

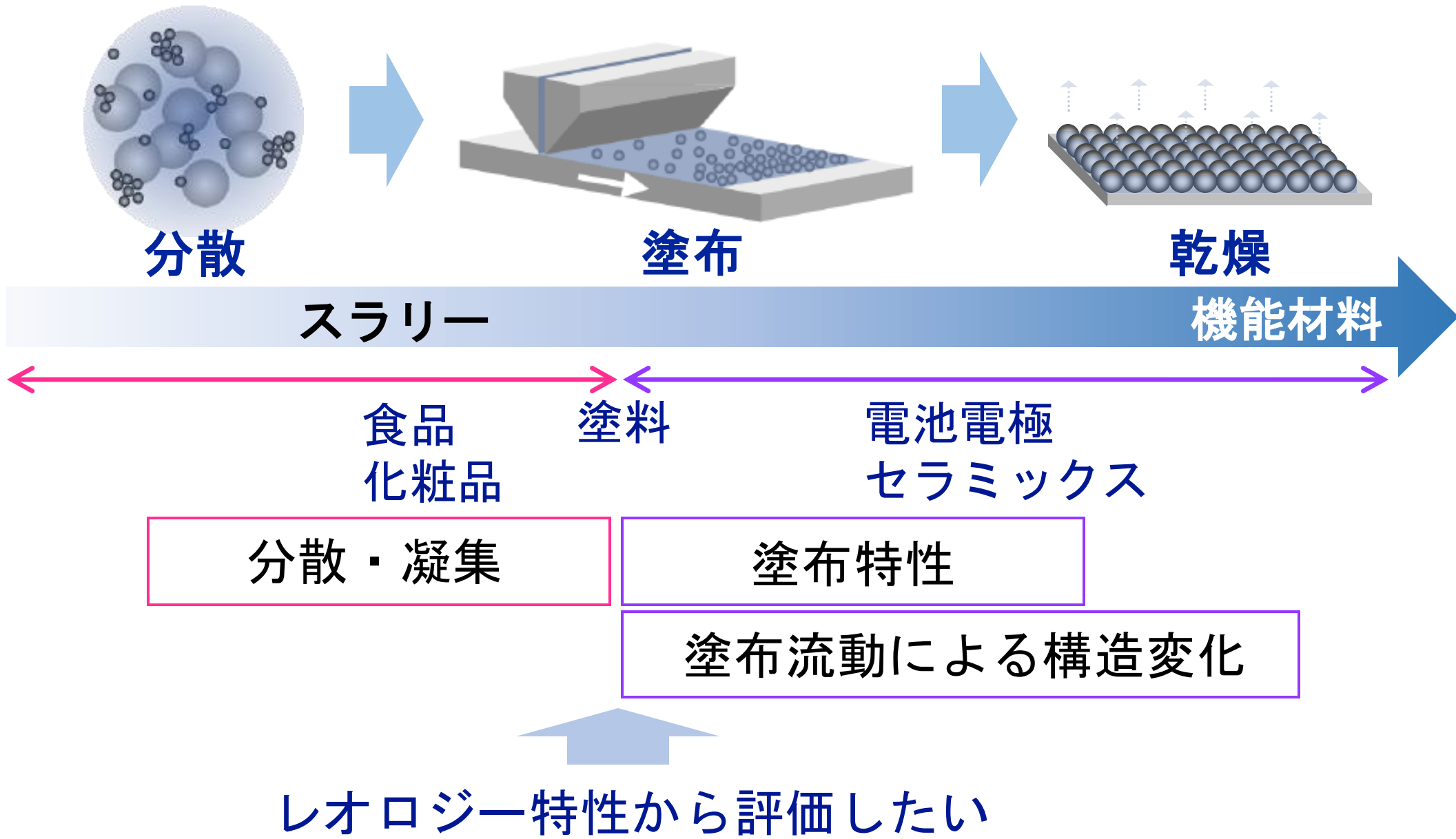
水系スラリーの粘弾性と粒子間ポテンシャルの関係

○ 辰巳 怜¹, 小池 修¹, 吉江 建一¹, 辻 佳子²

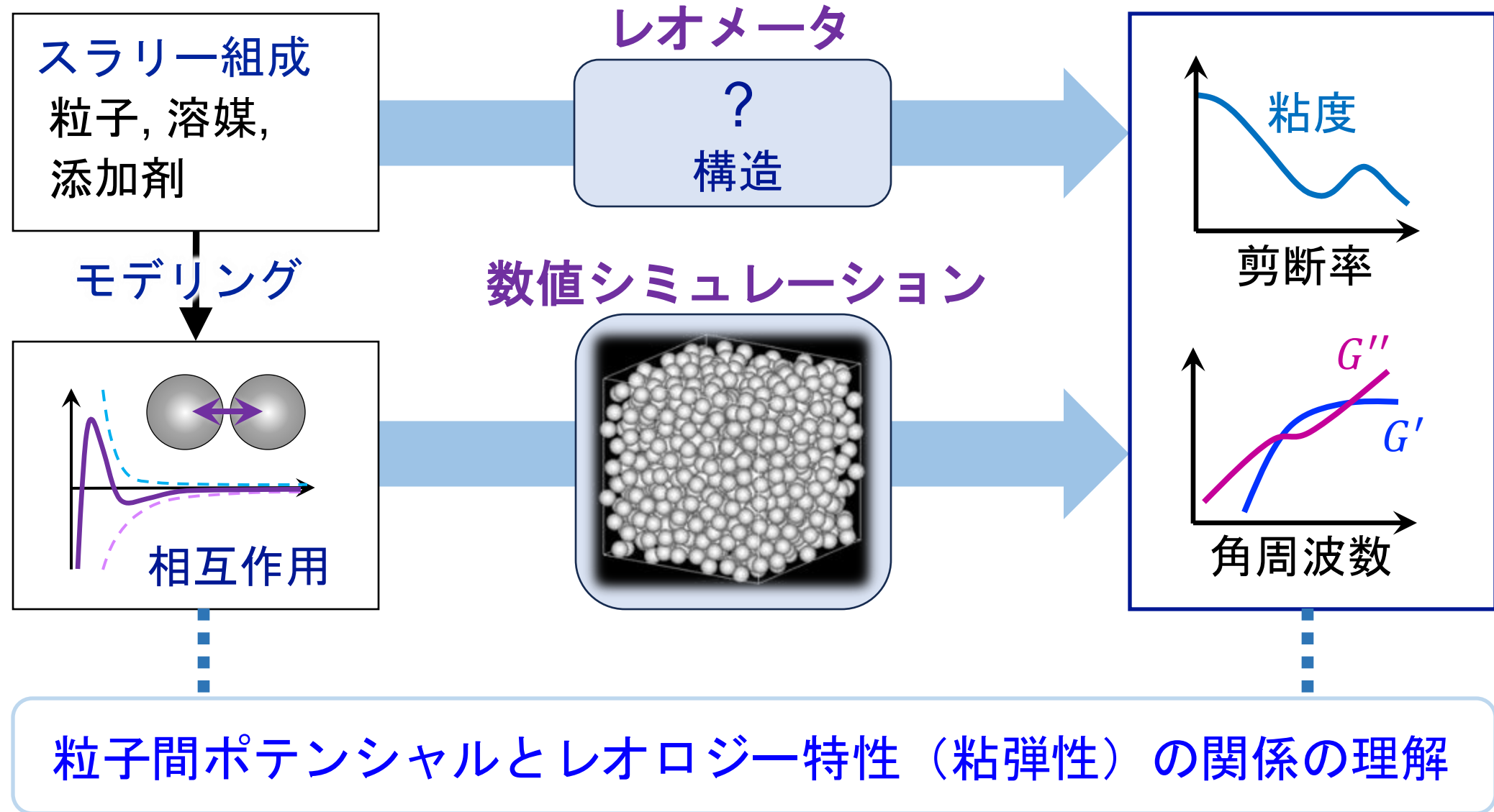
¹(一社)プロダクト・イノベーション協会

²東京大学 環境安全研究センター/大学院工学系研究科

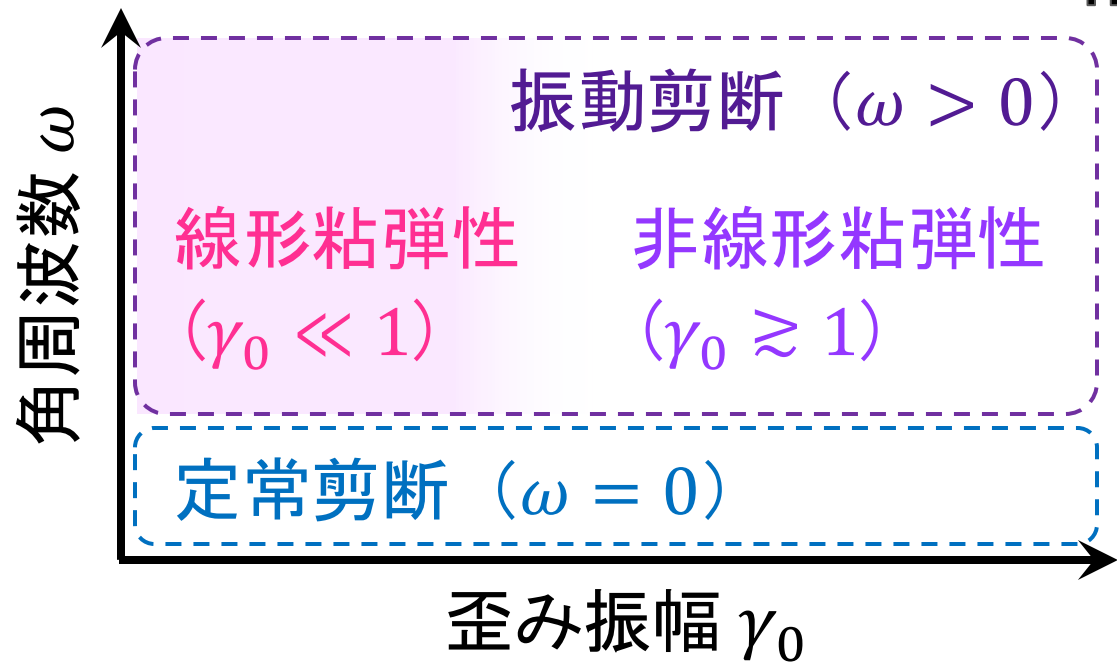
ものづくりとレオロジー



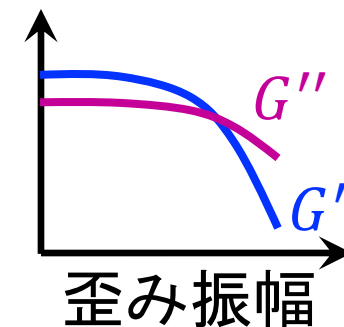
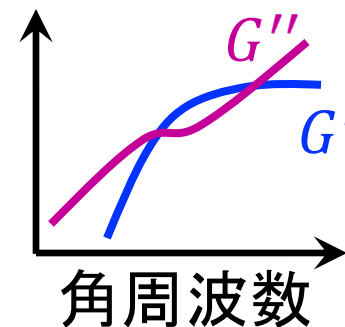
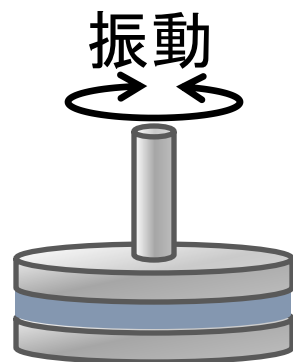
目的



