Morphology and Rheology of Immiscible Polymer Blends under Electric Fields

H. Orihara[1], Y. Nishimoto[1], K. Aida[1], Y. H. Na[1], T. Nagaya[2]

[1]Hokkaido University, [2] Oita University

Immiscible polymer blends

Rheology ⟺ Morphology

Close relationship

Doi and Ohta, 1991

Constitutive equations

Interface tensor

$$q_{\alpha\beta} = \frac{1}{V}\int_S \left(n_\alpha n_\beta - \frac{1}{3}\delta_{\alpha\beta} \right) dS$$

Interface area density

$$Q = \frac{1}{V}\int_S dS$$

V : system volume $\boldsymbol{n}$: unit normal vector

Excess stress from Interfacial tension(Batchelor, Doi, Onuki)

$-\Gamma q_{\alpha\beta}$ Γ : interfacial tension

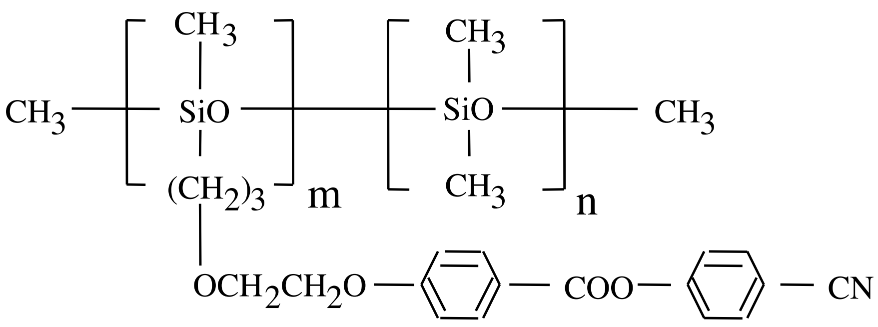
Experimental tests (Takahashi et al.)

Effect of electric fields

Immiscible polymer blend electro-rheological (ER) fluid

（Inoue et al. 1995）

LCP



m/(m+n) = 0.2, m+n =50

\+

OIL

PDMS

PIB

MPS

ER effect is due to morphological change.

Tajiri, K., K. Ohta, T. Nagaya, H. Orihara, Y. Ishibashi, M. Doi and M. Inoue, J. Rheol. **41**, 335-341 (1997).

Kimura, H., K. Aikawa, Y. Masubuchi, J. Takimoto, K. Koyama and K. Minagawa, Rheol. Acta **37** 54-60 (1998).

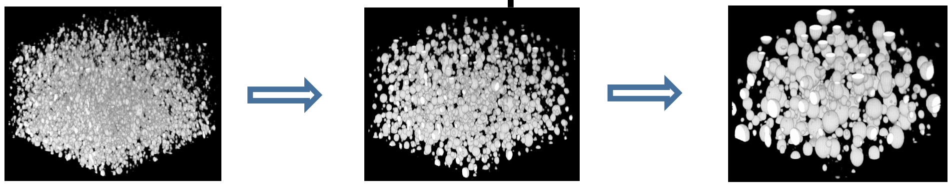
3D observations!

System combining CLSM and rhe

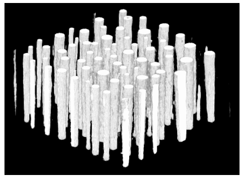
Outline

Subjected to a step electric field without shear flow

1. Coalescence of droplets



2. Shear modulus of columnar structure

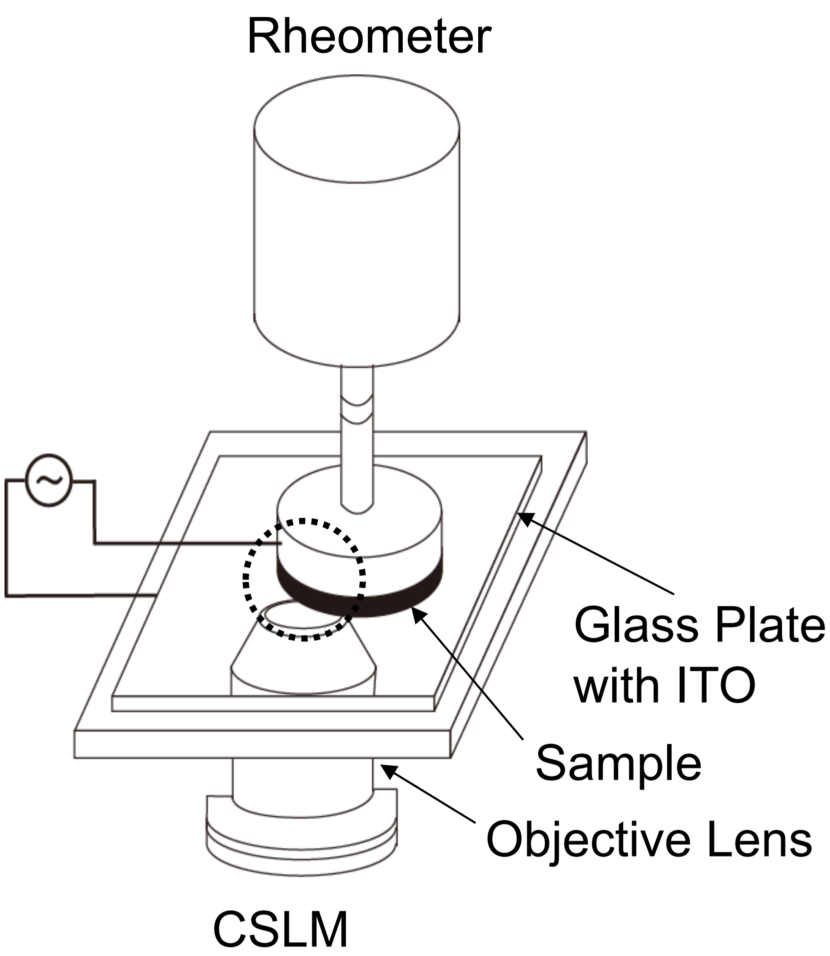


Subjected to a step electric field with shear flow

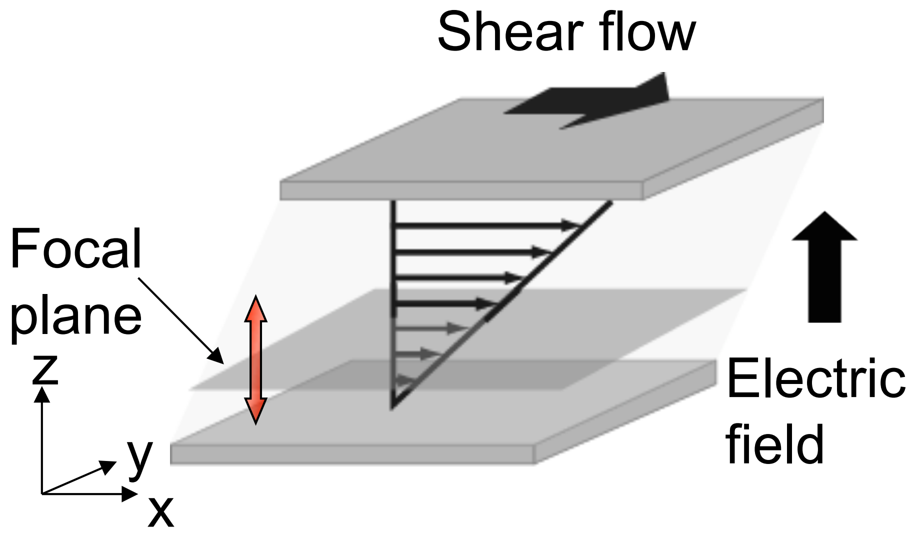
3. Interface tensor

4. Separation of viscous, interfacial and electric stresses
5. Relationship between excess stress and interface tensor

Experiment



Gap: 200mm, Diameter: 35 mm



Piezo-actuator 5Hz

Frame rate 500 f/s

400x390x50 pixels

163x163x56 μm^3

Blend of LCP and PIB(Polyisobutylene)

LCP: $\varepsilon_1 = 15,\ \sigma_1 = 8\times10^{-9}\Omega^{-1}m^{-1}$ PIB: $\varepsilon_2 = 2,\ \sigma_2 < 10^{-11}\Omega^{-1}m^{-1}$

Coalescence of droplets and column formation without shear flow

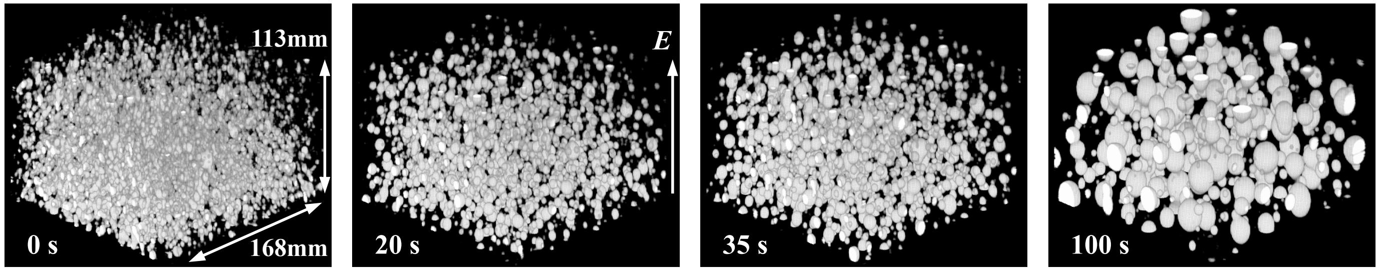
Blend: LCP(65 Pa s)/PIB(7.8 Pa s) at 25°C

