SCEJ 52nd Autumn Meeting
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Direct numerical simulation for viscoelastic analysis of concentrated colloidal suspensions

粒子系濃厚溶液の粘弾性特性の直接数値シミュレーション

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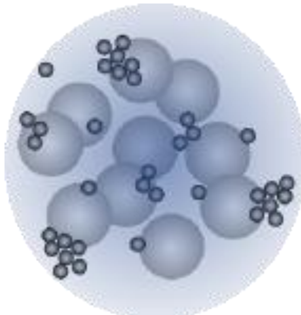
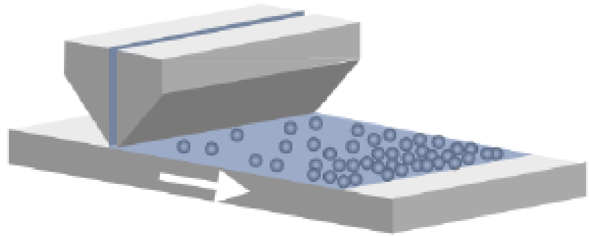
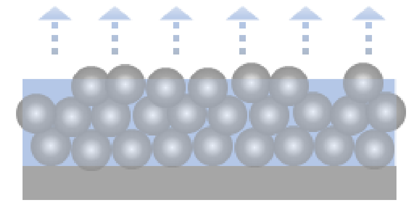
Material Fabrication from Colloidal Suspensions



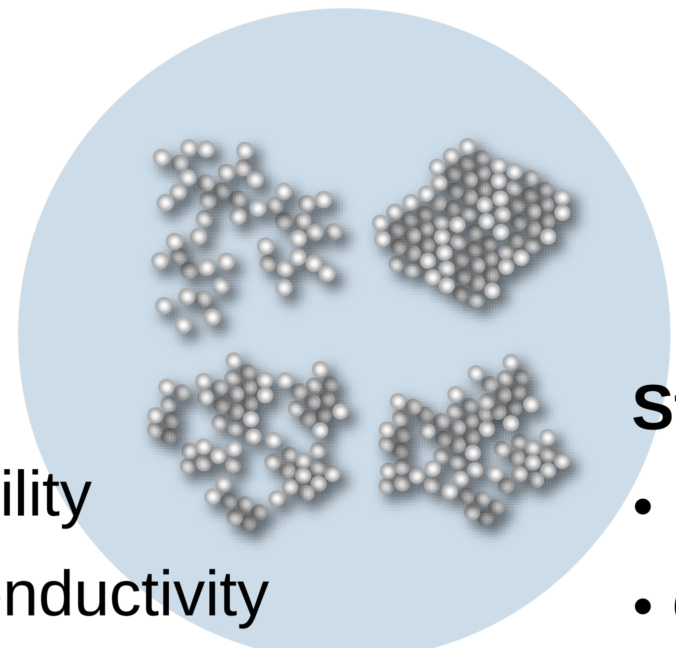
Dispersing



Coating



Drying



Functions

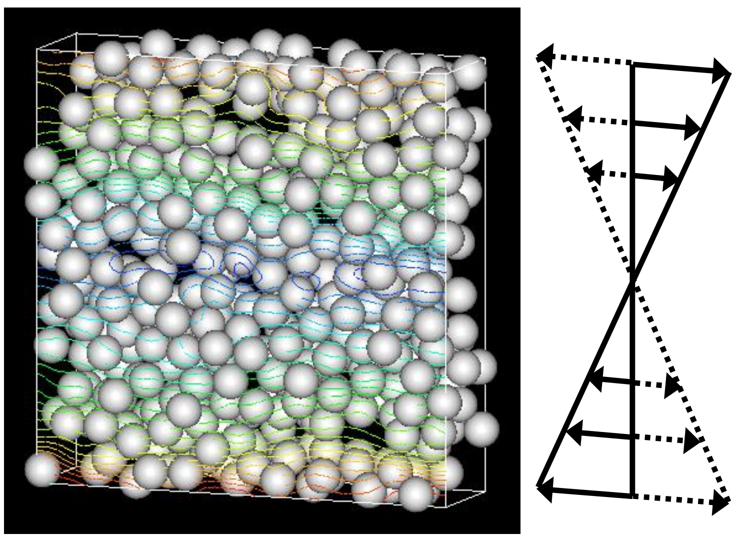
- Strength • Permeability
- Electrical/Thermal conductivity
- Optical property

Structures

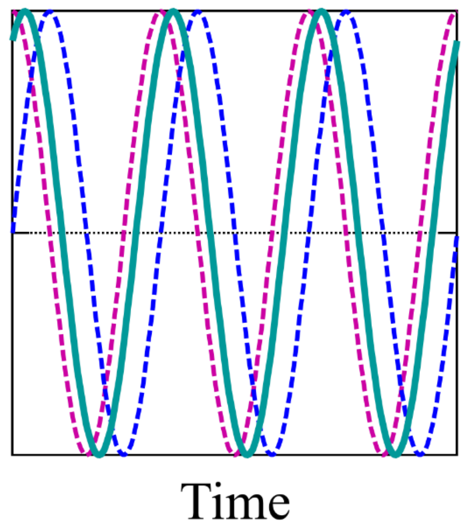
- Porosity
- Contact network

Objective

- Direct numerical simulation of viscoelastic behavior of concentrated colloidal suspensions
- Relation between dynamic modulus and the structure of particles