粘弾性



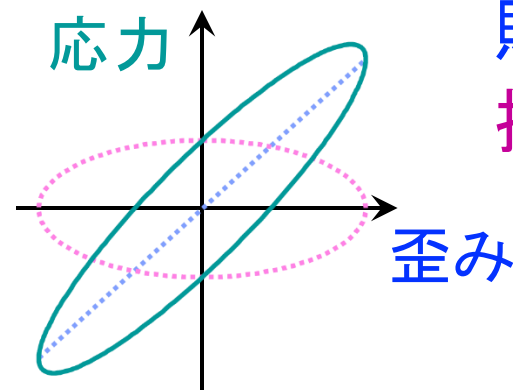
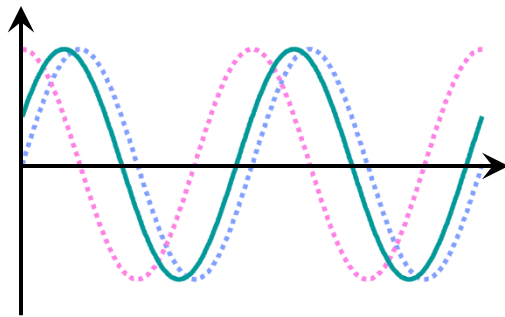
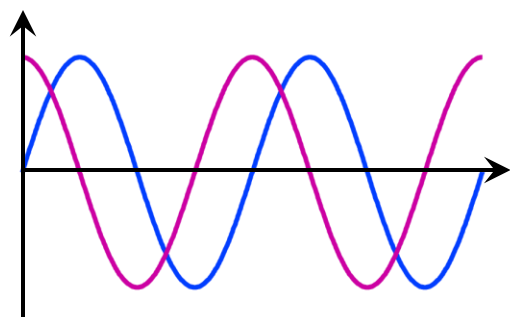
動的粘弾性測定



歪み: $\gamma_0 \sin \omega t$

剪断率: $\gamma_0 \omega \cos \omega t$

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



貯蔵弾性率: G'

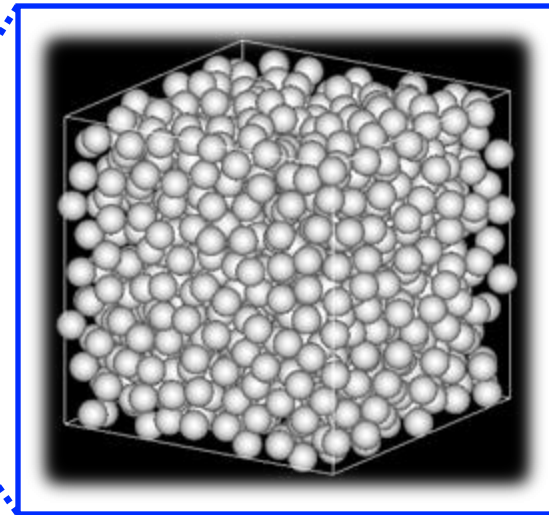
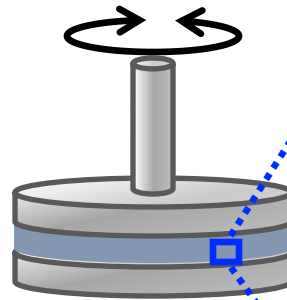
損失弾性率: G''

粒子の運動方程式

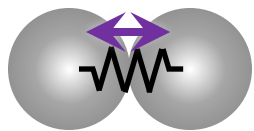
$$m\dot{\boldsymbol{v}}_i = -\underbrace{\zeta(\boldsymbol{v}_i - \boldsymbol{V}_i^{\text{ex}})}_{\text{流体抗力}} + \underbrace{\boldsymbol{F}_i^{\text{P}}}_{\text{粒子間力}}$$

- 抗力係数 : $\zeta = 3\pi\eta d$

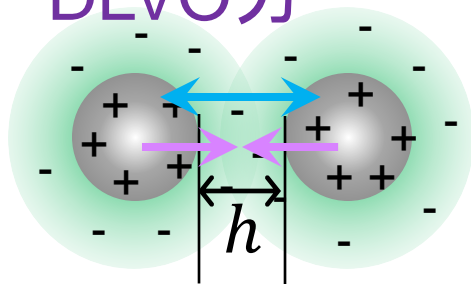
粒子直径: d 溶媒粘度: η



- 接触力



- DLVO力

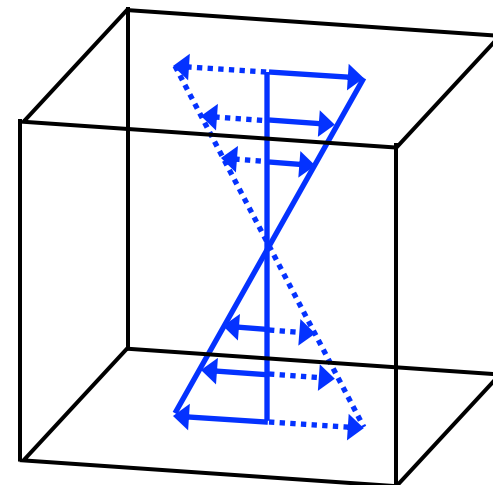
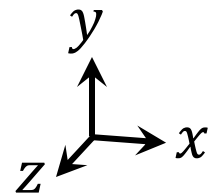


- 振動剪断場

$$\boldsymbol{V}_i^{\text{ex}} = \dot{\gamma}(t)y_i \boldsymbol{e}_x \quad \dot{\gamma}(t) = \gamma_0\omega \cos \omega t$$

- 境界条件 (剪断場に適合した周期境界)

x, z : Periodic, y : Lees-Edwards



粘弾性の評価

入力：振動剪断場

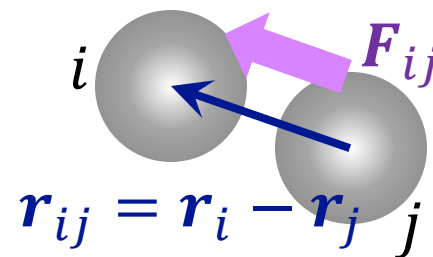
歪み： $\gamma(t) = \gamma_0 \sin \omega t$

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

出力：剪断応力

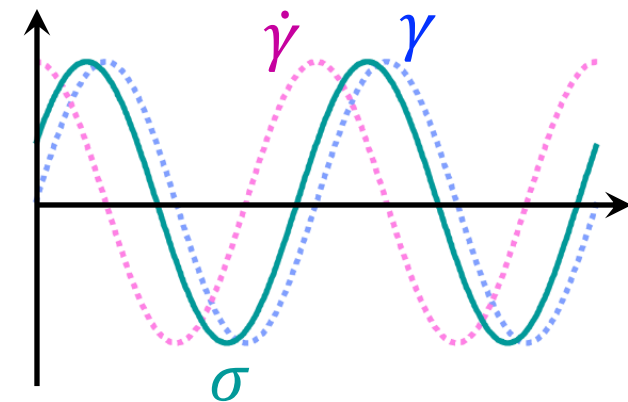
$$\sigma = -\frac{1}{V} \sum_{i < j} F_{ij}^x r_{ij}^y$$

* 粒子間力の寄与のみ考慮



貯蔵/損失弾性率

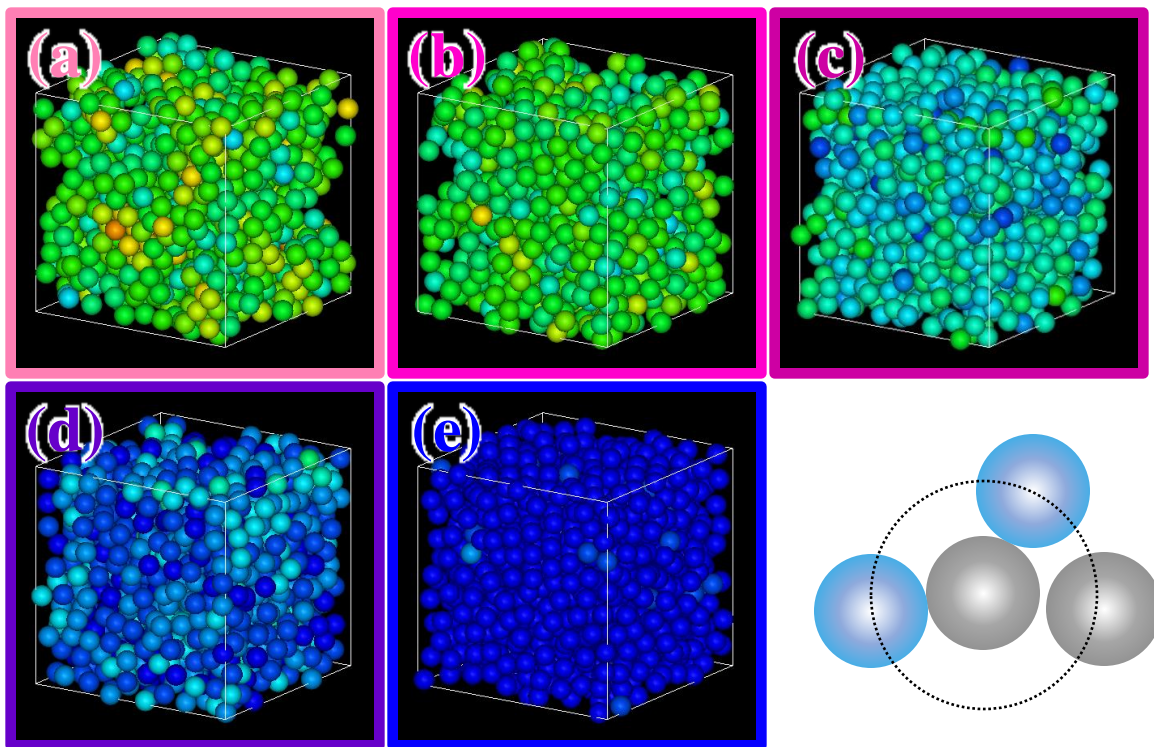
$$\begin{pmatrix} G'(\omega) \\ G''(\omega) \end{pmatrix} = \frac{\omega}{\pi \gamma_0} \int_0^{\frac{2\pi}{\omega}} \sigma(t) \begin{pmatrix} \sin \omega t \\ \cos \omega t \end{pmatrix} dt$$