Preshear of 200 s^{-1} for 20 min

⇩

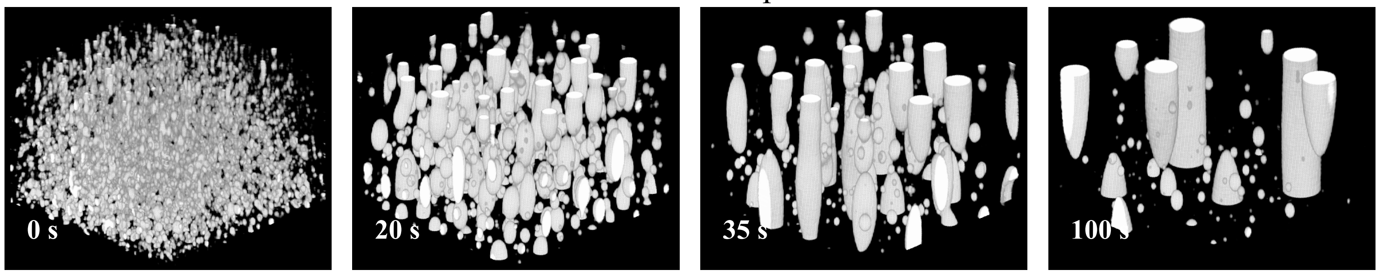
Application of ac electric field (512 Hz) without shear flow

LCP:PIB=1:6 (ϕ =0.14)



(a) 2 kV_{amp}/mm

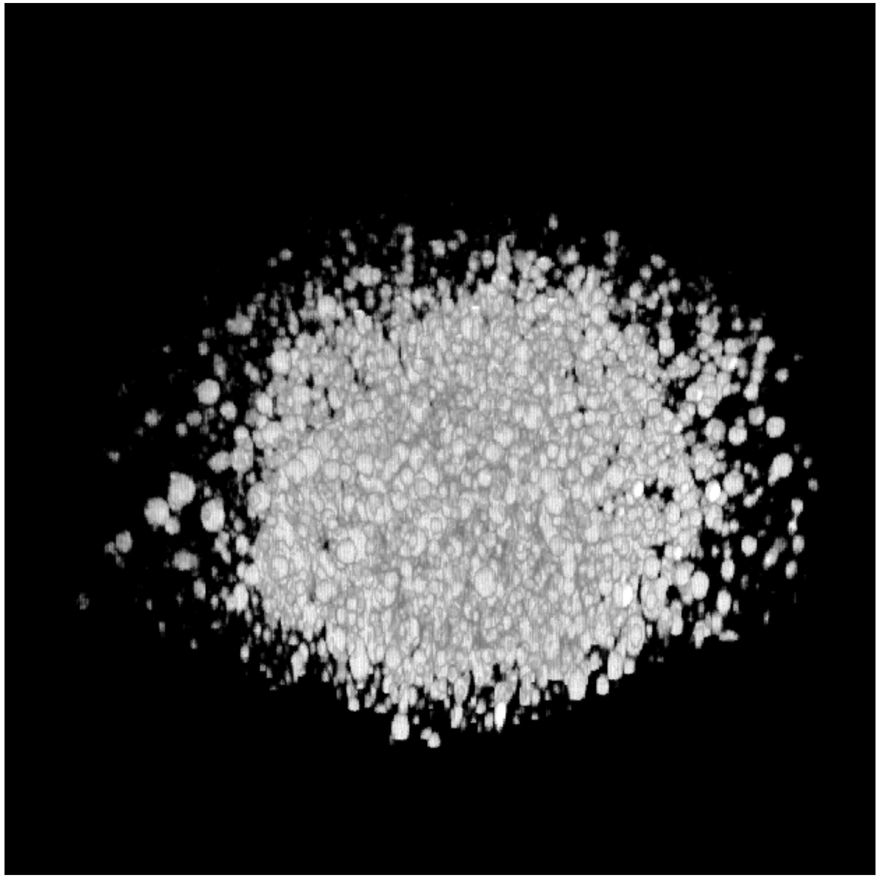
Coalescence



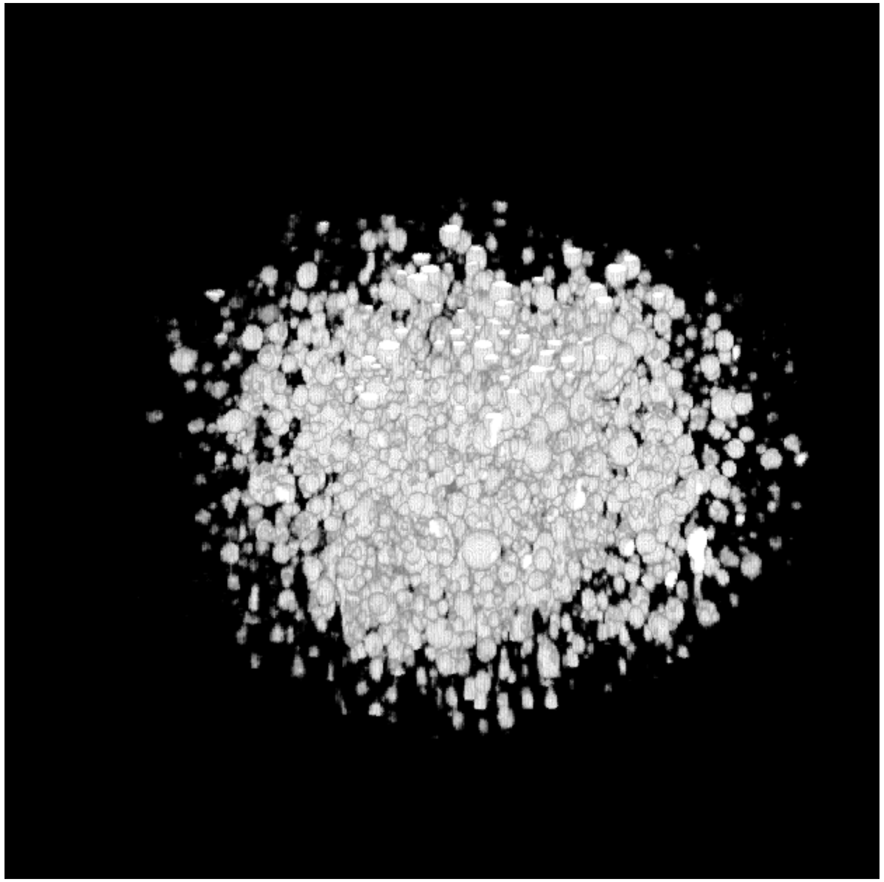
(b) 4 kV_{amp}/mm

Elongation

Movies (8 times as fast)



