

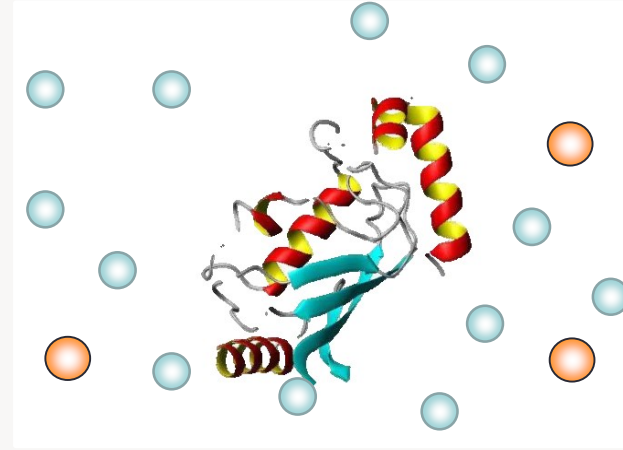
Effects of solvation structure on a large-particle diffusion

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Purpose	To study the validity of the Stokes-Einstein relation when a large-hard sphere is immersed in a binary hard-sphere mixture.
Method	We calculate the diffusion coefficient using a perturbation theory with respect to the size ratio of the solvent and solute particles.
Result	Large deviation from the Stokes-Einstein relation is observed when mixing binary solvent spheres with the size ratio of 1 : 5. The deviation is caused by the high density of solvent particles around the solute due to entropic effects.

1. Diffusion coefficient

- Diffusing particle:
size $R \sim$ biomolecule

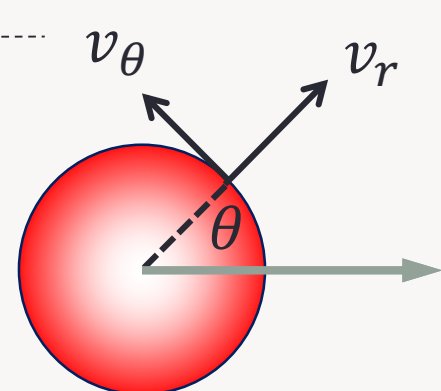


(solvent particle $\ll R <$ colloidal particle)

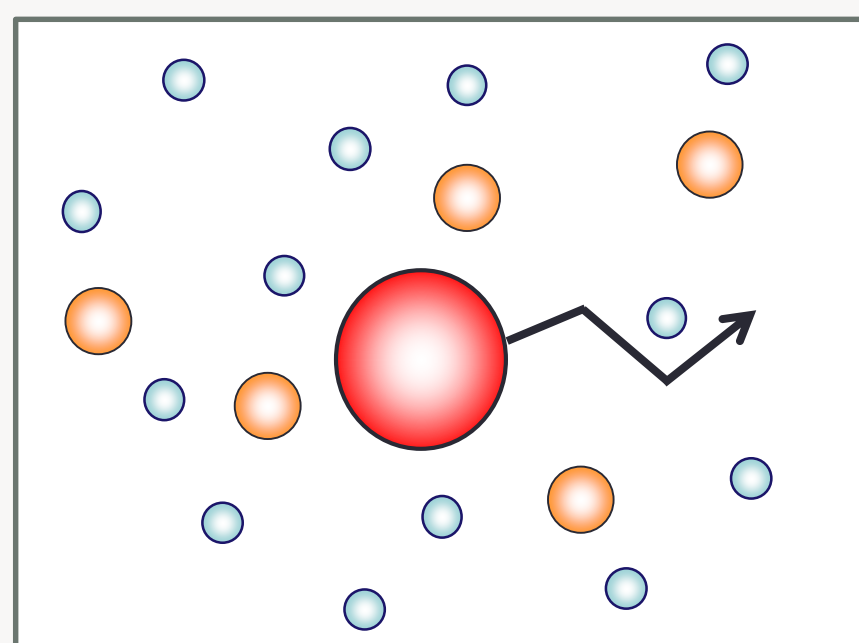
Stokes-Einstein relation

$$D_{SE} = \frac{k_B T}{8\pi\eta R} \quad \begin{array}{l} \eta : \text{viscosity} \quad R : \text{solute radius} \\ c : \text{depending on boundary condition} \\ 1/2 \text{ (slip)}, 3/4 \text{ (stick)} \end{array}$$