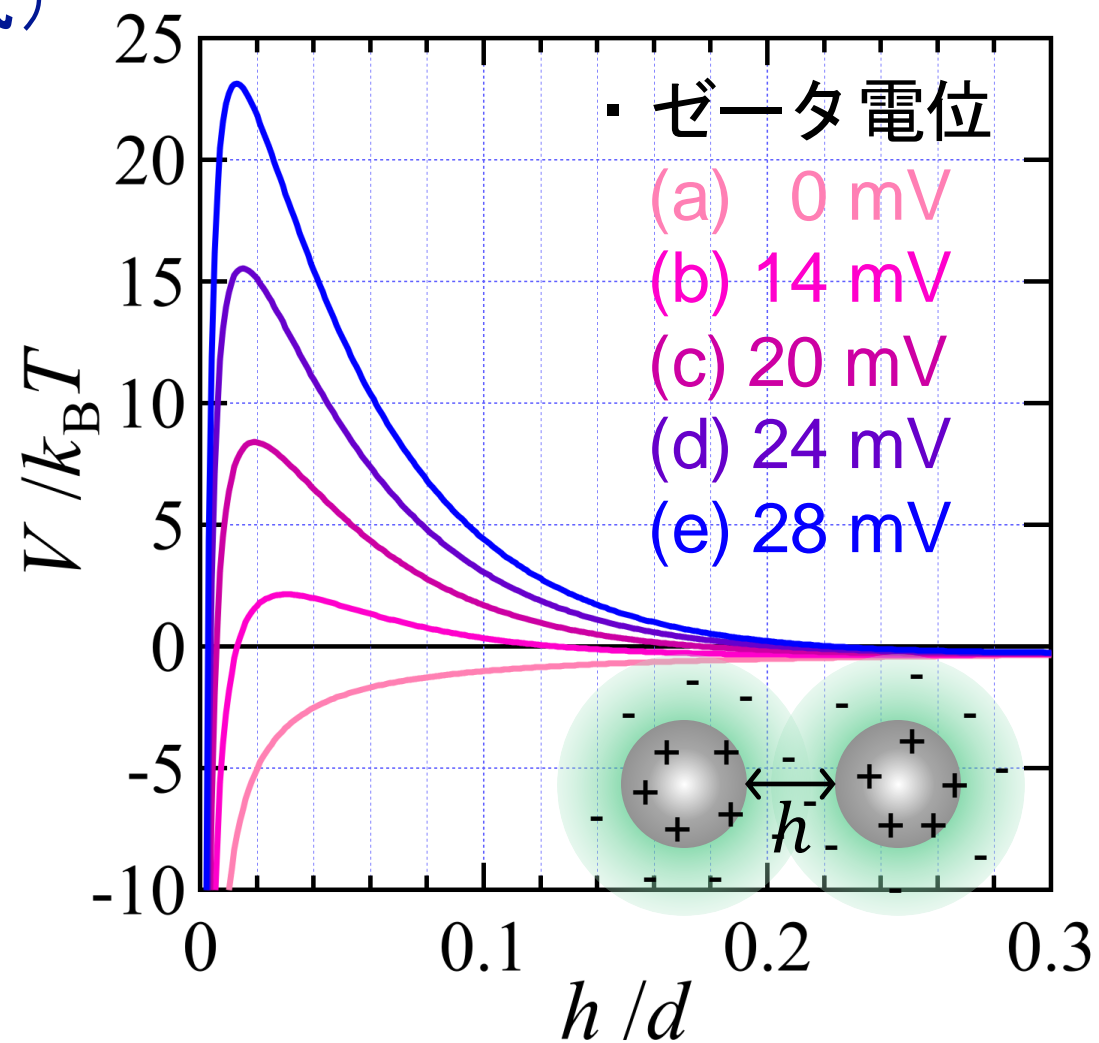
初期構造

Brown運動により形成 (Langevin方程式)

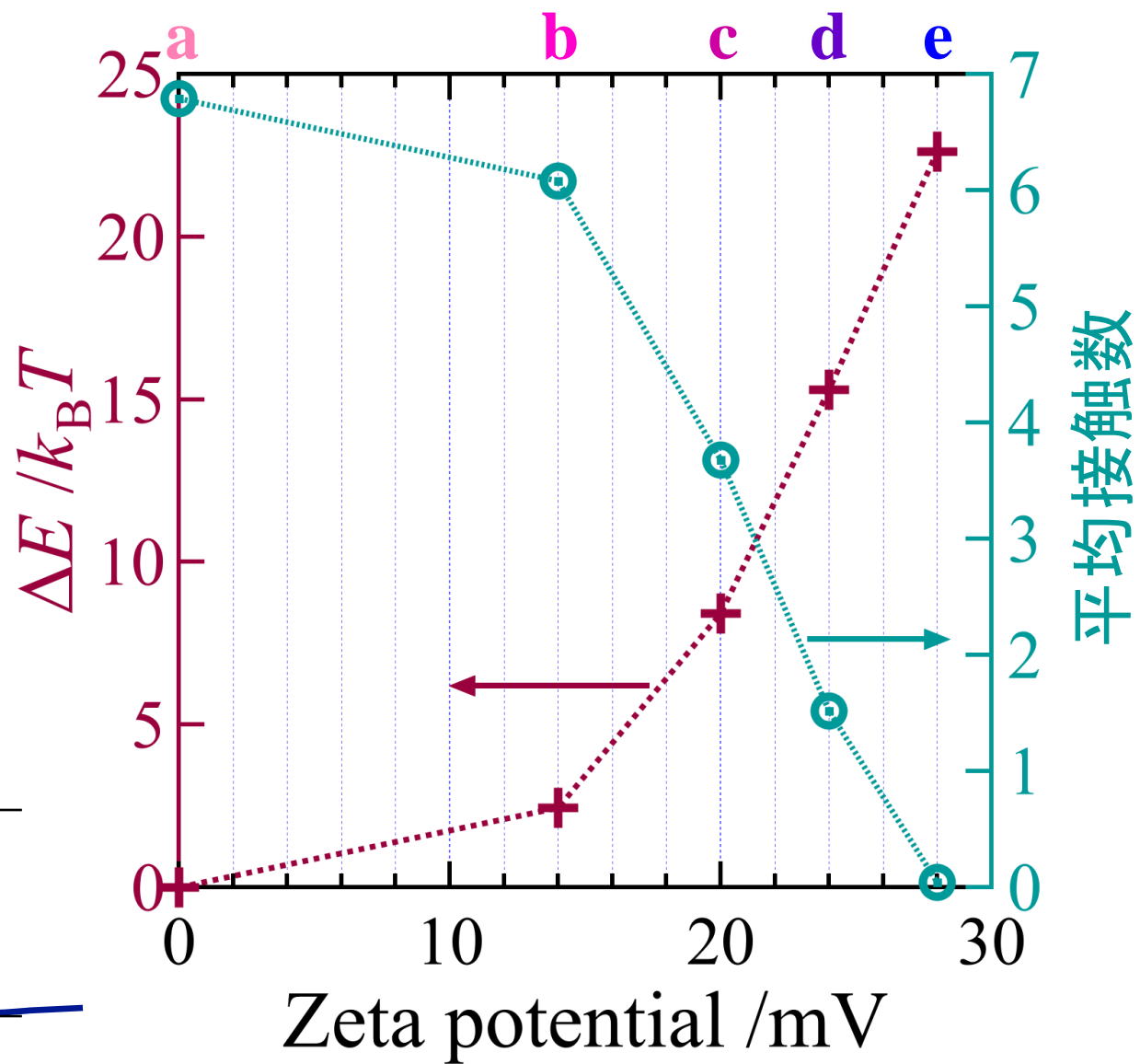
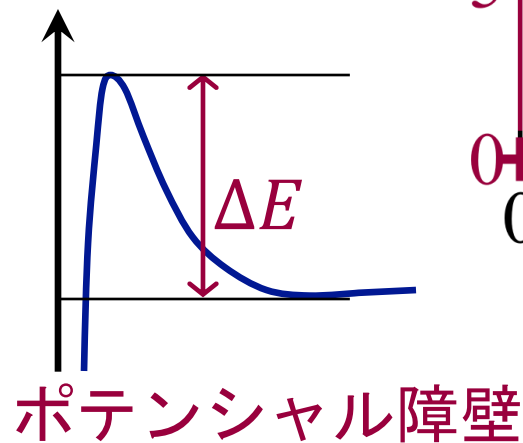
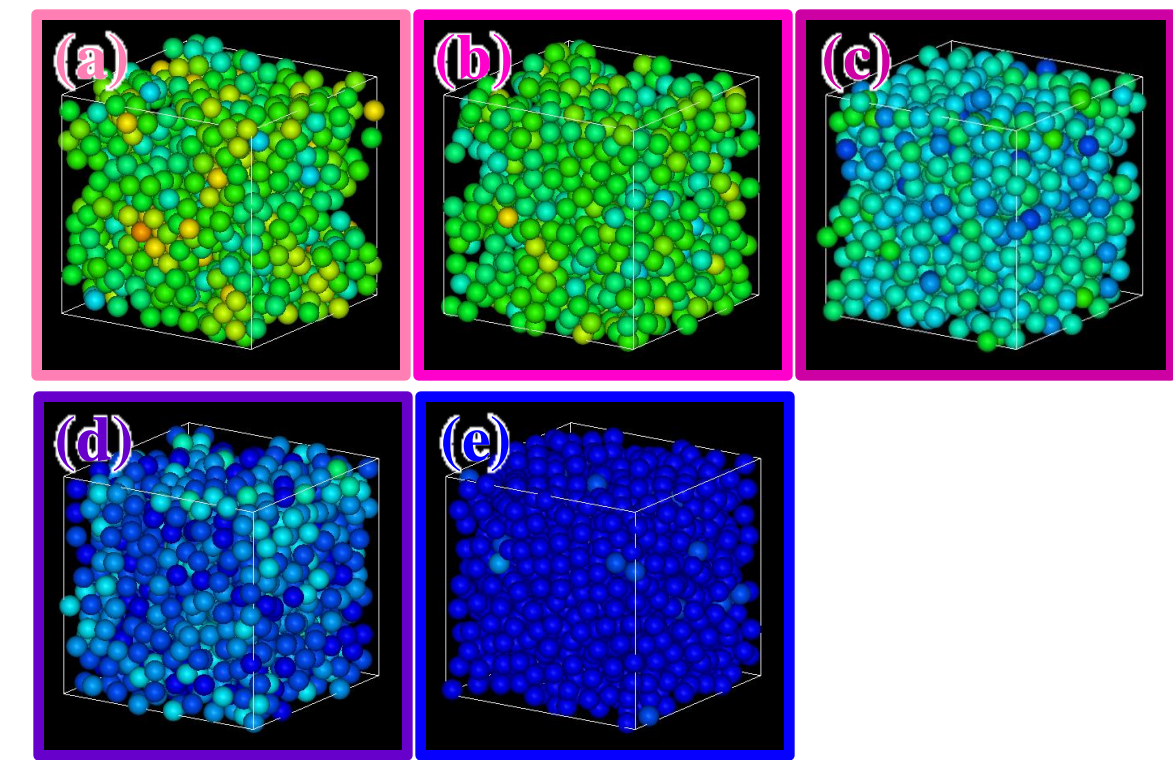
- ・ 粒子直径 : $d = 100 \text{ nm}$
- ・ 粒子濃度 : 45 vol%



