SCEJ 88th Annual Meeting

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Dynamic modulus reflecting aggregation state in aqueous slurries

水系スラリーの分散・凝集状態が示す貯蔵／損失弾性率プロファイル

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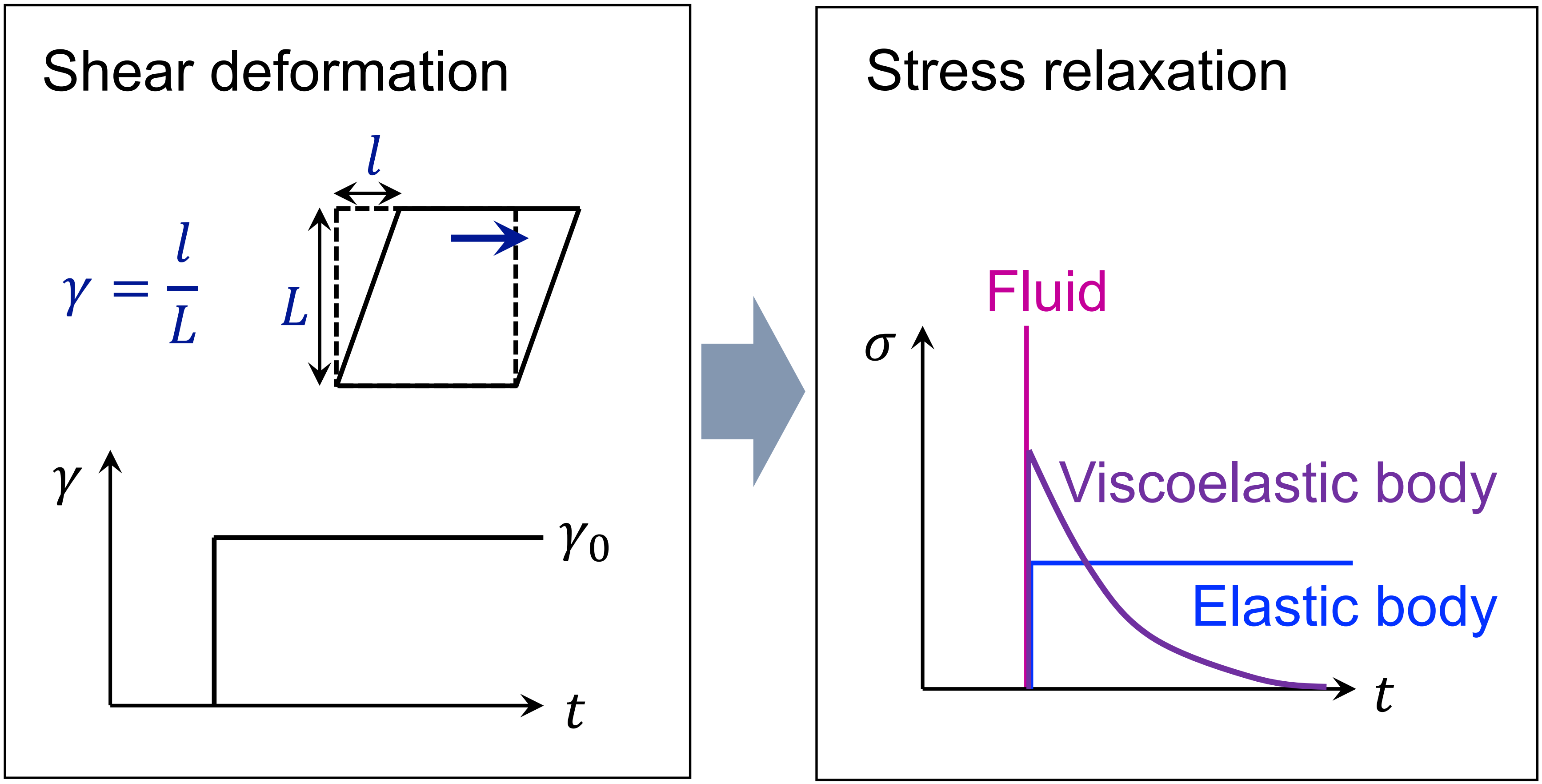
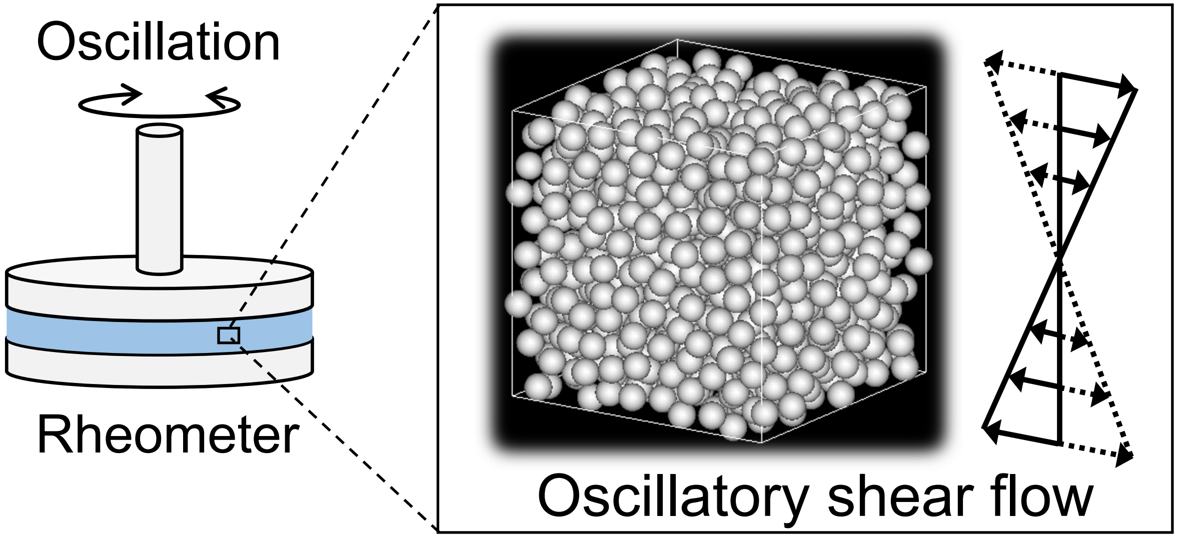
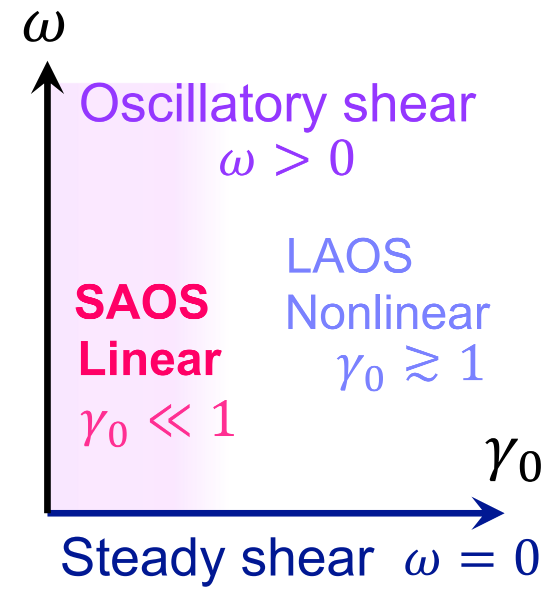
Viscoelasticity



