SCEJ 53rd Autumn Meeting
Sept. 14, 2022

Structural change in colloidal suspensions indicated by nonlinear viscoelasticity

微粒子分散液の非線形粘弾性が示す構造変化

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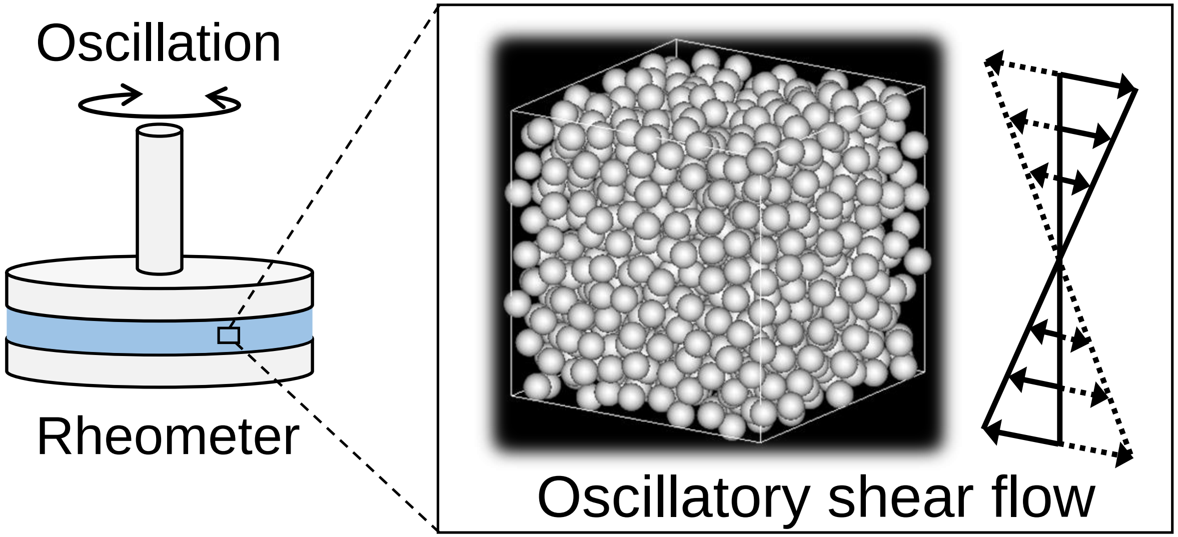
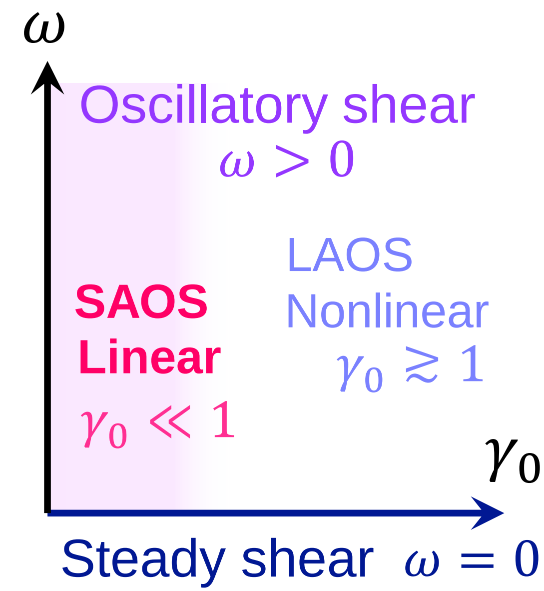
Viscoelasticity





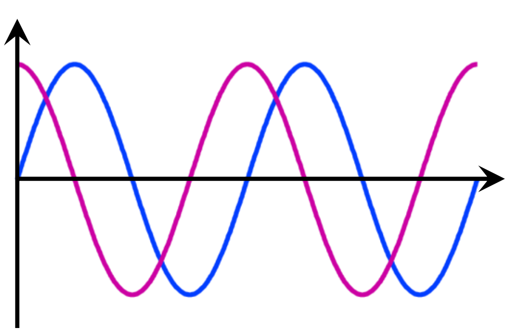
SAOS (Small Amplitude Oscillatory Shear; $\gamma_0 \ll 1$) → Linear response

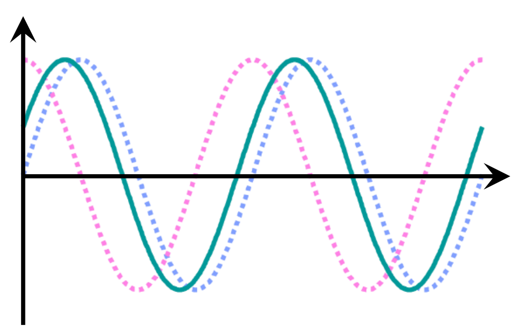
Strain: $\gamma_0 \sin \omega t$

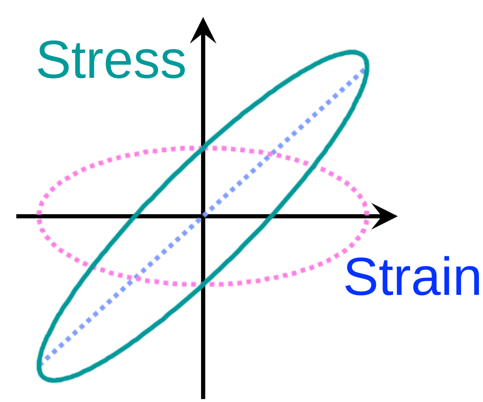
Shear rate: $\gamma_0 \omega \cos \omega t$

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

Storage modulus: G' Loss modulus: G''

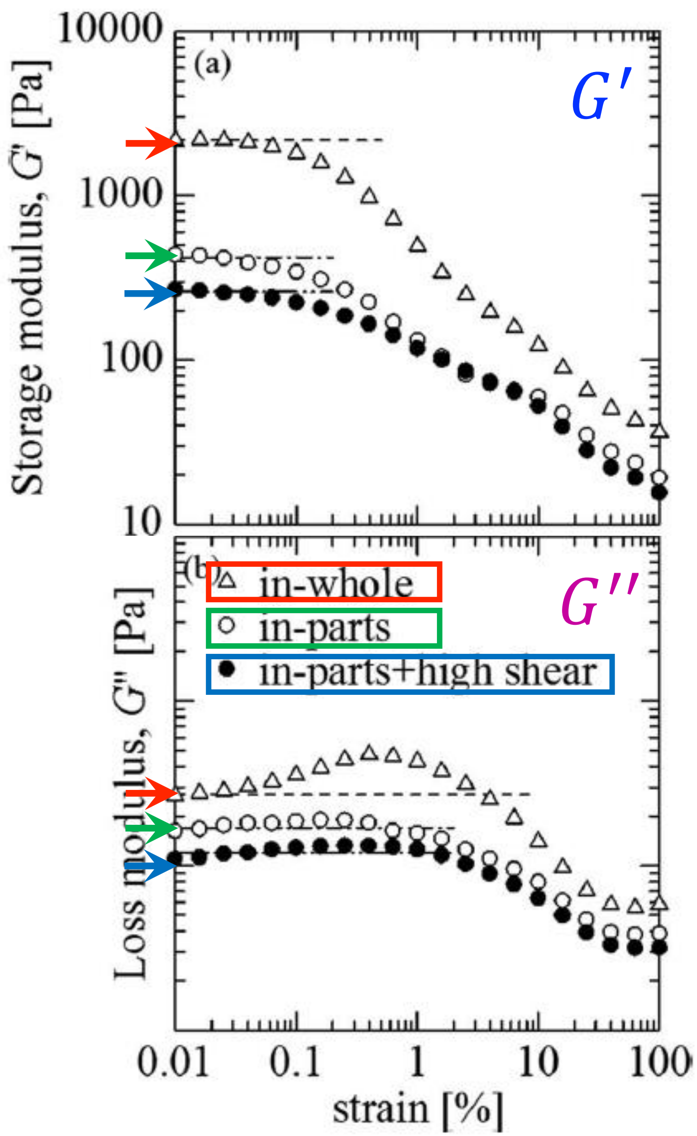




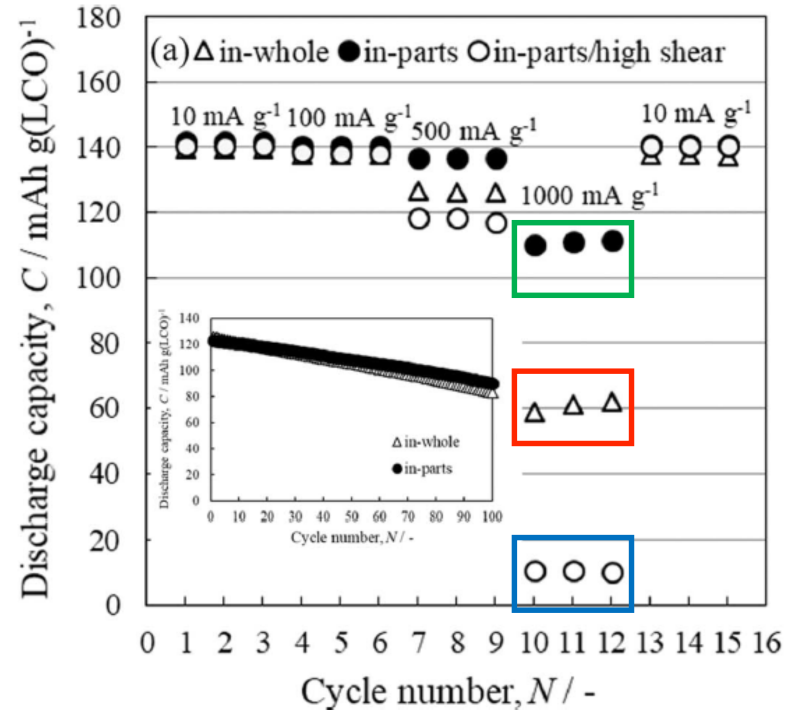


Structure estimation from viscoelasticity

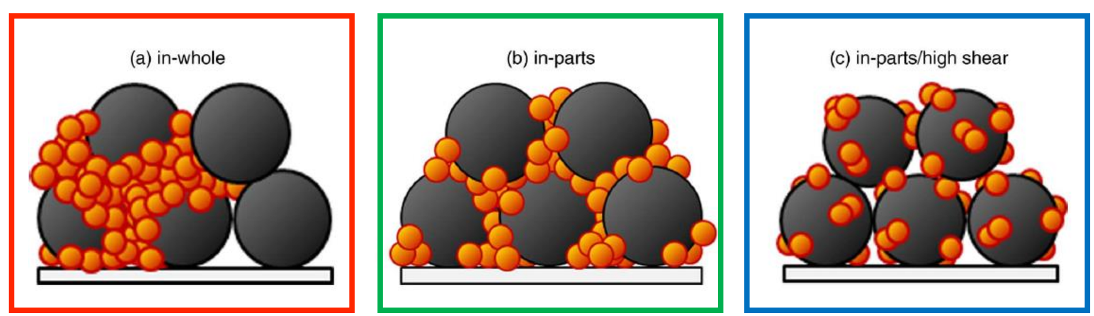
Slurry (LiCoO$_2$ + acetylene black)