Oscillatory shear



Shear strain/rate

$\gamma(t) = \gamma_0 \sin \omega t$

$\dot{\gamma}(t) = \gamma_0 \omega \cos \omega t$

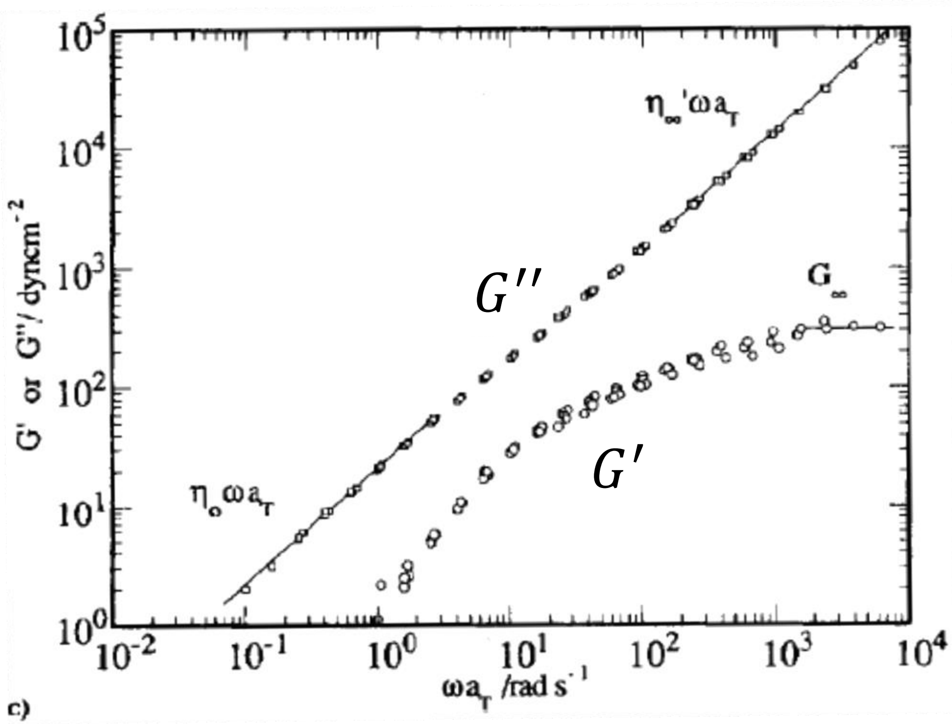
Stress

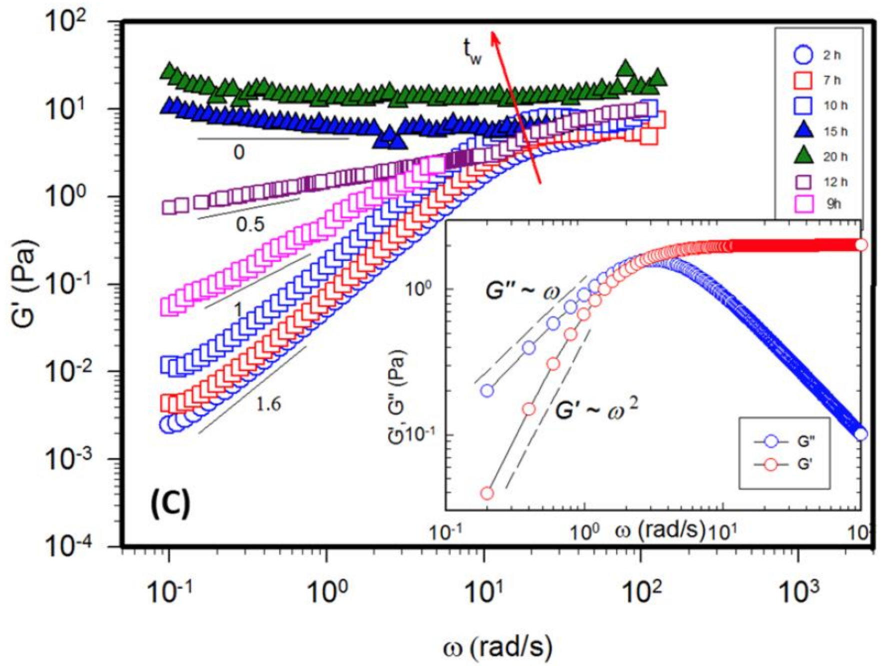
$\sigma(t) = \sigma_0 \sin(\omega t + \delta)$

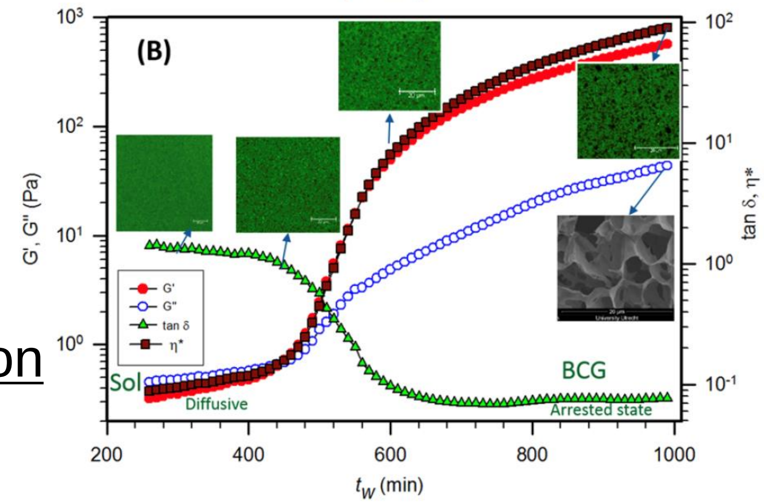
Dynamic modulus

$G' = \frac{\sigma_0}{\gamma_0} \cos \delta \quad G'' = \frac{\sigma_0}{\gamma_0} \sin \delta$

Dynamic modulus







Well-dispersed system

Silica (60 nm, 37 vol%)
Ethylene glycol/Glycerol solvent

Gelation

Laponite (25 nm, ~0.3%(w/v))
+ Montmorillonite(250 nm, ~3%(w/v))

Shikata & Pearson, J. Rheol. (1994).
Pujala et al., Sci. Rep. (2018).