Viscoelasticity





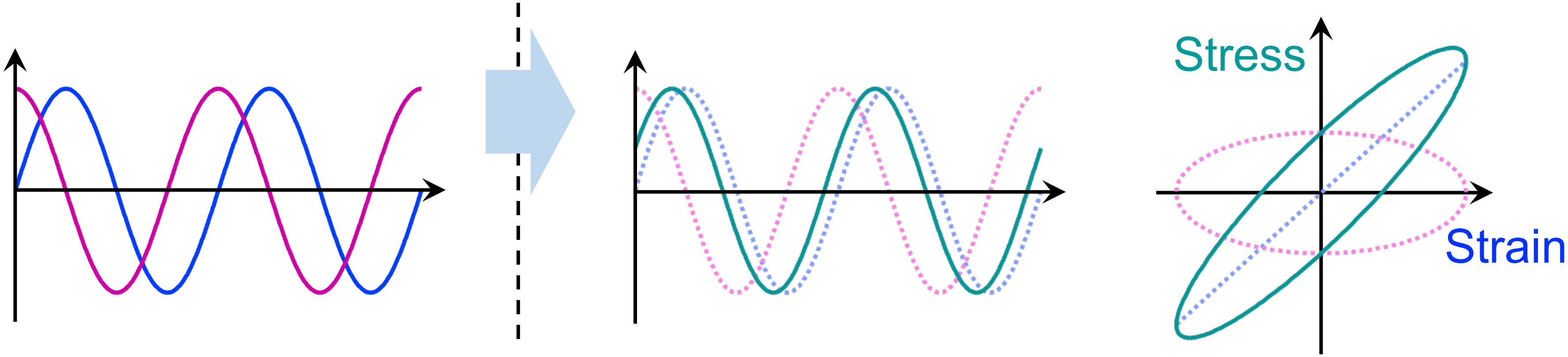
SAOS (Small Amplitude Oscillatory Shear; $\gamma_0 \ll 1$) → Linear response

Strain: $\gamma_0 \sin \omega t$

Shear rate: $\gamma_0 \omega \cos \omega t$

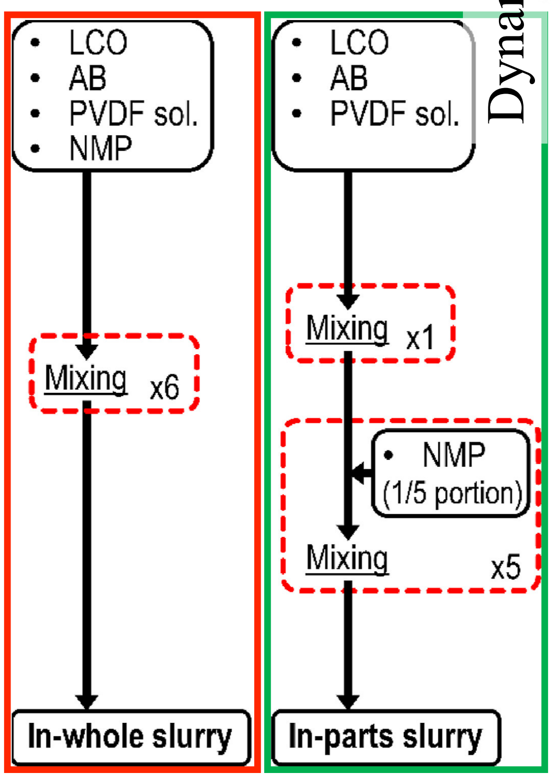
Stress: $\sigma_0 \sin(\omega t + \delta) = \gamma_0 (G' \sin \omega t + G'' \cos \omega t)$

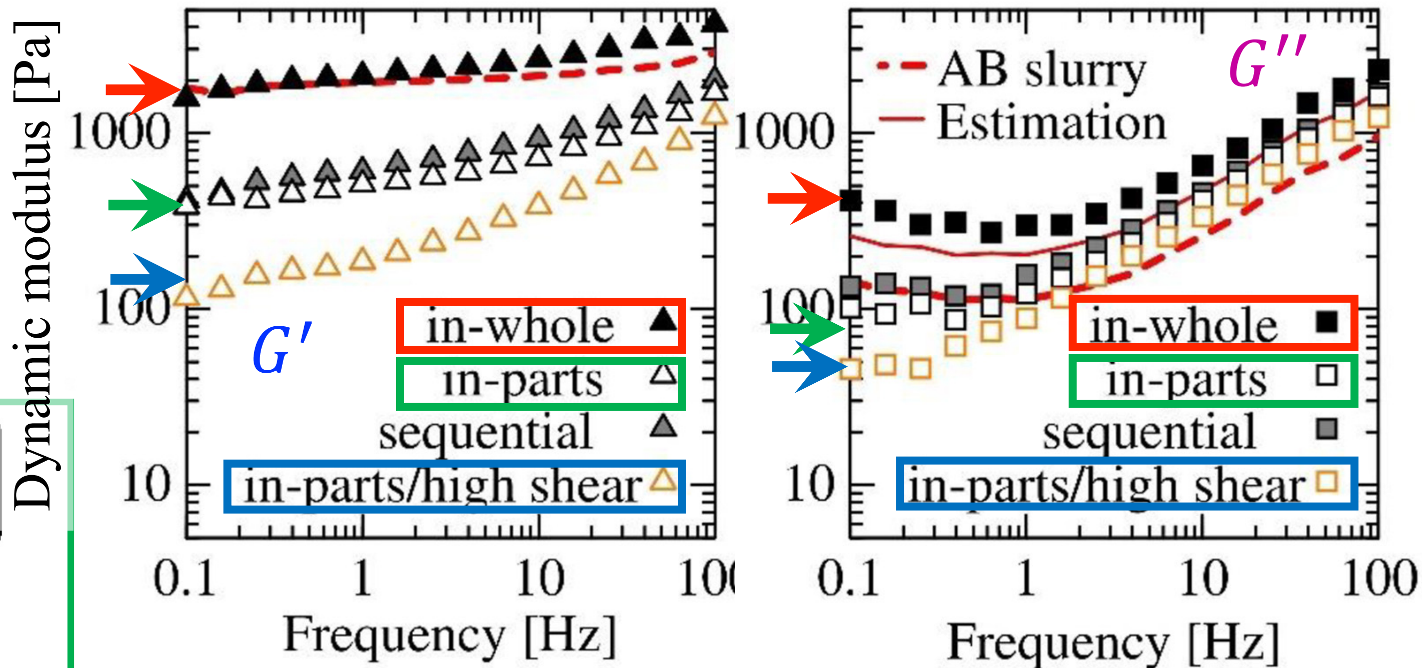
Storage modulus: G' Loss modulus: G''