Electrode

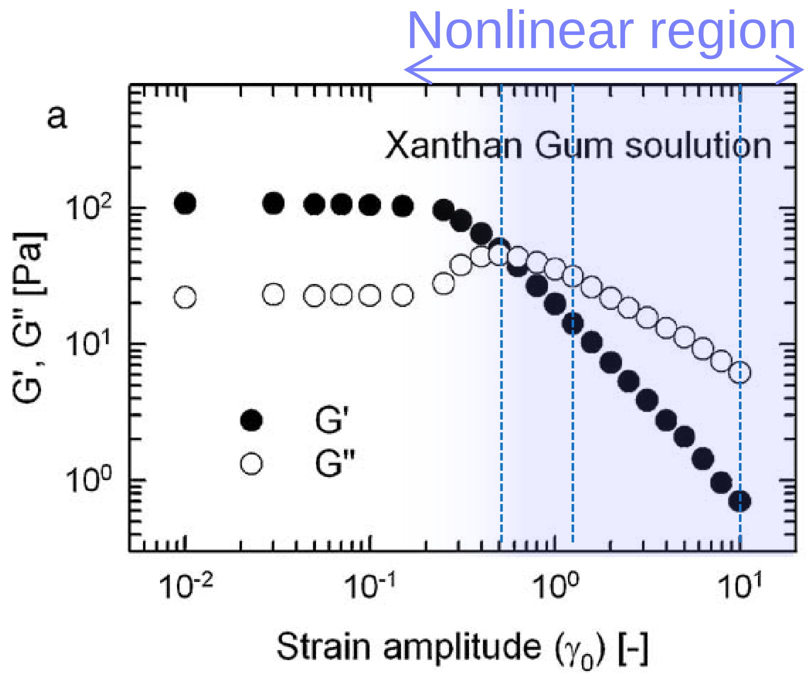


Discharge capacity

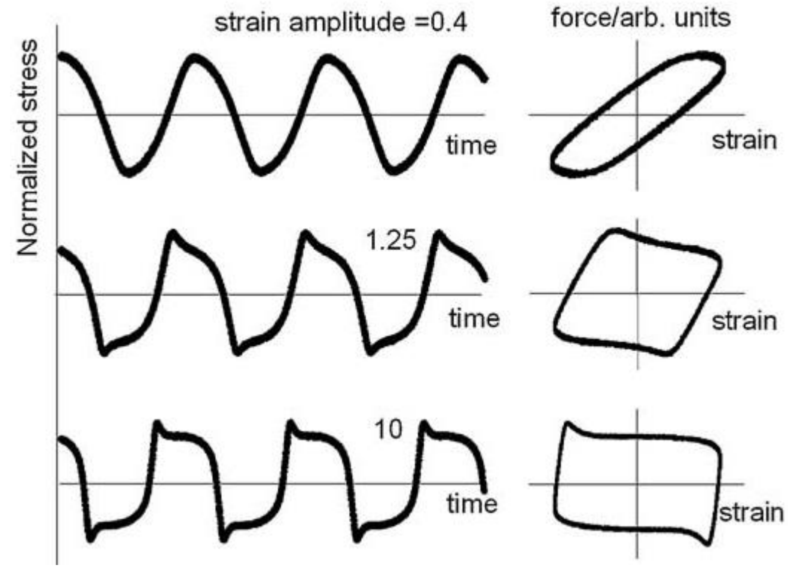


Kuratani *et al*., J. Electrochem. Soc. **166** A501 (2019).

Nonlinear viscoelasticity



Hyun *et al*., Prog. Polym. Sci. **36**, 1697 (2011).



LAOS (Large Amplitude Oscillatory Shear; $\gamma_0 \gtrsim 1$)

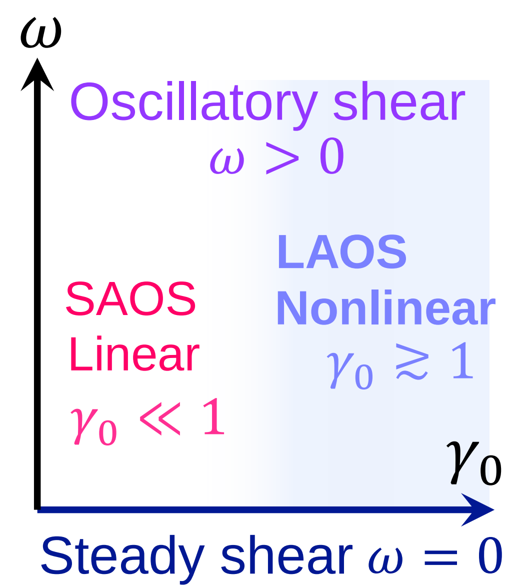
→ Nonlinear response

$$\sigma(t) = \gamma_0 \sum_{k:\,\mathrm{odd}} (G'_k \sin k\omega t + G''_k \cos k\omega t)$$

$$\begin{pmatrix} G'_k \\ G''_k \end{pmatrix} = \frac{\omega}{\pi \gamma_0} \int_0^{2\pi/\omega} \sigma(t) \begin{pmatrix} \sin k\omega t \\ \cos k\omega t \end{pmatrix} \mathrm{d}t$$

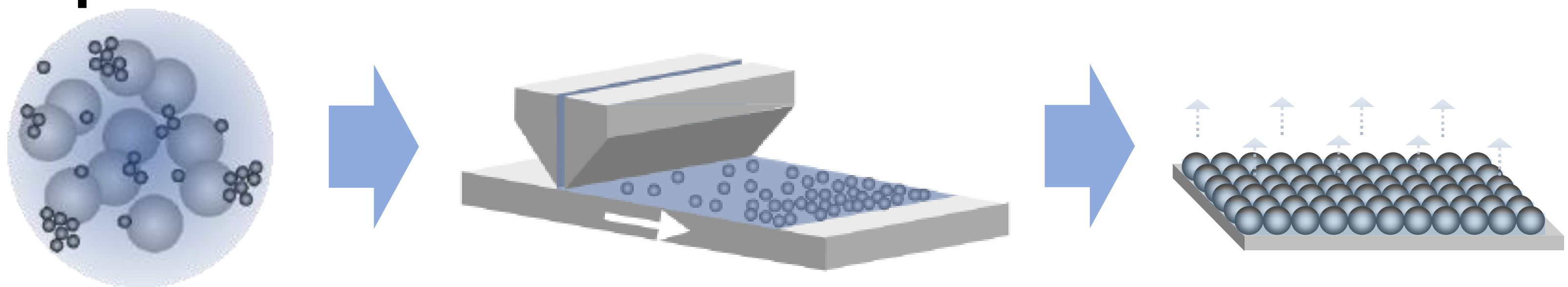
Fourier expansion → Higher harmonic contributions

Related to intracycle variation in viscoelasticity



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

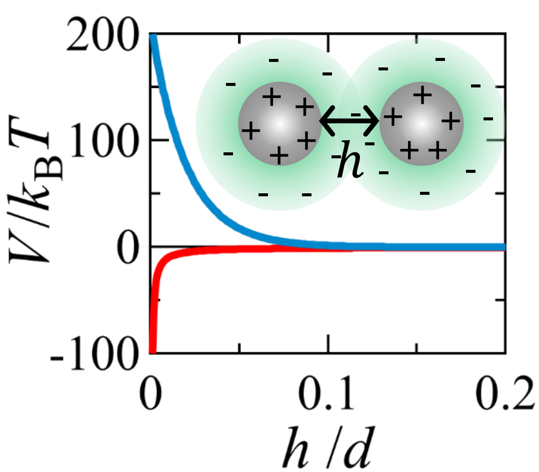
Numerical simulation

Materials

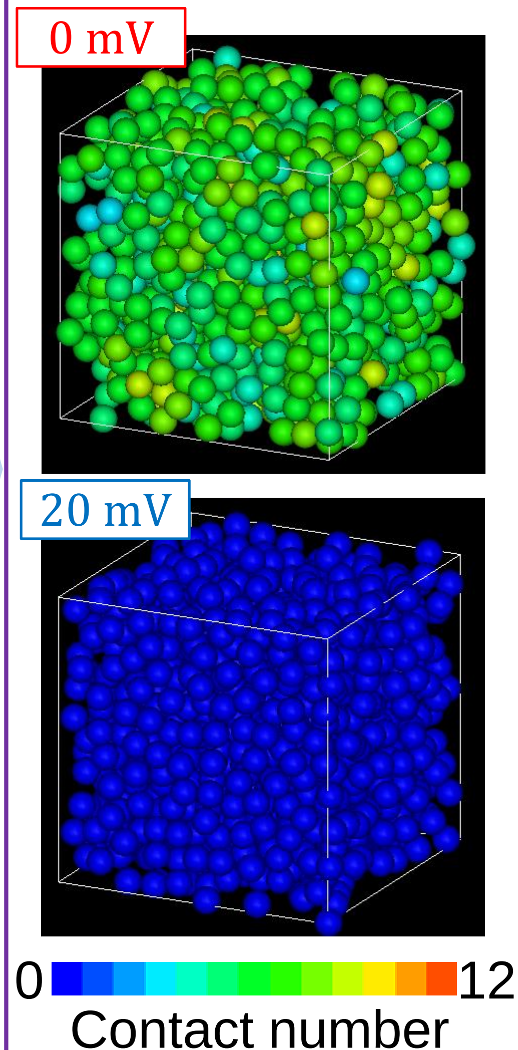
Solvent: water

Particles

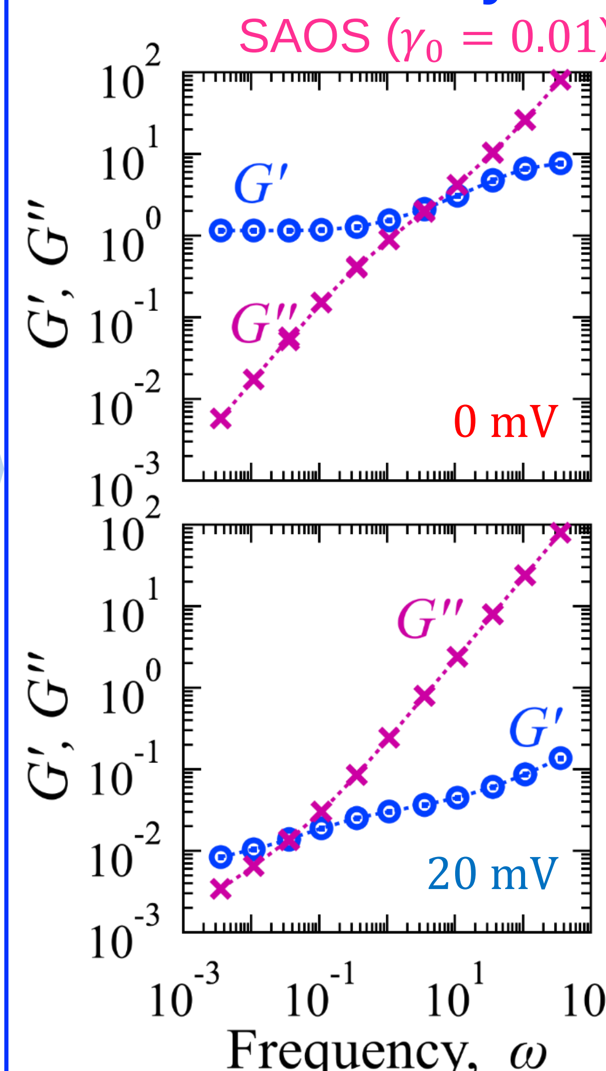
- Diameter: 1 μm
- Concentration: 45 vol%
- Zeta potential: 0 mV, 20 mV



Structure



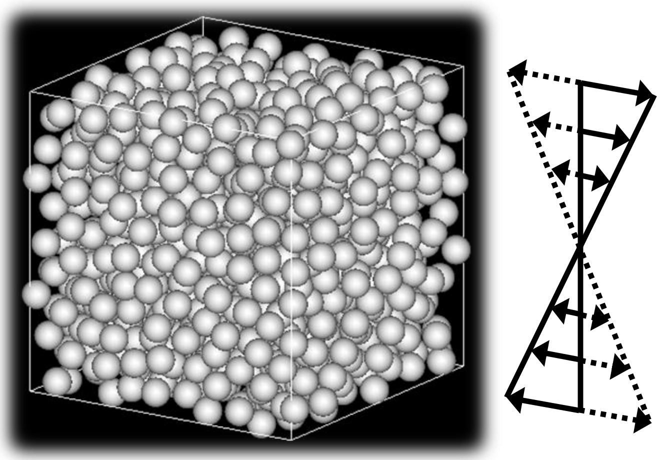
Viscoelasticity



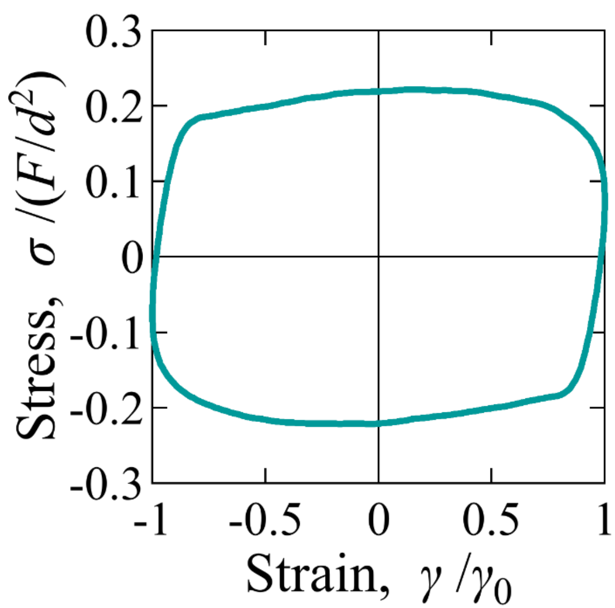
Tatsumi *et al.*, SCEJ 87th Annual meeting (2022).