2 kV_{amp}/mm

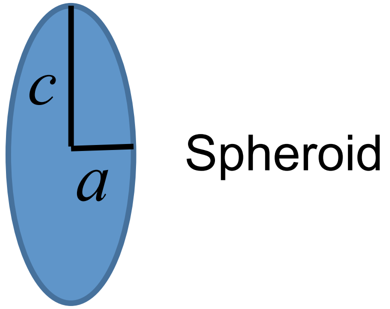


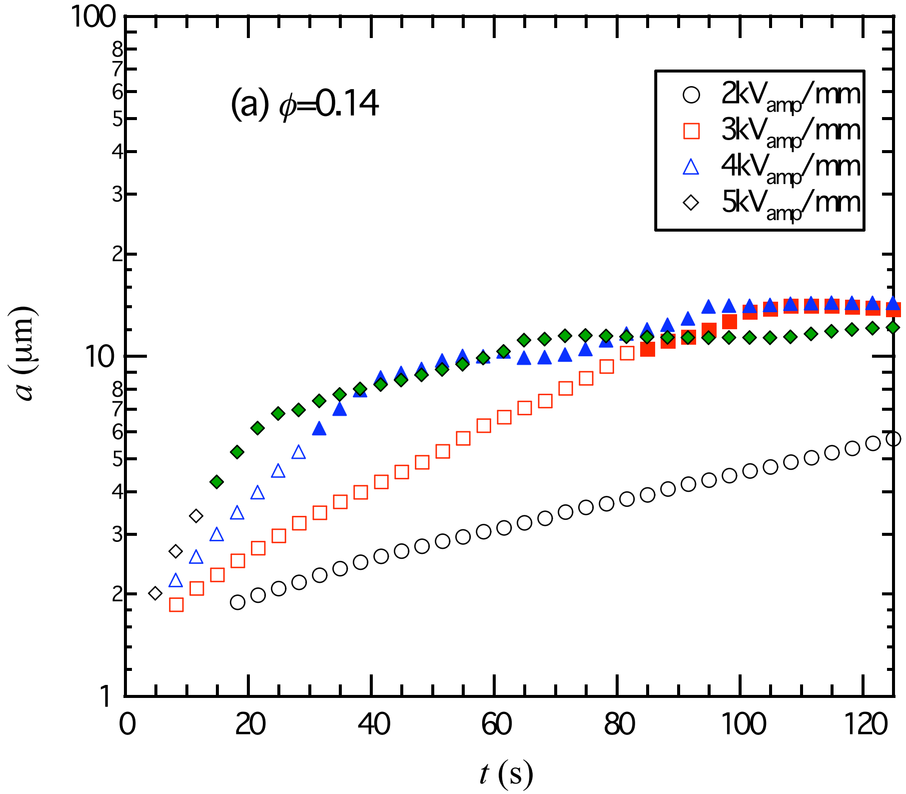
5 kV_{amp}/mm

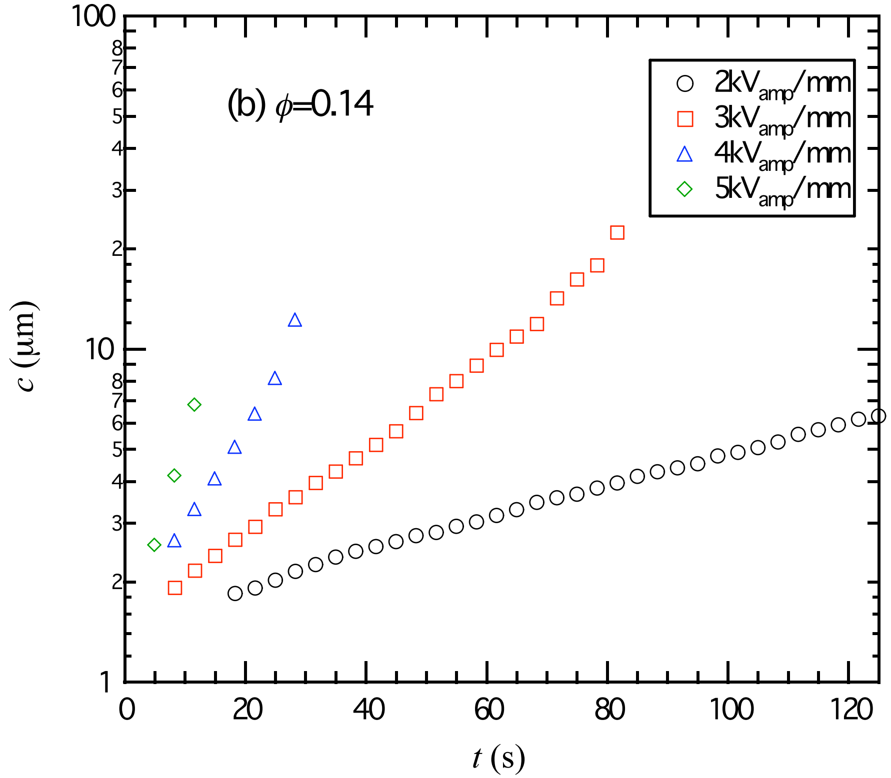
3D spatial correlation function

⇩

Average lenghts of semi-axes







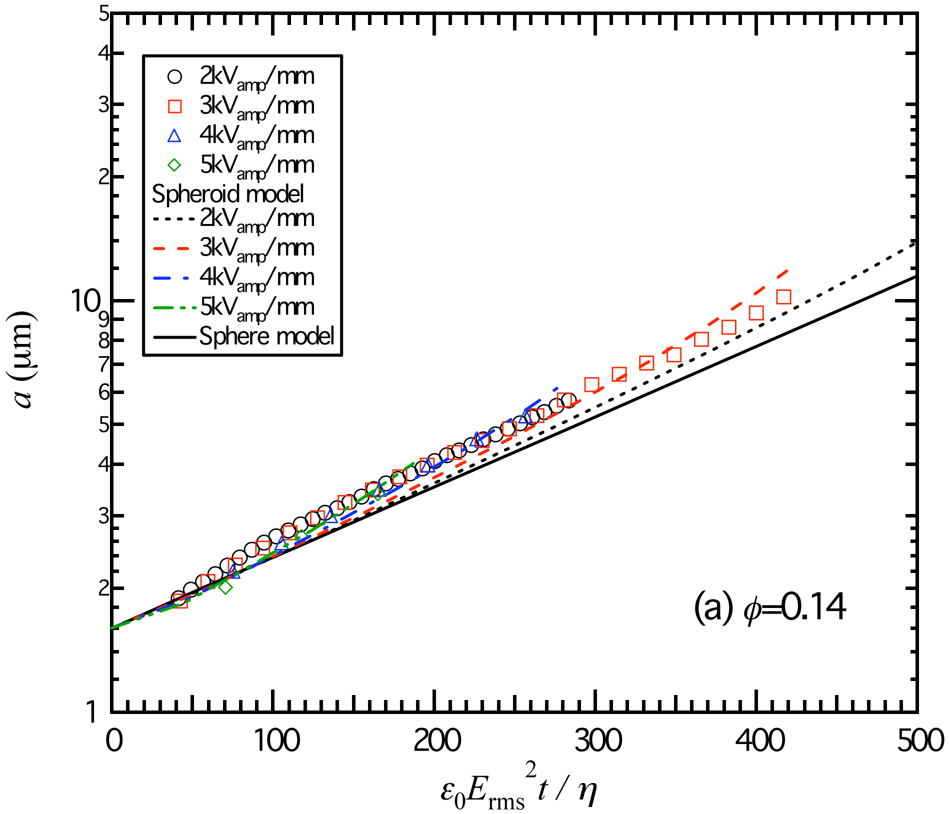
Scaling property

Assuming that all the droplets keep spherical shape,

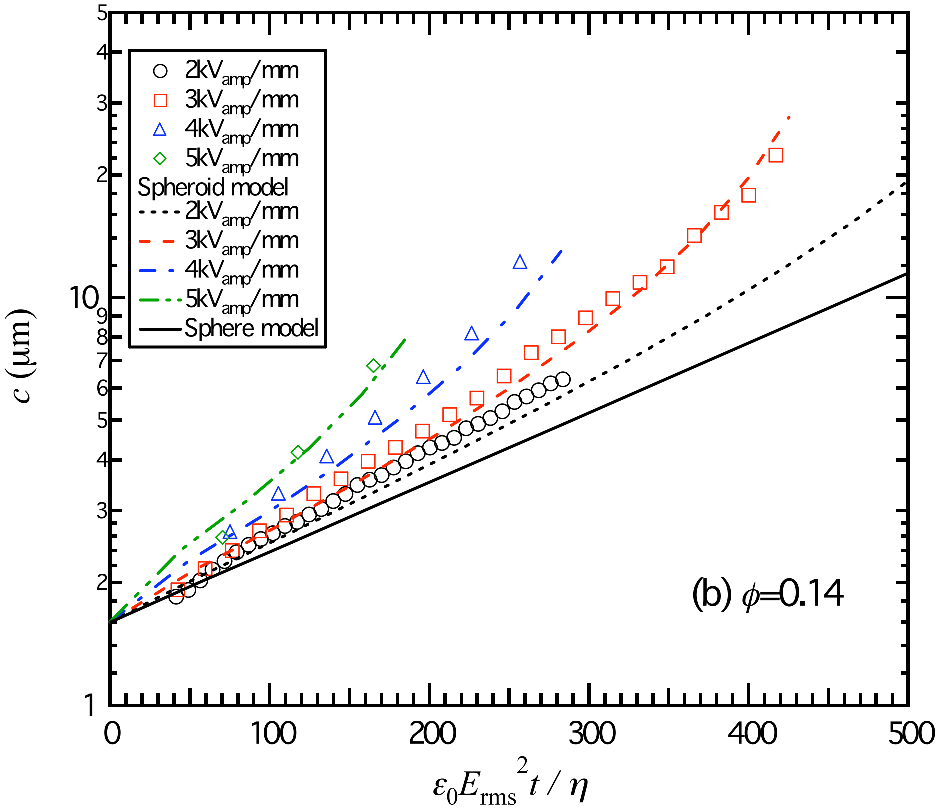
$$r = r_0 f\left(\frac{\varepsilon_0 E_{\mathrm{rms}}^2 t}{\eta}\right) \quad r(=a=c):\ \text{radius} \quad \eta:\ \text{viscosity of PIB}$$

Scaling property holds ?

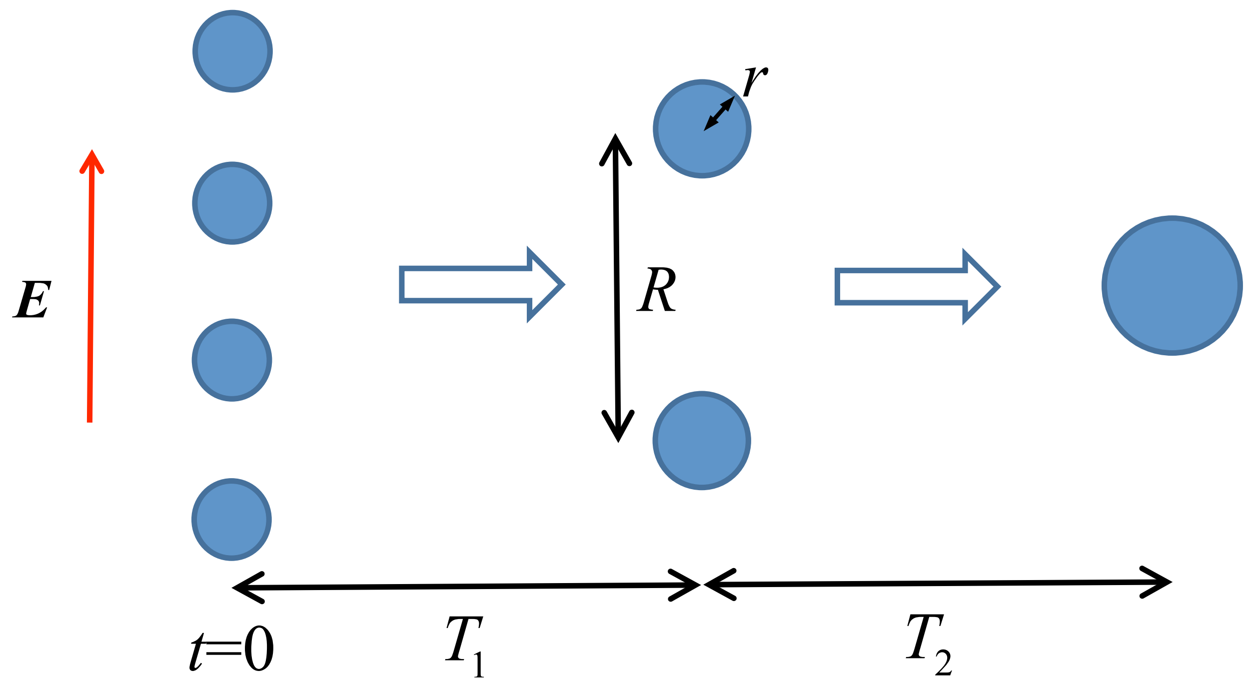
Yes ?