接触数 0  12



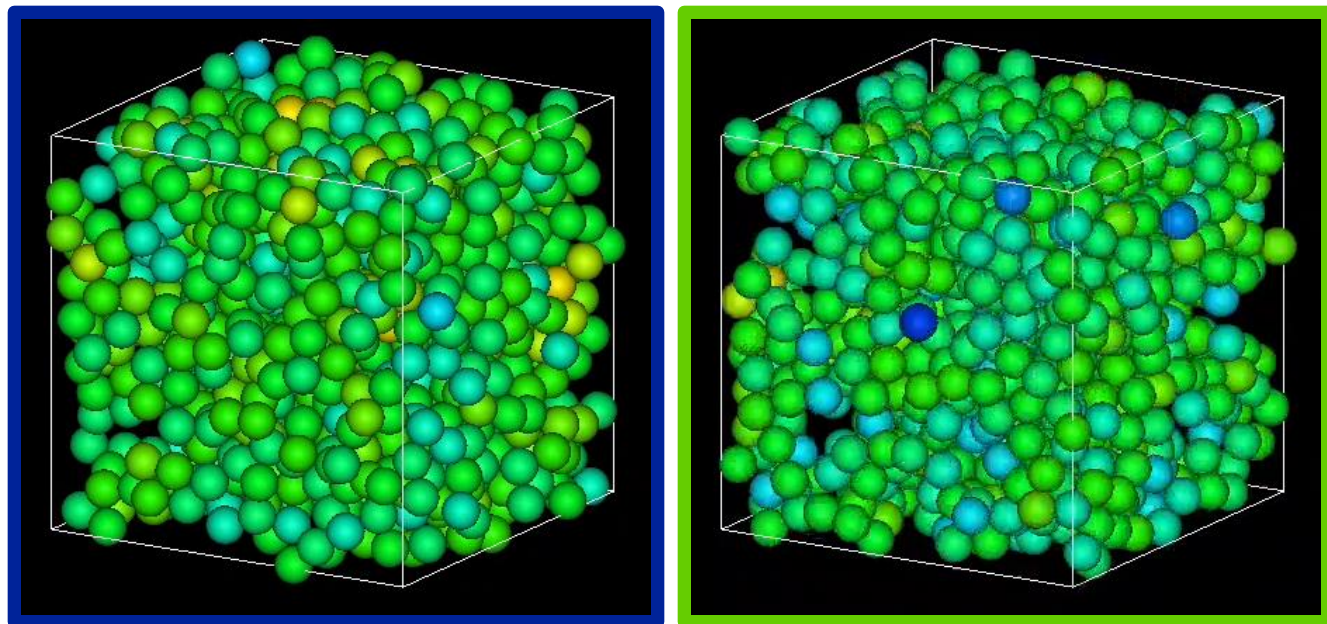
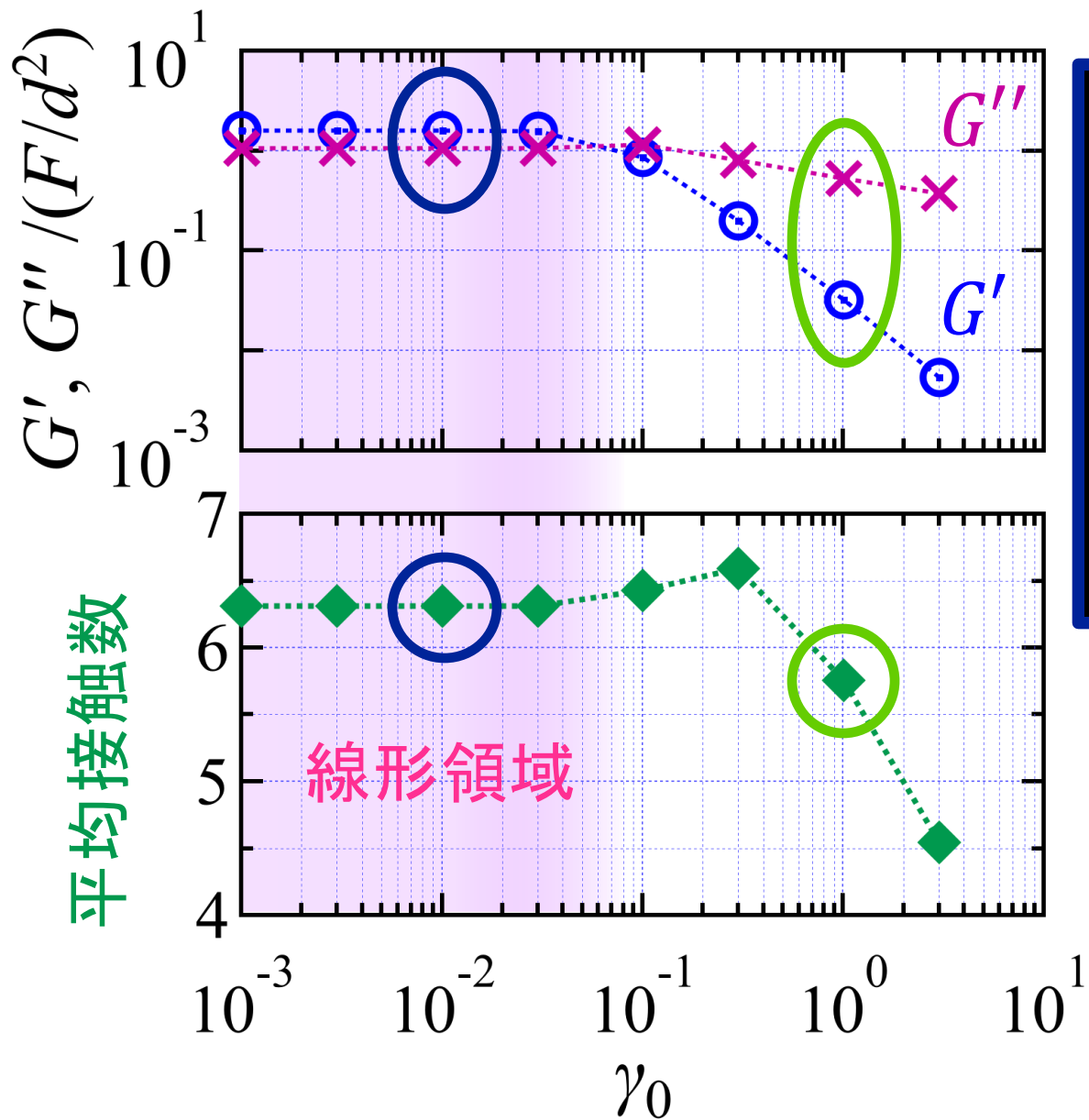
初期構造