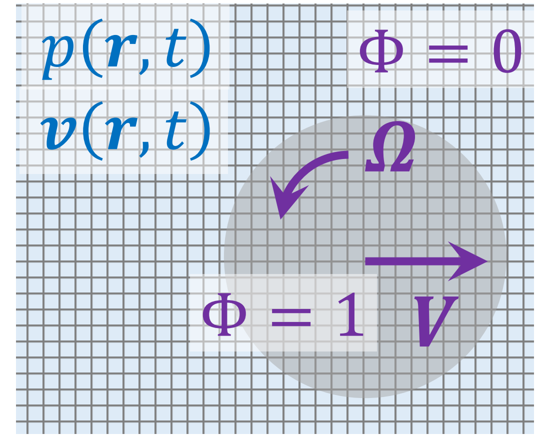
Equations

Particles

$$M\frac{\mathrm{d}\boldsymbol{V}}{\mathrm{d}t} = \boldsymbol{F}^{\mathrm{H}} + \boldsymbol{F}^{\mathrm{PP}}$$

$$I\frac{\mathrm{d}\boldsymbol{\Omega}}{\mathrm{d}t} = \boldsymbol{N}^{\mathrm{H}} + \boldsymbol{N}^{\mathrm{PP}}$$

- Van der Waals force
- Contact force



Hydrodynamic force

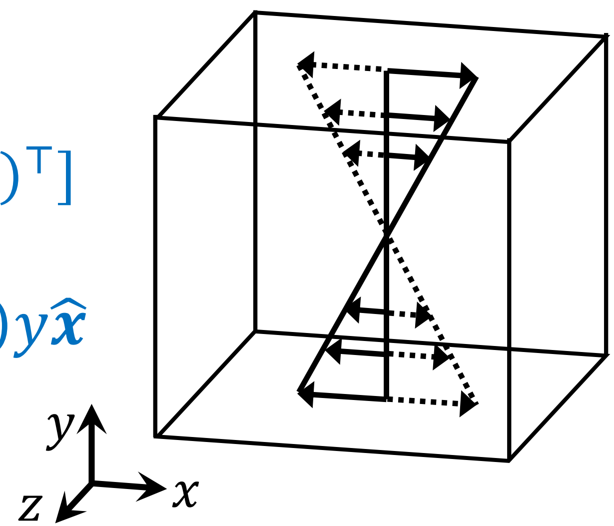
Fluid

Imposition of velocity in particle domains

$$\rho\left(\frac{\partial \boldsymbol{v}}{\partial t} + \boldsymbol{v}\cdot\nabla\boldsymbol{v}\right) = \nabla\cdot\boldsymbol{\sigma}_{\mathrm{F}} + \Phi\boldsymbol{f}_{\mathrm{P}}$$

$$\nabla\cdot\boldsymbol{v} = 0 \qquad \boldsymbol{\sigma}_{\mathrm{F}} = -p\boldsymbol{I} + \eta[\nabla\boldsymbol{v} + (\nabla\boldsymbol{v})^{\mathsf{T}}]$$

Calculation on peculiar velocity: $\boldsymbol{v}' = \boldsymbol{v} - \dot{\gamma}(t)y\hat{\boldsymbol{x}}$



Boundary conditions

x, z: Periodic, y: Lees-Edwards

Kobayashi & Yamamoto, J. Chem. Phys. **134**, 064110 (2011).

Dynamic modulus

Input

Shear strain $\gamma(t) = \gamma_0 \sin \omega t$

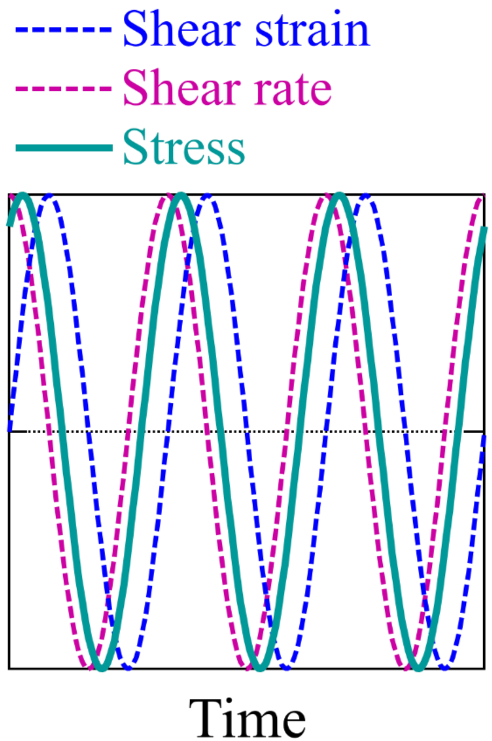
Shear rate $\dot{\gamma}(t) = \gamma_0 \omega \cos \omega t$