No !



Growth kinetics on the basis of hierarchical model



$$6\pi\eta r\frac{dR}{dt} = -48\pi\varepsilon_0\varepsilon_2\beta^2E_{\mathrm{rms}}^2r^2\left(\frac{r}{R}\right)^4 \qquad \beta = \frac{\varepsilon_1-\varepsilon_2}{\varepsilon_1+2\varepsilon_2}: \text{ polarizability}$$

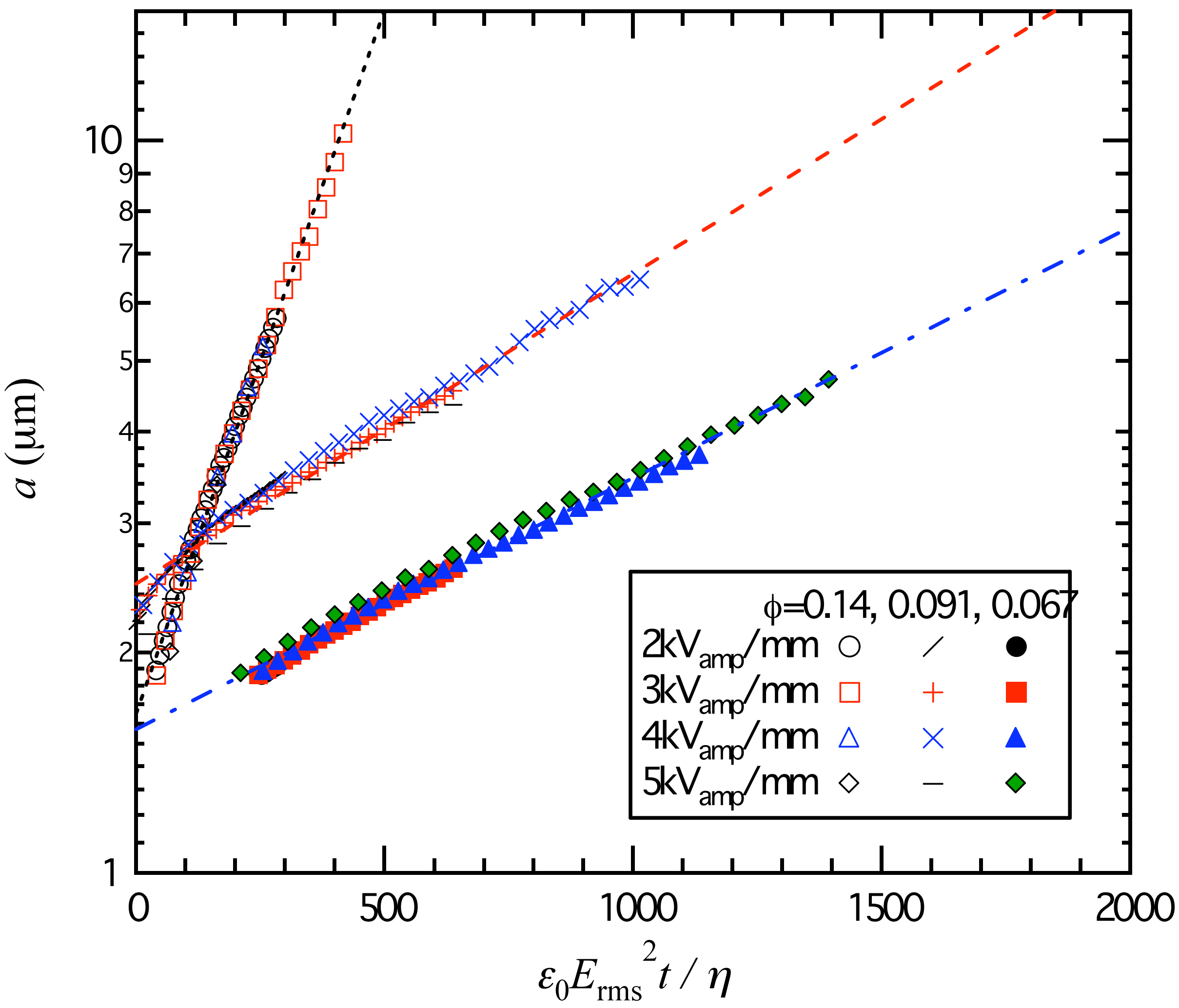
Viscous friction Dipole-dipole interaction

T_n is constant

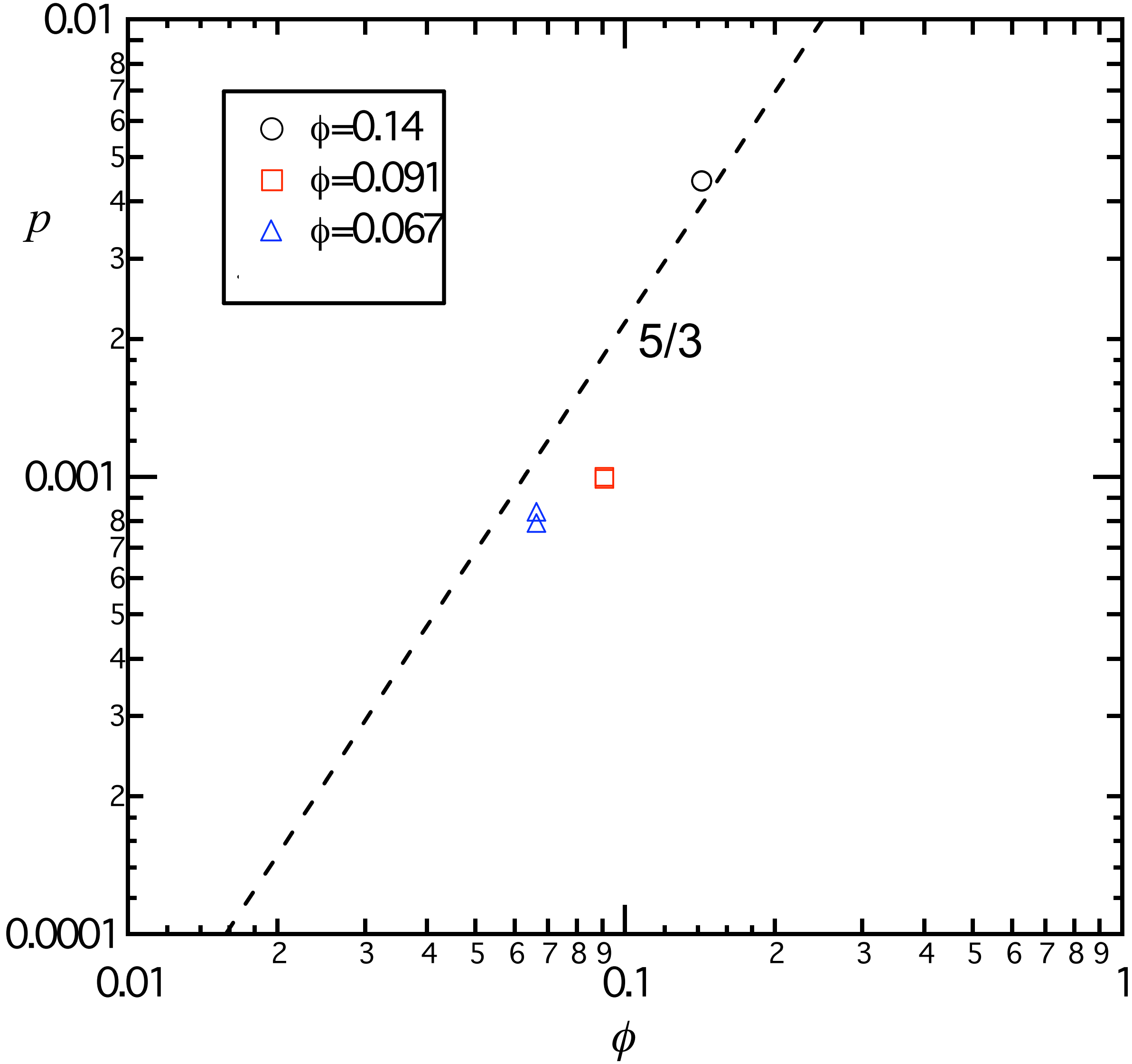
Exponential growth

$$r = r_0\exp\left(p\frac{\varepsilon_0E_{\mathrm{rms}}^2t}{\eta}\right) \qquad p = \frac{\ln 2}{3C}\varepsilon_2\beta^2\phi^{5/3}$$

