SCEJ 54th Autumn Meeting
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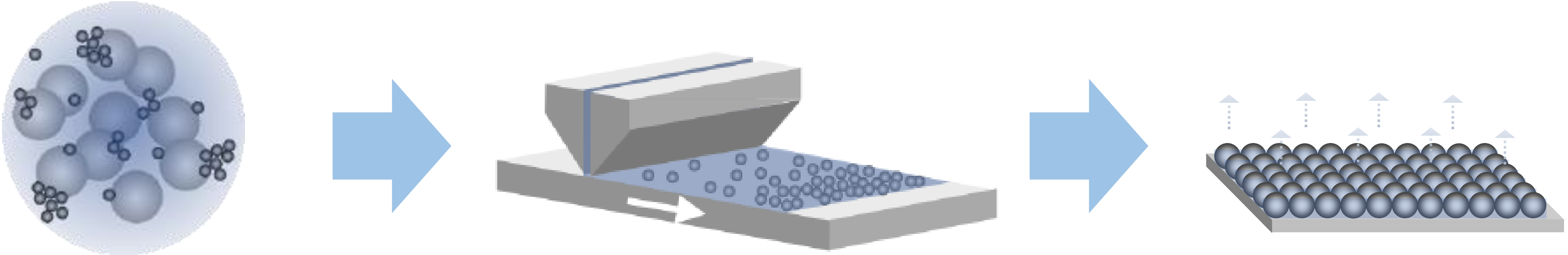
Viscoelastic analysis of structural change in slurry during mixing

混練によるスラリーの構造変化の粘弾性解析

○ 辰巳 怜 （PIA）
小池 修 （PIA）
山口 由岐夫 （PIA）
辻 佳子 （東大環安セ/東大院工）

Material fabrication from suspensions



Dispersing **Coating** **Drying**

Food Cosmetics Paint

Medicine

Electrode

Ceramics

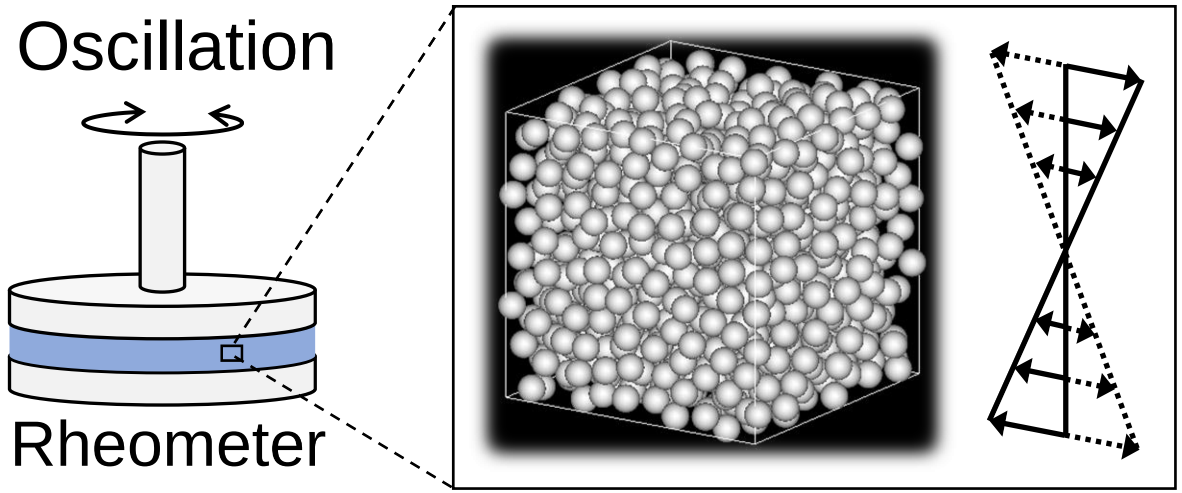
- Dispersion/Aggregation

- Coating properties
- Structural change by shear flow

Rheological properties: Viscosity, Viscoelasticity

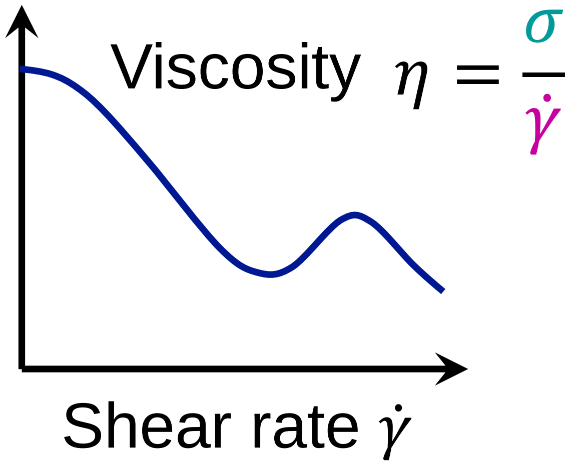
Rheological properties

(A) Rotation
(B) Oscillation



Shear rate $\dot{\gamma}$ ↔ Stress σ

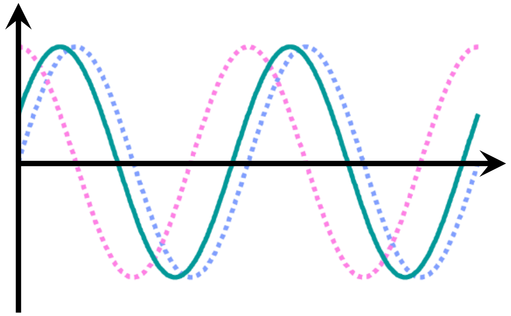
(A) Steady shear



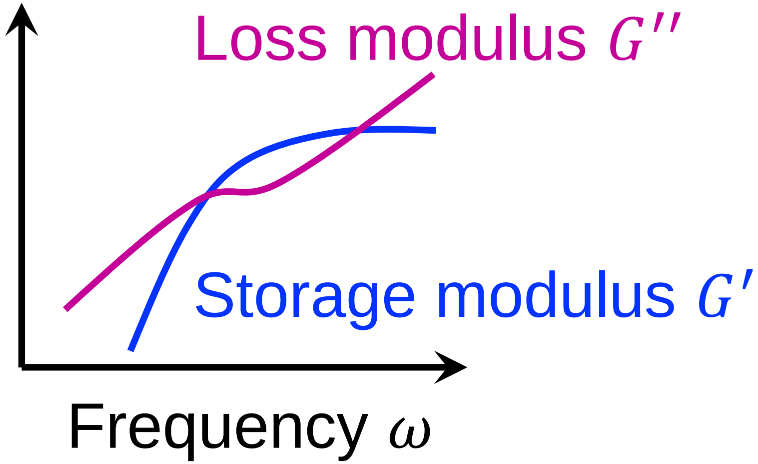
(B) Oscillatory shear

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

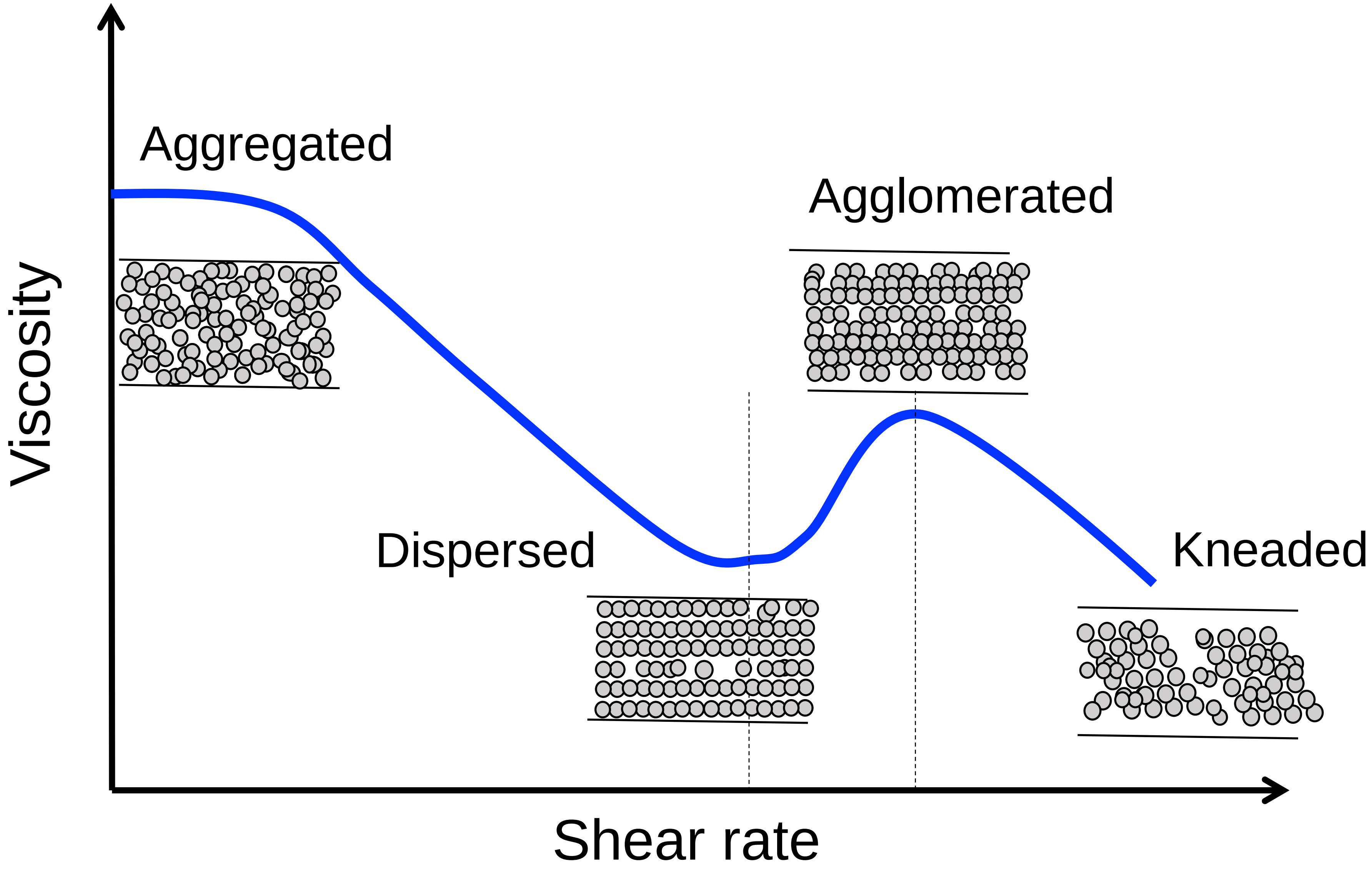
$$\dot{\gamma}(t) = \gamma_0 \omega \cos \omega t$$