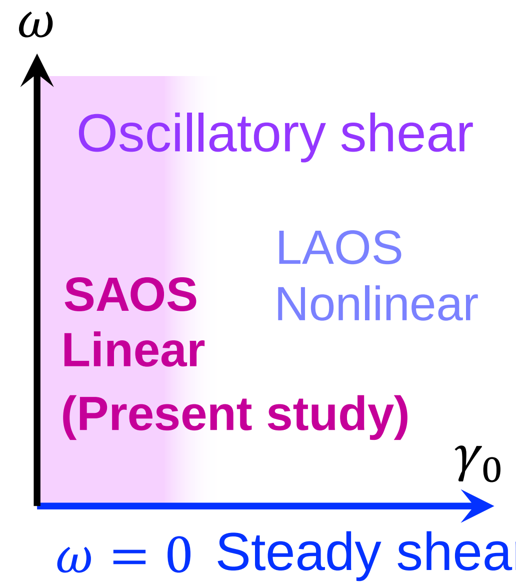
Output

Stress $\sigma(t) = \sigma_0 \sin(\omega t + \delta)$

$= \gamma_0 (G' \sin \omega t + G'' \cos \omega t)$

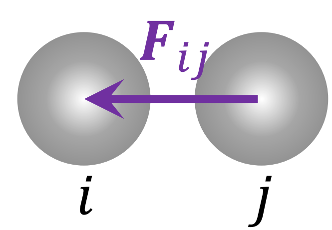
$G' = \dfrac{\sigma_0}{\gamma_0} \cos \delta \quad G'' = \dfrac{\sigma_0}{\gamma_0} \sin \delta$





Stress

$$\sigma = \eta \dot{\gamma} + \frac{1}{V} \sum_i \int_{\partial P_i} (\boldsymbol{\sigma}_{\mathrm{F}} \cdot \hat{\boldsymbol{n}})_x (y - y_i) \mathrm{d}S - \frac{1}{V} \sum_{i<j} F_{ij}^x (y_i - y_j)$$

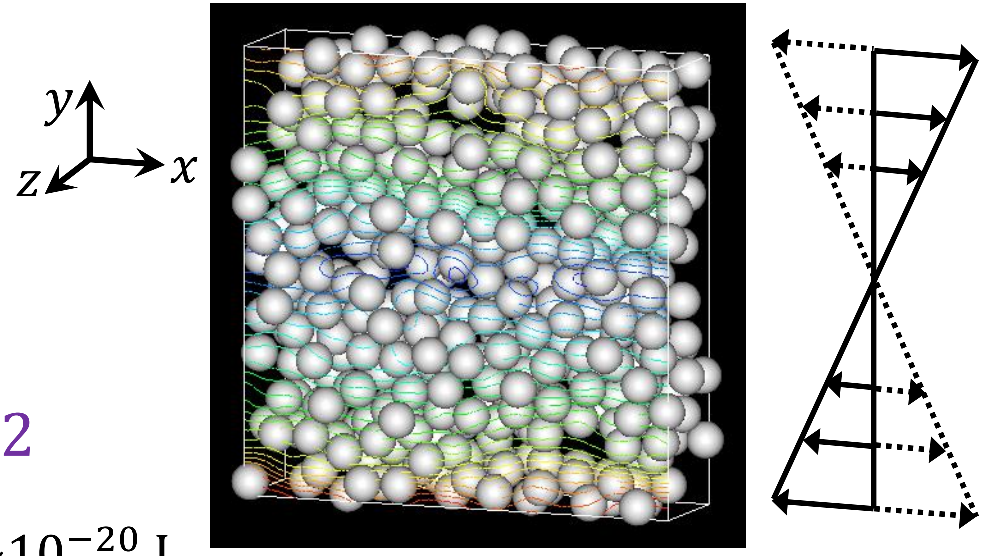


Dynamic modulus

$$G'(\omega) = \frac{\omega}{\pi \gamma_0} \int_0^{2\pi/\omega} \sigma(t) \sin \omega t \, \mathrm{d}t \qquad G''(\omega) = \frac{\omega}{\pi \gamma_0} \int_0^{2\pi/\omega} \sigma(t) \cos \omega t \, \mathrm{d}t$$

Simulation Conditions

$U_x(t) = \dot{\gamma}(t) y$



Domain size: $12d \times 12d \times 3d$

Particles

- Diameter: $d = 100\ \mathrm{nm}$
- Volume fraction: 0.5
- Zeta potential: $0\ \mathrm{mV}$
- Adhesive force:

$$F^* = \frac{\rho}{\eta^2} F = 4.2 \times 10^{-4} - 4.2$$

$F^* = 4.2 \rightarrow$ Hamaker constant $\sim 10^{-20}\ \mathrm{J}$

Fluid density: ρ

Viscosity: η

Fluid: Water

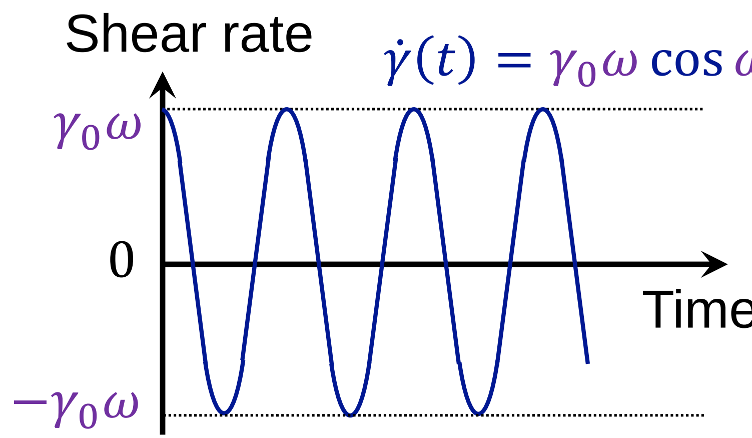
Shear flow

- Strain: $\gamma_0 = 3 \times 10^{-4} - 1 \times 10^{-1}$
- Frequency: $\omega \tau_{\mathrm{vis}} = 3 \times 10^{-2} - 3$