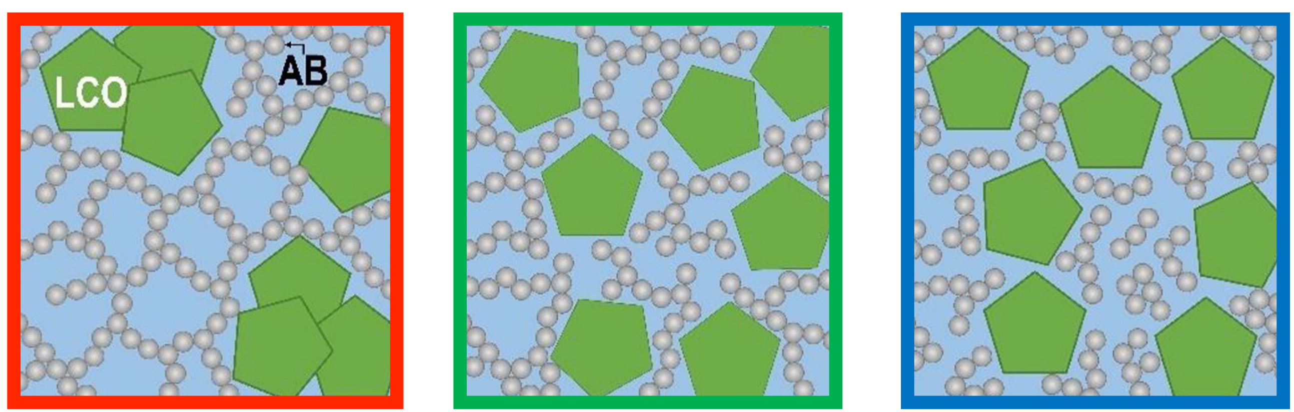


Structure estimation from viscoelasticity

Cathode slurry of LiB ($LiCoO_2$ + Acetylene black + NMP)



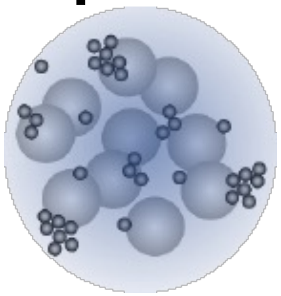


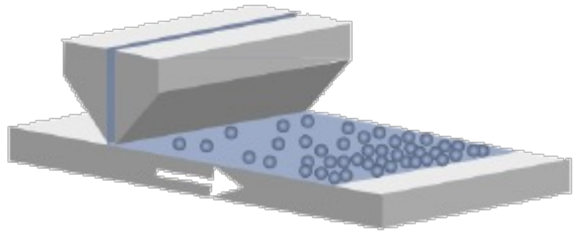


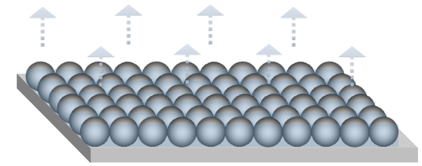
Komoda *et al.*, JCIS Open **5** 100038 (2022).

Material fabrication from suspensions

Suspensions **Functional materials**







Dispersing **Coating** **Drying**

Food Cosmetics Paint Electrode
Medicine Ceramics

- Dispersion/Aggregation

SAOS ($\gamma_0 \ll 1$)
Linear viscoelasticity

- Coating properties
- Structural change by shear flow

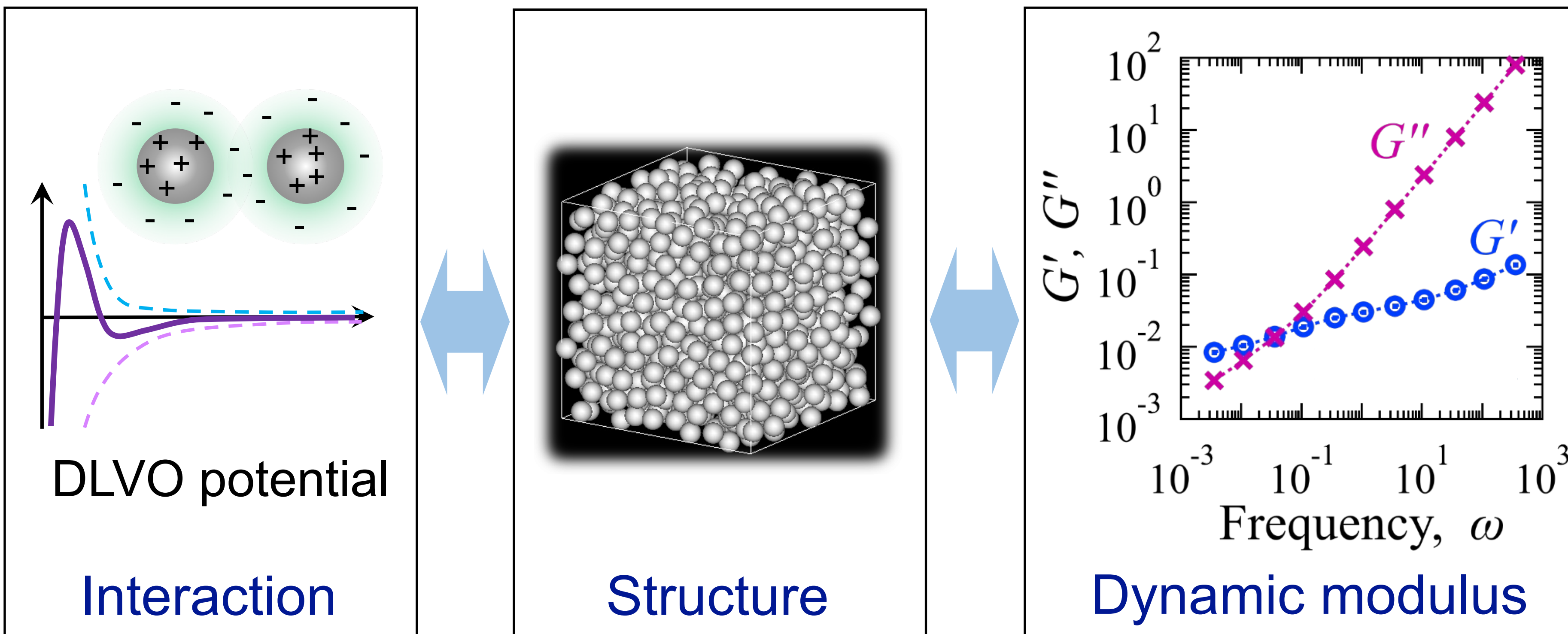
LAOS ($\gamma_0 \gtrsim 1$)
Nonlinear viscoelasticity