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



Shear thinning/thickening



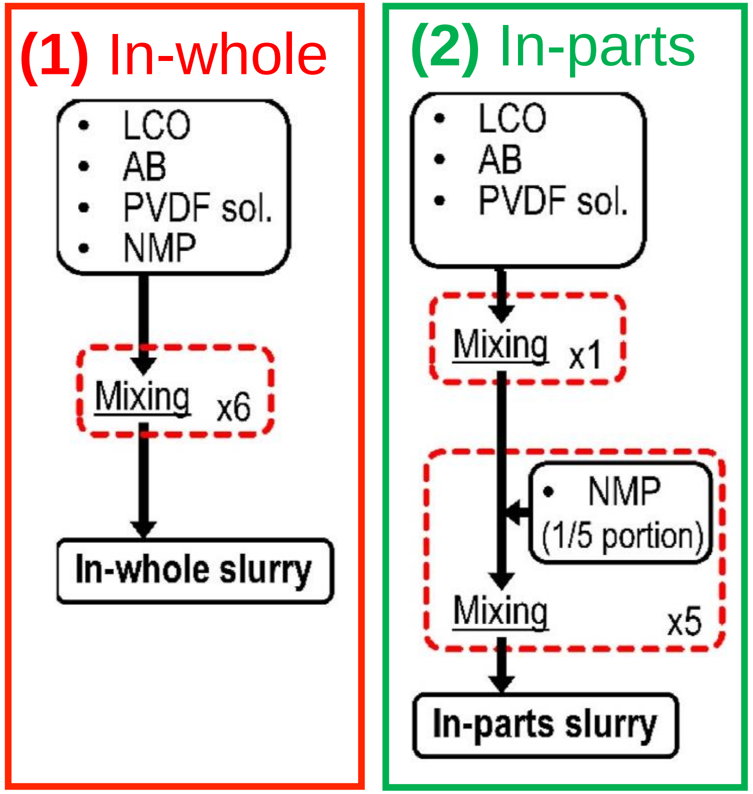
山口 由岐夫 「ものづくりの化学工学」, 丸善 (2015).

Structure estimation from viscoelasticity

Cathode slurry of LiB

(LiCoO$_2$ + Acetylene black + NMP)

Preparation process



(1) In-whole

- LCO
- AB
- PVDF sol.
- NMP

Mixing x6

In-whole slurry

(2) In-parts

- LCO
- AB
- PVDF sol.

Mixing x1

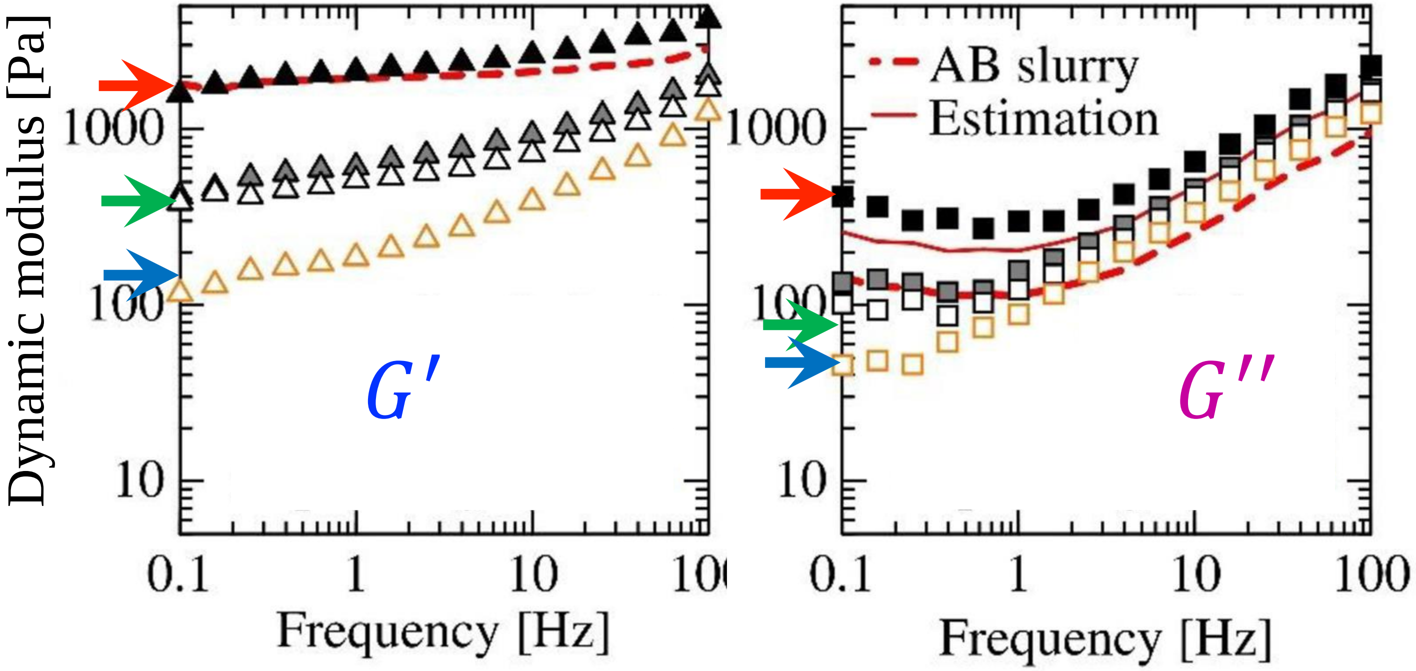
- NMP (1/5 portion)