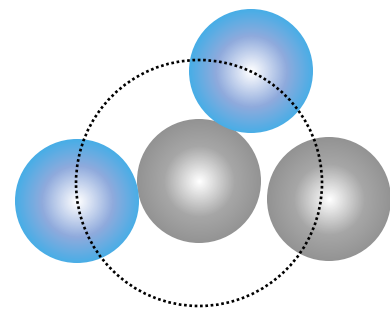
粘弾性の線形領域

(a) 0 mV

$\omega\tau = 1.2$

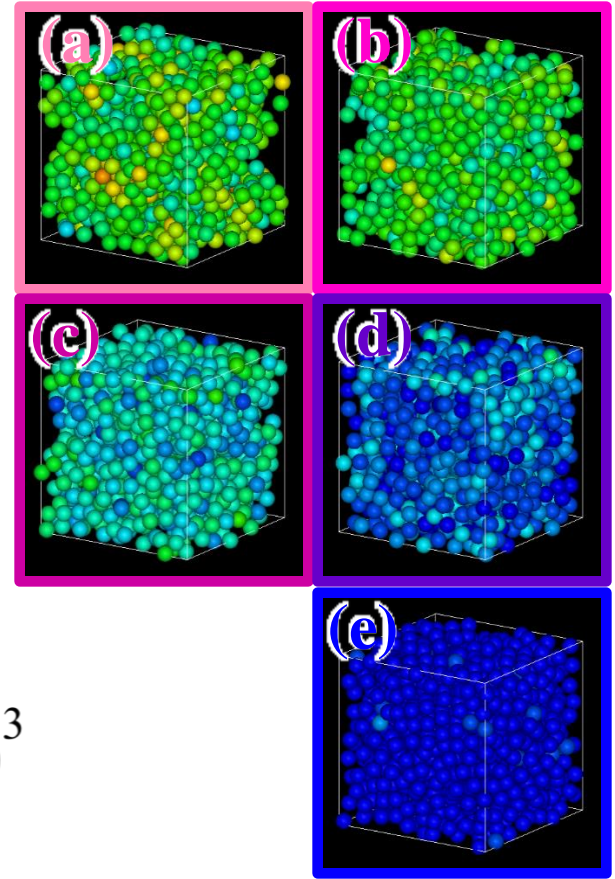
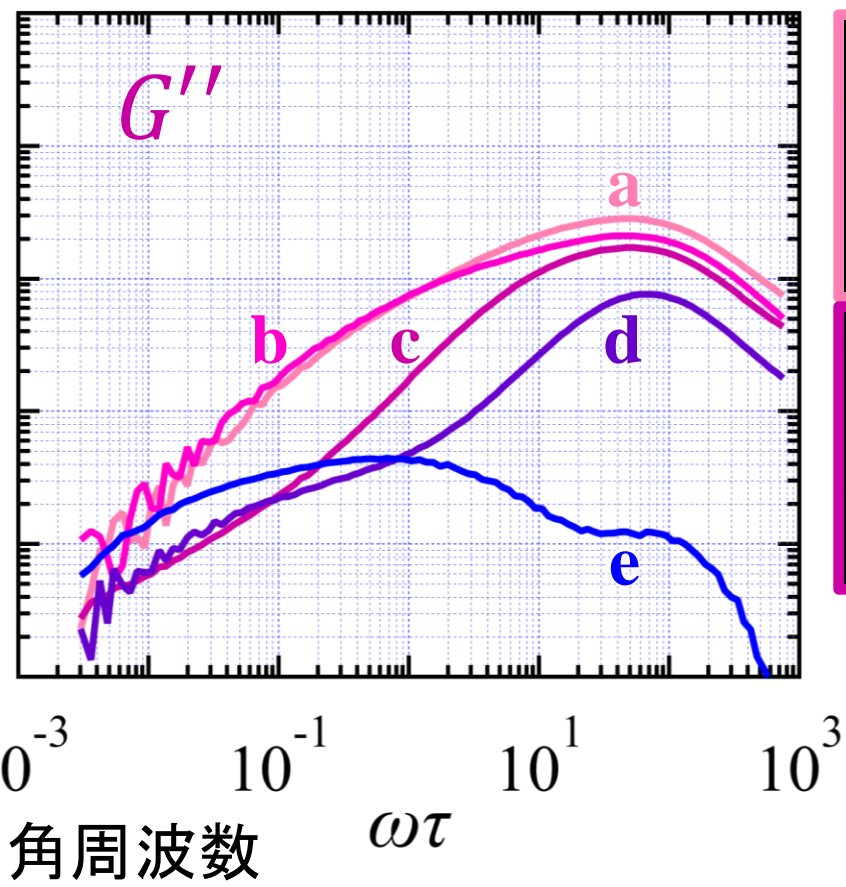
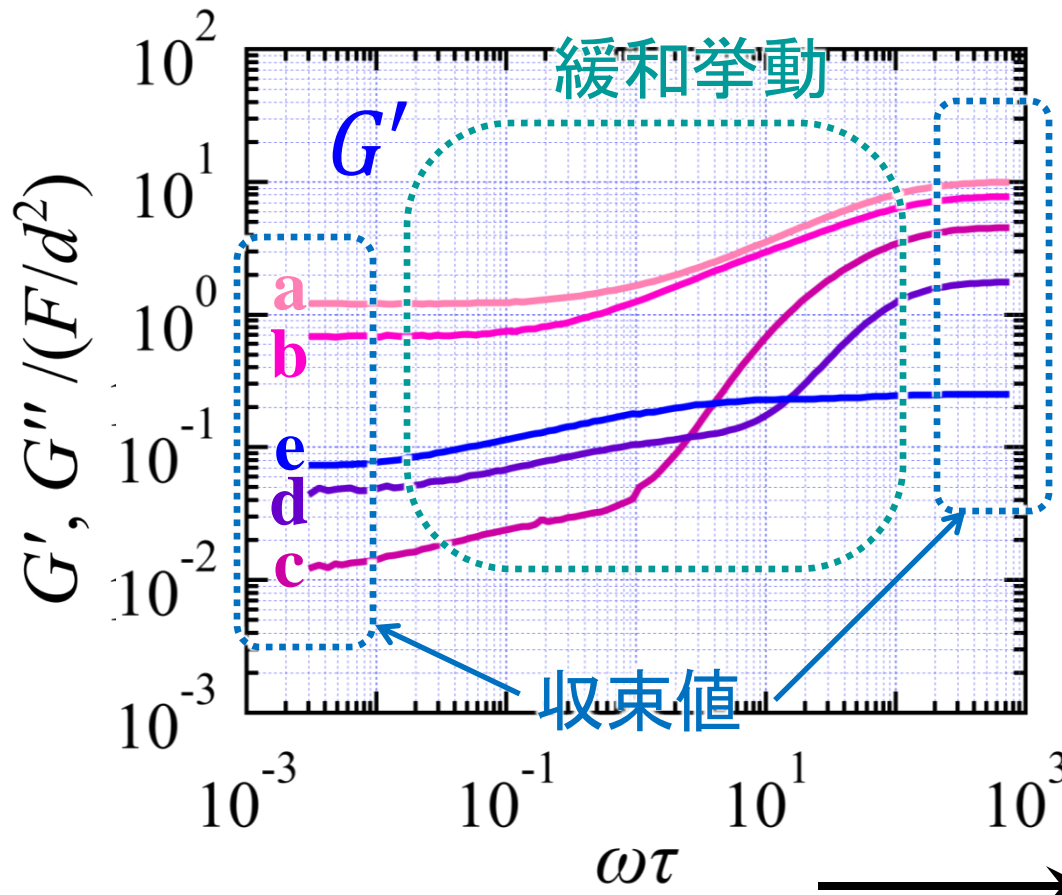


接触数



線形粘弾性

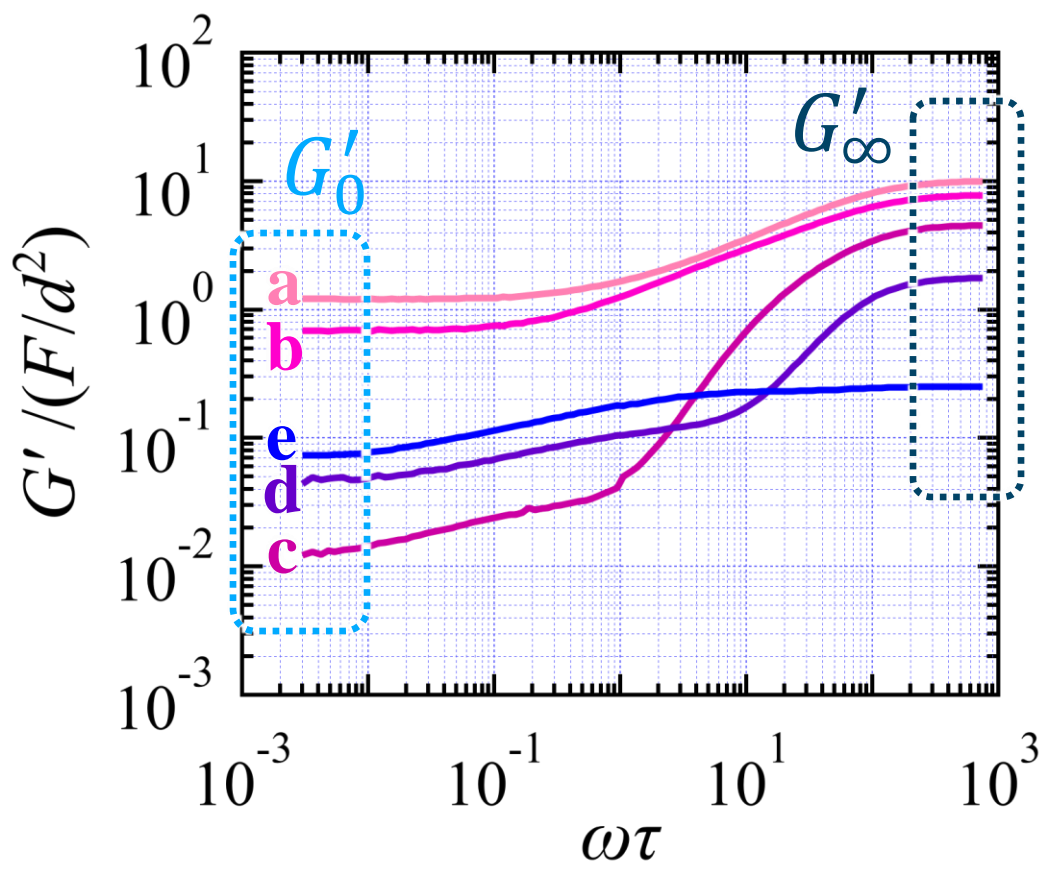
$\gamma_0 = 10^{-2}$ (線形領域)