Viscoelasticity can be a measure to control fabrication processes

← Relationship among starting materials, structure, and viscoelasticity

Objective

- Performing numerical simulations of particle dynamics under oscillatory shear flow to calculate linear viscoelasticity
- Investigating the relationship between structure and linear viscoelasticity (dynamic modulus) by changing DLVO interactions between particles

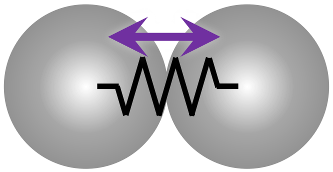


Motion of particles

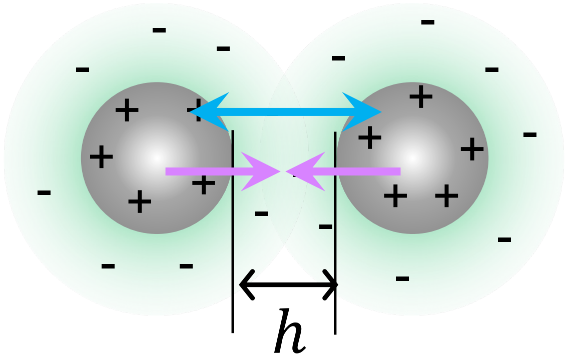
$$M\dot{\boldsymbol{V}} = \boldsymbol{F}^{\mathrm{H}} + \boldsymbol{F}^{\mathrm{P}}$$

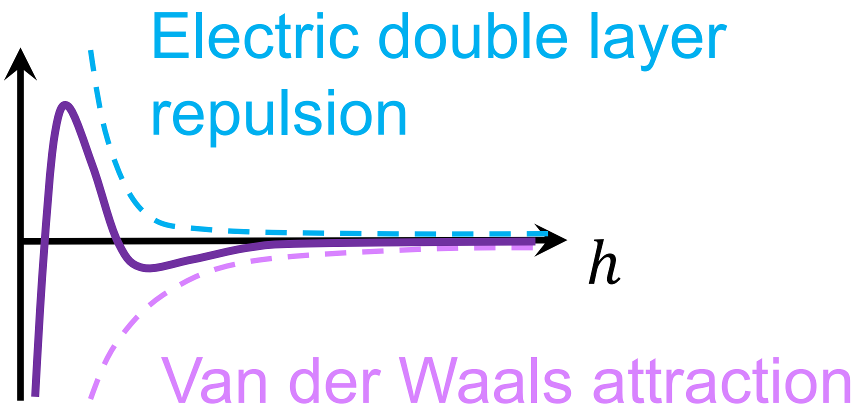
Fluid Inter-particle

- **Contact force**: $\boldsymbol{F}^{\mathrm{cnt}}$



- **DLVO force**: $\boldsymbol{F}^{\mathrm{DLVO}}$





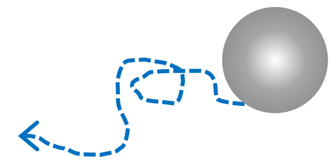
→ **Dispersion / Aggregation**

Motion of particles

$$M\dot{\boldsymbol{V}} = \boldsymbol{F}^{\mathrm{H}} + \boldsymbol{F}^{\mathrm{P}}$$

Numerical simulations in 2 steps

1. Structure formation : $\boldsymbol{F}^{\mathrm{H}} = -\zeta\boldsymbol{V} + \boldsymbol{F}^{\mathrm{R}}$



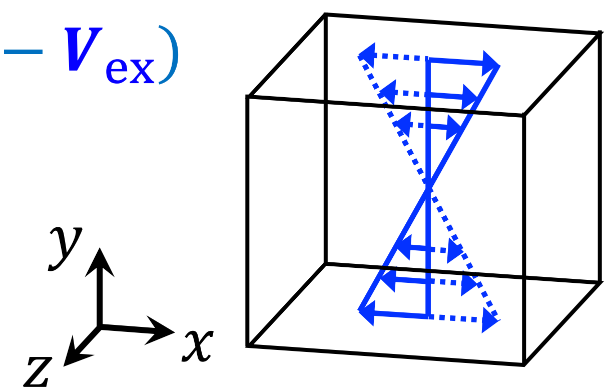
Brownian motion

- Drag: $-\zeta\boldsymbol{V}$ (Stokes' law)
- Fluctuations: $F_\alpha^{\mathrm{R}}(t) \sim N(0, 2\zeta k_{\mathrm{B}} T \Delta t)$ (Gaussian noise)

2. Rheological evaluation : $\boldsymbol{F}^{\mathrm{H}} = -\zeta(\boldsymbol{V} - \boldsymbol{V}_{\mathrm{ex}})$

- Oscillatory shear flow

$\boldsymbol{V}_{\mathrm{ex}} = \dot{\gamma}(t) y\, \boldsymbol{e}_x \quad \dot{\gamma}(t) = \gamma_0 \omega \cos \omega t$



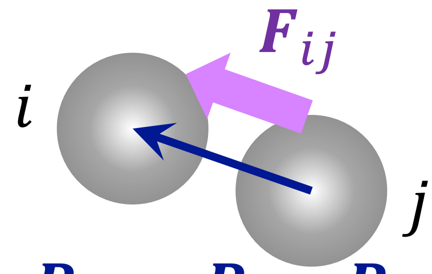
- Boundary conditions: Periodic (x, z), Lees-Edwards (y)

Rheological evaluation

Stress

$$\sigma = \sigma_\mathrm{f} + \sigma_\mathrm{p} = \eta_\mathrm{f}(\phi)\dot{\gamma} - \frac{1}{V}\sum_{i<j} F_{ij}^{x} R_{ij}^{y}$$

Fluid Particle



$$\boldsymbol{R}_{ij} = \boldsymbol{R}_i - \boldsymbol{R}_j$$

$$\eta_\mathrm{f}(\phi) = \eta_0\left(1 + \frac{5}{2}\phi\right)$$ (Einstein's eq.)