Mixing x5

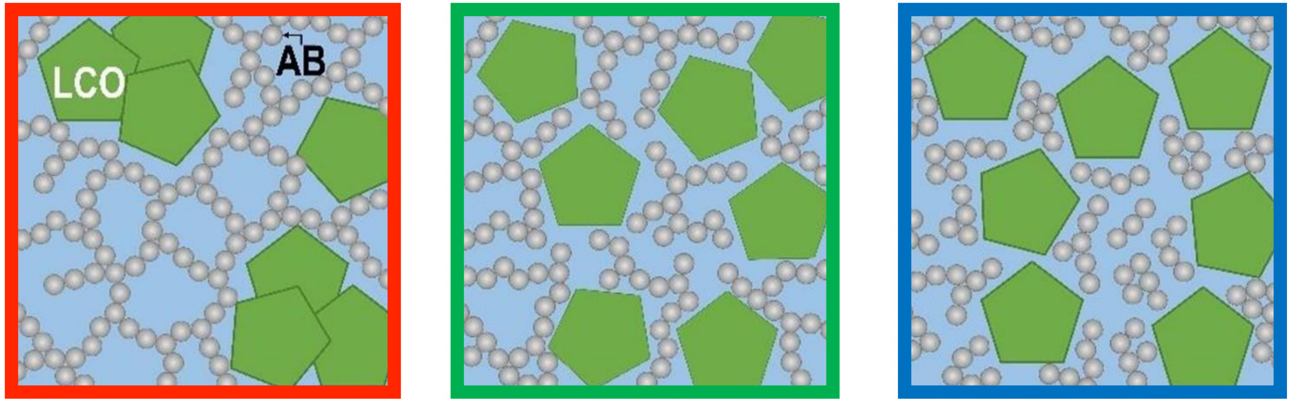
In-parts slurry

(3) (2) + high shear

Viscoelastic behavior

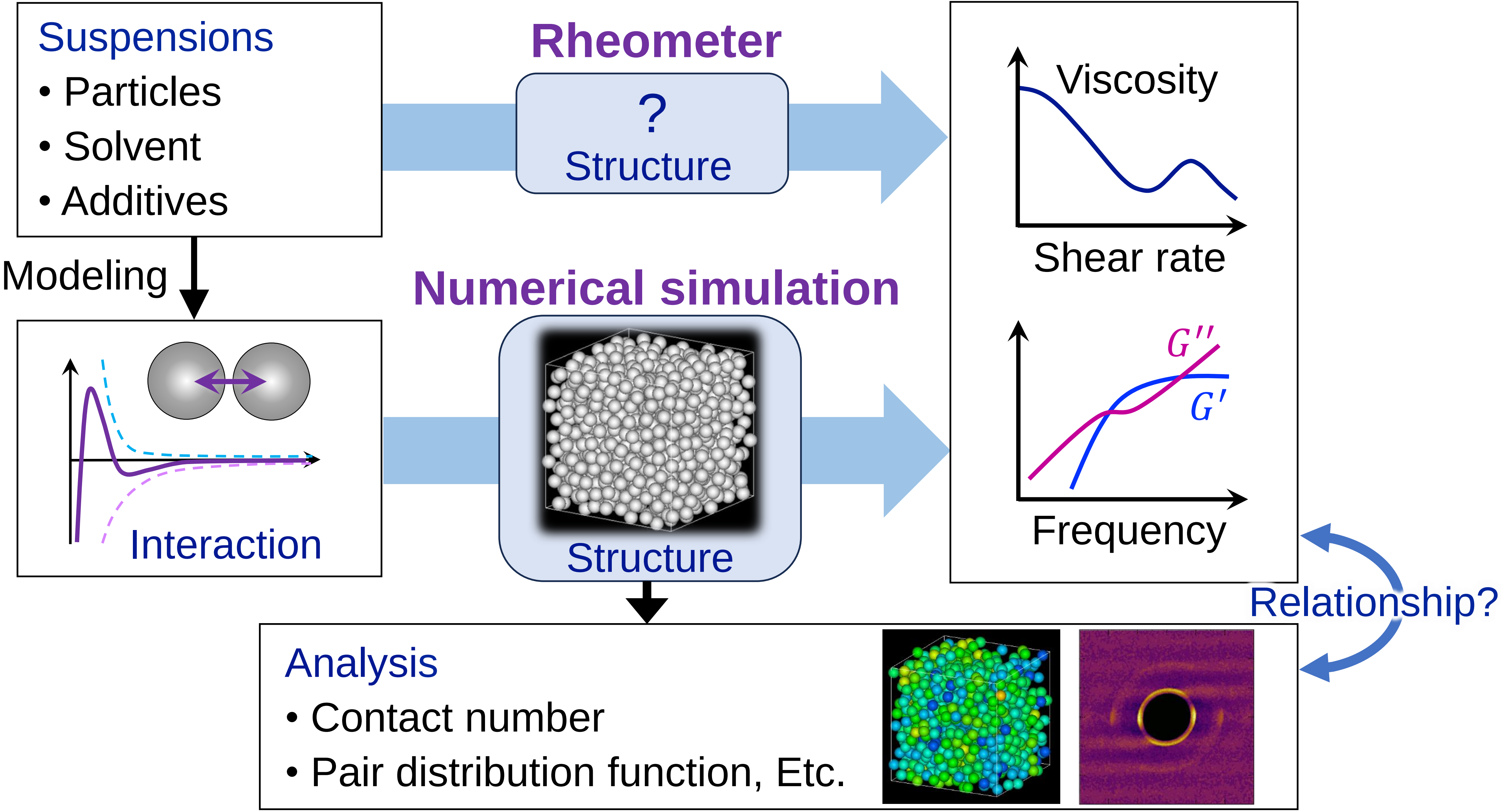


Structure



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

Objective & Method



Suspensions

- Particles
- Solvent
- Additives

Modeling

Rheometer

?

Structure

Numerical simulation

Structure

Relationship?

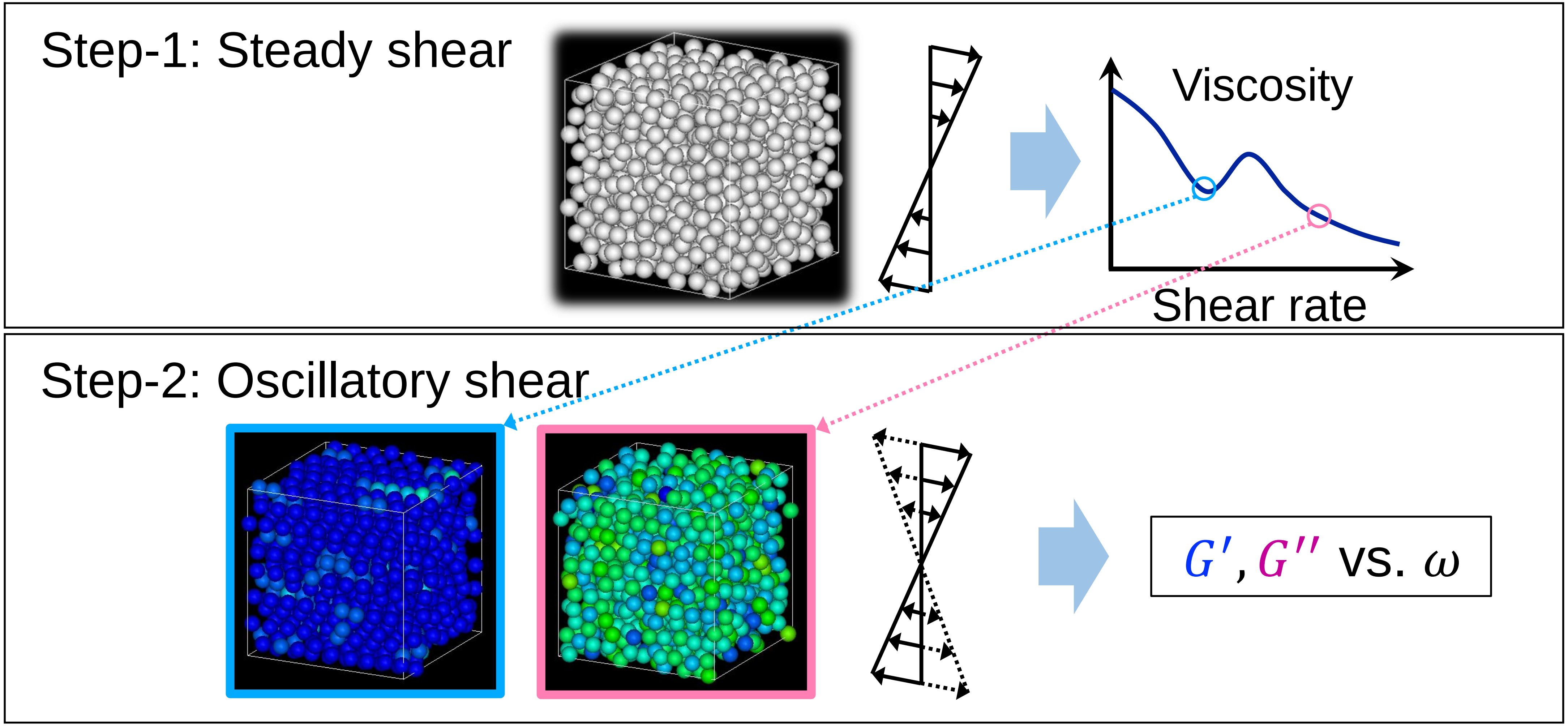
Analysis

- Contact number
- Pair distribution function, Etc.

Objective & Method

Viscoelastic analysis of structural change under shear flow

Numerical simulation



Step-1: Steady shear

Step-2: Oscillatory shear

G', G'' vs. ω

Motion of particles

$$m\dot{\boldsymbol{v}} = \boldsymbol{F}^{\mathrm{H}} + \boldsymbol{F}^{\mathrm{cnt}} + \boldsymbol{F}^{\mathrm{DLVO}}$$

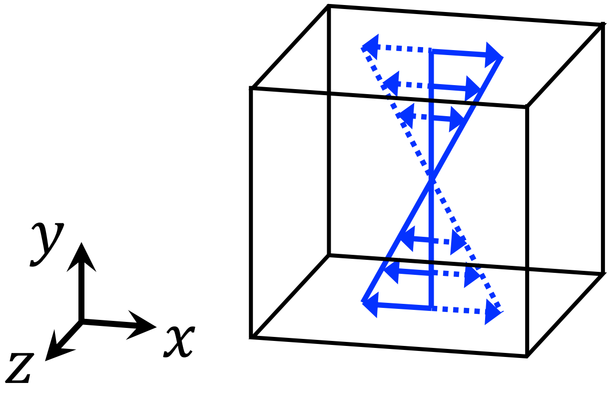
Fluid Inter-particle

- **Drag**: $\boldsymbol{F}^{\mathrm{H}} = -\zeta(\boldsymbol{v} - \boldsymbol{V}_{\mathrm{ex}})$ (Stokes' law)

- Shear flow

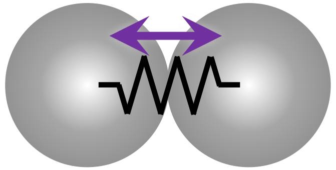
$$\boldsymbol{V}_{\mathrm{ex}} = \dot{\gamma}(t) y\, \boldsymbol{e}_x$$

$$\dot{\gamma}(t) = \dot{\gamma}_0 \cos \omega t$$

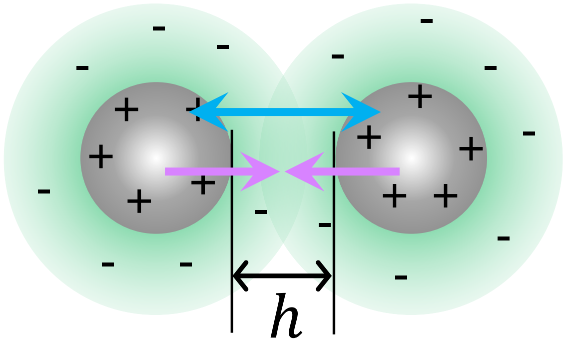


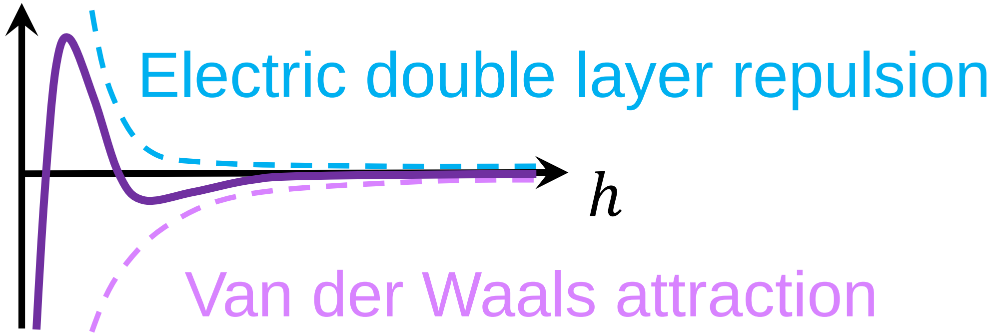
- Boundary conditions:
  Periodic (x, z), Lees-Edwards (y)