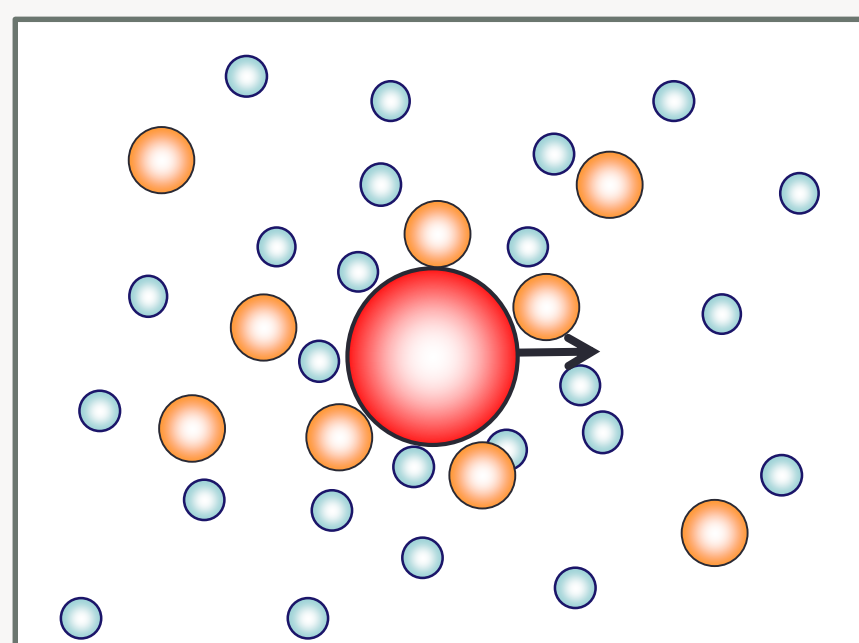
$$\begin{array}{ll} \text{slip} & \text{stick} \\ v_r = 0, \quad \frac{\partial v_\theta}{\partial r} = \frac{v_\theta}{R} & v_r = 0, \quad v_\theta = 0 \end{array}$$



- The effects of solvation structure



D : Large



D : Small

The solvation effects are not included in the SE relation.

Purpose

To study the validity of the SE relation when the solute particle is smaller than macroscopic size.

2. Perturbation theory

- Assuming that a solvent particle is much smaller than a solute, we expand microscopic equations.
- $\epsilon = a/R \ll 1$ (a, R : radii of solvent and solute particles)

$$D = \frac{k_B T}{8\pi\eta R} \quad c = \frac{6 - 3\epsilon\alpha - 3\epsilon\beta}{12 - 4\epsilon\alpha + (\epsilon\beta)^2}$$

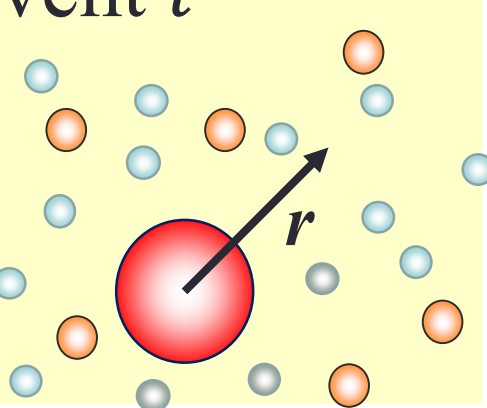
- ✓ α and β are calculated from $g_i(r)$.
- Considering the solvation effect

$g_i(r)$: radial distribution function of solvent i

$$g_i(r) = \rho_i(r)/\rho_i$$

$\rho_i(r)$: equilibrium mass density field

ρ_i : average mass density



- ✓ analytical expression

- Avoiding the finite-size effect

Derivation

Microscopic equations [1]