Dynamic modulus

- Storage modulus

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

- Loss modulus

$$G''(\omega) = \frac{\omega}{\pi\gamma_0}\int_0^{2\pi/\omega} \sigma(t)\cos\omega t\,\mathrm{d}t = \eta_\mathrm{f}(\phi)\omega + G''_\mathrm{p}$$

Simulation conditions

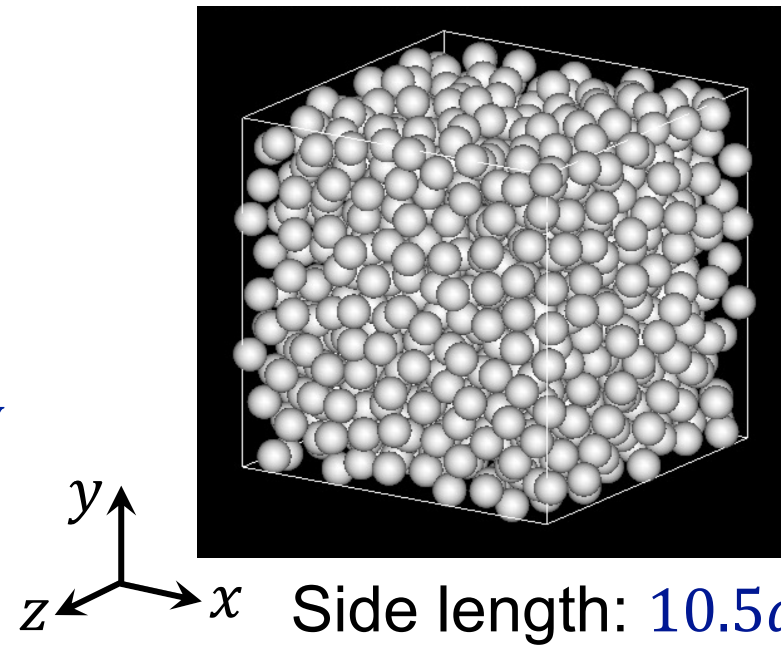
Step-1: Structure formation

Particles

- Diameter: $d = 100$ nm
- Concentration: 45 vol%
- Zeta potential: 0, −20, −28 mV