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



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





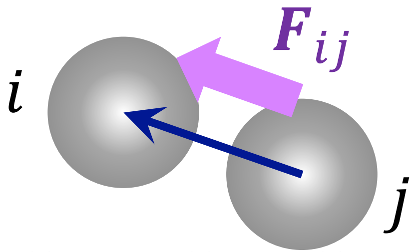
Rheological evaluation

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



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

$$\eta_\mathrm{f}(\phi) = \eta_0\left(1 + \frac{5}{2}\phi\right)$$

Viscosity (Steady shear)

$$\eta = \frac{\sigma}{\dot{\gamma}} = \eta_\mathrm{f}(\phi) + \eta_\mathrm{p}$$

Dynamic modulus (Oscillatory shear)

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

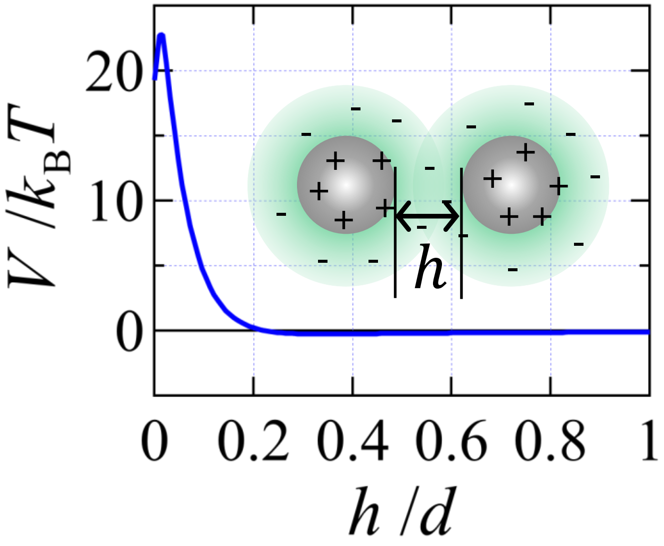
Particles

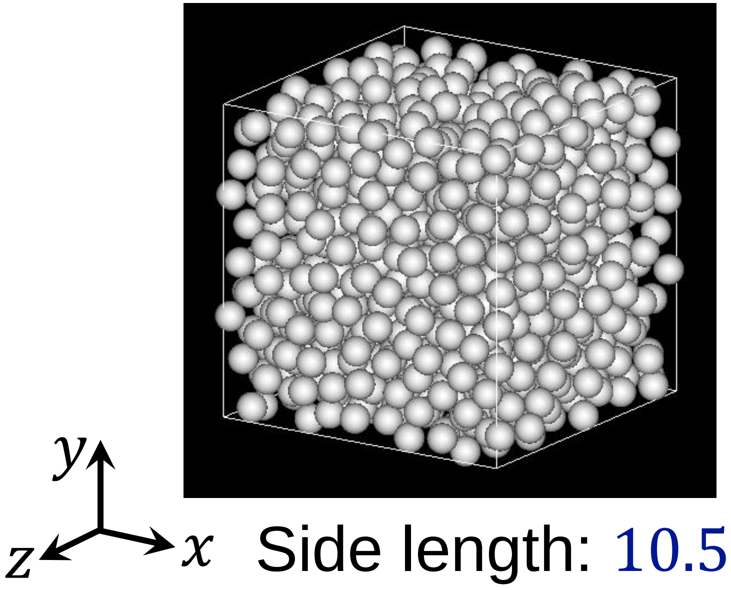
- Diameter: $d = 100\ \mathrm{nm}$
- Concentration: $45\ \mathrm{vol\%}$
- Zeta potential: $-28\ \mathrm{mV}$

Solvent: Water

- Ion concentration: $3.8\ \mathrm{mM}$

DLVO potential



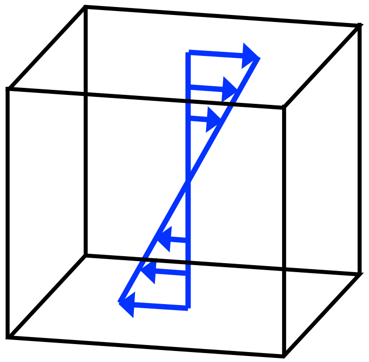


Side length: $10.5d$

Step-1: Steady shear

- Shear rate :

$$\dot{\gamma}\tau = 10^{-3} - 10$$

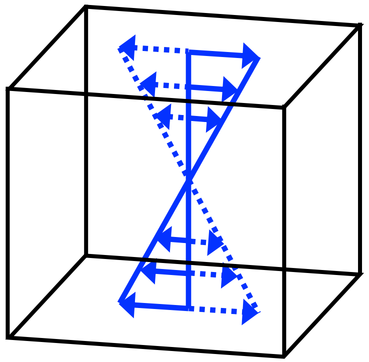


Structural change

Step-2: Oscillatory shear

- Strain: $\gamma_0 = 1 \times 10^{-2}$
- Frequency:

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



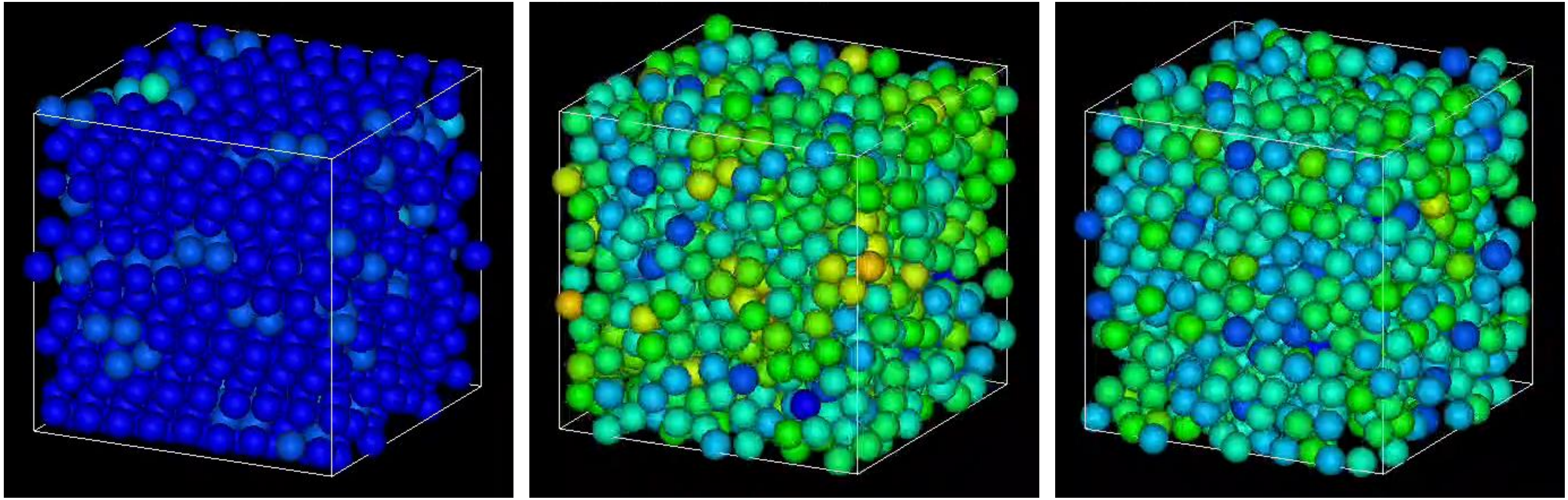
Viscoelastic analysis

Step-1: Structural change under shear flow

Characteristic time

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

Drag = Adhesion force



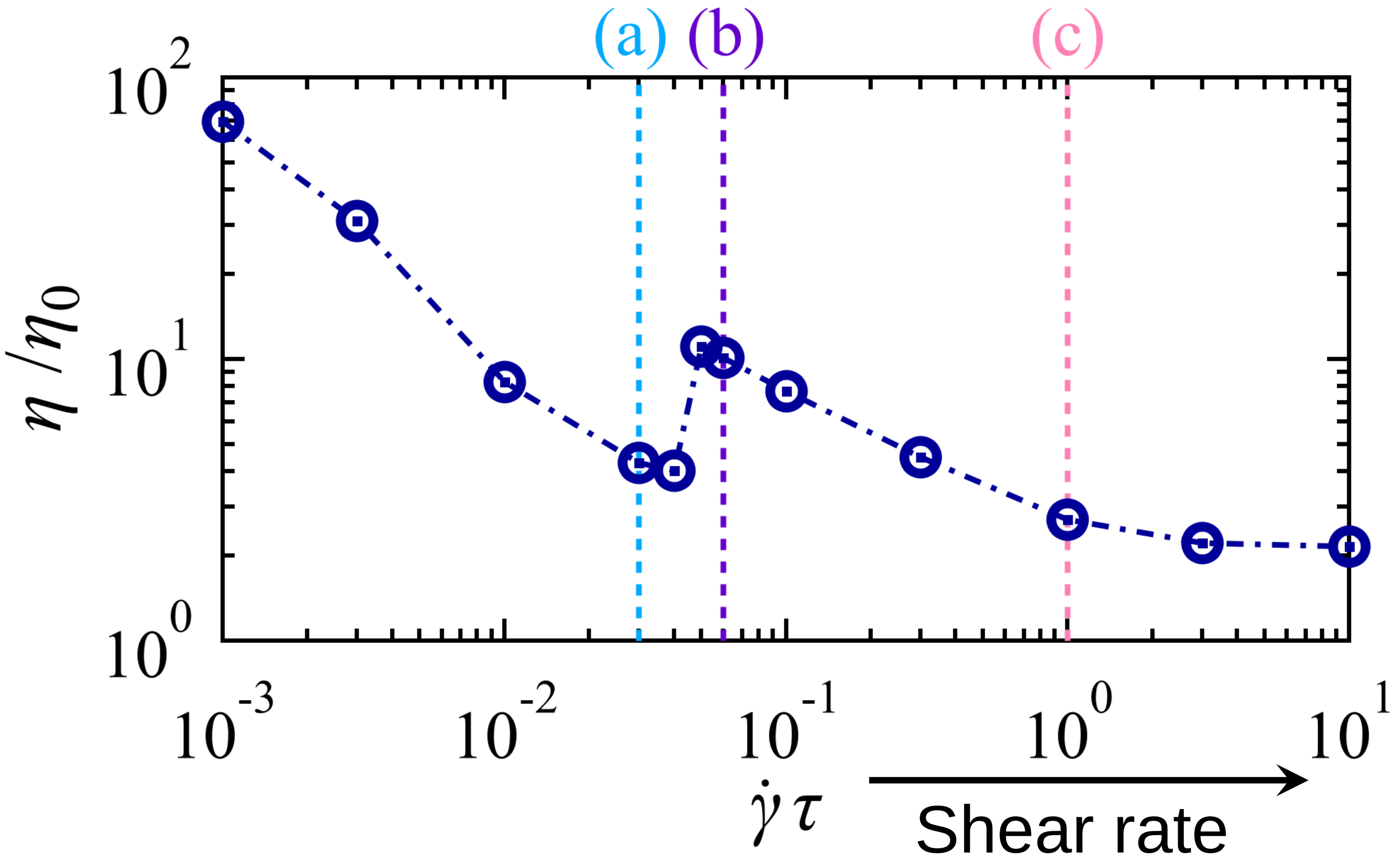
(a) $\dot{\gamma}\tau = 0.03$

(b) $\dot{\gamma}\tau = 0.06$

(c) $\dot{\gamma}\tau = 1$

$\longrightarrow$ Shear rate

Viscosity

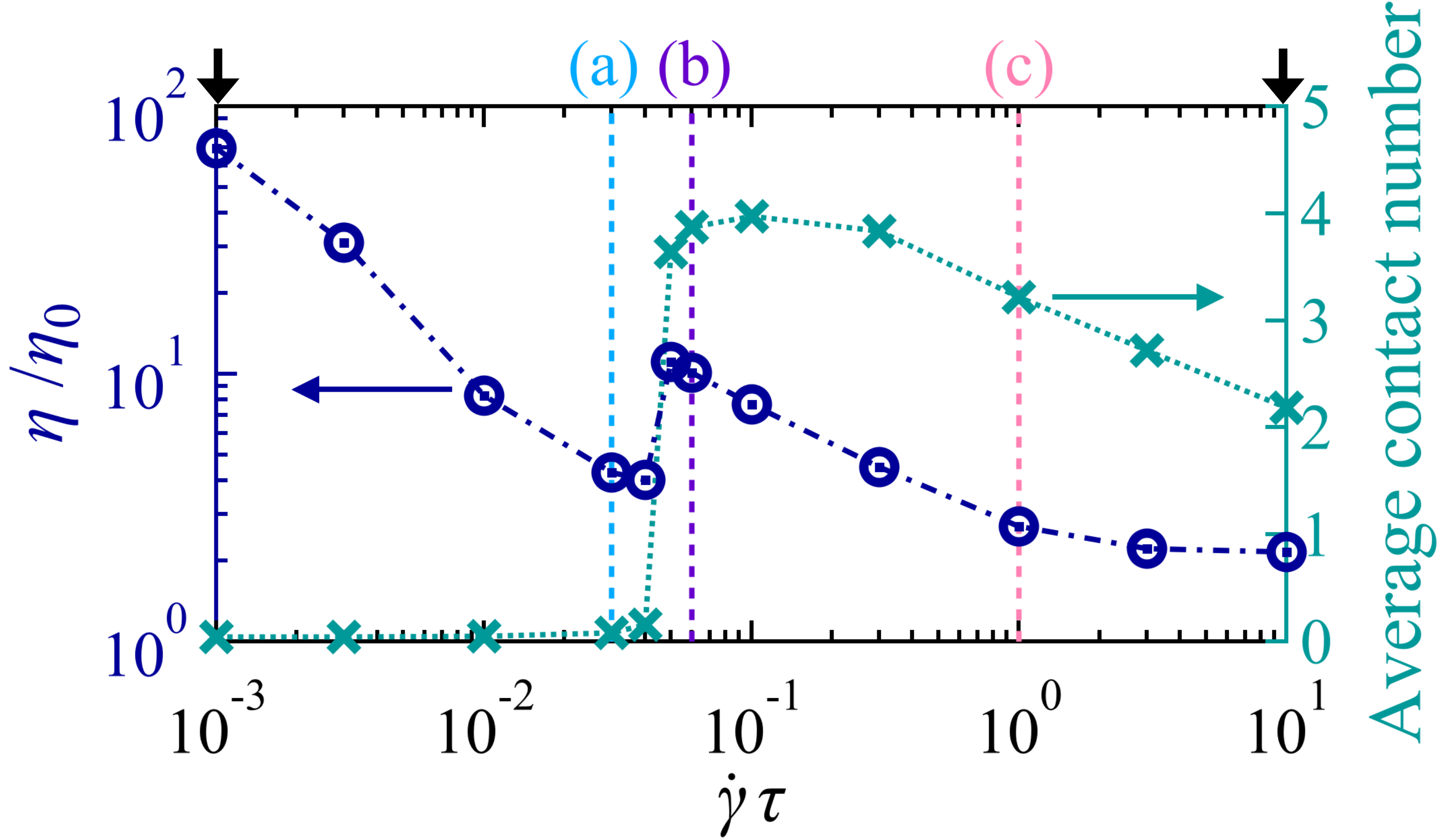


Dimensionless shear rate

$$\dot{\gamma}\tau = \frac{3\pi\eta\dot{\gamma}d^2}{F}$$

$$= \frac{\text{(Shear force)}}{\text{(Adhision force)}}$$

Structure

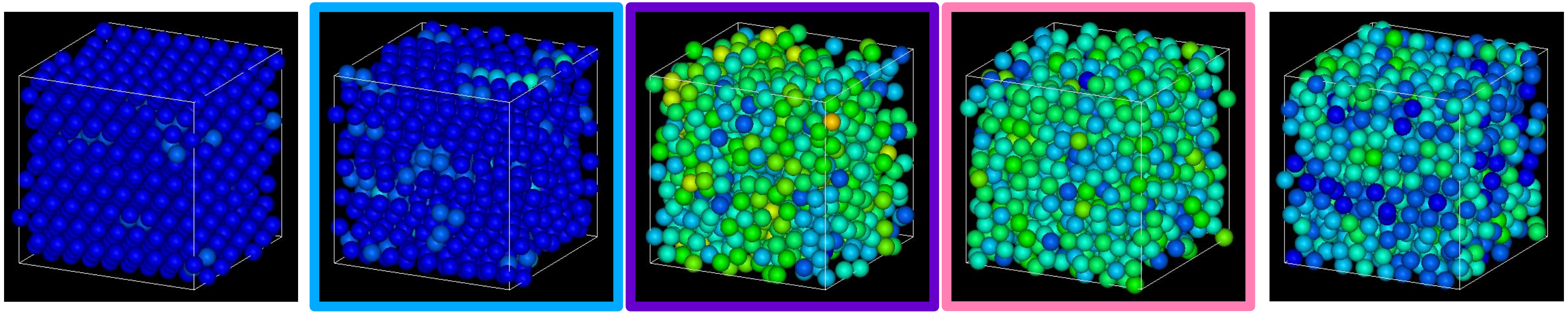


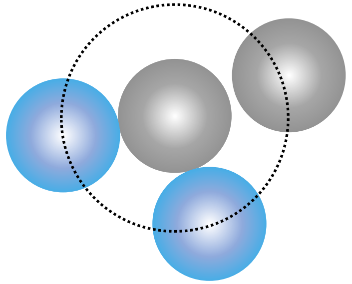
Dimensionless shear rate

$$\dot{\gamma}\tau = \frac{3\pi\eta\dot{\gamma}d^2}{F}$$

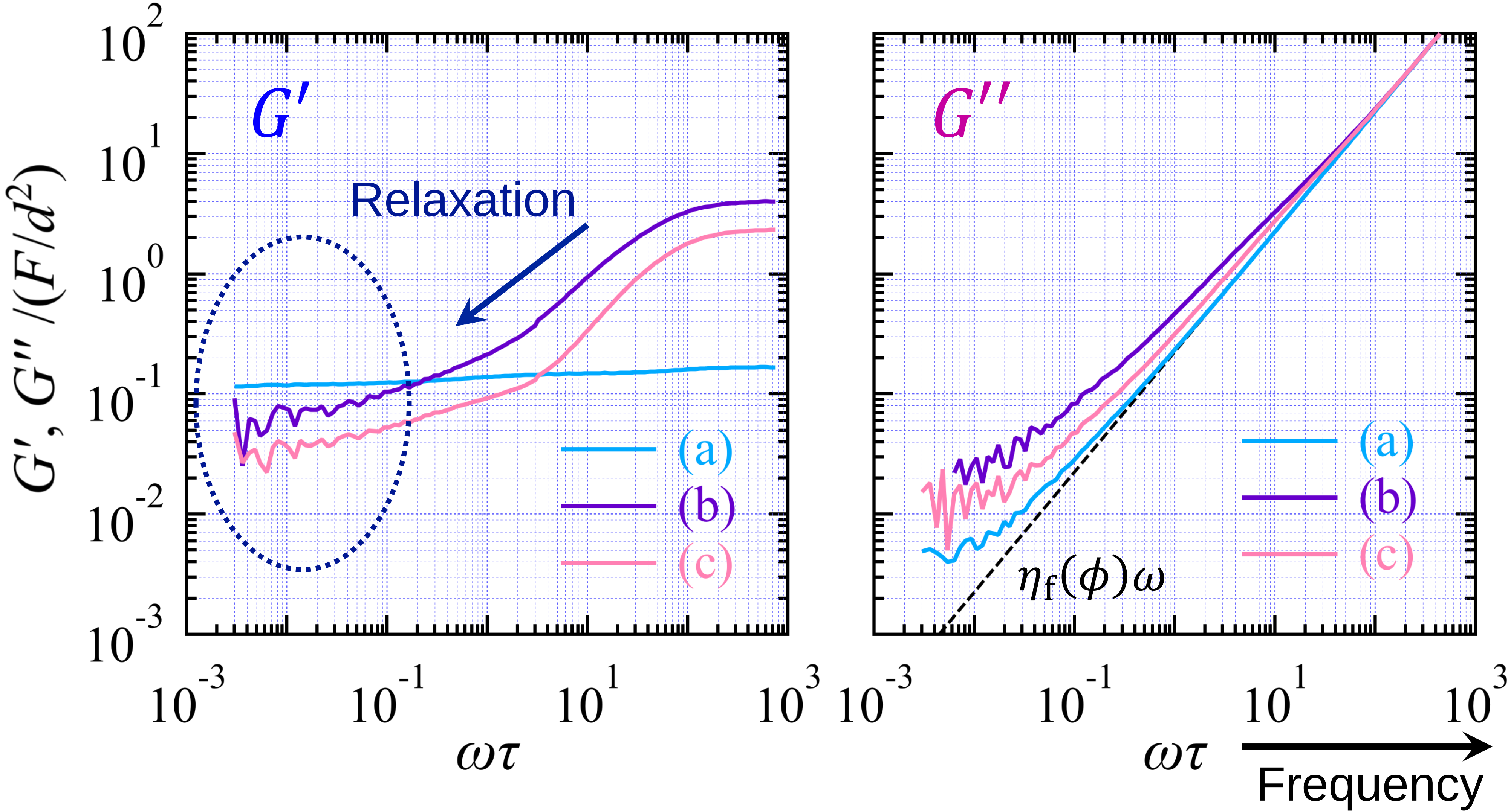
$$= \frac{(\text{Shear force})}{(\text{Adhision force})}$$

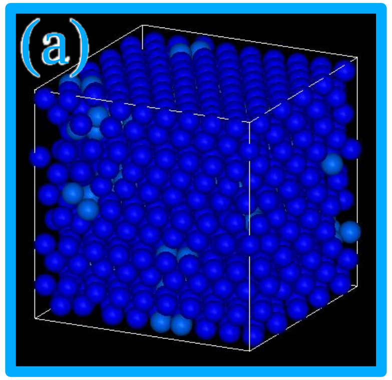
Contact number

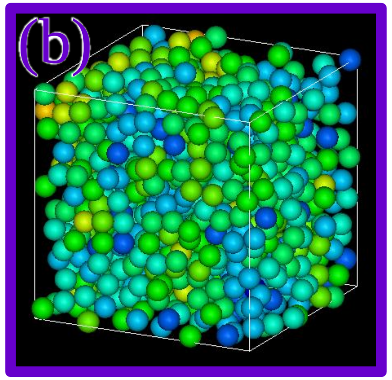


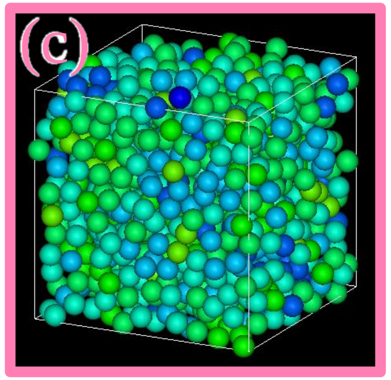


Step-2: Viscoelasticity









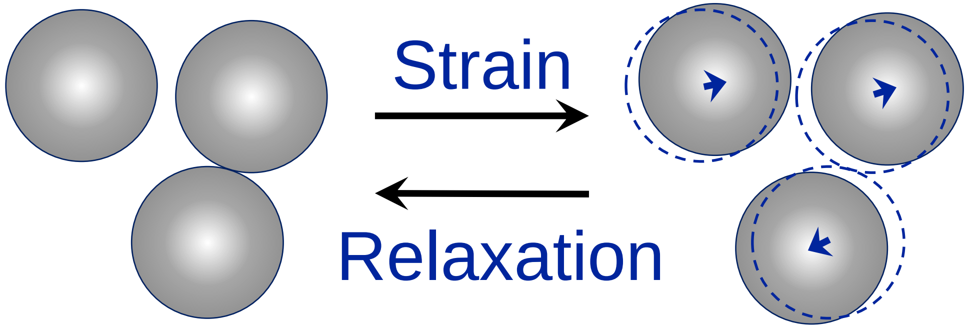
Structural strength at rest ($\omega\tau \to 0$)