Continuity equations $\nabla \cdot \rho_i(r) \mathbf{v}_i(r) = 0$

Equations of motion

$$-\rho_i(r) \nabla \mu_i(r) + \frac{\rho_i(r)}{\rho_T(r)} [\eta \nabla^2 \mathbf{v}(r) + \gamma \nabla (\nabla \cdot \mathbf{v}(r))] + \nabla L [\mathbf{v}_1(r) - \mathbf{v}_2(r)] = 0$$

Irreversible terms are approximated by the long wavelength limit.

$\mathbf{v}_i(r)$: velocity, $\mu_i(r)$: chemical potential, $\rho_T(r) = \rho_1(r) + \rho_2(r)$

$\mathbf{v}(r) = (\rho_1(r) \mathbf{v}_1(r) + \rho_2(r) \mathbf{v}_2(r)) / \rho_T(r)$,

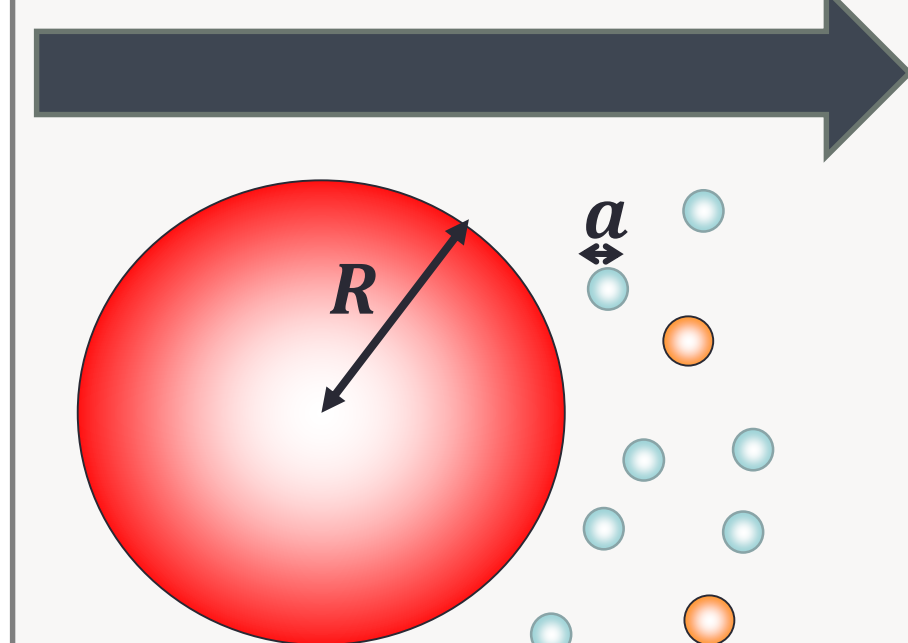
η : share viscosity, $\gamma = \zeta + \eta/3$, ζ : bulk viscosity

L : the strength of the friction between solvents 1 and 2.

[1] T.Yamaguchi *et al.* J. Chem. Phys. **123**, 034504 (2005)