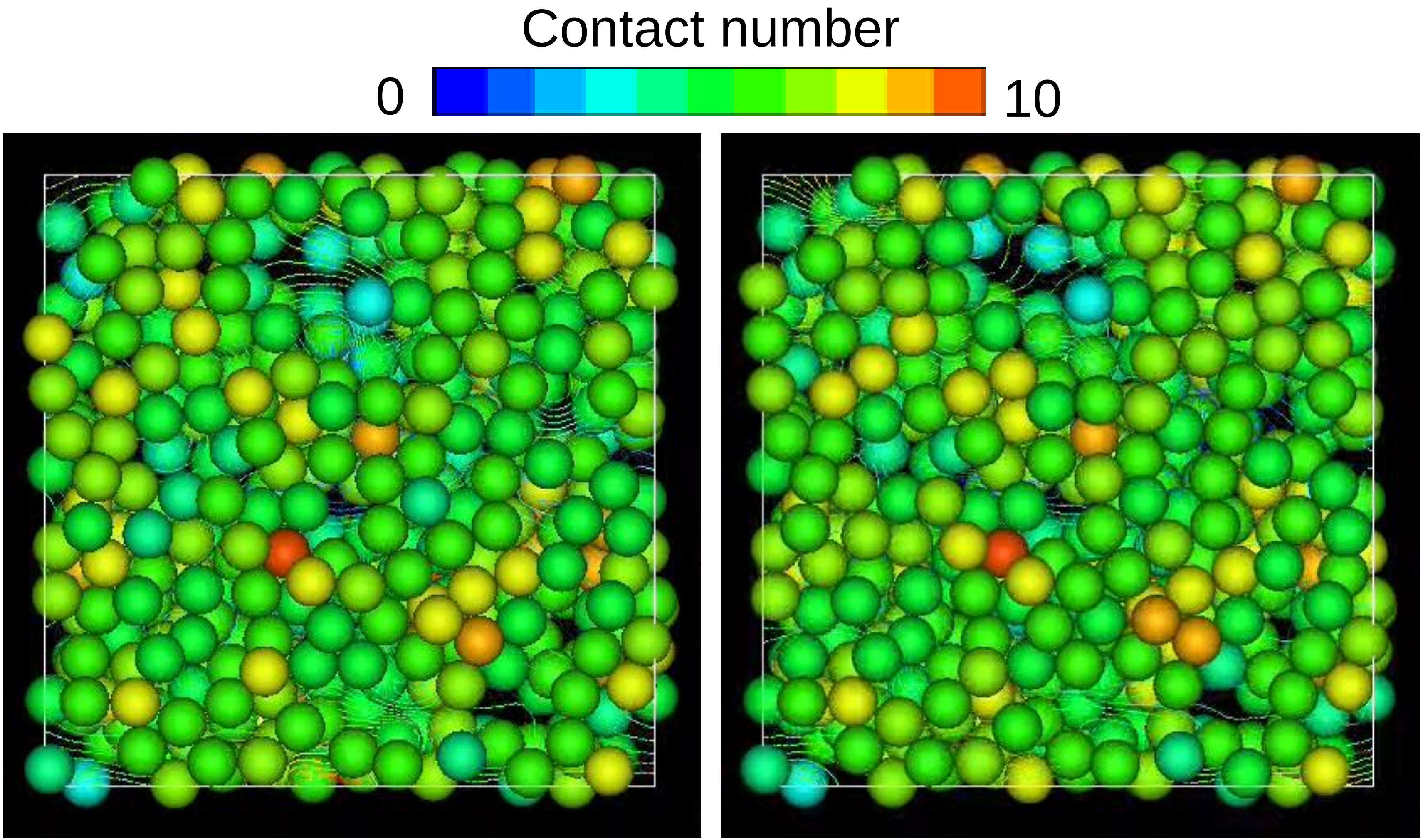
$$\tau_{\mathrm{vis}} = \frac{\rho d^2}{\eta}$$