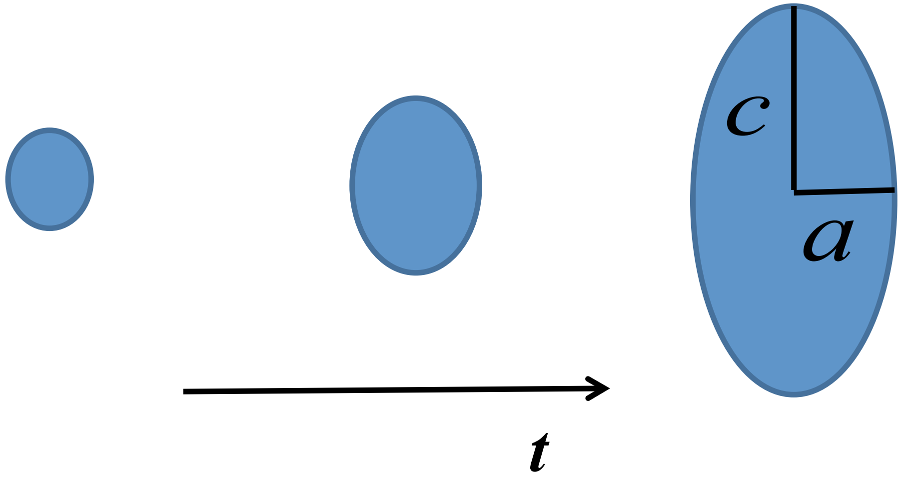
Volume fraction dependence



$$p = \frac{\ln 2}{3C} \varepsilon_2 \beta^2 \phi^{5/3}$$



Sphere ⟹ Spheroid



Deformation

$$D = \frac{(c-a)}{(c+a)} \qquad D = \frac{9\varepsilon_0\varepsilon_2}{16\Gamma}\Phi E_{\mathrm{rms}}^2 r \quad \text{(Torza et al, 1971)}$$

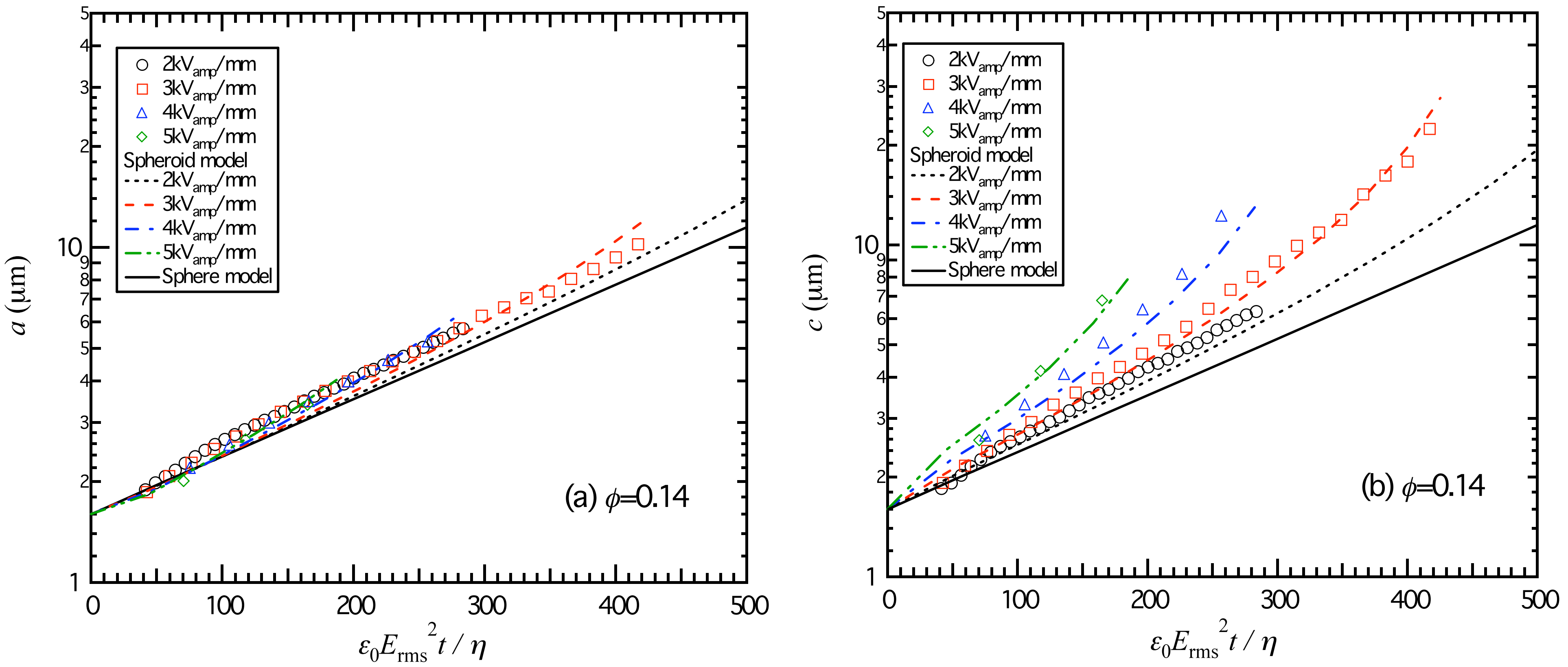
$$\beta = \frac{1}{3}\frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_1 + (\varepsilon_1 - \varepsilon_2)n^{(c)}}$$