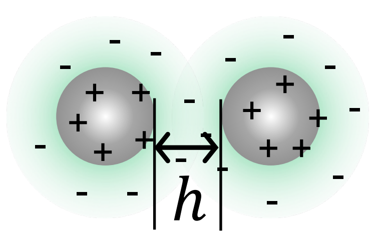
Fluid: Water

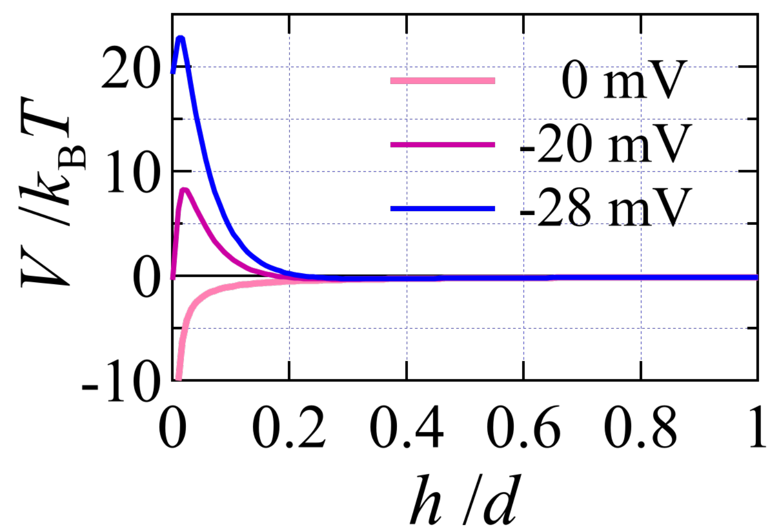
- Ion concentration : 3.8 mM



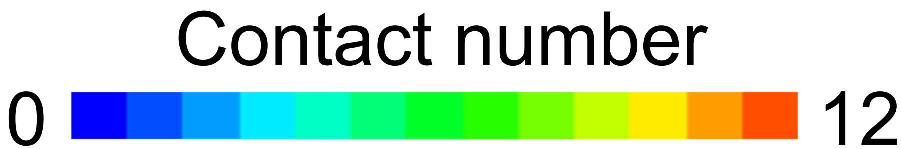
Side length: $10.5d$

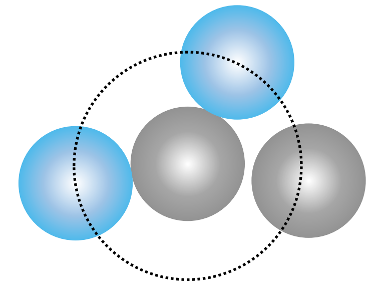
DLVO potential

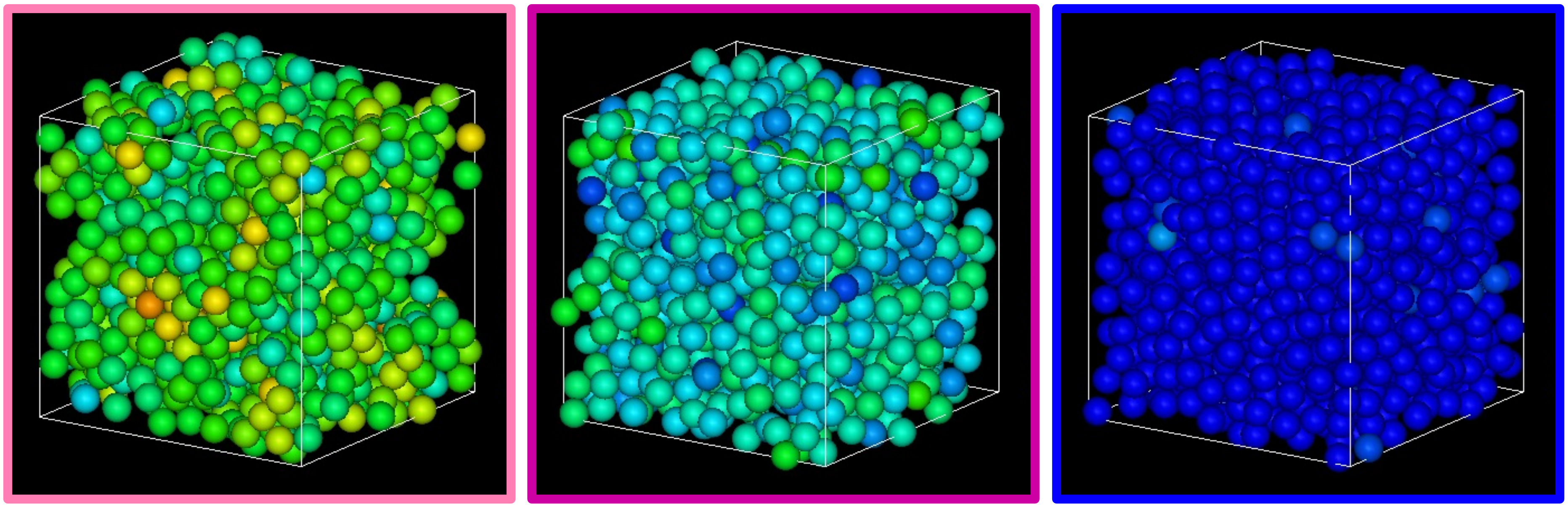




Structure







Zeta potential /mV	0	-20	-28
Average contact number	6.8	3.7	0.0

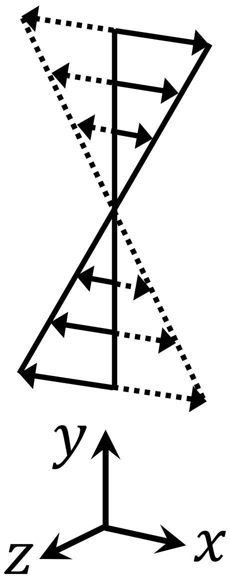
Simulation conditions

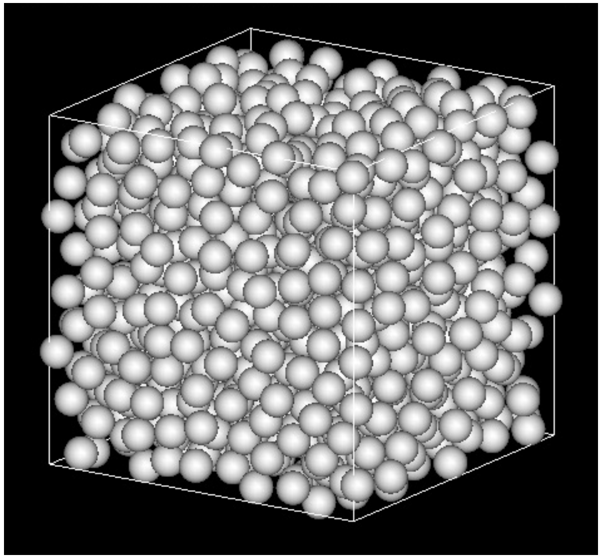
Step-2: Rheological evaluation

Shear flow

- Strain: $\gamma_0 = 1\times10^{-2}$
- Frequency:

$$\omega\tau = 3\times10^{-3} - 10^{3}$$





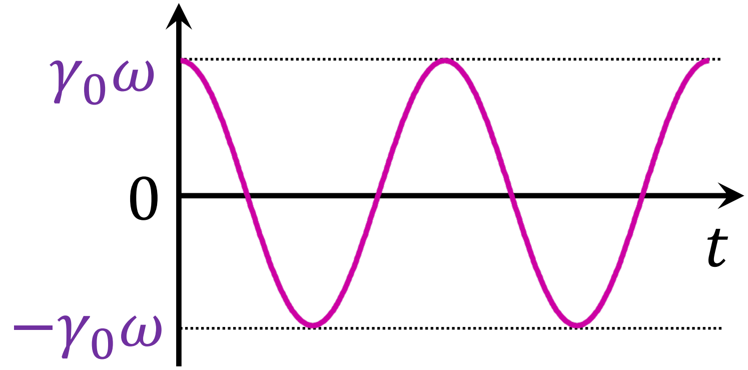
Side length: $10.5d$

Relaxation time

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

Drag force = Adhesive force

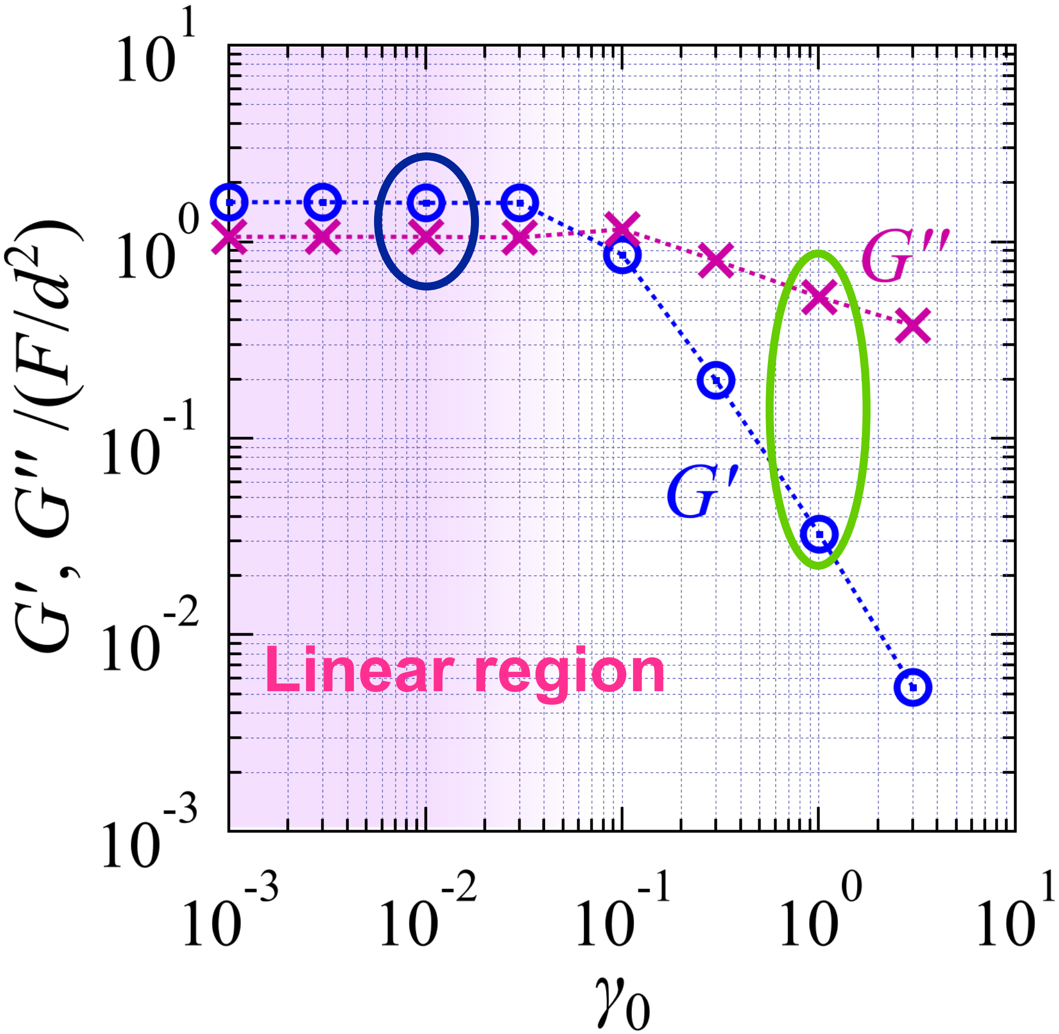
Shear rate: $\dot{\gamma}(t) = \gamma_0\omega\cos\omega t$

