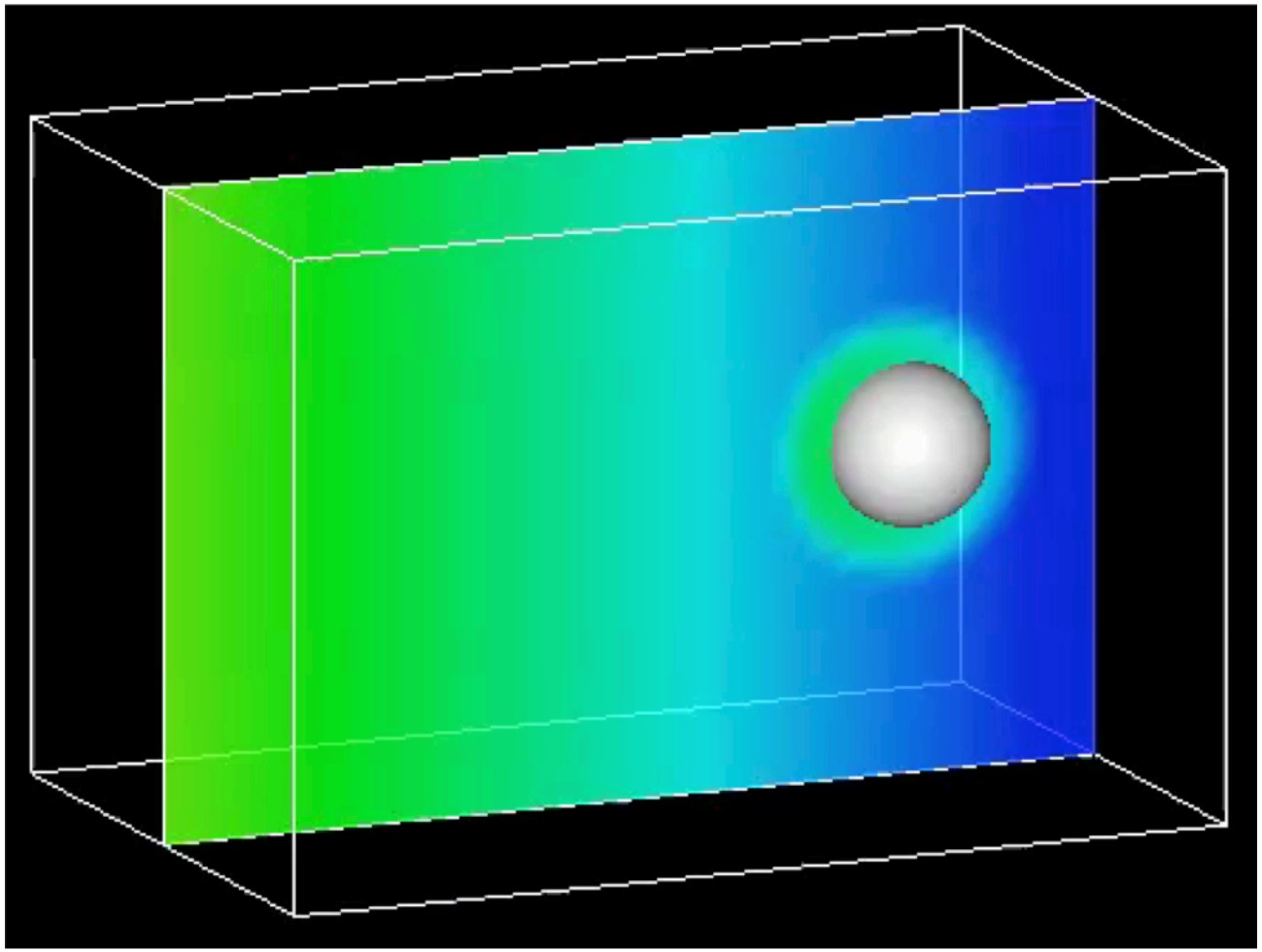
system size: $7d \times 4d \times 4d$
(x: fixed; y, z: periodic)

adsorption layer thickness:
$w = 0.25d$

energy:
$\beta\varepsilon = 0.5$

concentration
average:
$1\ \mathrm{mol/L}$

gradient:
$2 \times 10^{9}\ \mathrm{mol\,m^{-4}}$



Aggregation by Adsorption

particle diameter:

$d = 100\ \mathrm{nm}$

adsorption layer thickness:

$w = 0.25d$

energy:

$\beta\varepsilon = 0.5$

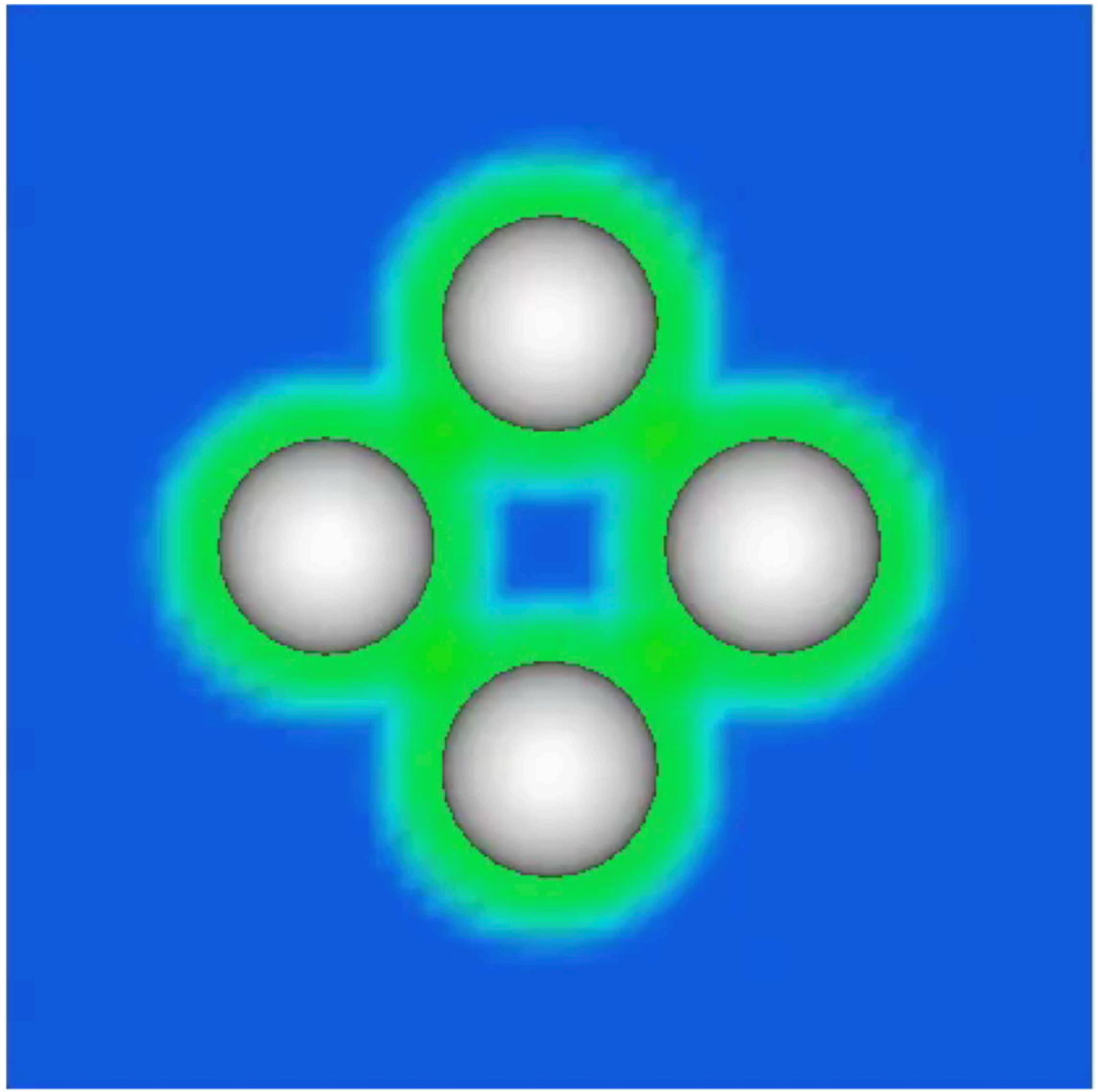
concentration average:

$0.1\ \mathrm{mol/L}$

system size:

$5d \times 5d \times 3d$

(periodic)



Shear Flow

Particle diameter: $d = 100$ nm System size: $5d \times 5d \times 3d$