Structure maintained by repulsion (a) / attraction (b, c)

Relaxation time

$$m\ddot{\boldsymbol{r}}_i = -\zeta\dot{\boldsymbol{r}}_i + \boldsymbol{F}_i \quad (i = 1, \ldots, N)$$

Fluid Inter-particle



Equilibrium state: $\boldsymbol{r}_0$

Ignoring inertia term

Linearization

$$\dot{\boldsymbol{r}} = \zeta^{-1}\boldsymbol{H} \cdot (\boldsymbol{r} - \boldsymbol{r}_0)$$

$$\boldsymbol{r} = \begin{pmatrix} \boldsymbol{r}_1 \\ \boldsymbol{r}_2 \\ \vdots \\ \boldsymbol{r}_N \end{pmatrix} \quad \boldsymbol{H} = \begin{pmatrix} \boldsymbol{H}_{11} & \boldsymbol{H}_{12} & \cdots & \boldsymbol{H}_{1N} \\ \boldsymbol{H}_{21} & \boldsymbol{H}_{22} & \ddots & \vdots \\ \vdots & \ddots & \ddots & \vdots \\ \boldsymbol{H}_{N1} & \cdots & \cdots & \boldsymbol{H}_{NN} \end{pmatrix} \quad \boldsymbol{H}_{ij} = -\frac{\partial \boldsymbol{F}_i}{\partial \boldsymbol{r}_j} \quad \boldsymbol{F}_i = \sum_{j \neq i} \boldsymbol{F}_{ij}$$

Hessian matrix: $\boldsymbol{H}$

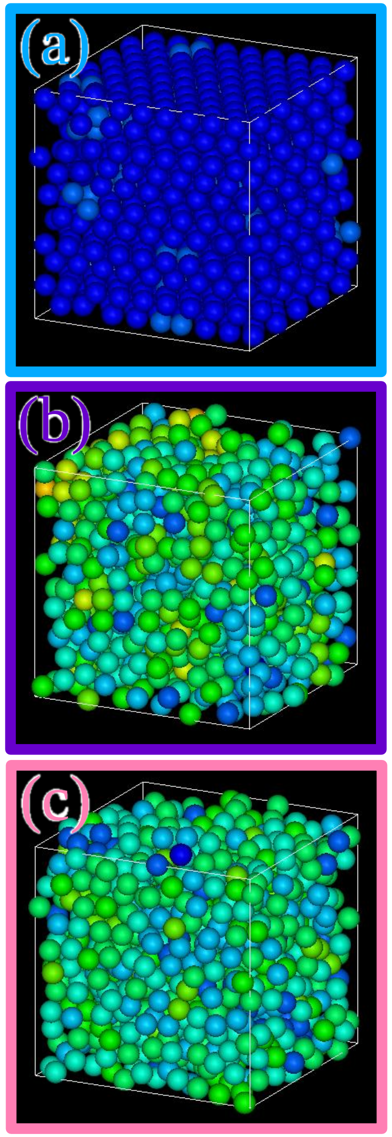
Diagonalization

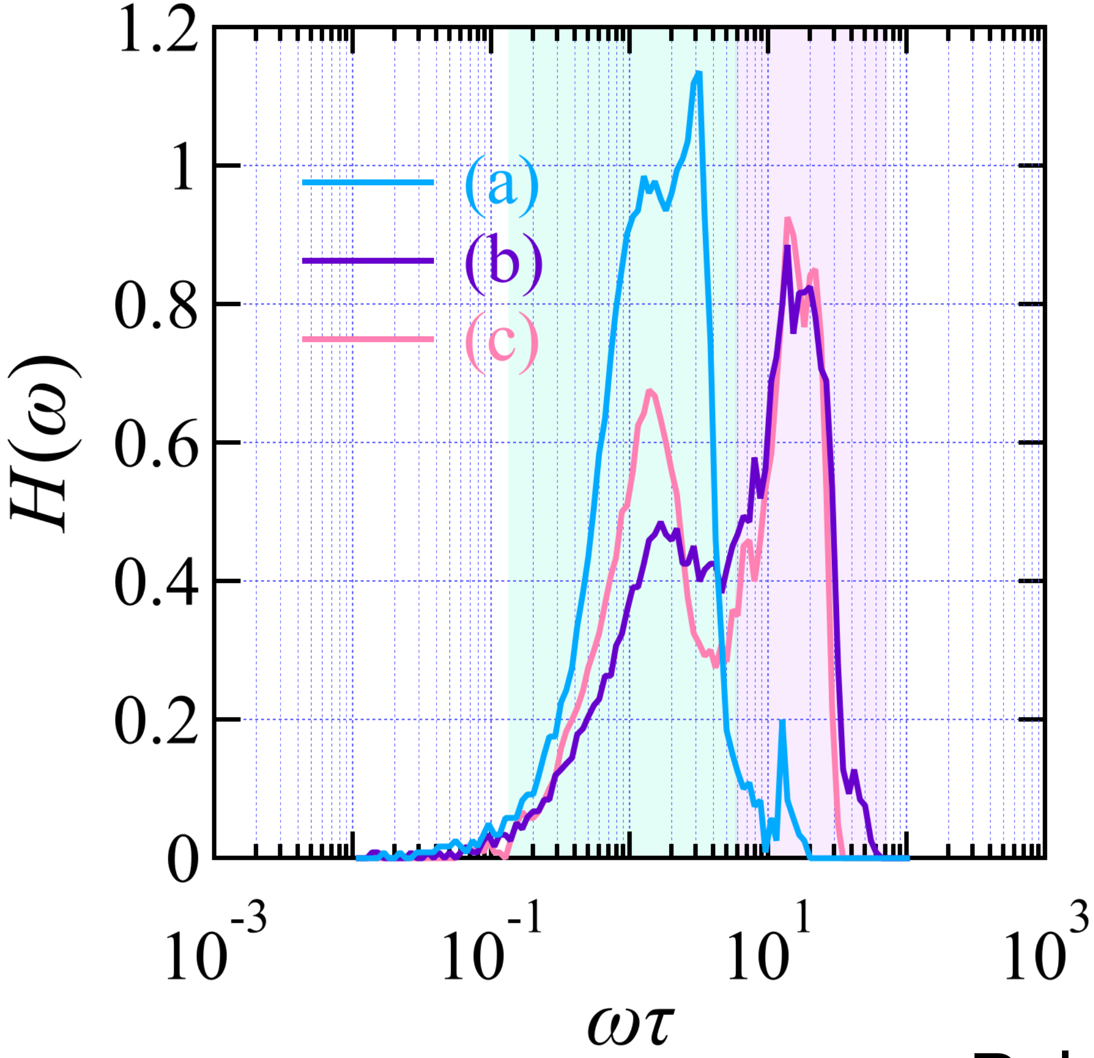
$$\dot{q}_k = -\frac{1}{\tau_k} q_k \quad (k = 1, \ldots, 3N) \qquad q_k = \boldsymbol{u}_k \cdot \boldsymbol{r}$$