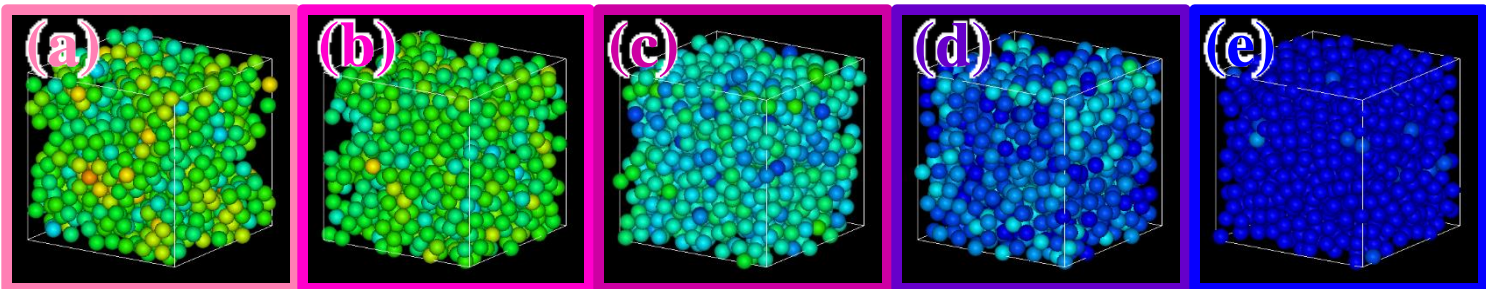
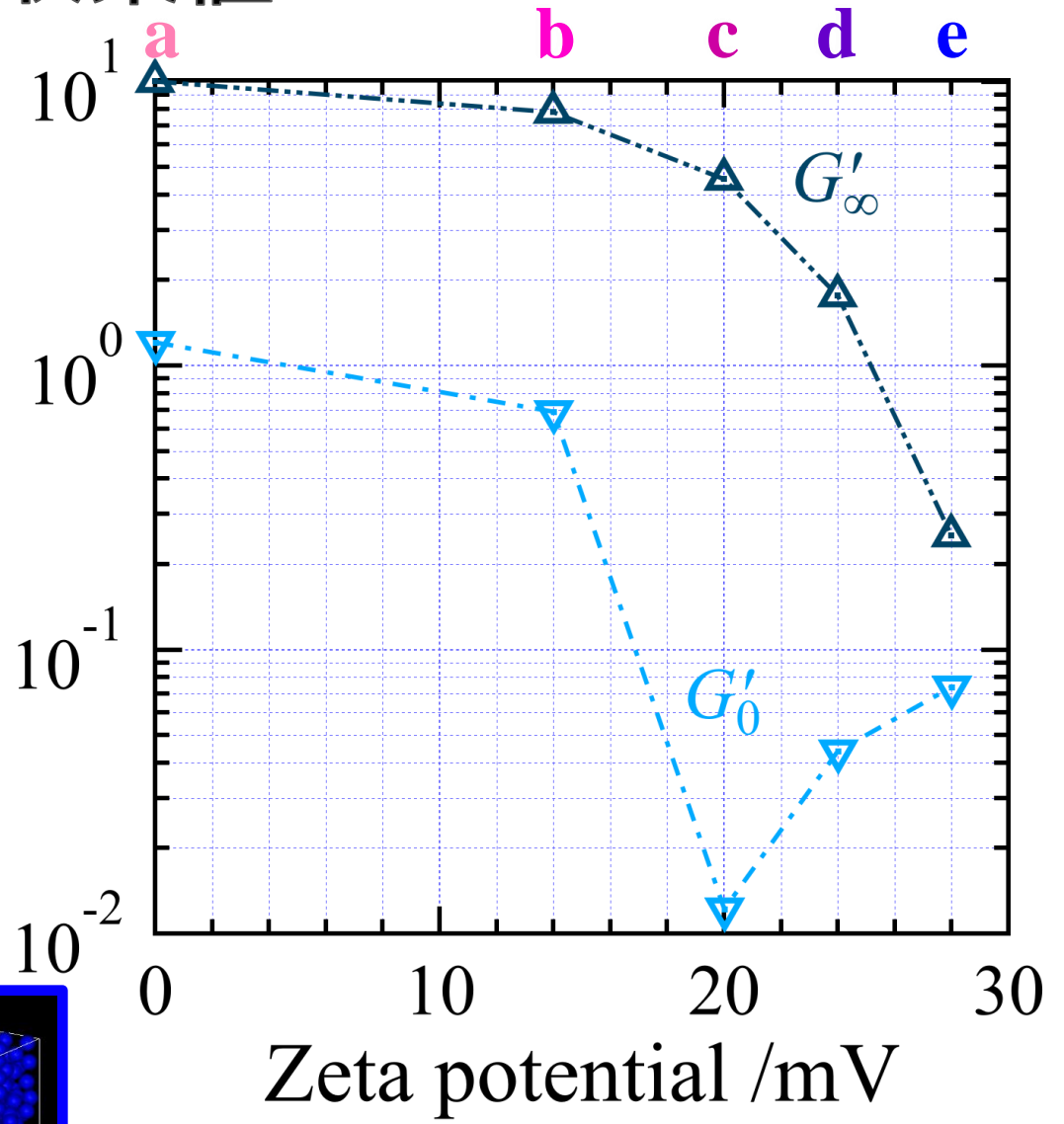
特性時間 $\tau = \frac{d}{U} = \frac{3\pi\eta d^2}{F} \leftarrow 3\pi\eta dU = F$

流体抗力 = 粒子間付着力

貯蔵弾性率の収束値



$G'_0, G'_\infty / (F/d^2)$



構造の緩和時定数

粘弾性挙動と構造との関係を考察

$$m\ddot{\mathbf{r}}_i = -\zeta\dot{\mathbf{r}}_i + \mathbf{F}_i^{\text{P}} \quad (i = 1, \dots, N)$$

流体抗力 粒子間力

慣性項の無視, 線形化

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

$$\mathbf{r} = \begin{pmatrix} \mathbf{r}_1 \\ \mathbf{r}_2 \\ \vdots \\ \mathbf{r}_N \end{pmatrix} \quad \mathbf{H} = \begin{pmatrix} \mathbf{H}_{11} & \mathbf{H}_{12} & \cdots & \mathbf{H}_{1N} \\ \mathbf{H}_{21} & \mathbf{H}_{22} & \ddots & \vdots \\ \vdots & \ddots & \ddots & \vdots \\ \mathbf{H}_{N1} & \cdots & \cdots & \mathbf{H}_{NN} \end{pmatrix}$$

$$\mathbf{H}_{ij} = -\frac{\partial \mathbf{F}_i^{\text{P}}}{\partial \mathbf{r}_j} = \frac{\partial}{\partial \mathbf{r}_j} \sum_{j \neq i} \frac{\partial \phi(r_{ij})}{\partial \mathbf{r}_i} = \frac{\partial^2 \Phi}{\partial \mathbf{r}_j \partial \mathbf{r}_i}$$

$$\Phi(\mathbf{r}) = \sum_{j \neq i} \phi(r_{ij}) \quad \mathbf{H} : \text{Hessian行列}$$