Objective

- Performing numerical simulations of particle dynamics under oscillatory shear flow to calculate nonlinear viscoelasticity
- Investigating the relationship between structural change and the nonlinear viscoelasticity of aggregated suspensions



Structure



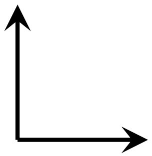
$$S = \frac{G'_{\mathrm{L}} - G'_{\mathrm{M}}}{G'_{\mathrm{L}}}$$

$$T = \frac{\eta'_{\mathrm{L}} - \eta'_{\mathrm{M}}}{\eta'_{\mathrm{L}}}$$

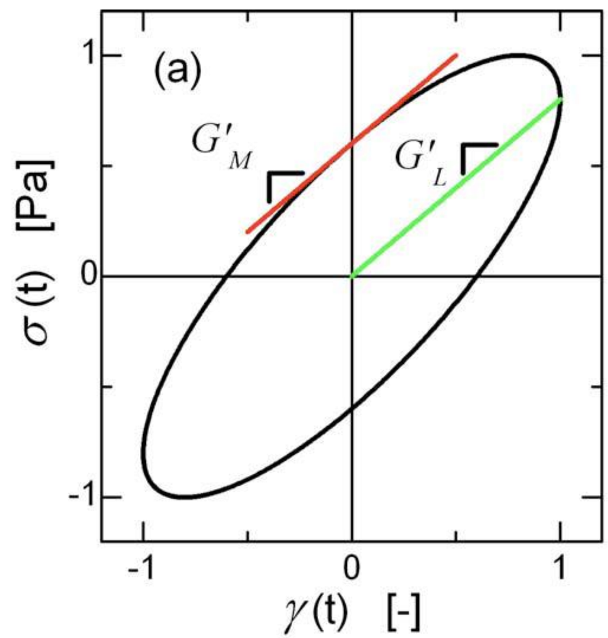
Nonlinear viscoelasticity

Measures of nonlinear viscoelasticity

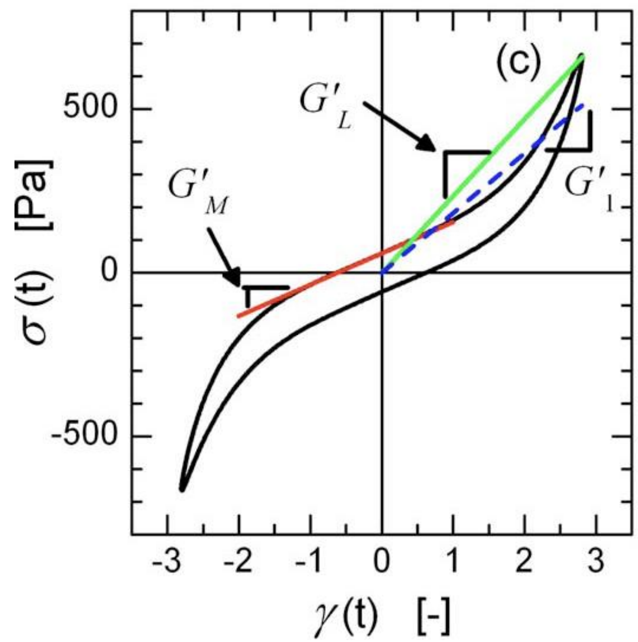
Stress



Strain



Linear ($\gamma_0 \ll 1$)



Nonlinear ($\gamma_0 \gtrsim 1$)

$$G'_{\mathrm{M}} = \left(\frac{\mathrm{d}\sigma}{\mathrm{d}\gamma}\right)_{\gamma=0}$$

Minimum-strain modulus

$$G'_{\mathrm{L}} = \left(\frac{\sigma}{\gamma}\right)_{|\gamma|=\gamma_0}$$

Large-strain modulus

Intracycle change in elasticity

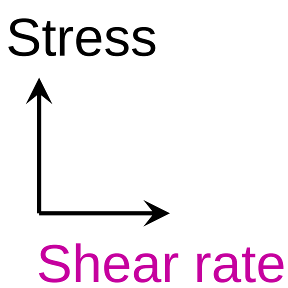
$$S = \frac{G'_{\mathrm{L}} - G'_{\mathrm{M}}}{G'_{\mathrm{L}}}$$

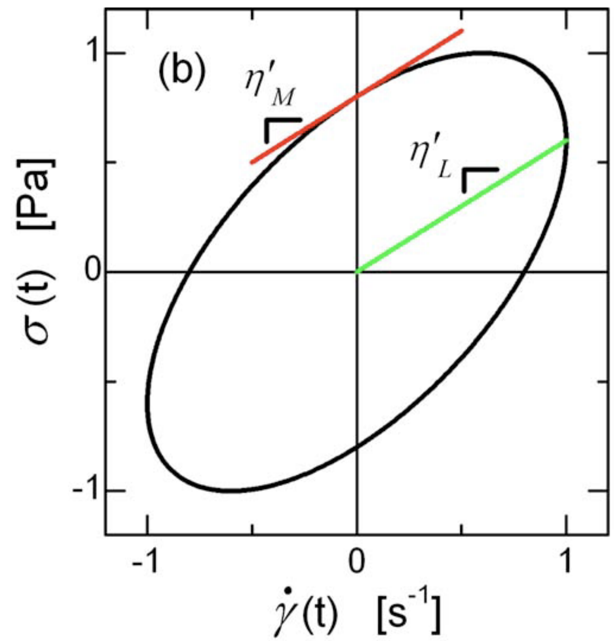
$S > 0$: strain stiffening

$S < 0$: strain softening

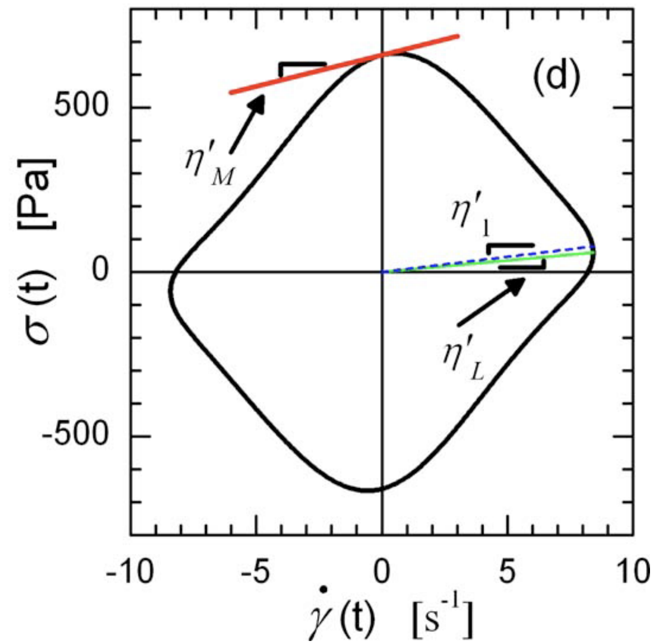
Ewoldt *et al*. J. Rheol. **52**, 1427 (2008).

Measures of nonlinear viscoelasticity





Linear ($\gamma_0 \ll 1$)



Nonlinear ($\gamma_0 \gtrsim 1$)

$$\eta'_{\mathrm{M}} = \left(\frac{\mathrm{d}\sigma}{\mathrm{d}\dot{\gamma}}\right)_{\dot{\gamma}=0}$$

Minimum-rate viscosity

$$\eta'_{\mathrm{L}} = \left(\frac{\sigma}{\dot{\gamma}}\right)_{|\dot{\gamma}|=\dot{\gamma}_0}$$

Large-rate viscosity

Intracycle change in viscosity

$$T = \frac{\eta'_{\mathrm{L}} - \eta'_{\mathrm{M}}}{\eta'_{\mathrm{L}}}$$

$T > 0$: shear thickening

$T < 0$: shear thinning

Ewoldt *et al*. J. Rheol. **52**, 1427 (2008).

Measures of nonlinear viscoelasticity

Fourier expansion of stress response

$$\sigma(t) = \gamma_0 \sum_{k:\,\mathrm{odd}} (G'_k \sin k\omega t + G''_k \cos k\omega t)$$

$$S = \frac{G'_\mathrm{L} - G'_\mathrm{M}}{G'_\mathrm{L}} = \frac{-4G'_3 + \cdots}{G'_1 - G'_3 + \cdots}$$

$G'_3 < 0$: strain stiffening

$$T = \frac{\eta'_\mathrm{L} - \eta'_\mathrm{M}}{\eta'_\mathrm{L}} = \frac{4G''_3 + \cdots}{G''_1 + G''_3 + \cdots}$$

$G''_3 > 0$: shear thickening

S & T can be calculated from $\{G'_k\}$ & $\{G''_k\}$

Equation of motion of particles

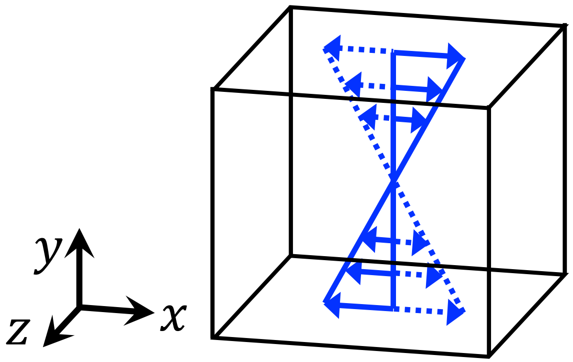
$$M\dot{\boldsymbol{V}} = -\zeta(\boldsymbol{V}-\boldsymbol{V}_{\rm ex}) + \boldsymbol{F}^{\rm cnt} + \boldsymbol{F}^{\rm DLVO}$$

Fluid — Interparticle

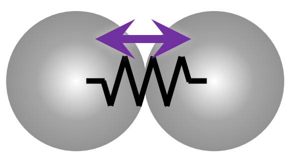
- **Hydrodynamic drag**: $-\zeta(\boldsymbol{V}-\boldsymbol{V}_{\rm ex})$

  Oscillatory shear flow

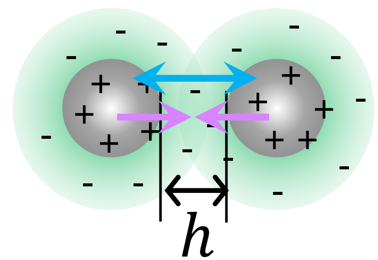
  $\boldsymbol{V}_{\rm ex} = \dot{\gamma}(t) y\, \boldsymbol{e}_x \qquad \dot{\gamma}(t) = \gamma_0 \omega \cos \omega t$