Relaxation time: τ_k

Eigenvector: $\boldsymbol{u}_k$

Distribution of relaxation frequency





Relaxation frequency

$$\omega_k = \tau_k^{-1}$$

Distribution of $\{\log \omega_k\}$: $H(\omega)$

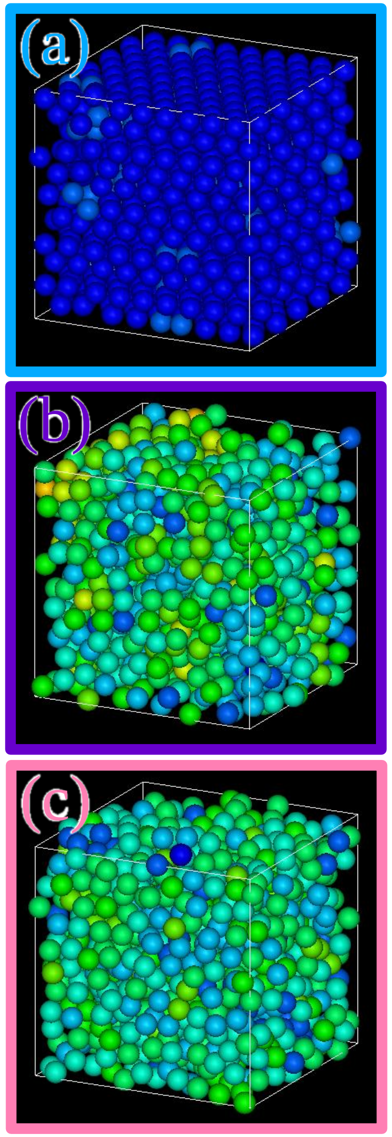
(Probability density function)

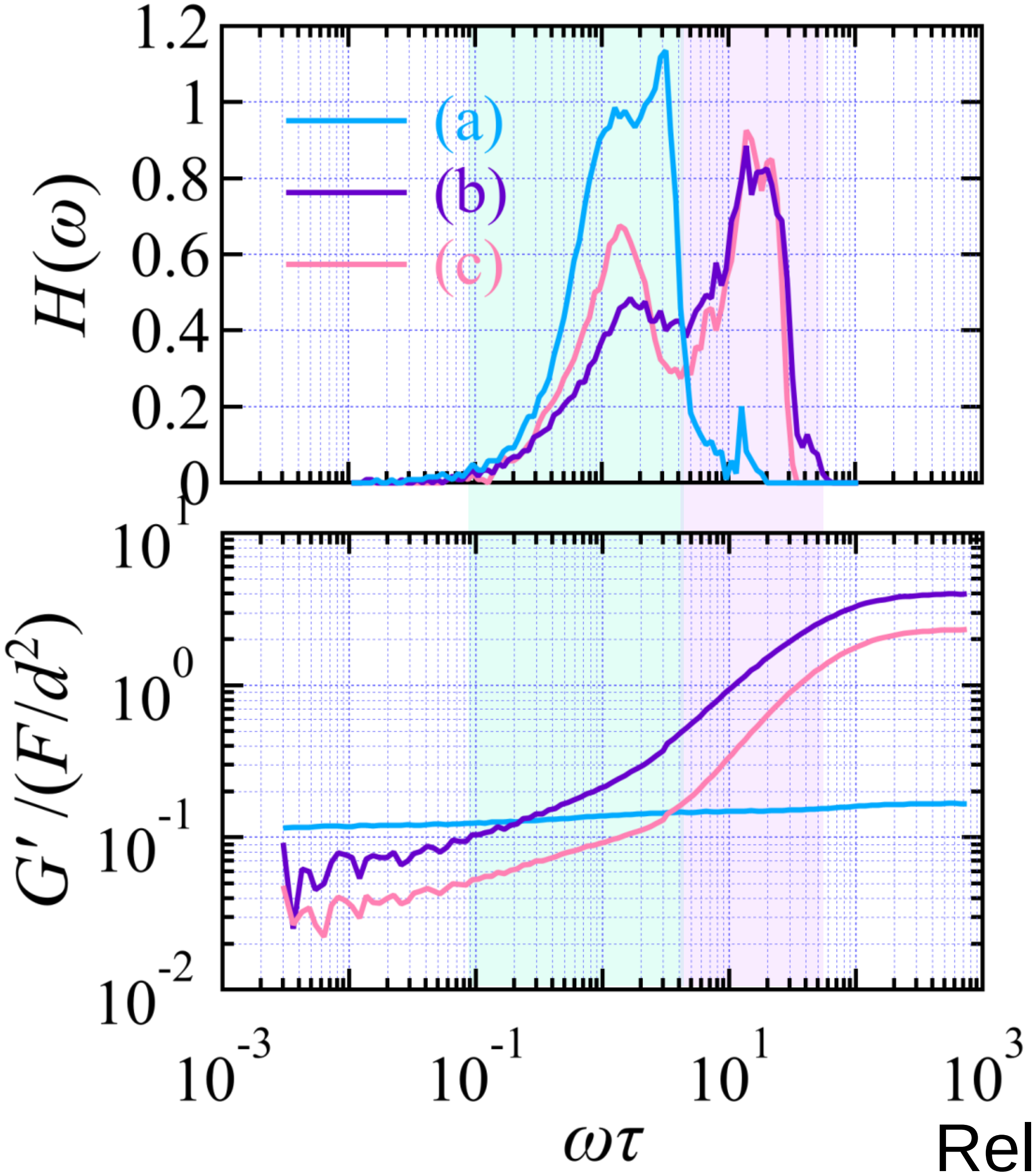
$$H(\omega)|\mathrm{d}\log\omega| = D(\omega)|\mathrm{d}\omega|$$