$n^{(c)}$: depolarization factor depending on D

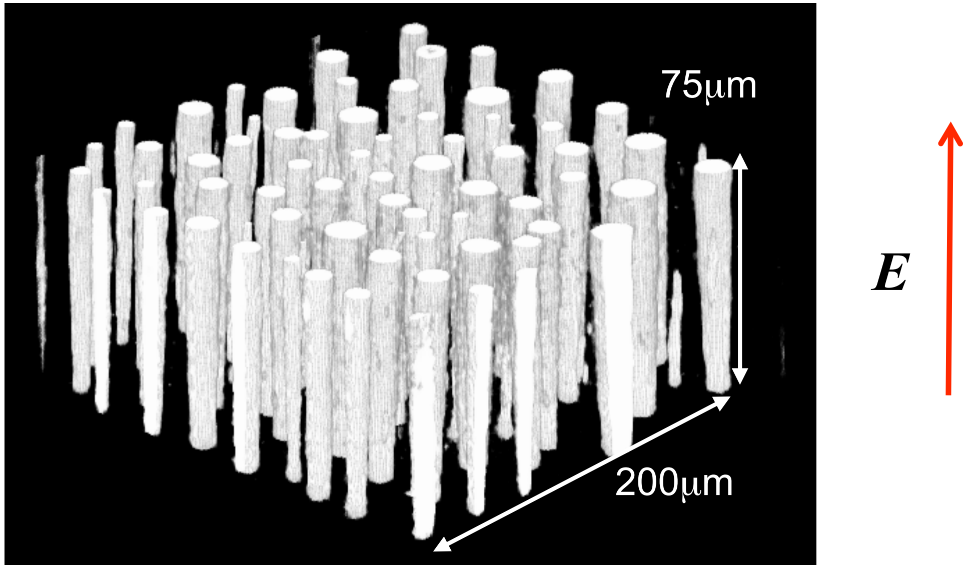
⇩

$$T_n \quad (n = 1, 2, \cdots)$$

Numerical calculation

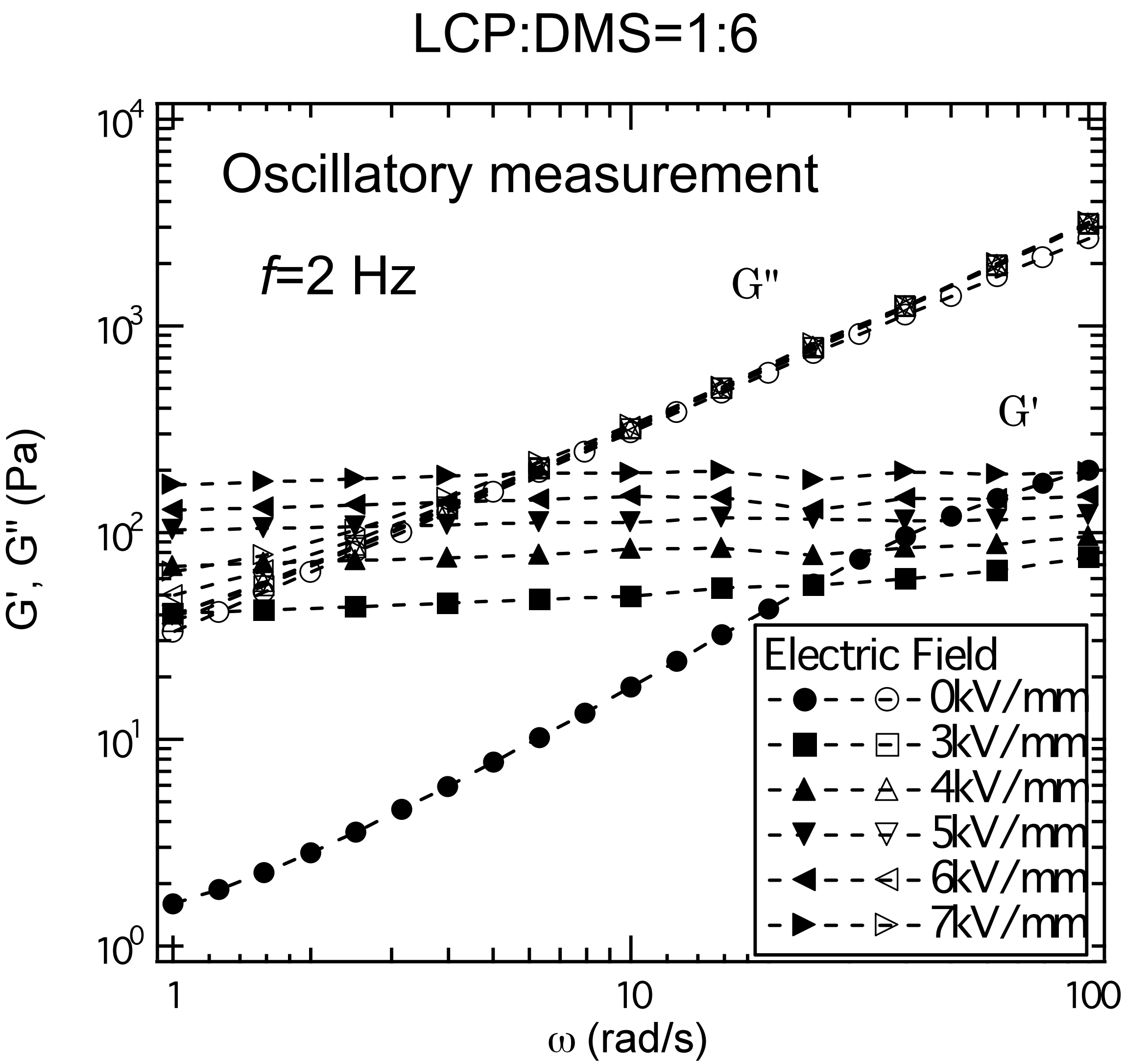


Storage Shear Modulus of Columnar Structure



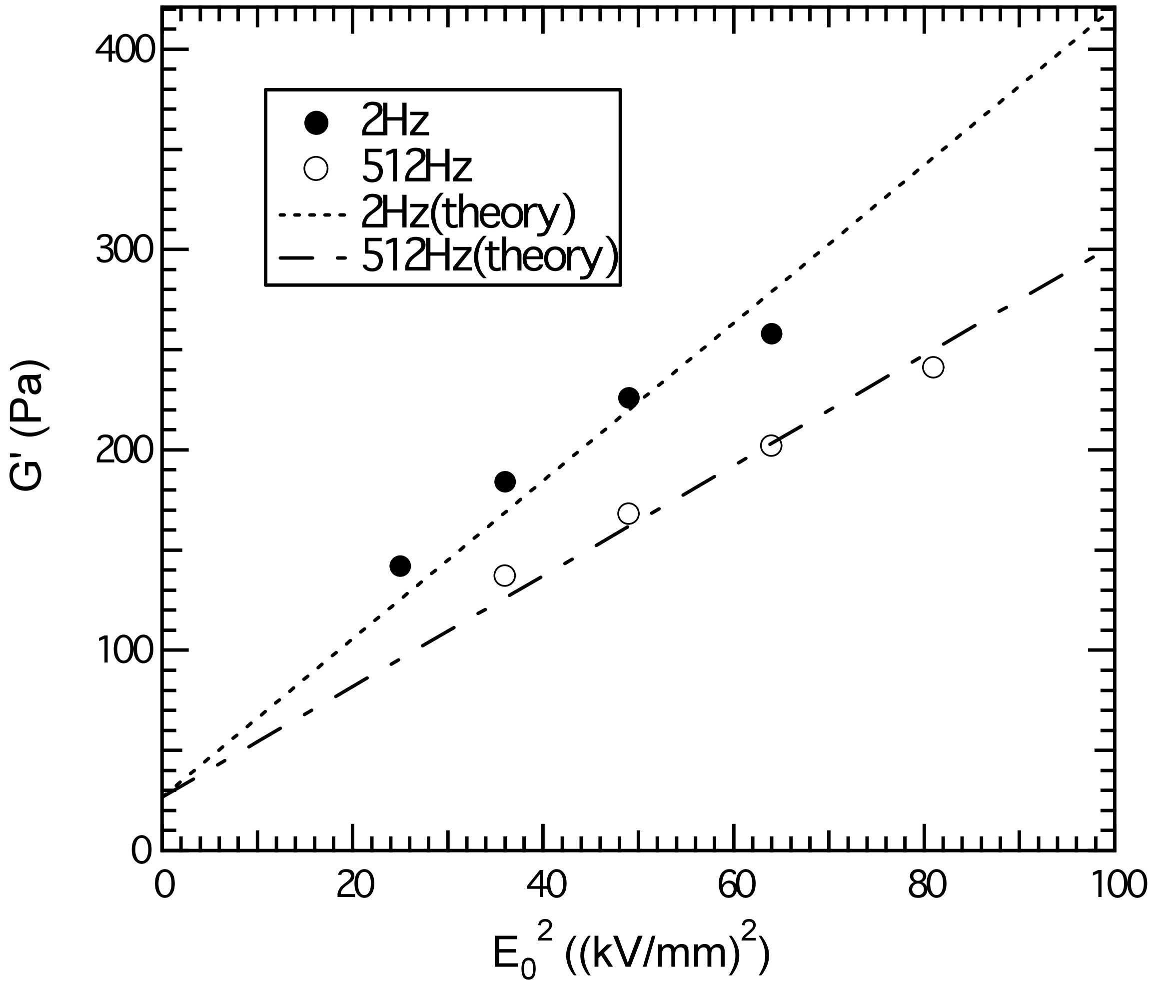
100 sec later after applying an ac electric field with an amplitude of 5kV/mm and a frequency of 2Hz.

Emergence of elasticity

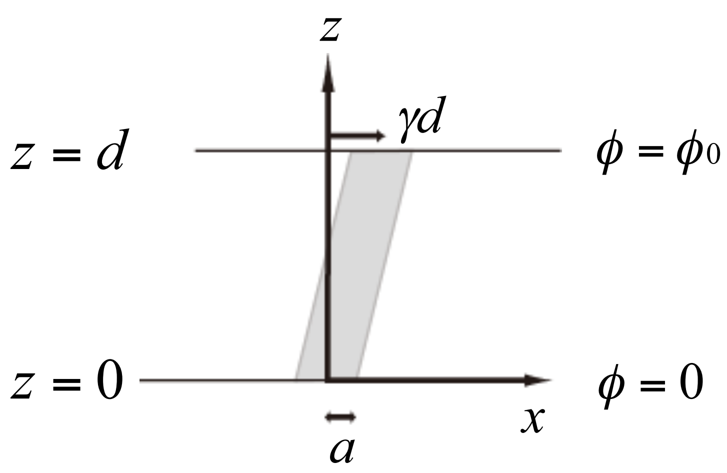


Dependence of G’ on electric field strength

$\omega = 10$ rad/s (oscillation)



Electric stress on slant column



$$G'(0) = \pi n a \Gamma + 2nad(\varepsilon_1 - \varepsilon_2)E_0^2$$

$$\times \mathrm{Re}\left[\sum_{m=1}^{\infty} \frac{[1-(-1)^m](\tilde{\varepsilon}_1 - \tilde{\varepsilon}_2)/m^3\pi^2}{\tilde{\varepsilon}_1 I_1'(m\pi a/d)/I_1(m\pi a/d) - \tilde{\varepsilon}_2 K_1'(m\pi a/d)/K_1(m\pi a/d)}\right]$$