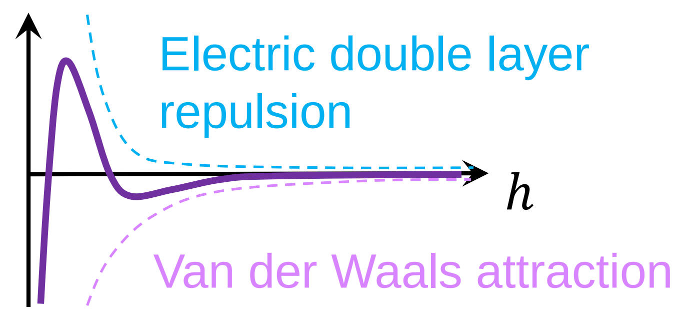


- **Contact force**: $\boldsymbol{F}^{\rm cnt}$



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



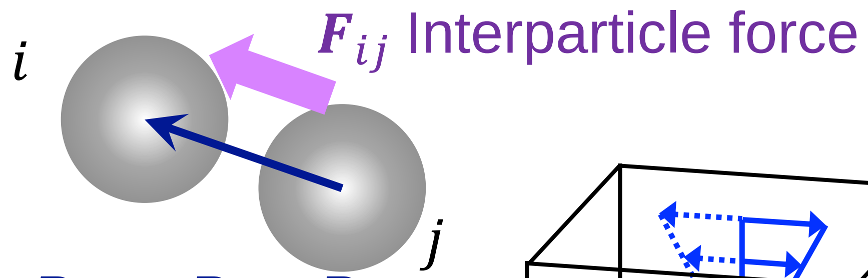


→ **Dispersion / Aggregation**

- **Boundary conditions**

  x, z: Periodic, y: Lees-Edwards

Estimation of nonlinear viscoelasticity

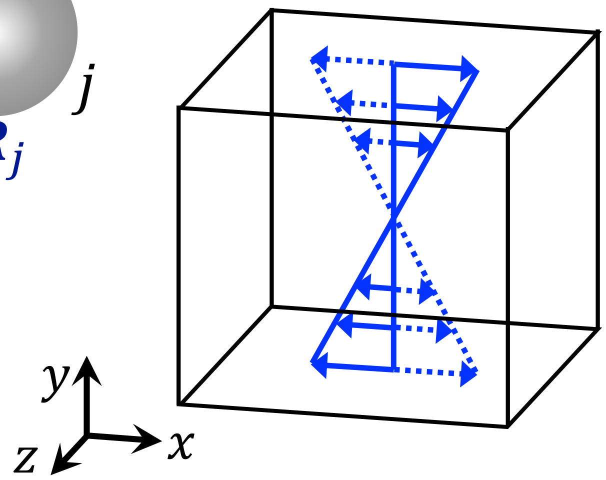


$$\boldsymbol{R}_{ij} = \boldsymbol{R}_i - \boldsymbol{R}_j$$

Stress

$$\sigma(t) = -\frac{1}{V}\sum_{i<j} F_{ij}^{x} R_{ij}^{y}$$

$$= \gamma_0 \sum_{k:\,\mathrm{odd}} \left(G_k' \sin k\omega t + G_k'' \cos k\omega t\right)$$



Intracycle change in elasticity/viscosity

$$S = \frac{G_{\mathrm{L}}' - G_{\mathrm{M}}'}{G_{\mathrm{L}}'} = \frac{-4G_3' + \cdots}{G_1' - G_3' + \cdots} \qquad T = \frac{\eta_{\mathrm{L}}' - \eta_{\mathrm{M}}'}{\eta_{\mathrm{L}}'} = \frac{4G_3'' + \cdots}{G_1'' + G_3'' + \cdots}$$

Simulation conditions

Fluid: Water

Particles

- Diameter: $d = 100\ \text{nm}$
- Concentration: $45\ \text{vol\%}$
- Zeta potential: $0\ \text{mV}$

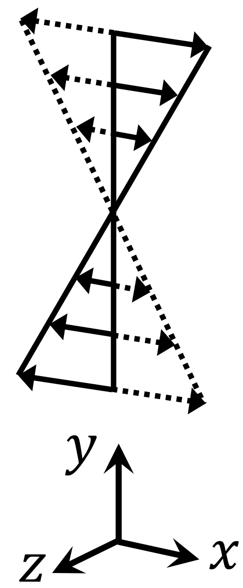
Shear flow

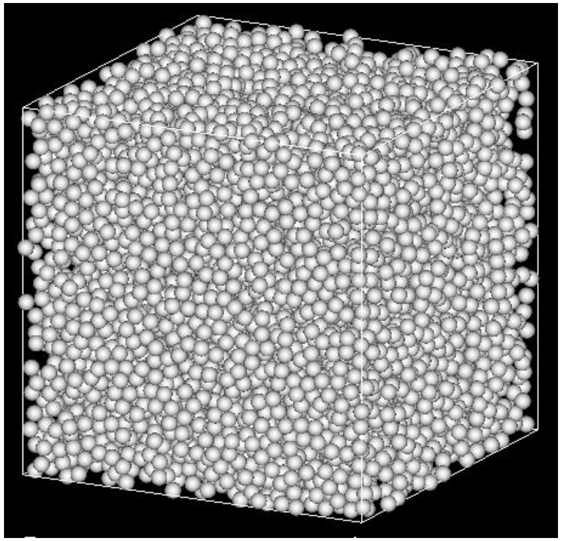
- Strain: $\gamma_0 = 1 \times 10^{-3} - 3$
- Frequency: $\omega\tau = 1.2$

$$\tau = 3\pi\eta d^2/F$$

F : Attractive force between contacting particles

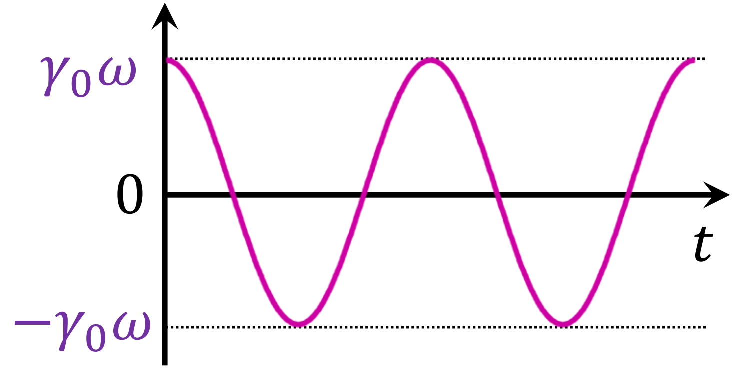
$U_x(t) = \dot{\gamma}(t) y$



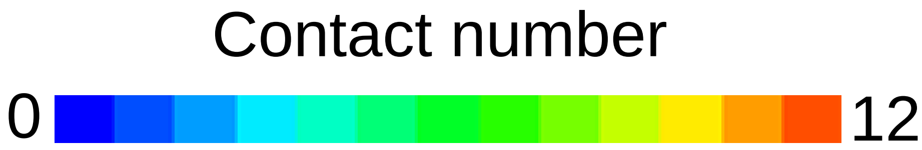


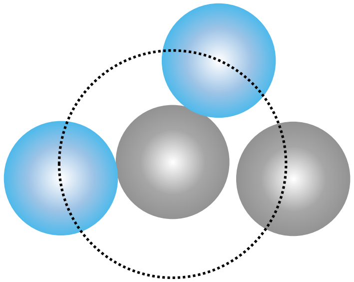
Side length: $22.7d$

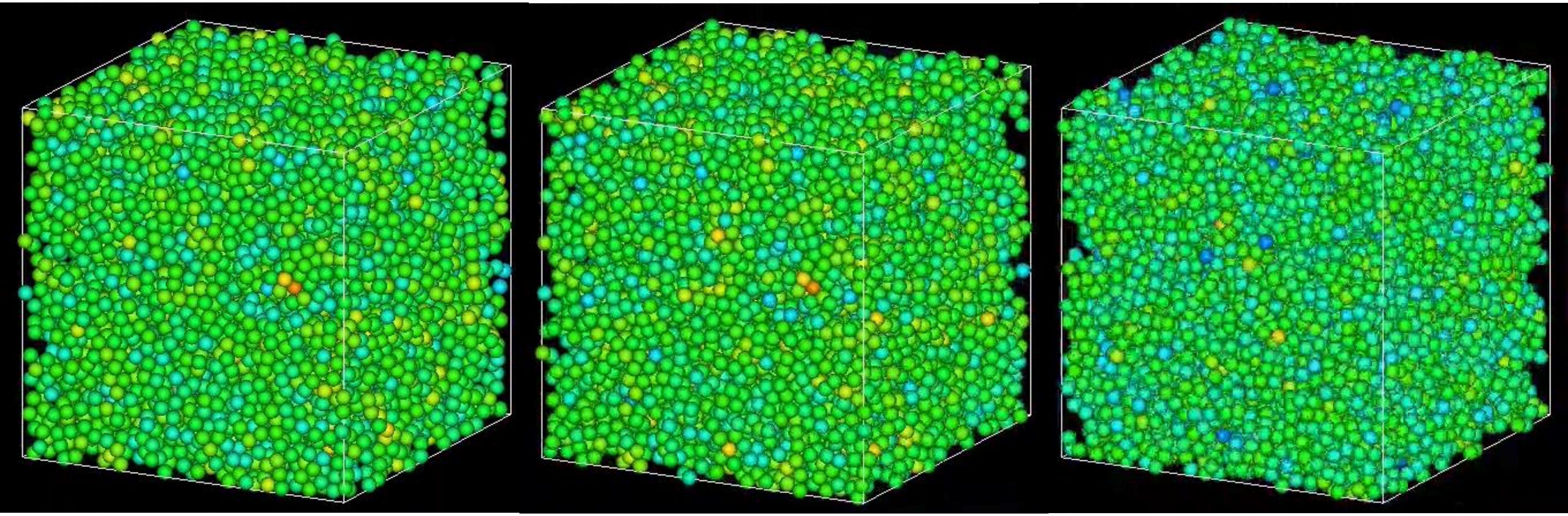
Shear rate: $\dot{\gamma}(t) = \gamma_0 \omega \cos \omega t$