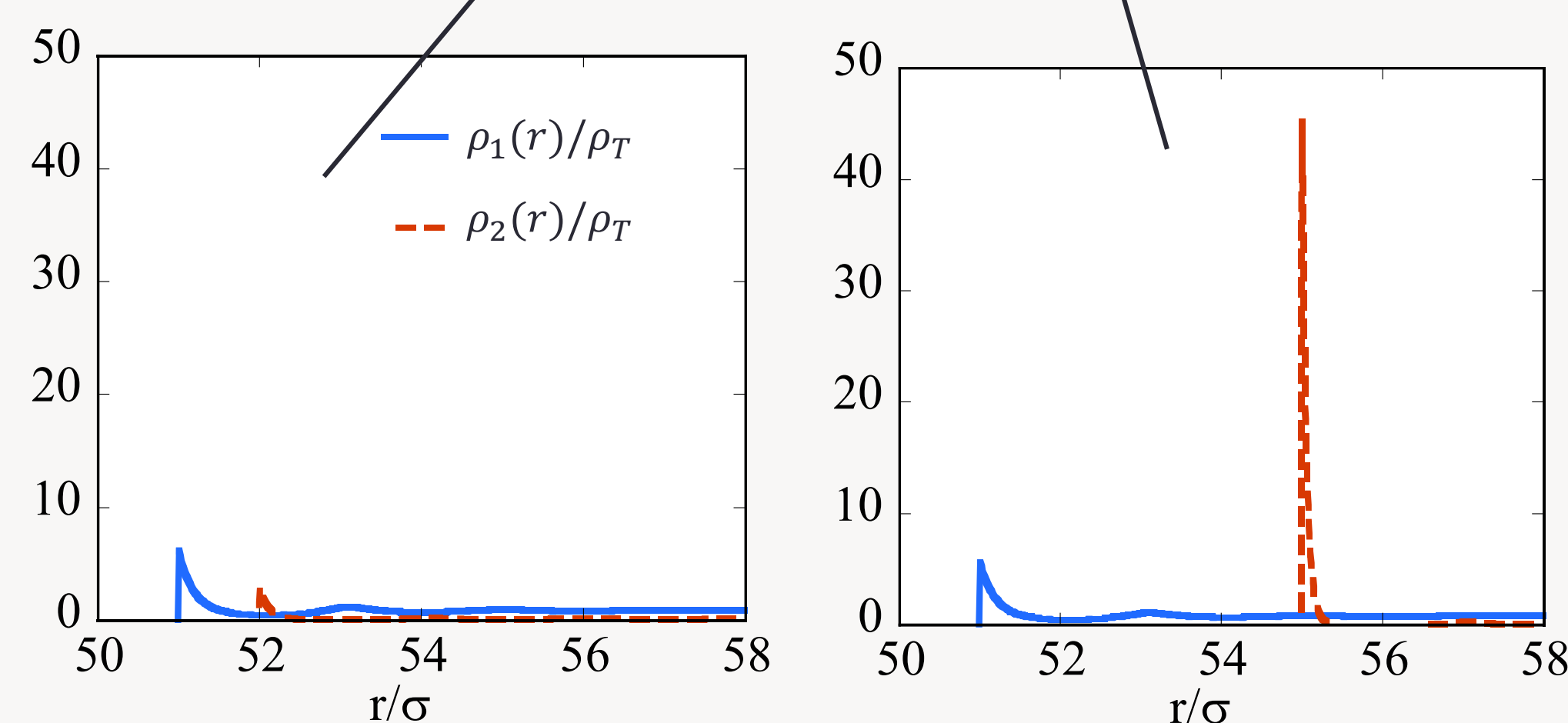