Timescale of momentum diffusion

$\dot{\gamma}(t) = \gamma_0 \omega \cos \omega t$



Structures in oscillatory shear flow

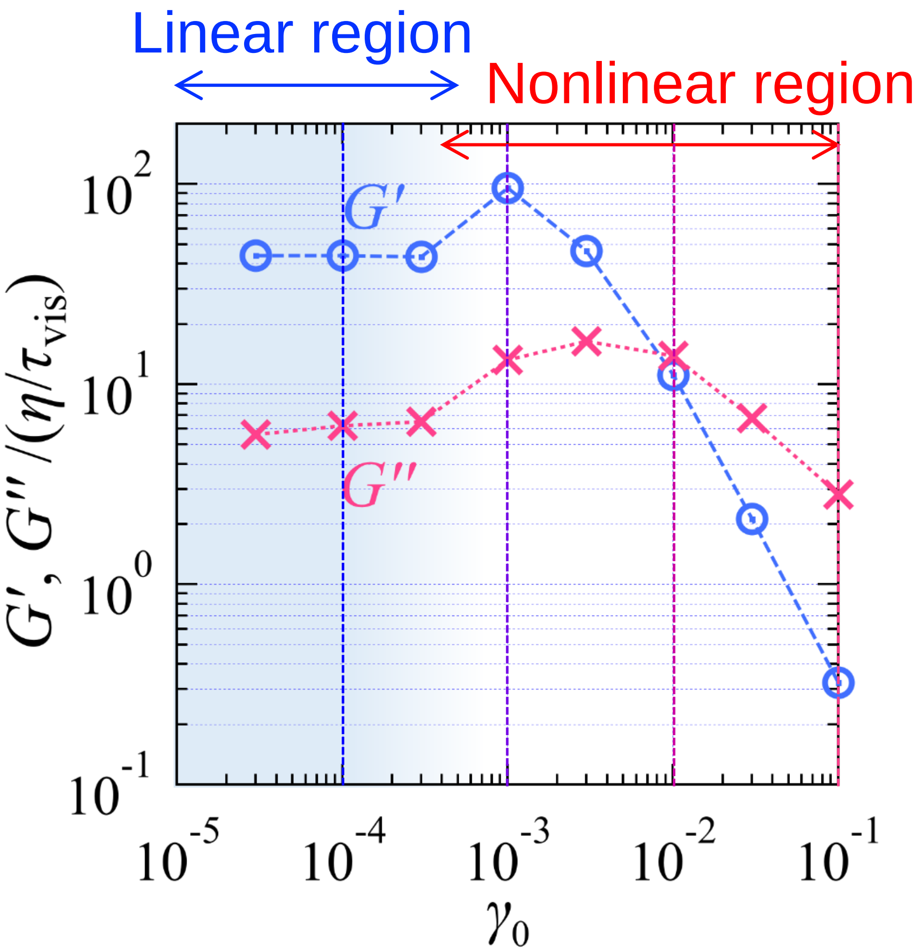


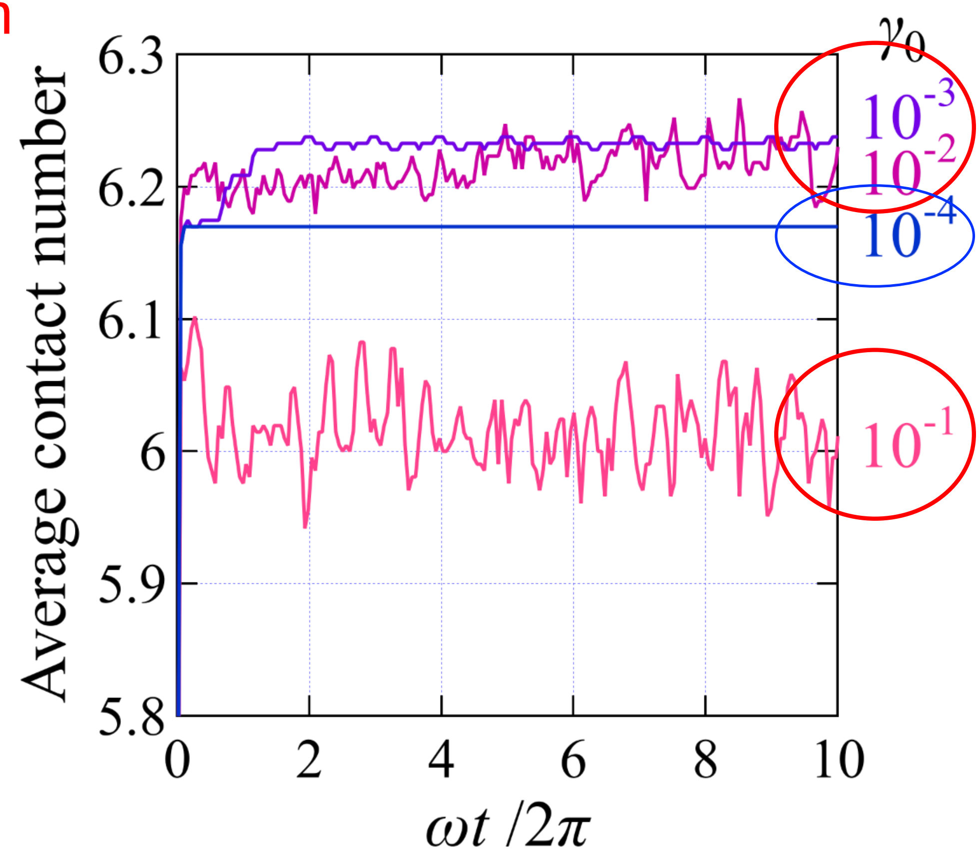
$\gamma_0 = 1.0 \times 10^{-4}$ $\gamma_0 = 1.0 \times 10^{-2}$