Structure of particles

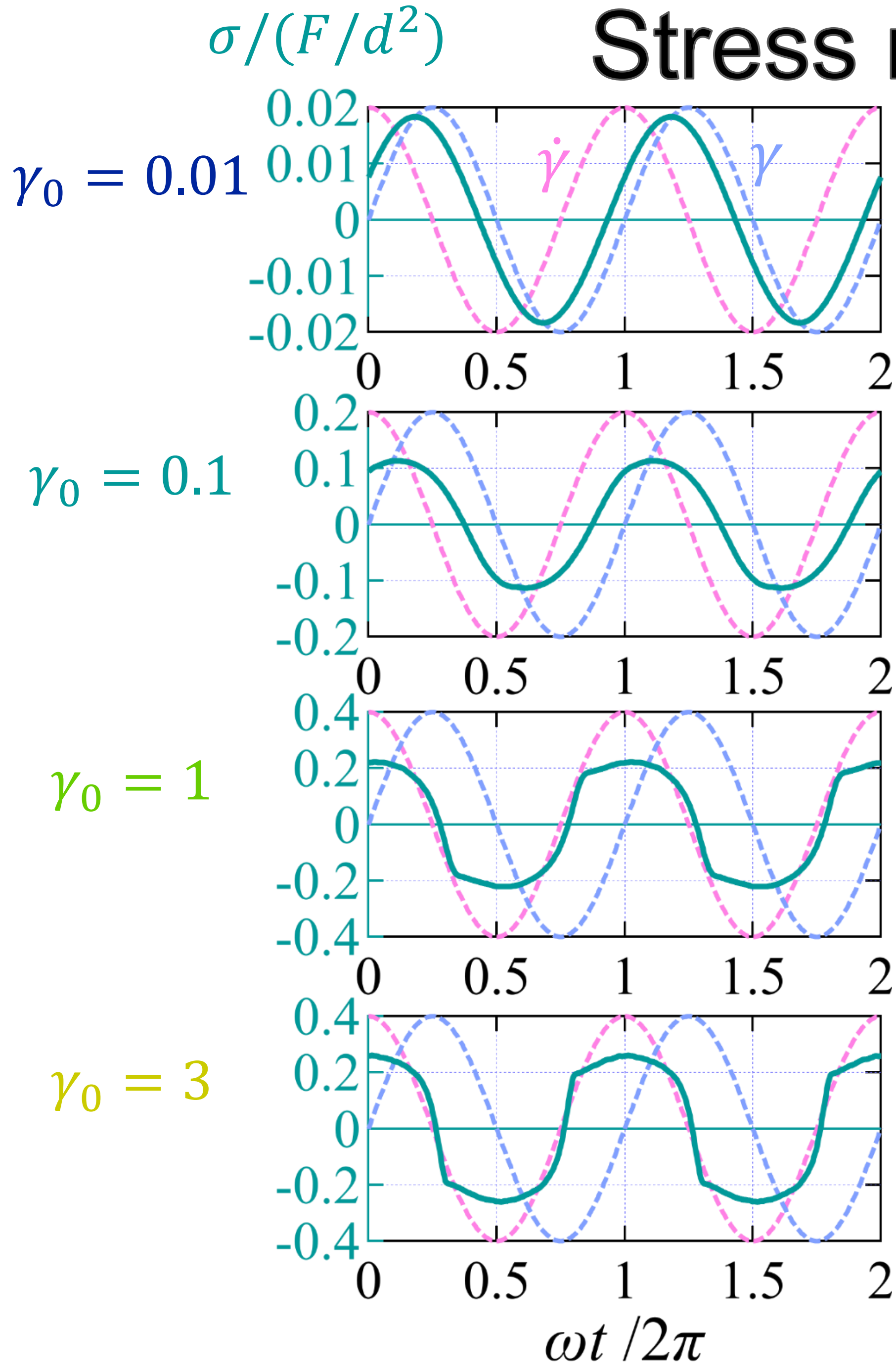


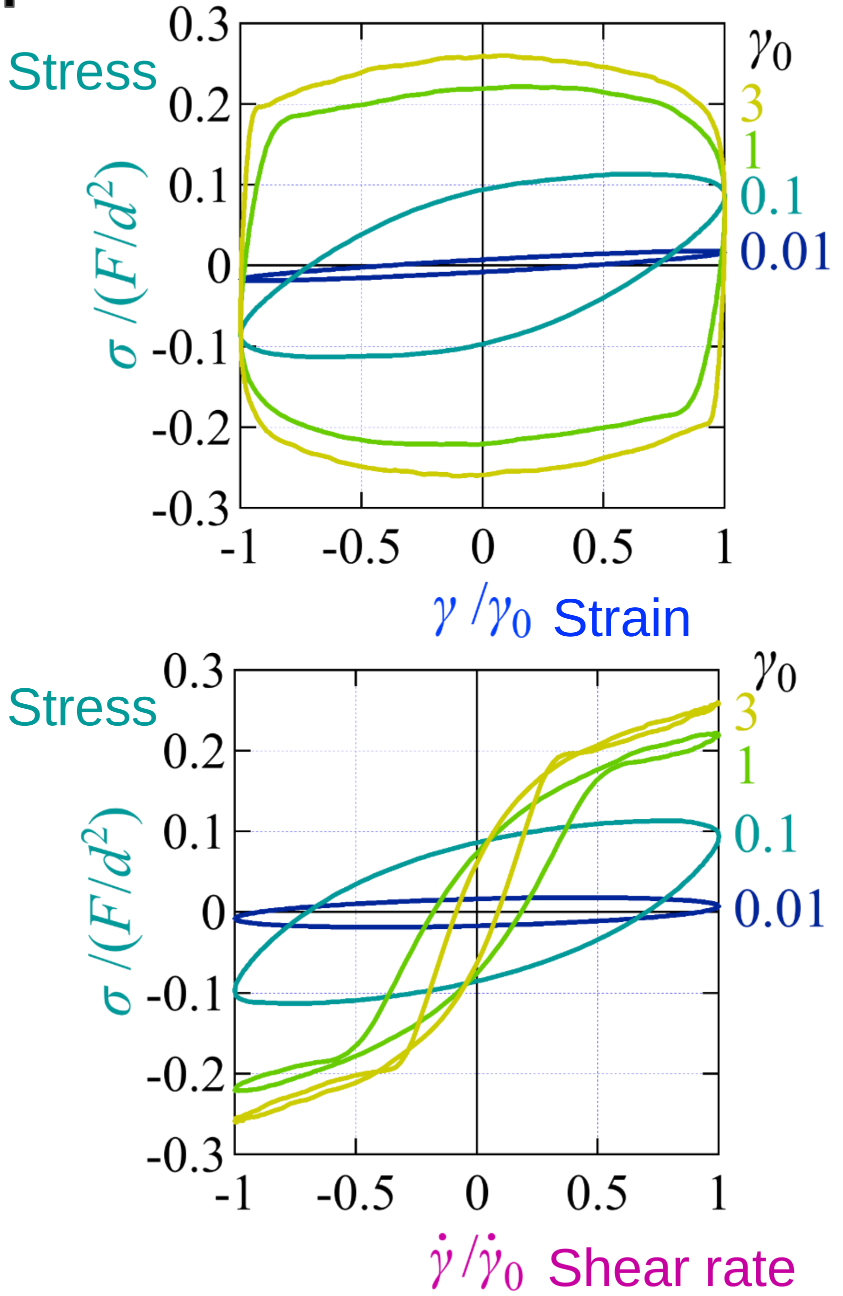




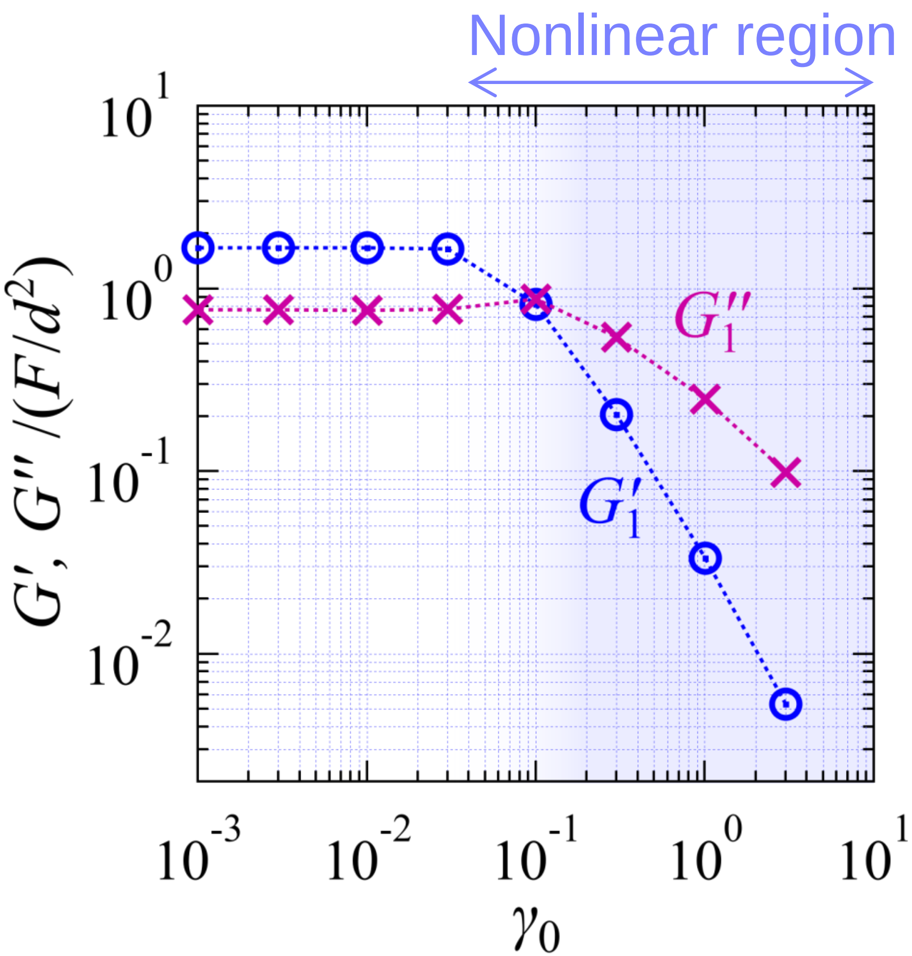
$\gamma_0 = 0.01$ | $\gamma_0 = 0.1$ | $\gamma_0 = 1$

Stress response

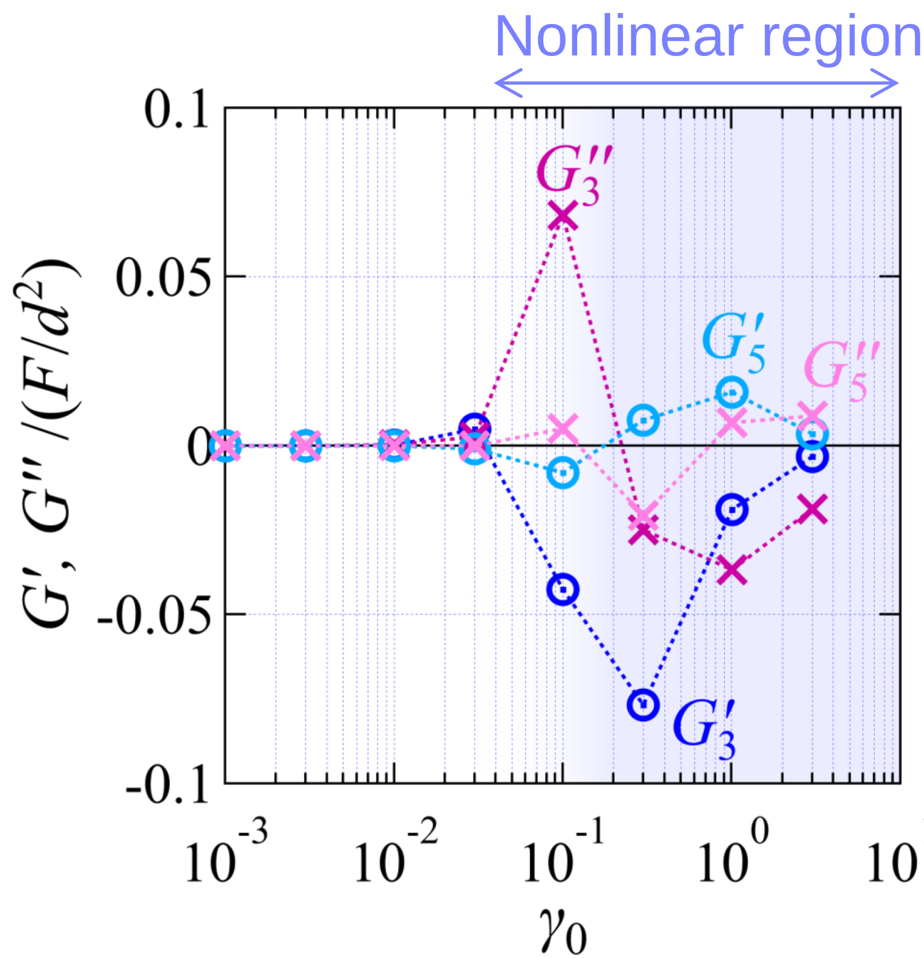




Fourier coefficients of stress



Dynamic modulus ($k = 1$)