$\phi : \text{粒子間ポテンシャル}$

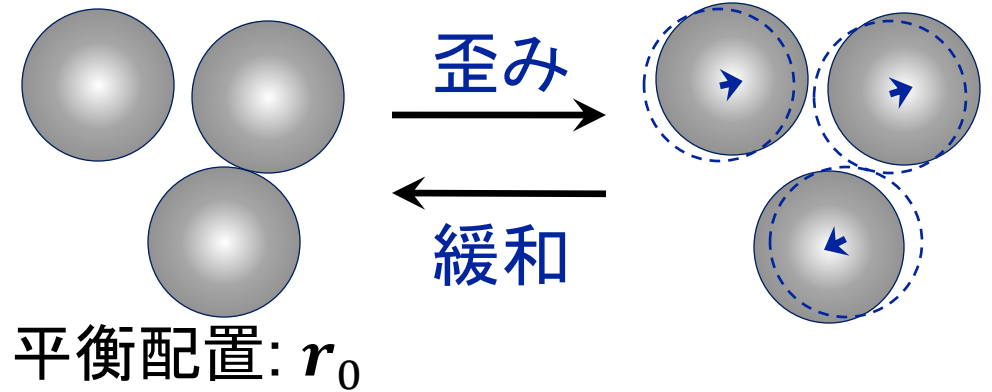
対角化

$$\dot{q}_k = -\frac{1}{\tau_k} q_k \quad (k = 1, \dots, 3N)$$

$$q_k = \mathbf{u}_k \cdot \mathbf{r}$$

τ_k : 緩和時定数

\mathbf{u}_k : 固有ベクトル



緩和周波数の分布

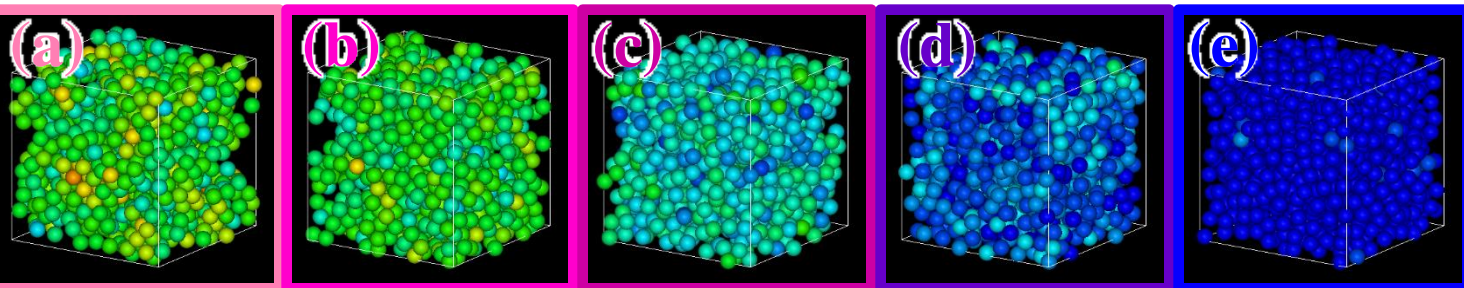
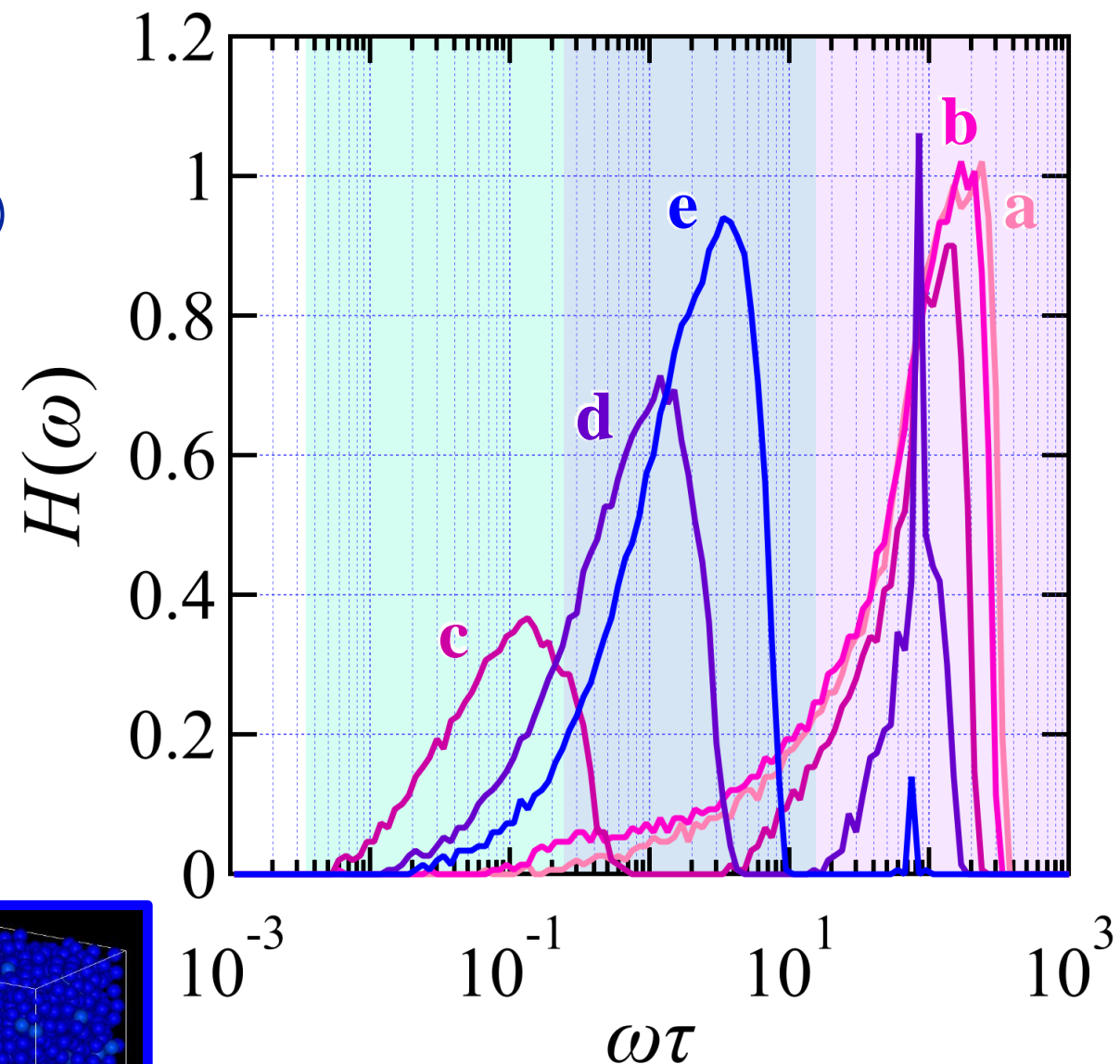
緩和周波数: $\omega_k = \tau_k^{-1}$

$\{\log \omega_k\}$ の分布: $H(\omega)$ (確率密度関数)

$$H(\omega)|d\log\omega| = D(\omega)|d\omega|$$

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

斥力 / 引力 による構造緩和は
周波数域が異なる



緩和周波数の分布

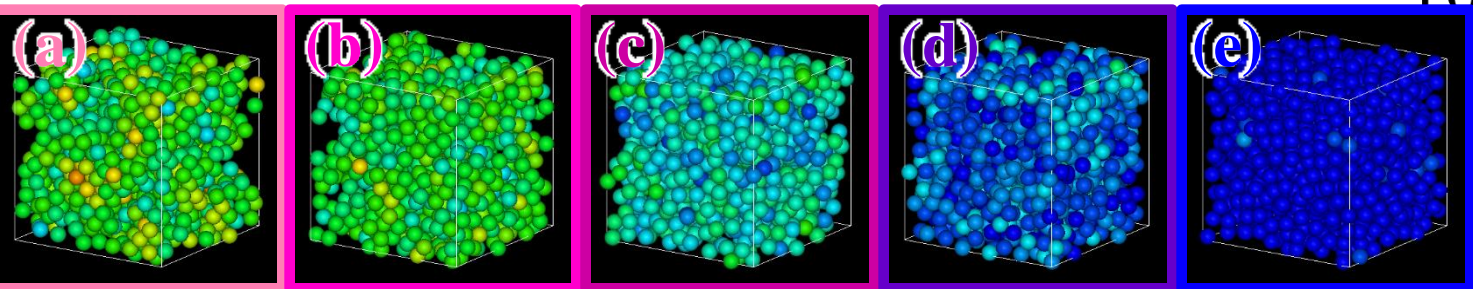
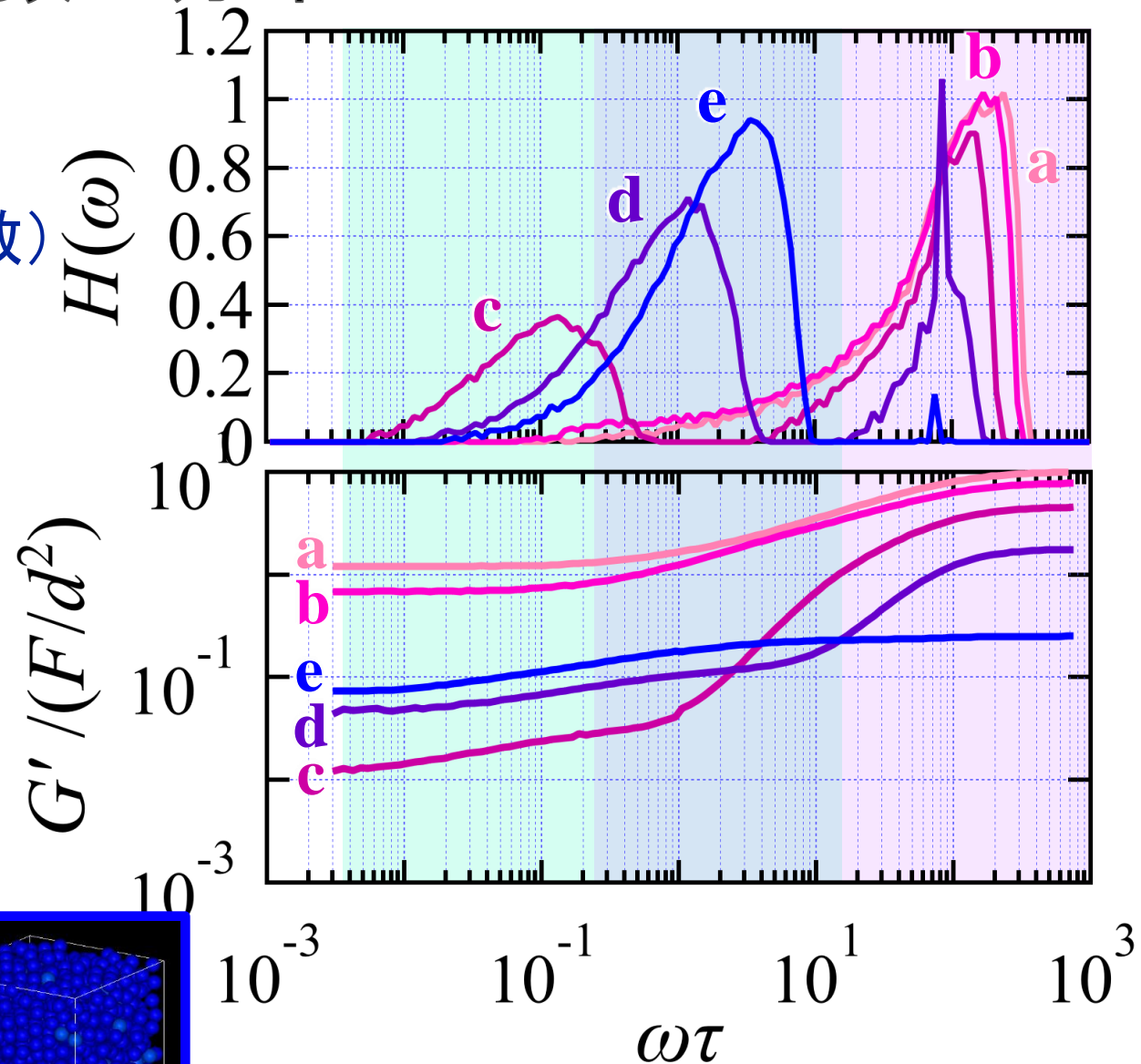
緩和周波数: $\omega_k = \tau_k^{-1}$

$\{\log \omega_k\}$ の分布: $H(\omega)$ (確率密度関数)

$$H(\omega) |d \log \omega| = D(\omega) |d \omega|$$

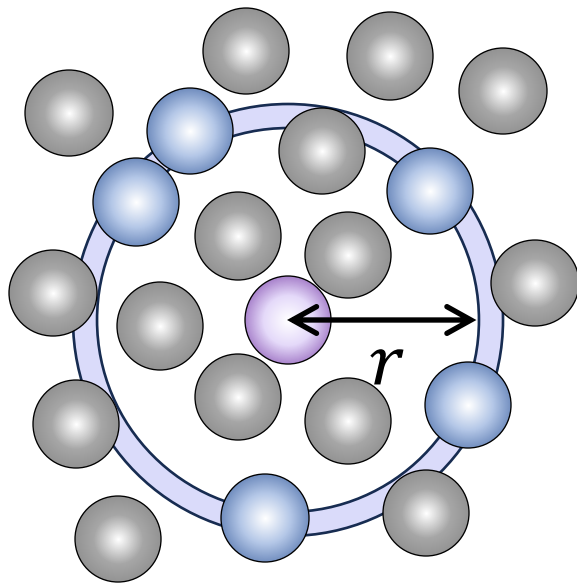
$$D(\omega) = \frac{1}{3N - 3} \sum_k \delta(\omega - \omega_k)$$