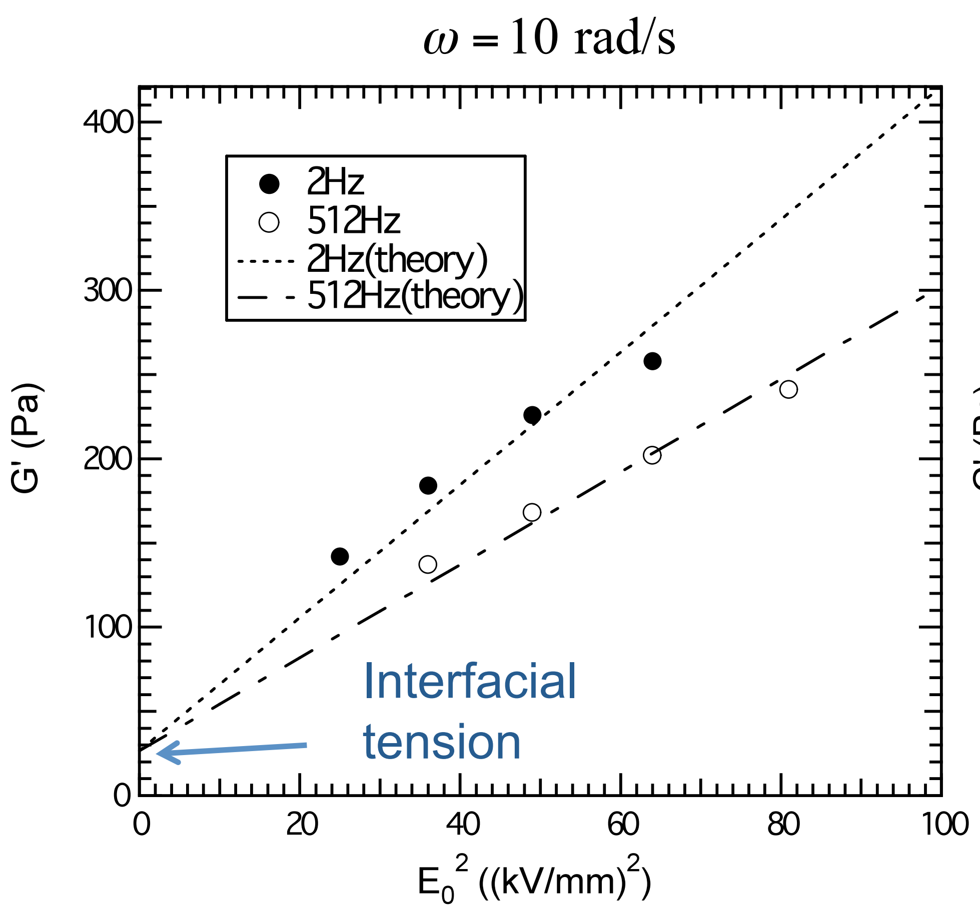
Interfacial stress Electric stress

$$\tilde{\varepsilon}_j = \varepsilon_j + \frac{\sigma_j}{i2\pi f}$$

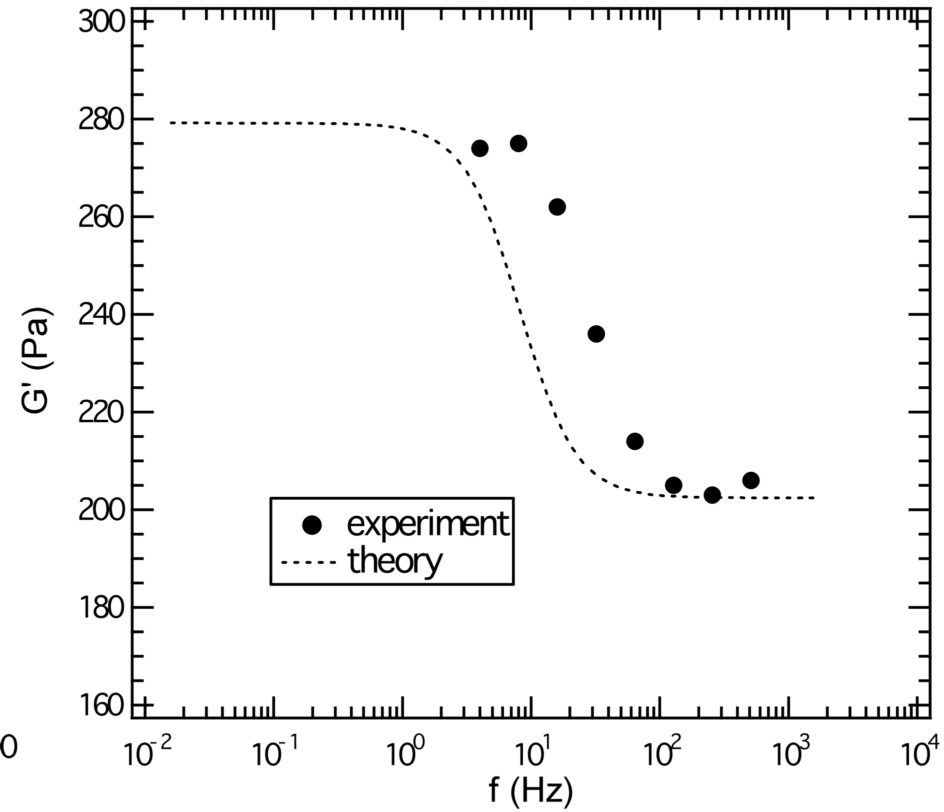
f: frequency of ac electric field

n: column density Γ: interfacial tension

$I_1(x),\ K_1(x)$: modified Bessel function



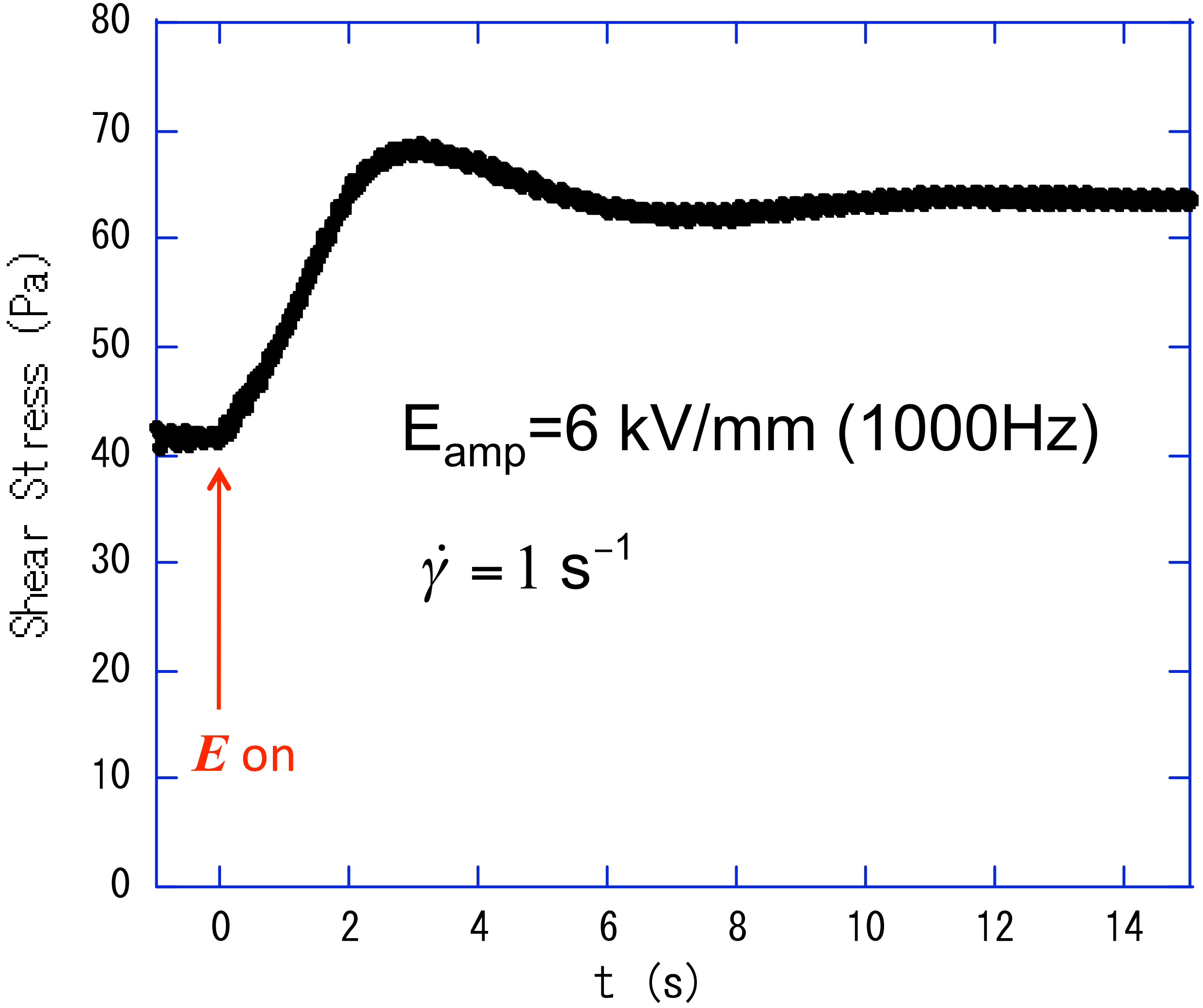
E dependence



f dependence

Transient process
subjected to a step electric field
with shear flow

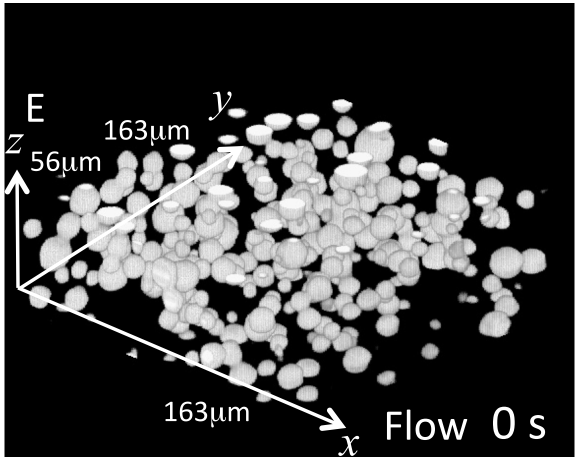
Transient shear stress

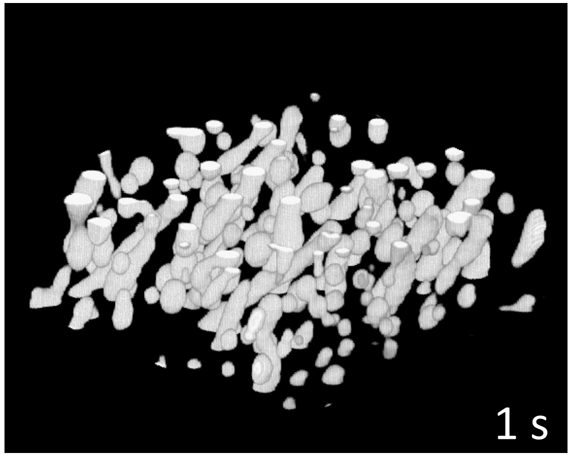


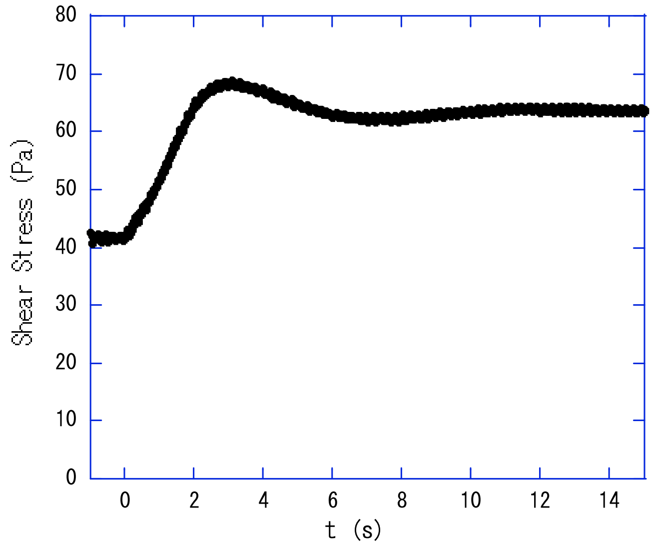
Blend with the same viscosity

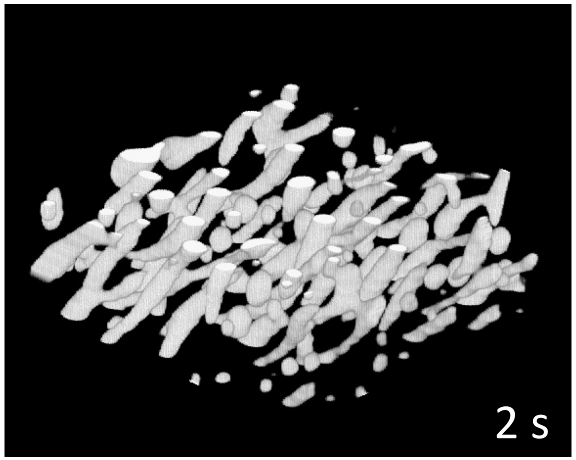
LCP:PIB=1:6
(η=33.5 Pa s at 28℃)

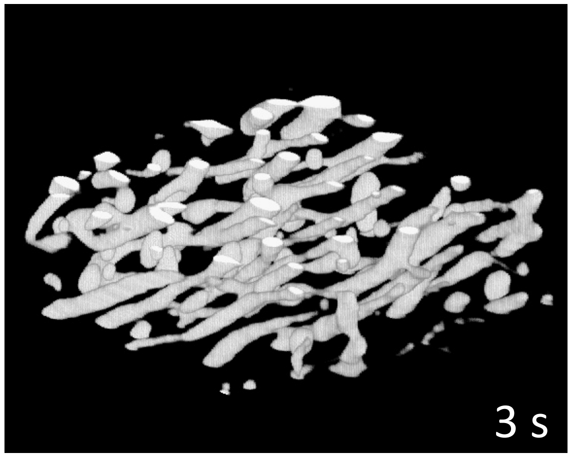