Higher harmonic contributions ($k = 3, 5$)

$$\sigma(t) = \gamma_0 \sum_{k:\,\mathrm{odd}} \left(G'_k \sin k\omega t + G''_k \cos k\omega t \right)$$

Measures of nonlinear viscoelasticity

$$S = \frac{G'_\mathrm{L} - G'_\mathrm{M}}{G'_\mathrm{L}}$$

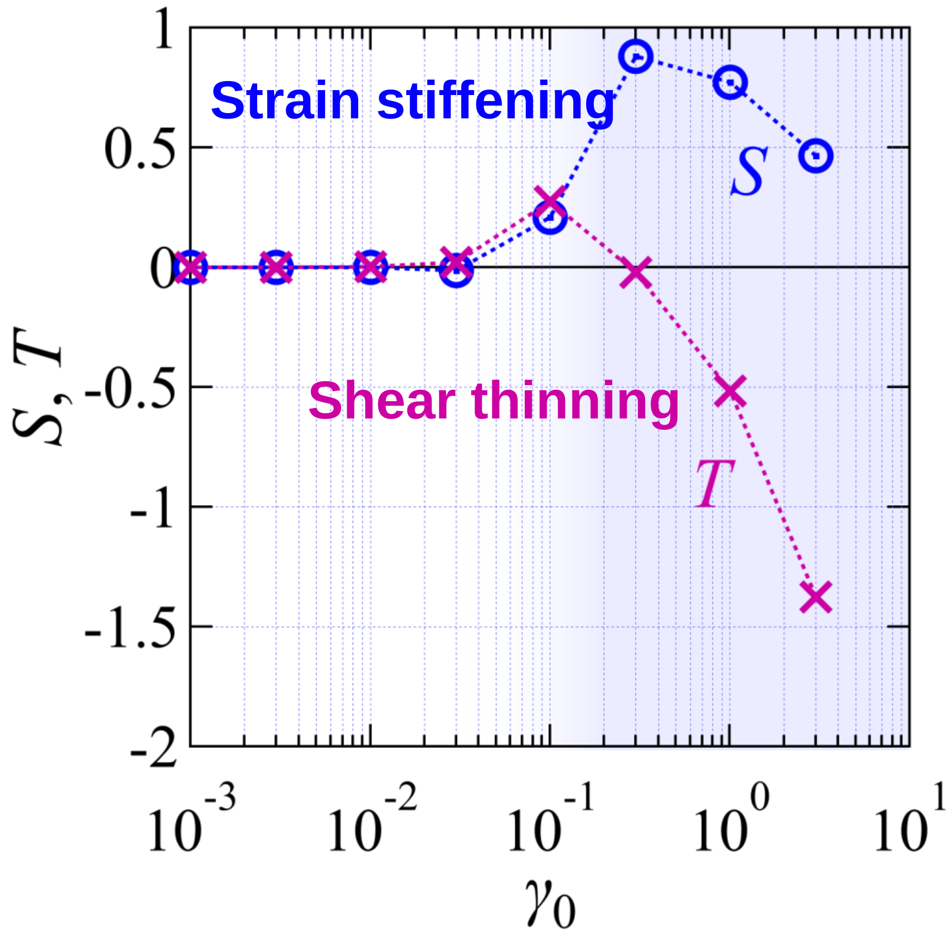
$S > 0$: strain stiffening

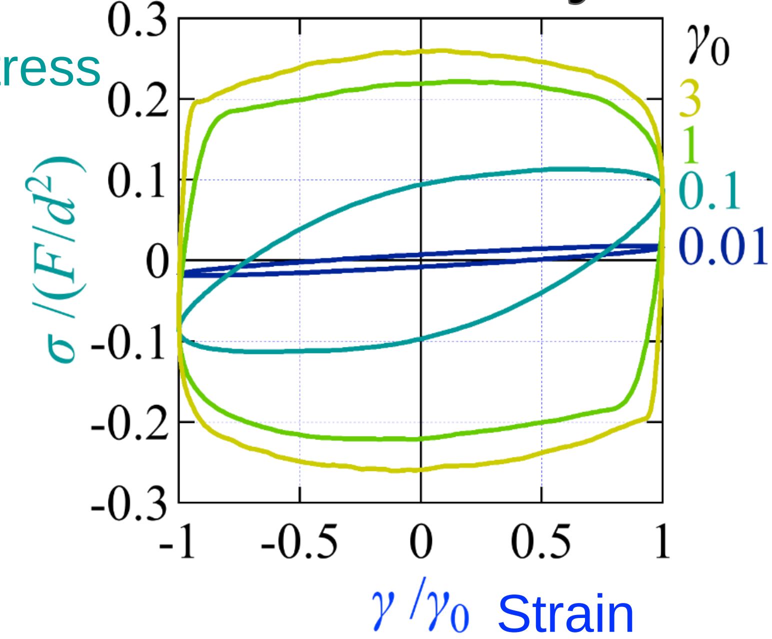
$S < 0$: strain softening

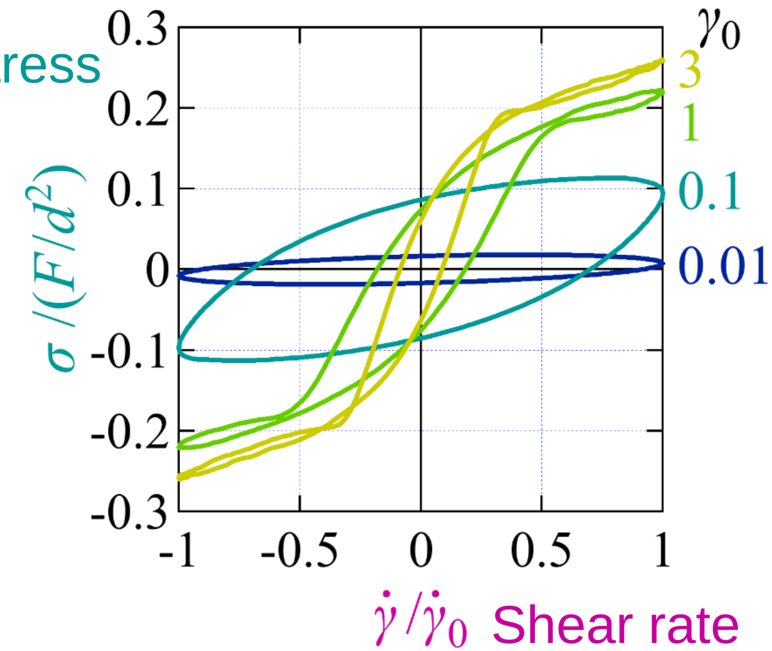
$$T = \frac{\eta'_\mathrm{L} - \eta'_\mathrm{M}}{\eta'_\mathrm{L}}$$