$$D(\omega) = \frac{1}{3N-3}\sum_k \delta(\omega - \omega_k)$$

Relaxation by repulsion / attraction

Distribution of relaxation frequency





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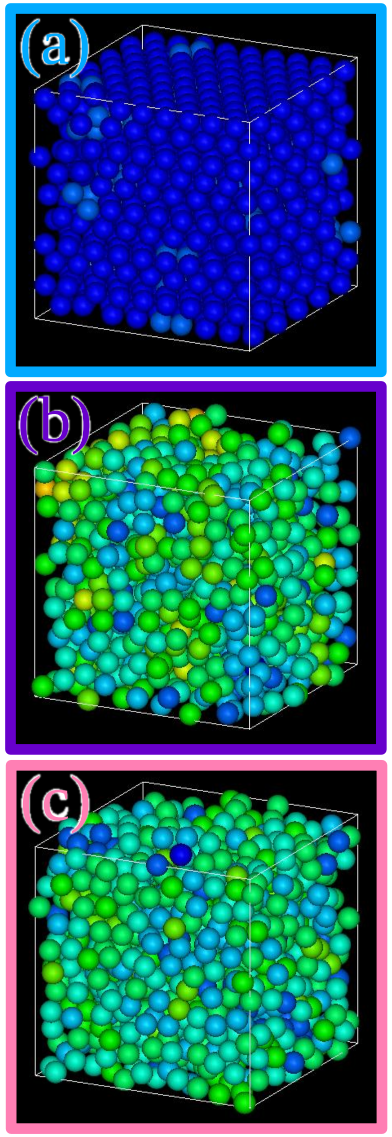
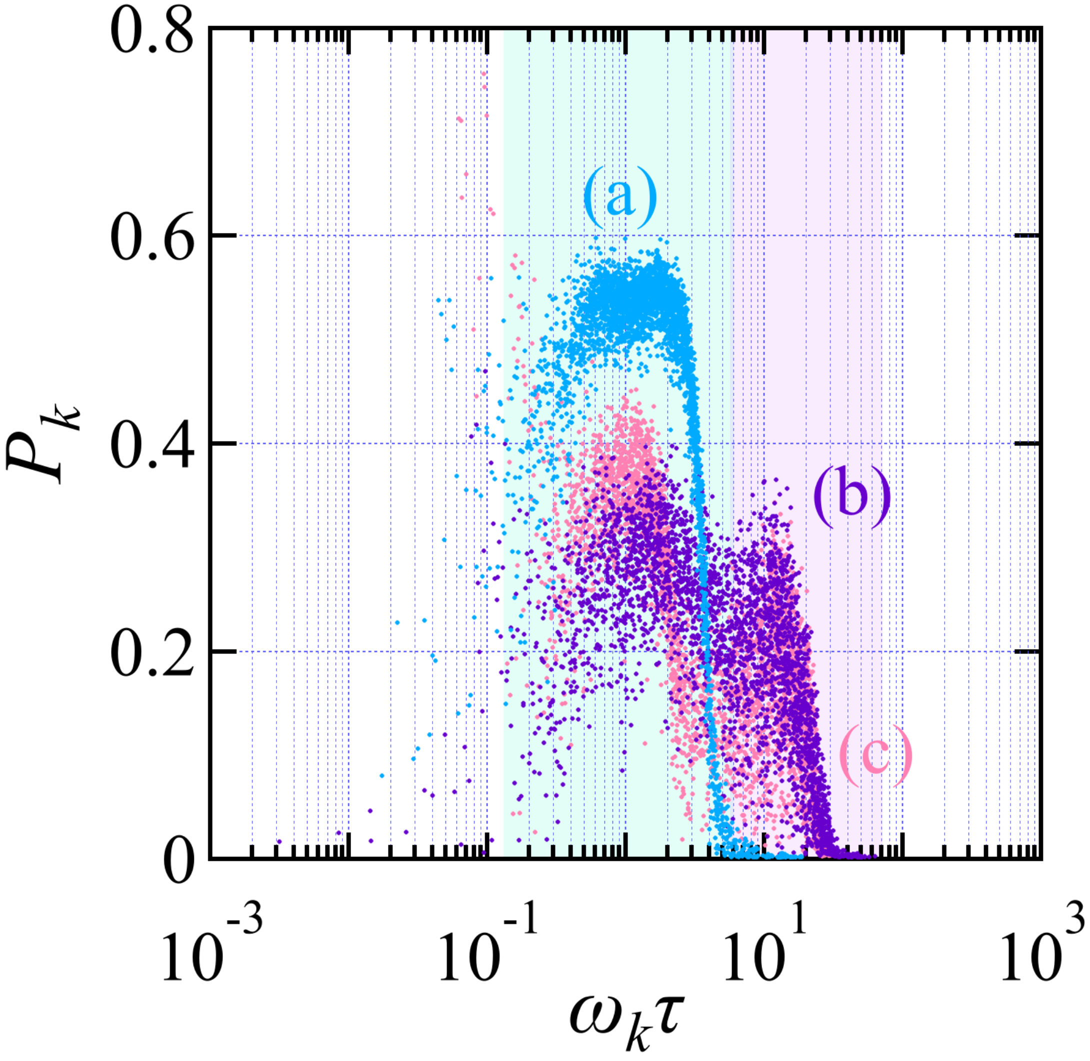
Relaxation by repulsion / attraction

Eigenmodes of particles' motion





Participation ratio

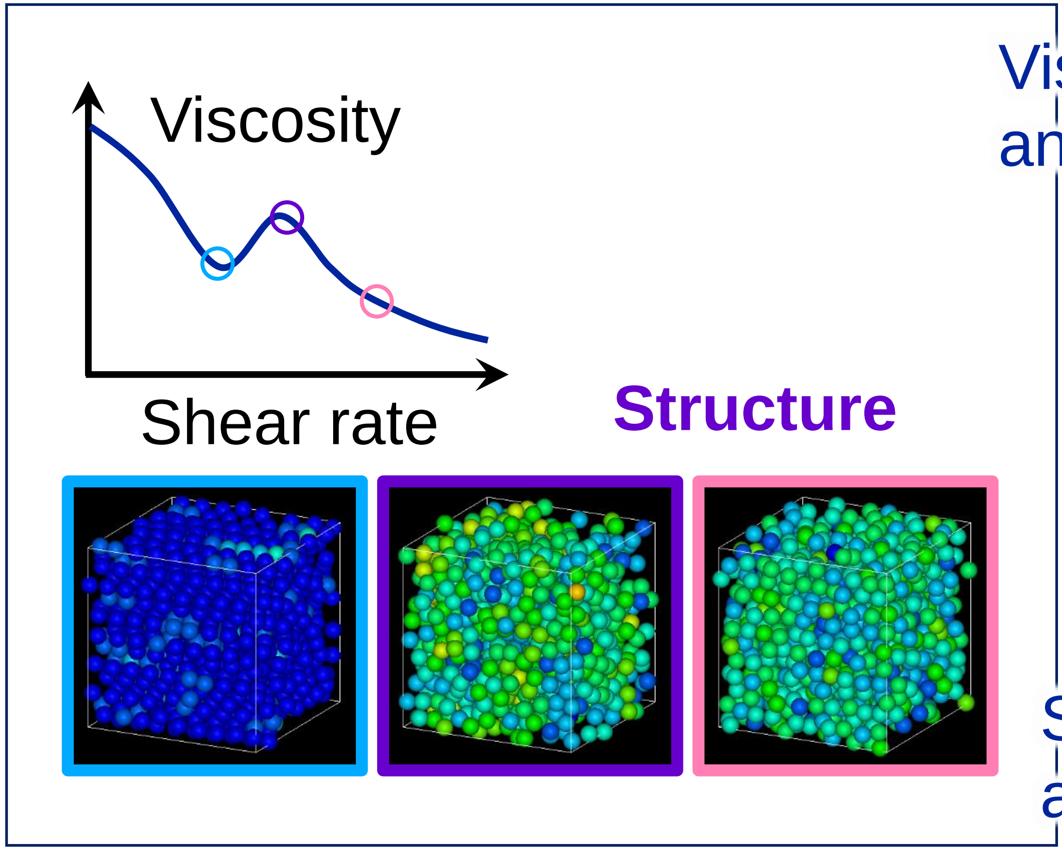
$$P_k = \frac{\left(\sum_i |\boldsymbol{u}_k \cdot \boldsymbol{r}_i|^2\right)^2}{N \sum_i |\boldsymbol{u}_k \cdot \boldsymbol{r}_i|^4}$$

Ratio of particles participating in an eigenmode of motion

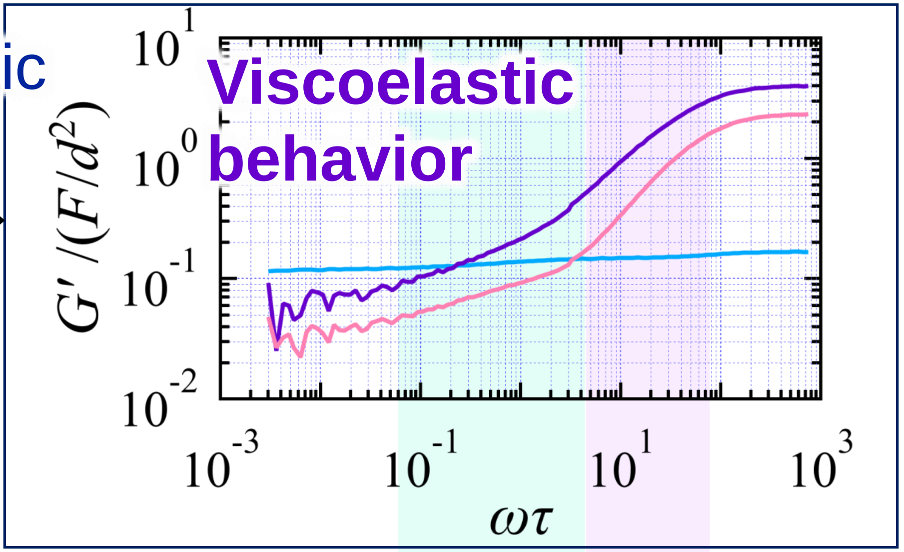
Relaxation frequency:
Repulsion < Attraction

Extent of collective motion:
Repulsion > Attraction

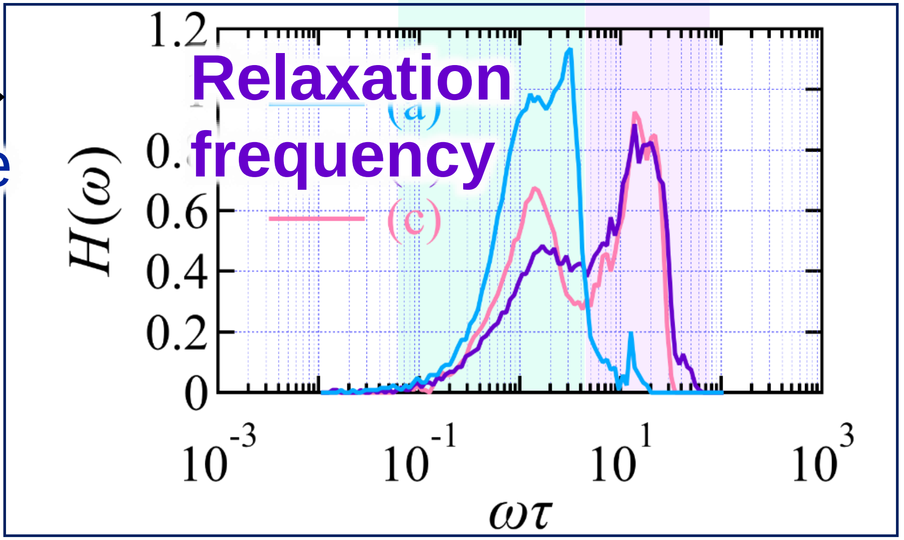
Summary



Viscoelastic analysis



Structure analysis



Viscoelastic behavior may show inter-particle interactions determining structure

→ Knowledge how to prepare slurry to control its viscoelasticity