Strain dependence

$F^* = 4.2$

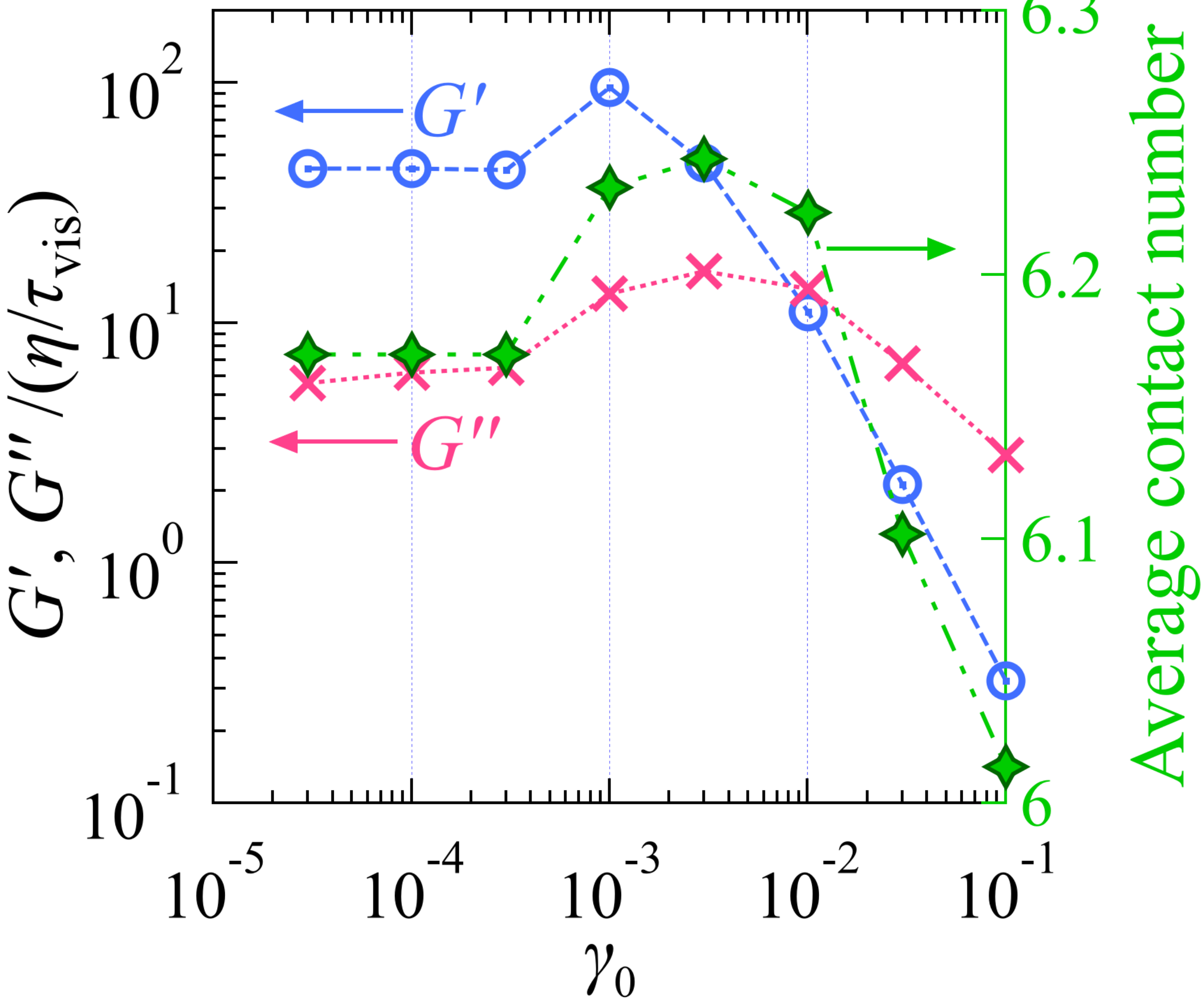
$\omega\tau_{\mathrm{vis}} = 0.1$





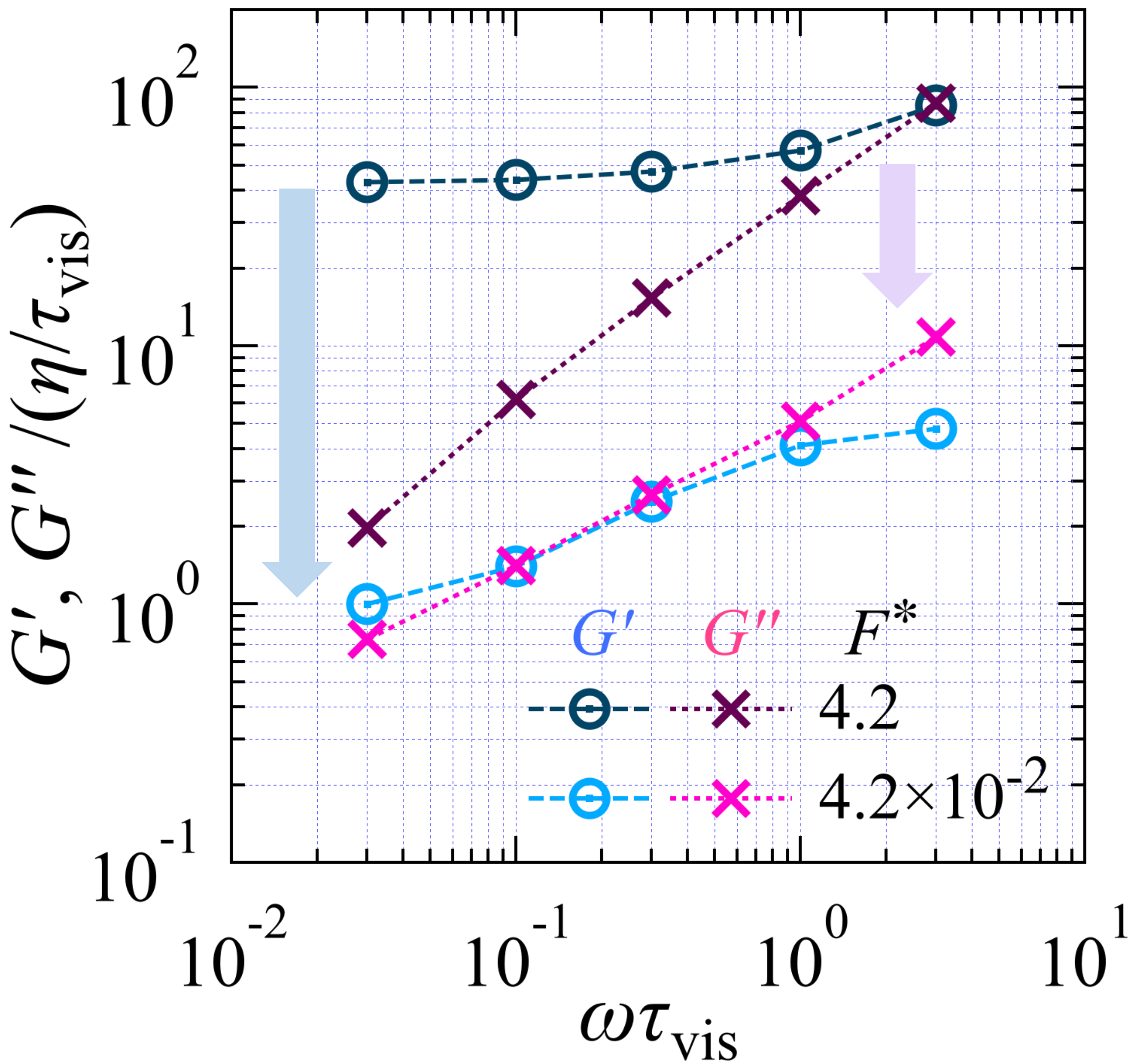
Linear region ← Little change in structure