$T > 0$: shear thickening

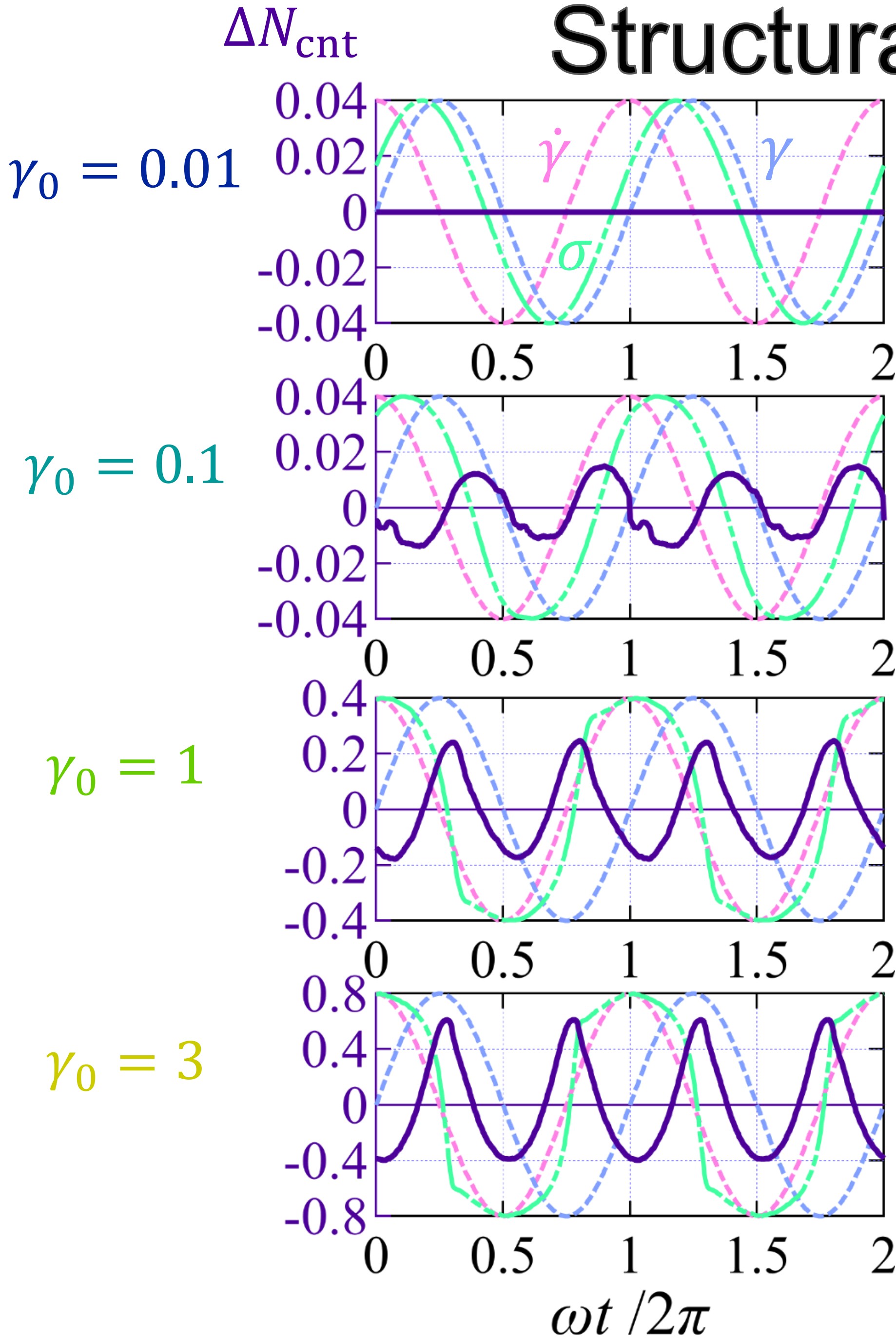
$T < 0$: shear thinning







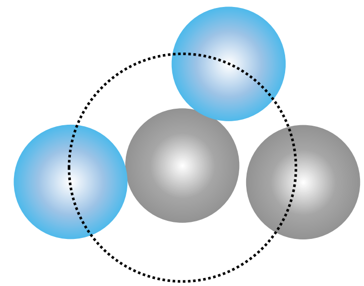
Structural change

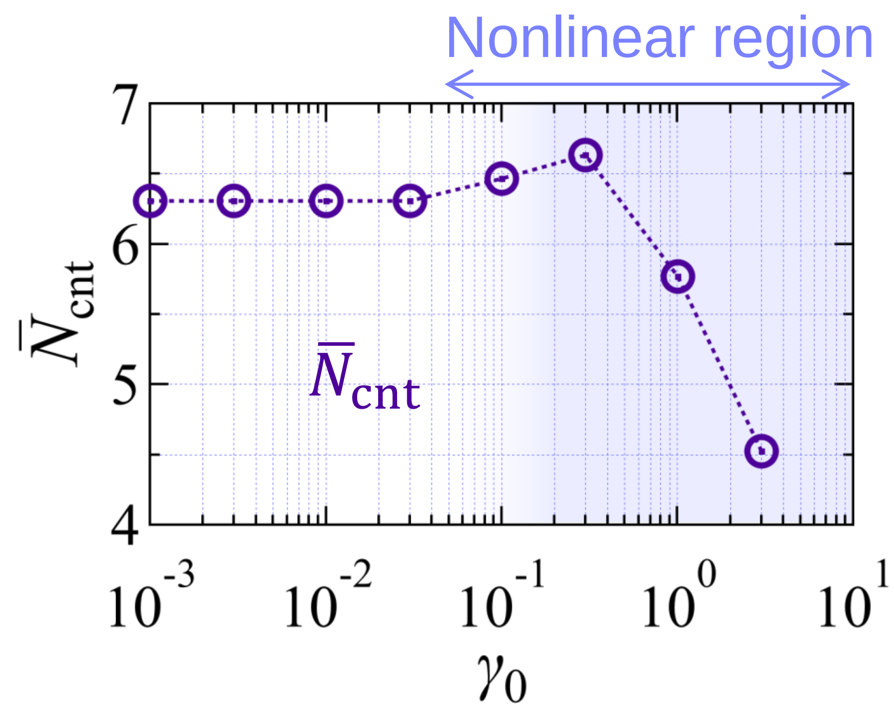


Contact number

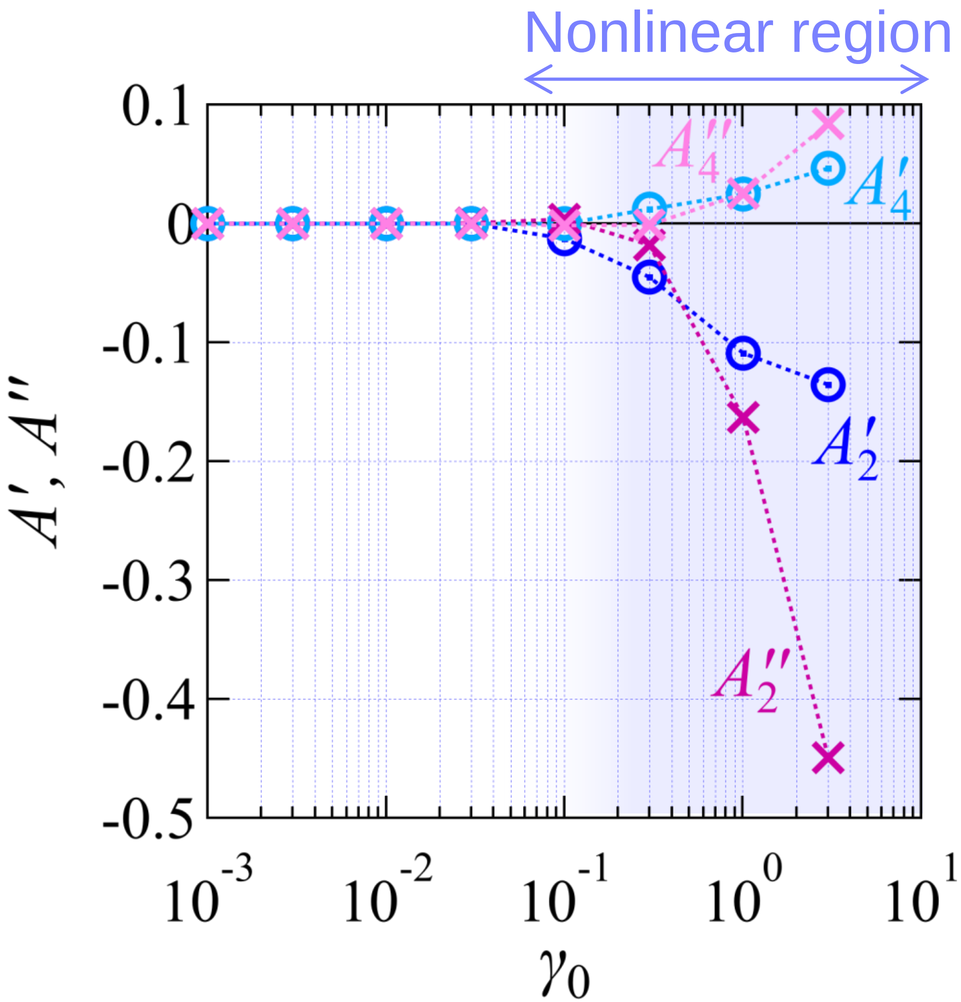
$\bar{N}_{\mathrm{cnt}} + \Delta N_{\mathrm{cnt}}(t)$

Mean Variation



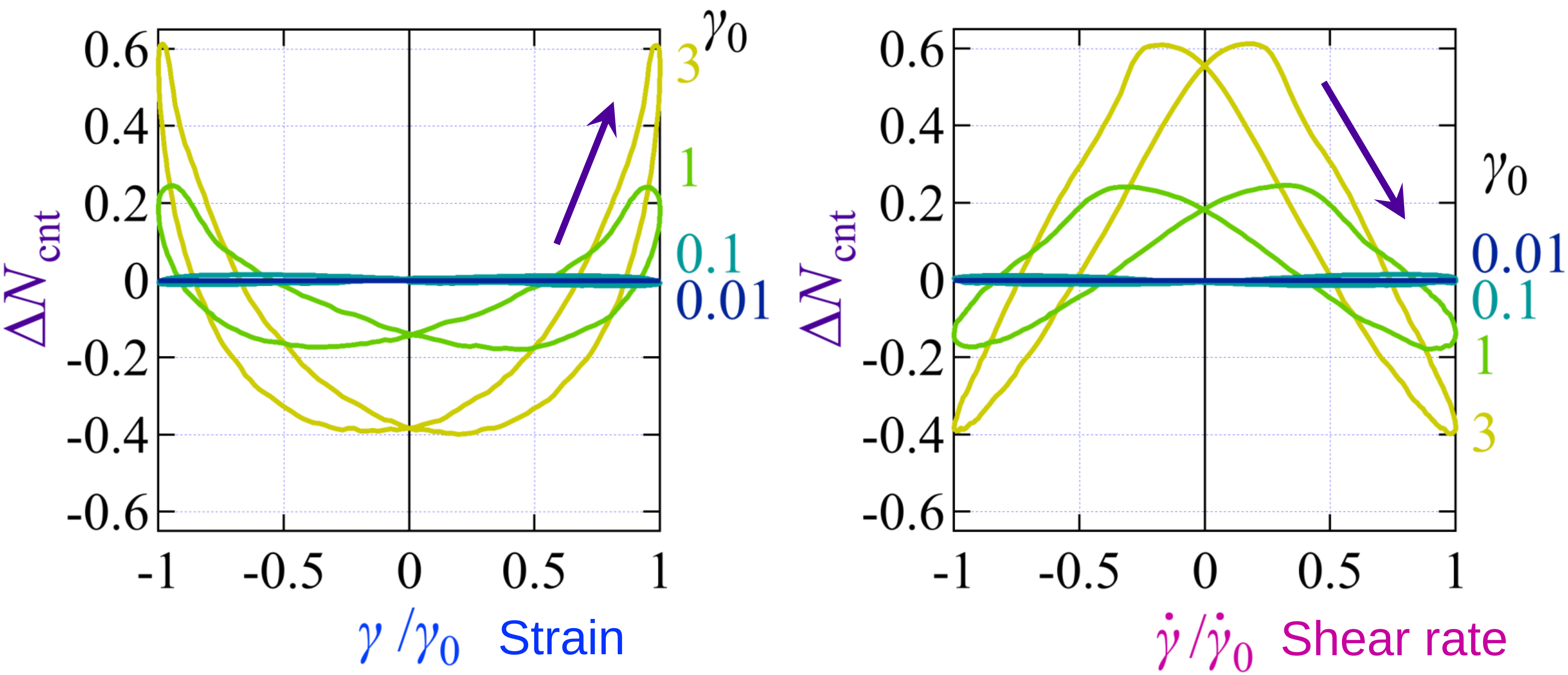


Fourier coefficients of contact number



$$\Delta N_{\mathrm{cnt}}(t) = \sum_{k:\mathrm{even}} \left(A_k' \sin k\omega t + A_k'' \cos k\omega t\right)$$