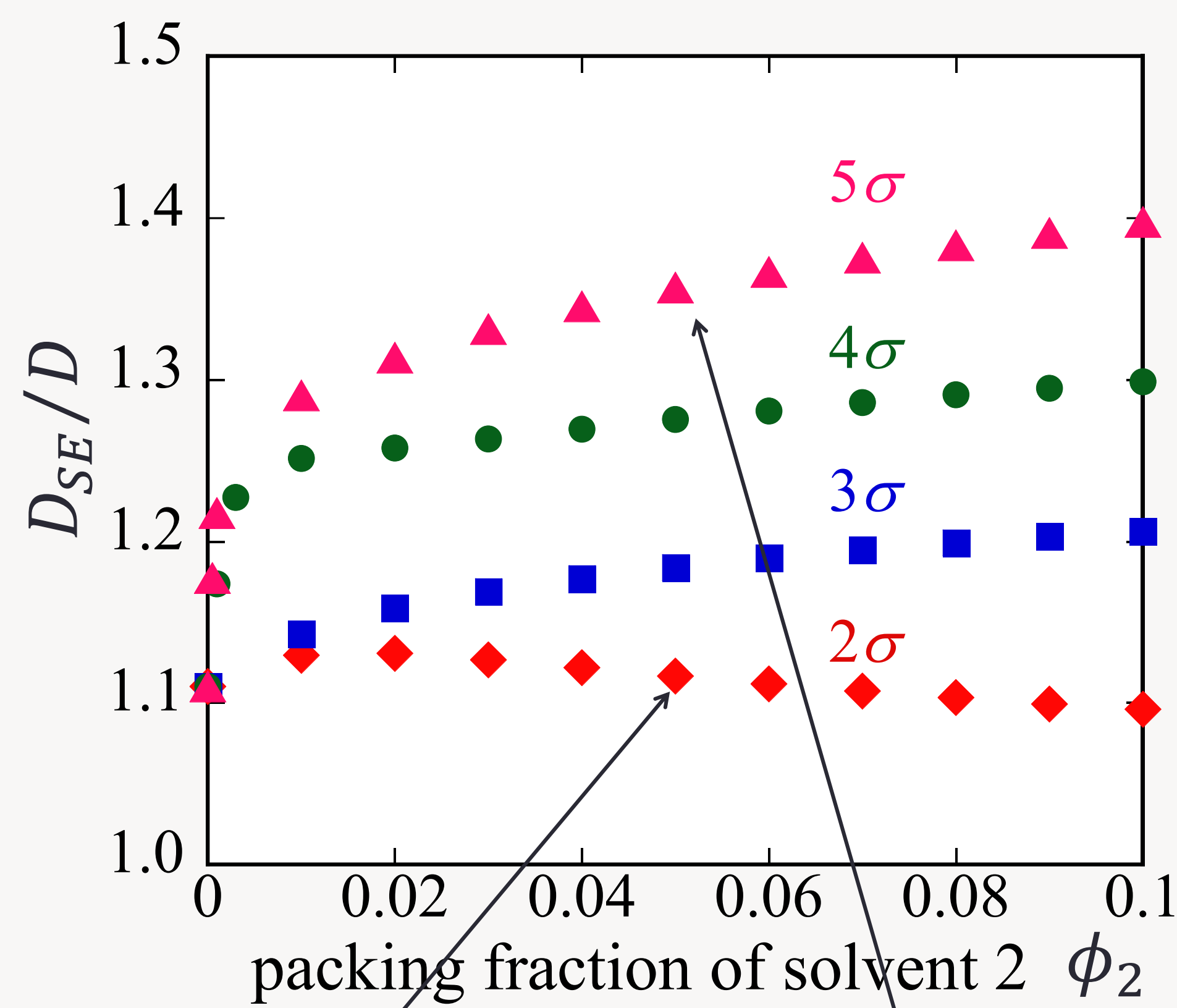
perturbation expansion