Strain dependence



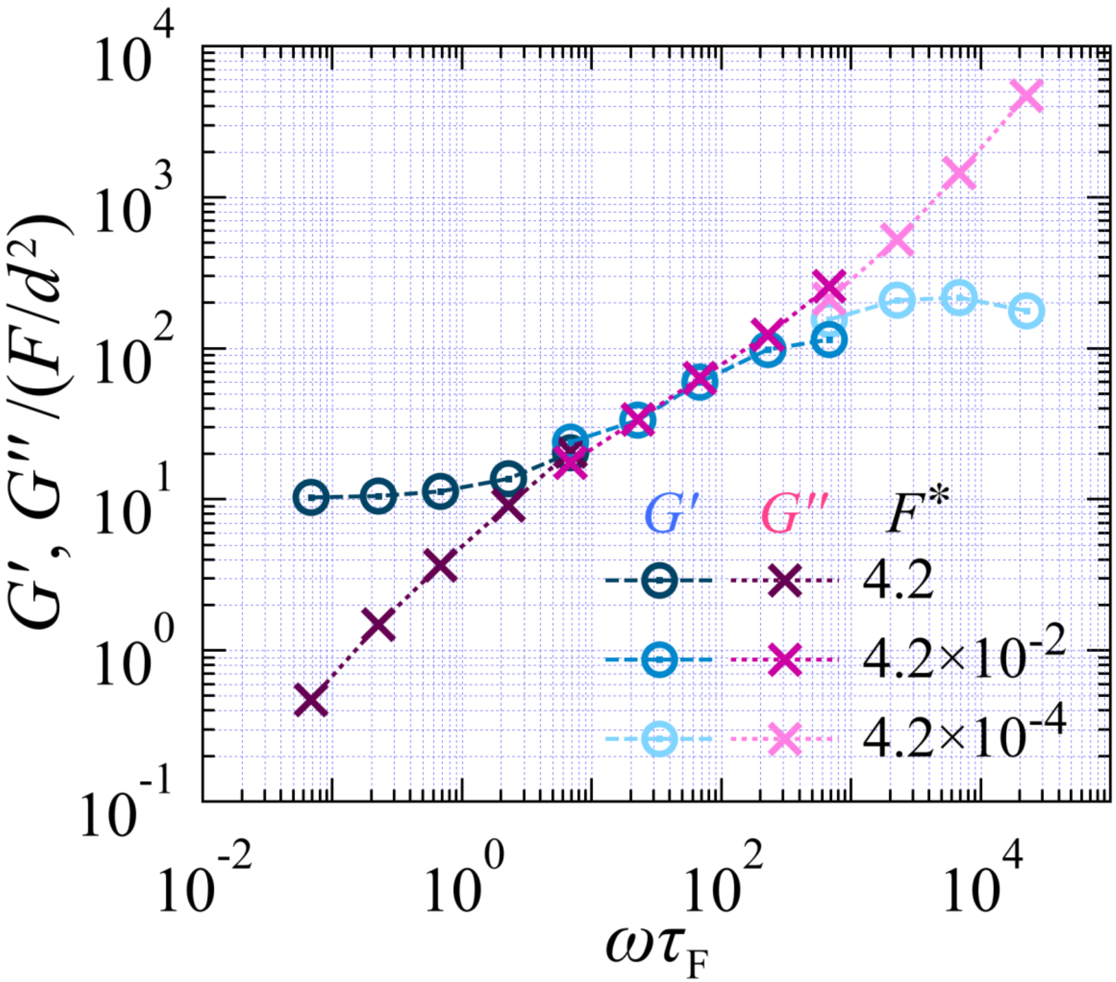
Effects of adhesive force

$\gamma_0 = 10^{-4}$



Frequency dependence

$\gamma_0 = 10^{-4}$



Adhesive force ~ Drag force

$$F \sim 3\pi\eta d U$$

Velocity of adhesion

$$U = \frac{F}{3\pi\eta d}$$

Relaxation time

$$\tau_F = \frac{d}{U} = \frac{3\pi\eta d^2}{F}$$

← Larger adhesive force, Lower frequency

Summary

- Direct numerical simulation of viscoelastic behavior of concentrated colloidal suspensions
- Calculation of dynamic modulus in oscillatory shear flow
- Strain dependence reflects the structure change of particles
- Frequency dependence reflects relaxation of particle motion by adhesive force
- Increasing frequency corresponds to decreasing adhesive force