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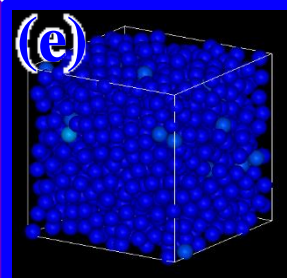
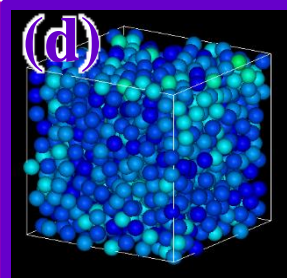
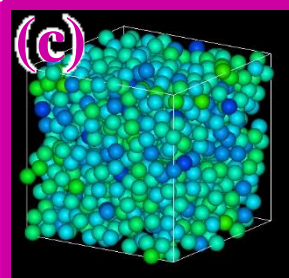
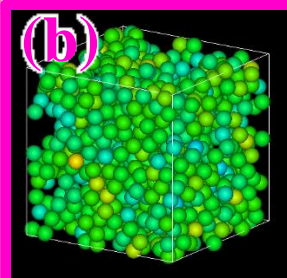
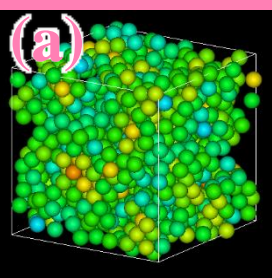
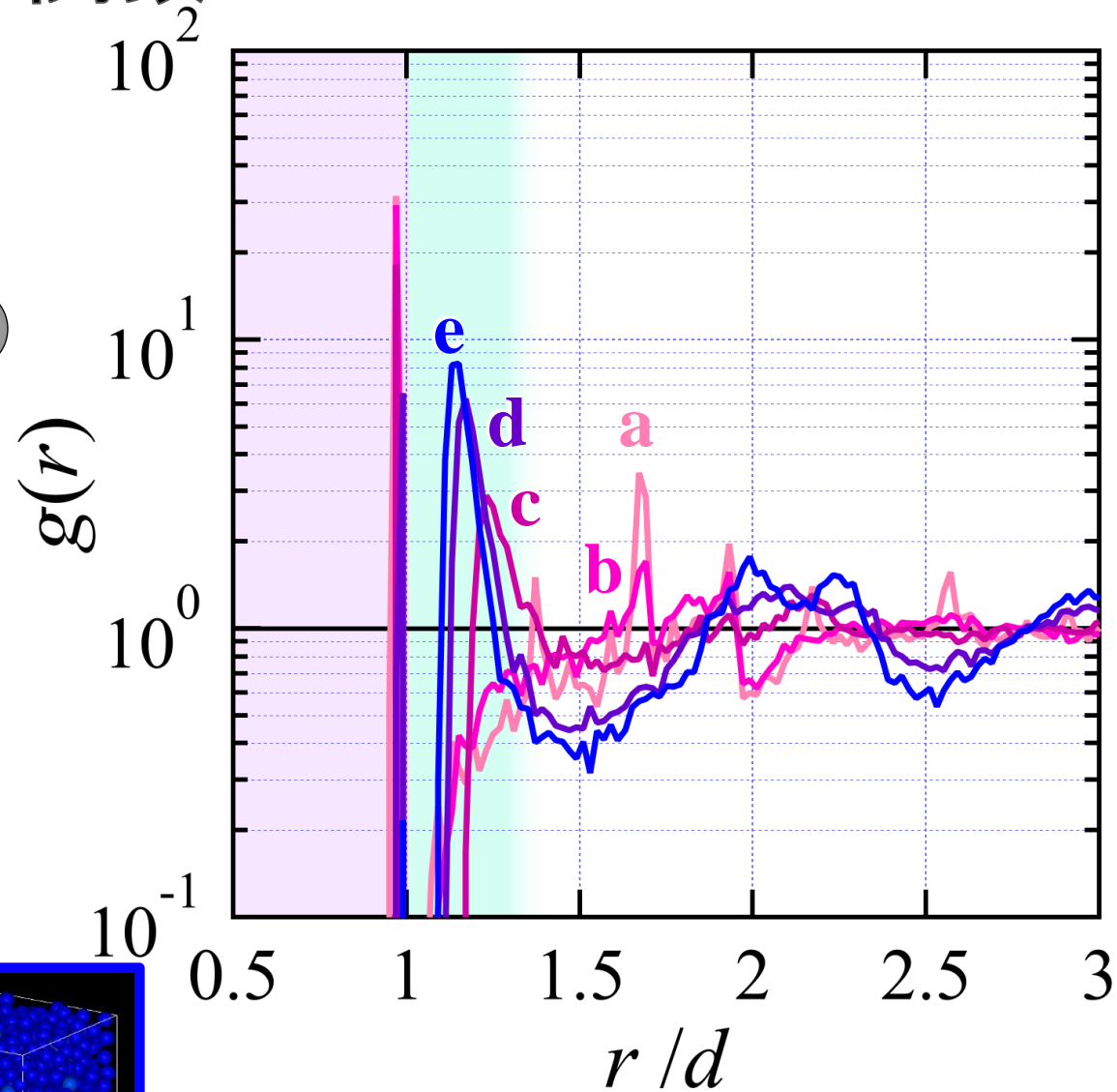
動径分布関数

$$g(r) = \frac{1}{4\pi r^2 \rho} \frac{dn(r)}{dr}$$

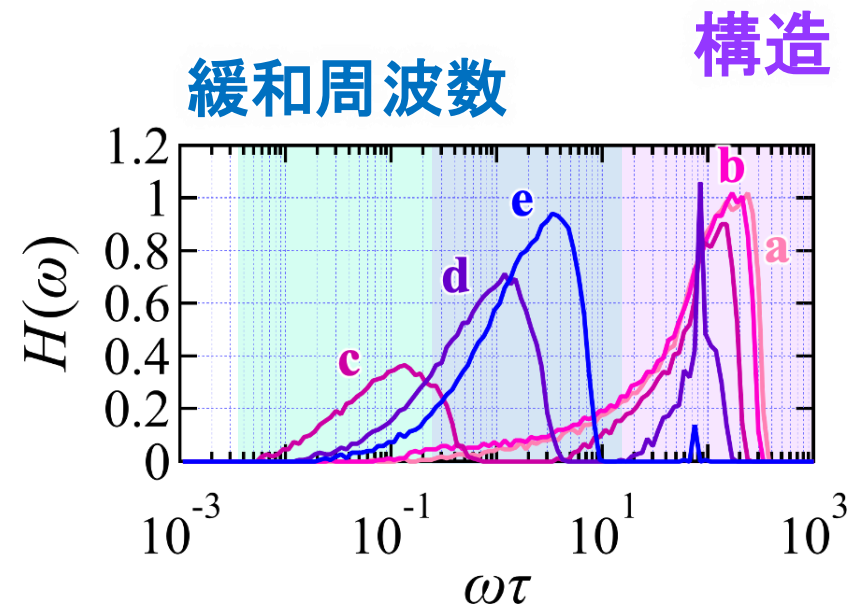
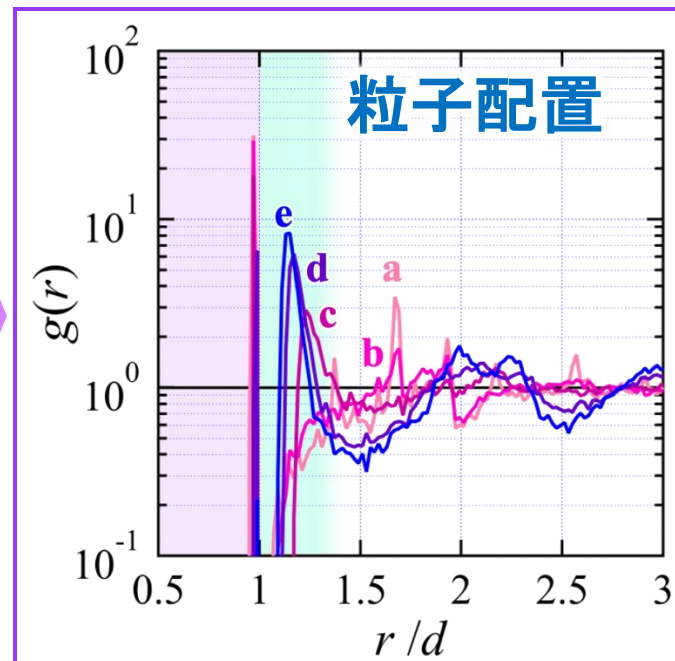
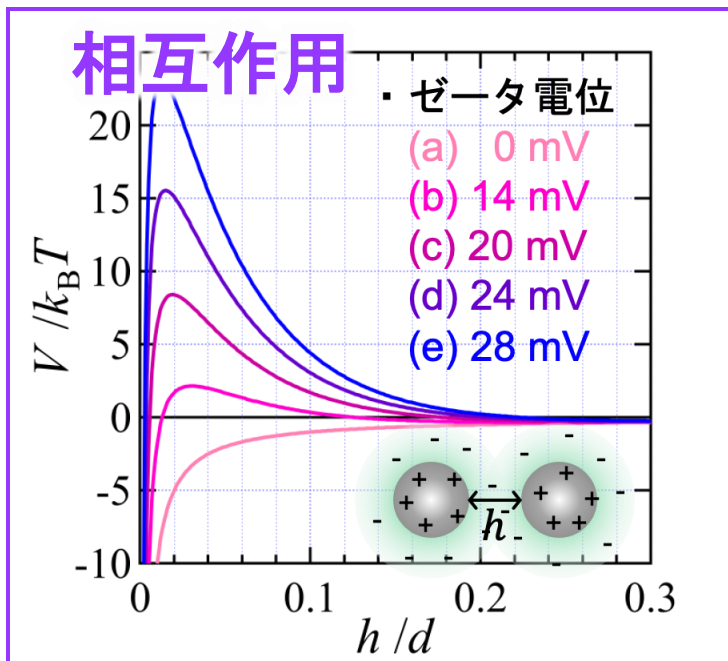


厚み dr の球殻に存在する平均粒子数 : $dn(r)$

粒子の平均数密度 : ρ



まとめ



粘弾性挙動： 粒子間ポテンシャルと、
それにより決定付けられる構造を反映

→ 粘弾性制御のためのスラリー調製の知見へ