$$\epsilon = a/R \ll 1$$



[2] Y. Nakamura *et al.* J. Phys. Soc. Jpn. **83**, 064601 (2014)

3. Binary hard spheres

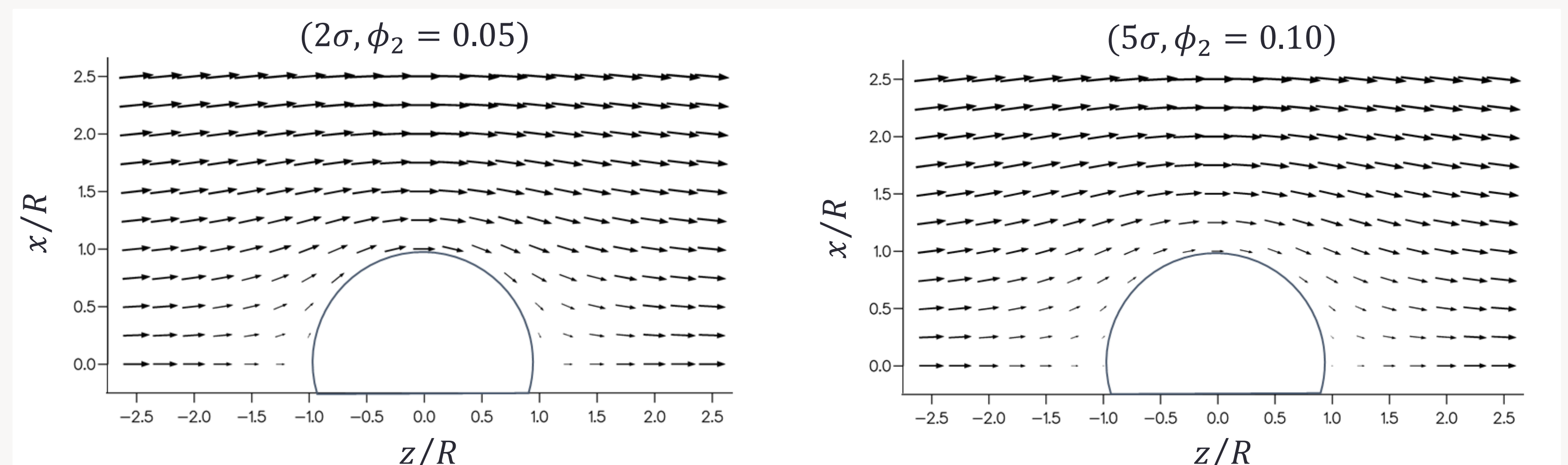


$\rho_1(r), \rho_2(r)$: the equilibrium mass densities

$$\rho_1(r) = \rho_1 g_1(r), \quad \rho_2(r) = \rho_2 g_2(r)$$

[3] We thank Professor Masahiro Kinoshita for software program used in the numerical calculations of $g_1(r)$ and $g_2(r)$.

- Velocity field



High density around the solute surface makes a solvent sticky.

- Hydrodynamic equations

$$\nabla \cdot \mathbf{v}(r) = 0, \quad -\nabla P(r) + \eta \nabla^2 \mathbf{v}(r) = 0$$

$P(r)$: pressure

These equations are solved analytically.

- Boundary conditions

$$v_r = -\epsilon\beta v_\theta \cot \theta, \quad \frac{\partial v_\theta}{\partial r} = \frac{1 - \epsilon\alpha}{R} v_\theta - \frac{\epsilon\beta}{2\eta} P \tan \theta$$

α, β are calculated from $g_i(r)$

$$\begin{aligned} \epsilon\alpha &= \frac{1}{R} \left[\int_{R+a}^{R+b} \Delta v_1(r) dr + \int_{R+b}^{\infty} \Delta v_T(r) dr \right. \\ &\quad \left. - \left(1 + \frac{\gamma}{\eta} \right) \left\{ \int_{R+a}^{R+b} \rho_1(r) \int_r^{\infty} \frac{\omega_1(r')}{\rho_1(r')} \Delta v_1(r') dr' dr + \int_{R+a}^{R+b} \rho_T(r) \int_r^{\infty} \frac{\omega_T(r')}{\rho_T(r')} \Delta v_T(r') dr' dr \right\} \right. \\ &\quad \left. - \left(1 + \frac{\gamma}{\eta} \right) \int_{R+a}^{R+b} \rho_1(r) dr \left\{ \int_r^{\infty} \frac{\omega_T(r')}{\rho_T(r')} \Delta v_T(r') dr + \Delta v_1(R+b) \left(\frac{1}{\rho_1(R+b)} - \frac{1}{\rho_T(R+b)} \right) \right\} \right] \\ \epsilon\beta &= \frac{1}{R} \int_R^{\infty} \left[\frac{\rho_T(r)}{\rho_T} - 1 \right] dr, \quad \Delta v_j(r) = \frac{2\omega_j(r)}{\rho_j(r)} \int_R^r \rho_j(r') dr', \quad \omega_j(r) = \frac{1}{\rho_j(r)} \frac{d\rho_j(r)}{dr} \end{aligned}$$

a, b : radii of solvent 1 and solvent 2 particles