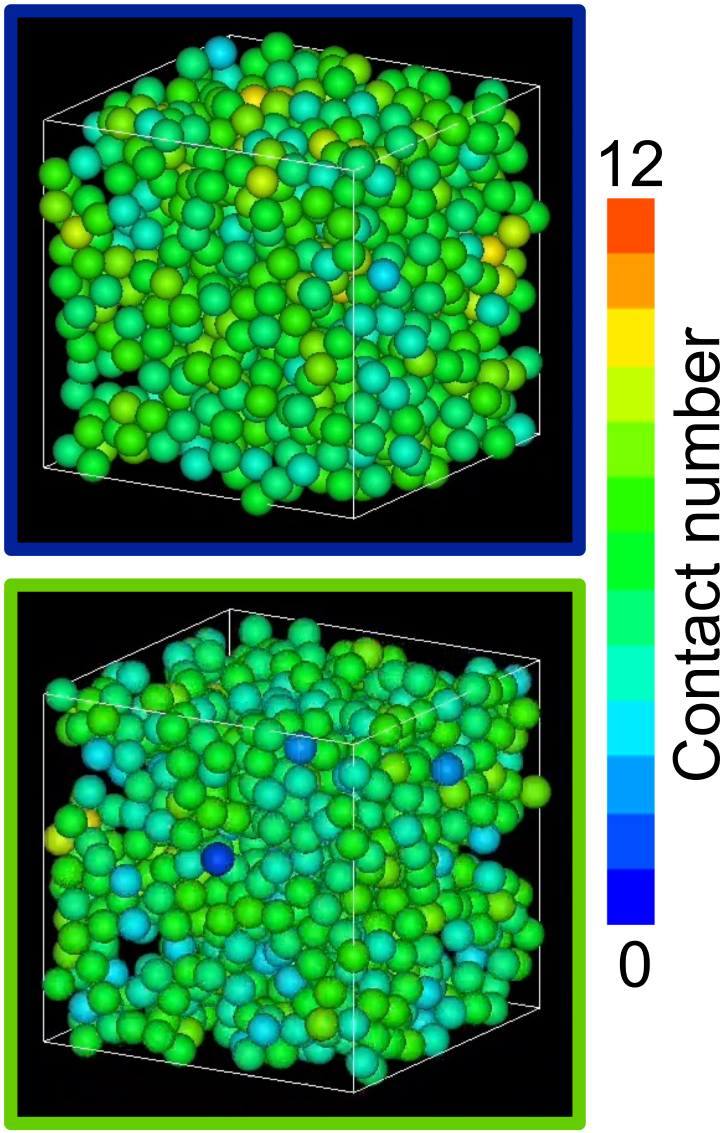


Strain dependence

0 mV

$\omega\tau = 1.2$

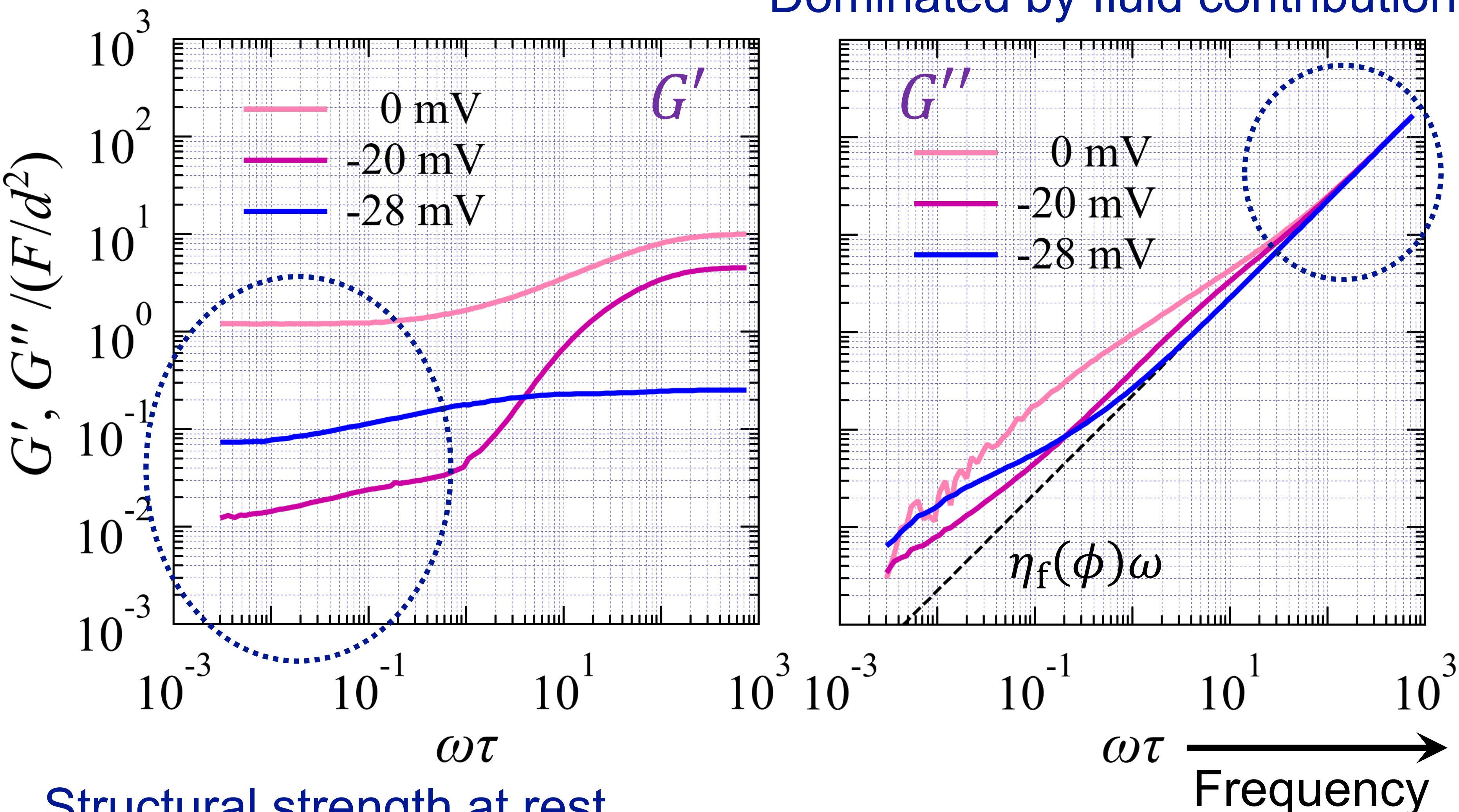




Strain amplitude

Dynamic modulus

Dominated by fluid contribution



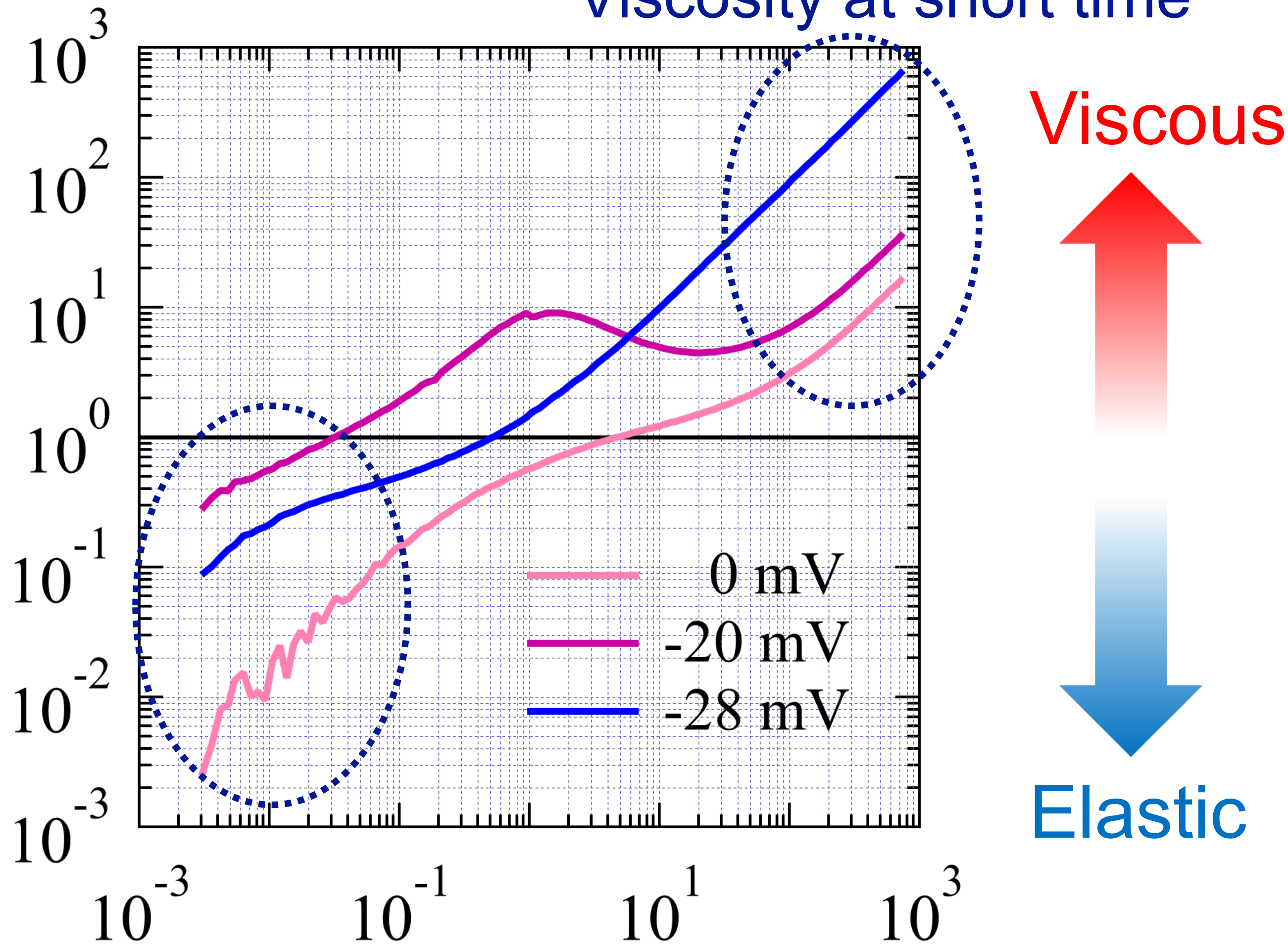
Structural strength at rest

Structure maintained by attraction (0, −20 mV) / repulsion (−28 mV)

Dynamic modulus

$\tan\delta = G''/G'$

Coating fluidity:
Viscosity at short time



Shape retention:
Elasticity at long time

$\omega\tau$ → Frequency

Summary

- Numerical simulations show dynamic modulus reflecting structure formed by DLVO potentials
- Non-monotonic dependence of dynamic modulus on the degree of aggregation at low frequency
- The non-monotonic dependence is to be noted in rheological control