Structural change



Contact number increases with increasing strain

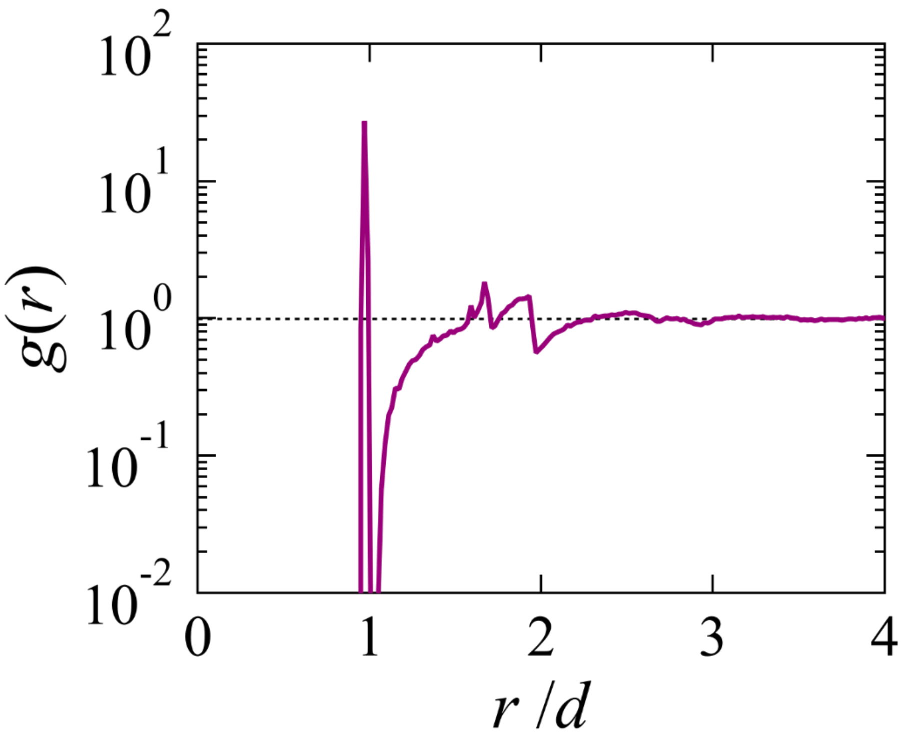
↔ Strain stiffening

Contact number decreases with increasing shear rate

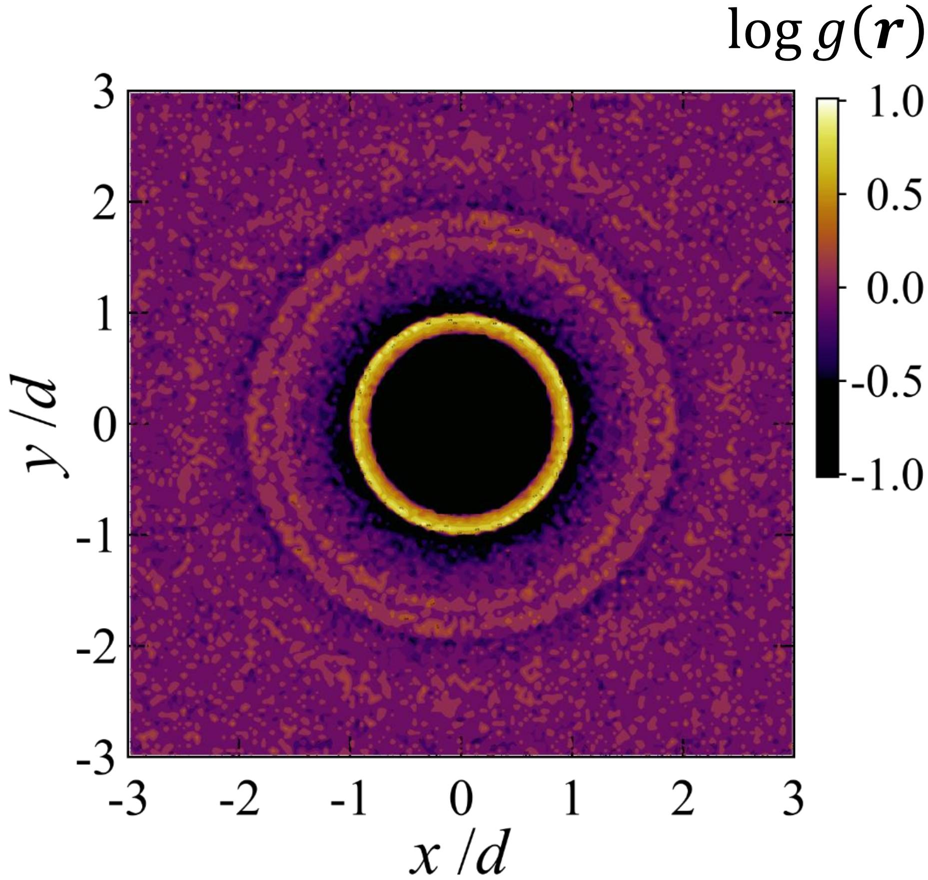
↔ Shear thinning

Pair distribution function

No-shear condition



Radial distribution function

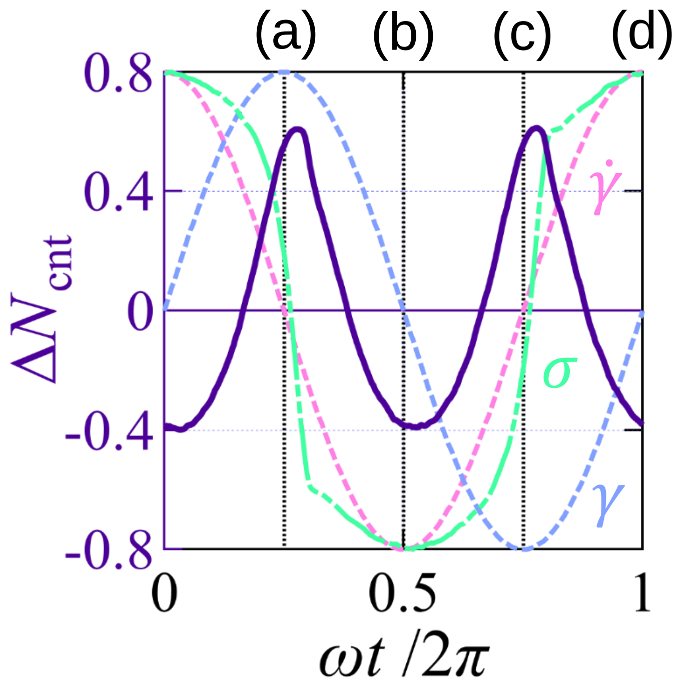


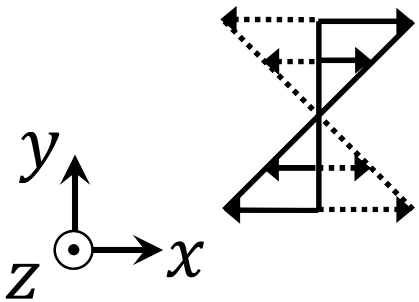
Distribution function on xy-plane

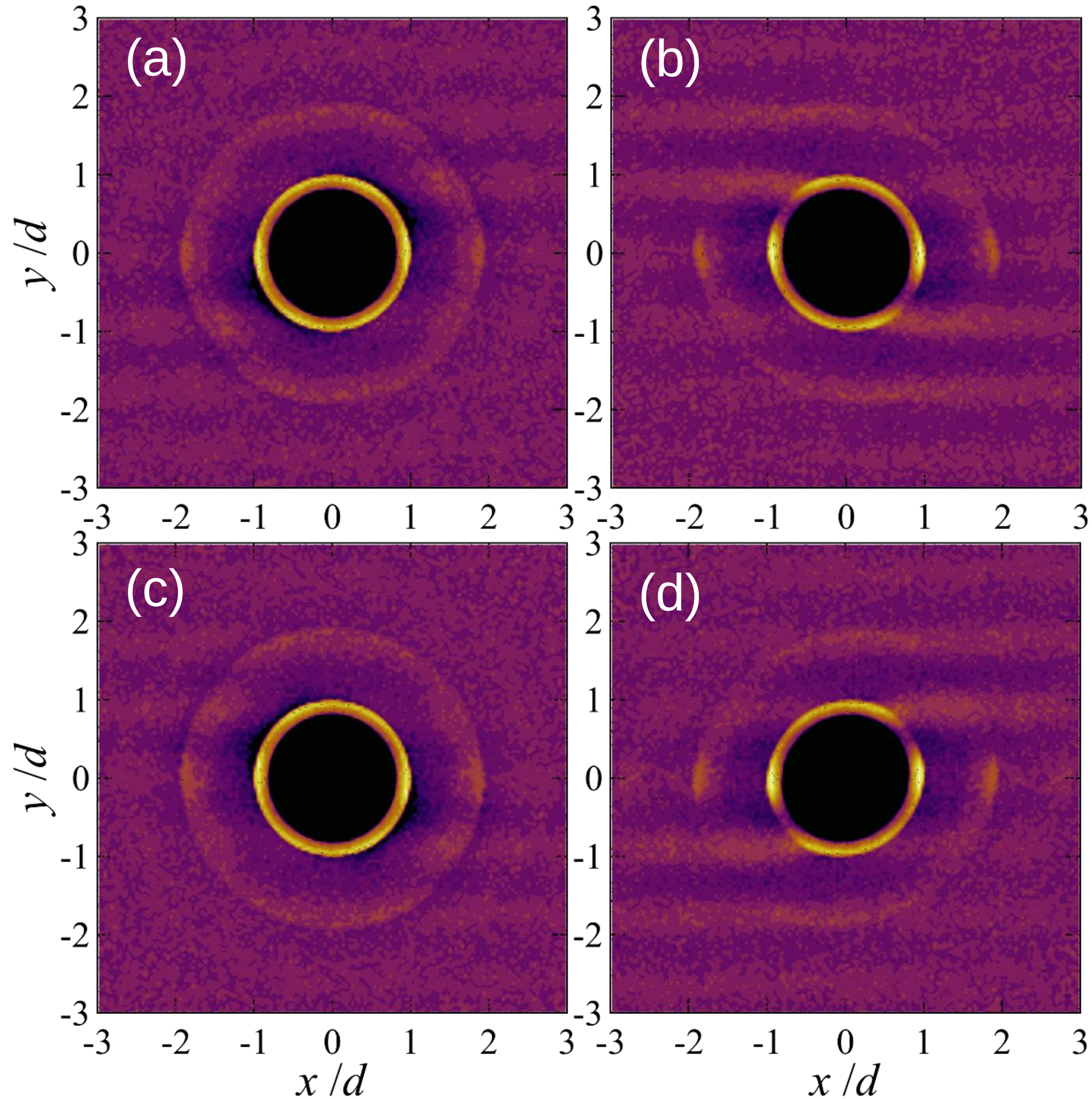
- Number density of particles around a particle
- Normalized by the bulk density of particles

Pair distribution function

$\gamma_0 = 3$

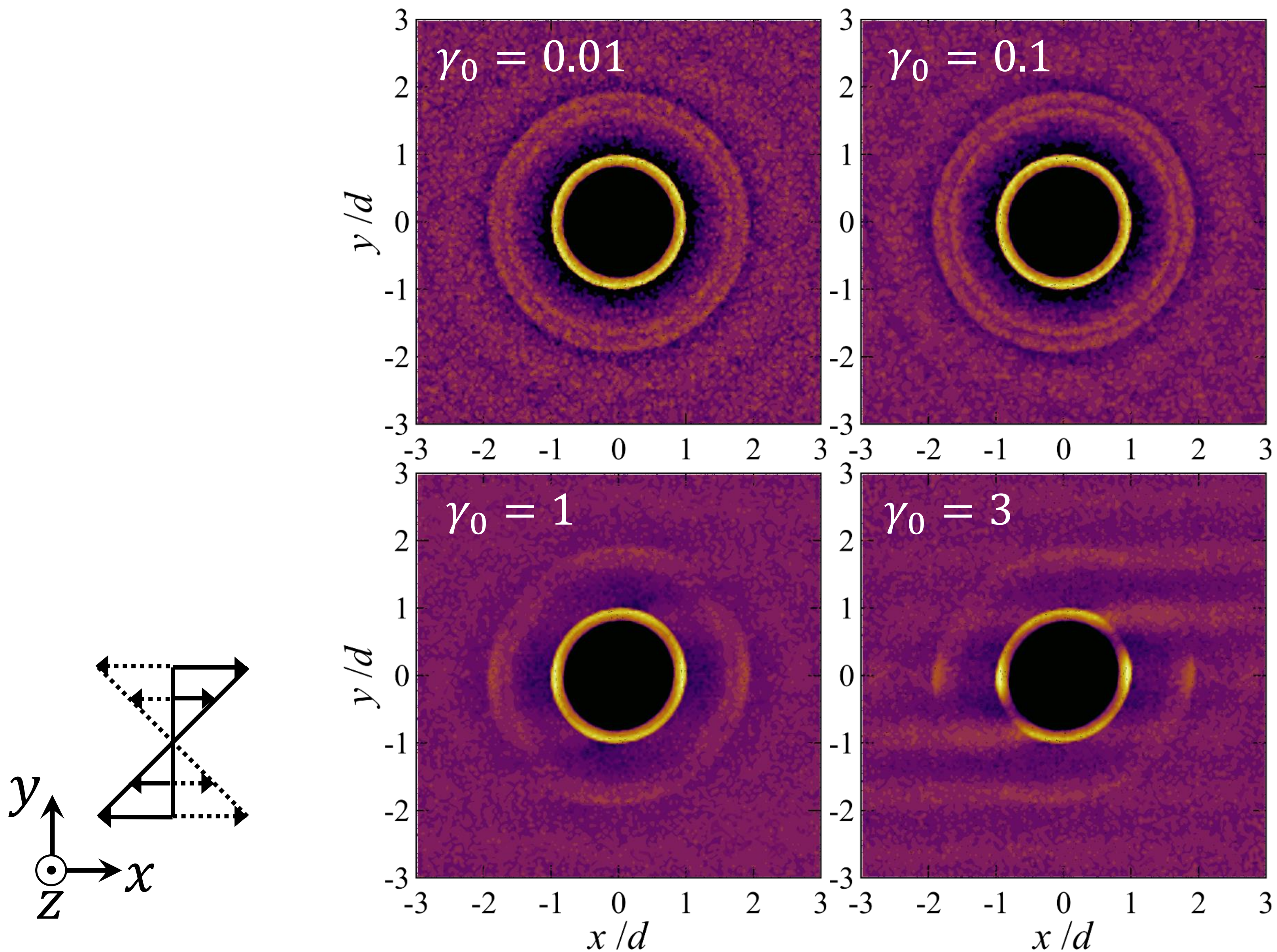






Anisotropic structure

Pair distribution function



Summary

- Nonlinear viscoelasticity describes change in elastic modulus and viscosity due to intracycle variation in shear strain/rate

  → Nonlinear viscoelasticity can be a measure to control coating operation in fabrication processes

- Nonlinear viscoelasticity of aggregated suspensions indicates strain stiffening and shear thinning

- Relationship between structural change and nonlinear viscoelasticity:
  - Contact number increases with increasing strain
    ↔ Strain stiffening
  - Contact number decreases with increasing shear rate
    ↔ Shear thinning
  - Decrease in contact number ↔ Anisotropic structural change