3D images in the transient process

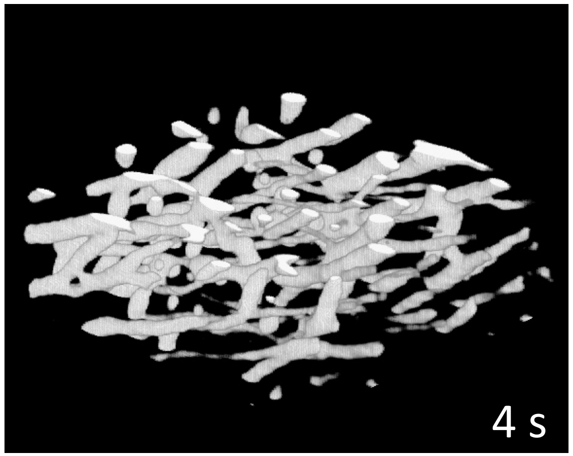




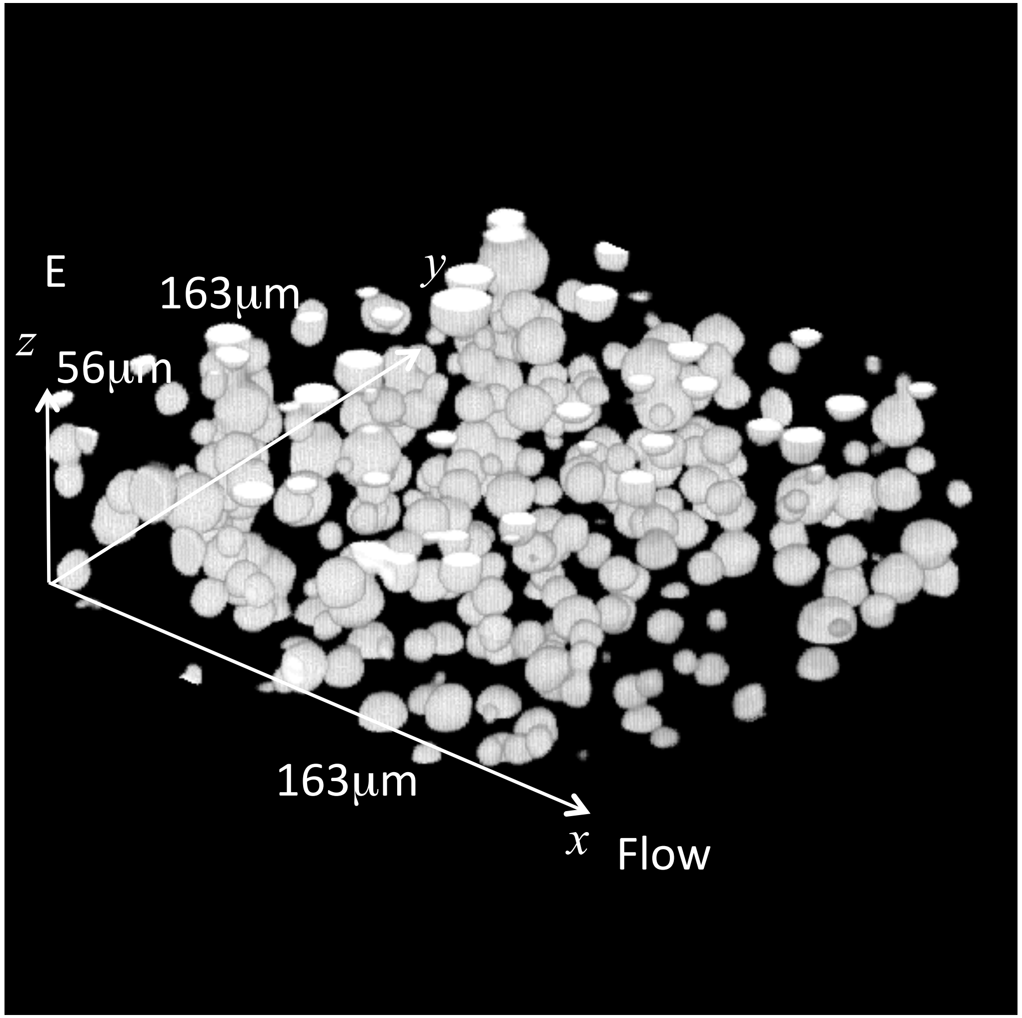








Movie in the transient process

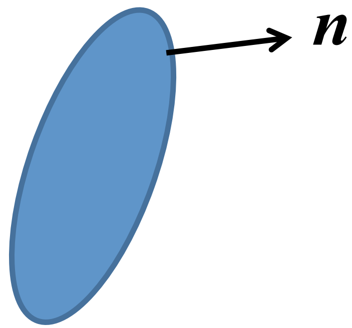


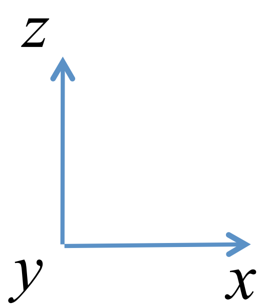
Real time speed

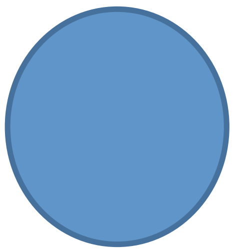
Interface tensor $q_{\alpha\beta}$

$$q_{\alpha\beta} = \frac{1}{V}\int_{S_0}\left(n_\alpha n_\beta - \frac{1}{3}\delta_{\alpha\beta}\right)dS$$

Symmetrical and traceless

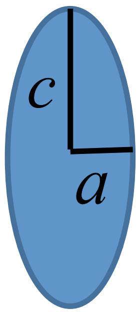






Sphere

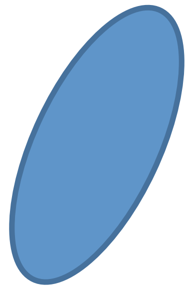
$$\begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$



Ellipsoid

$$\begin{pmatrix} q_{xx} & 0 & 0 \\ 0 & q_{yy} & 0 \\ 0 & 0 & q_{zz} \end{pmatrix}$$

$c > a \Rightarrow q_{zz} < q_{xx}$

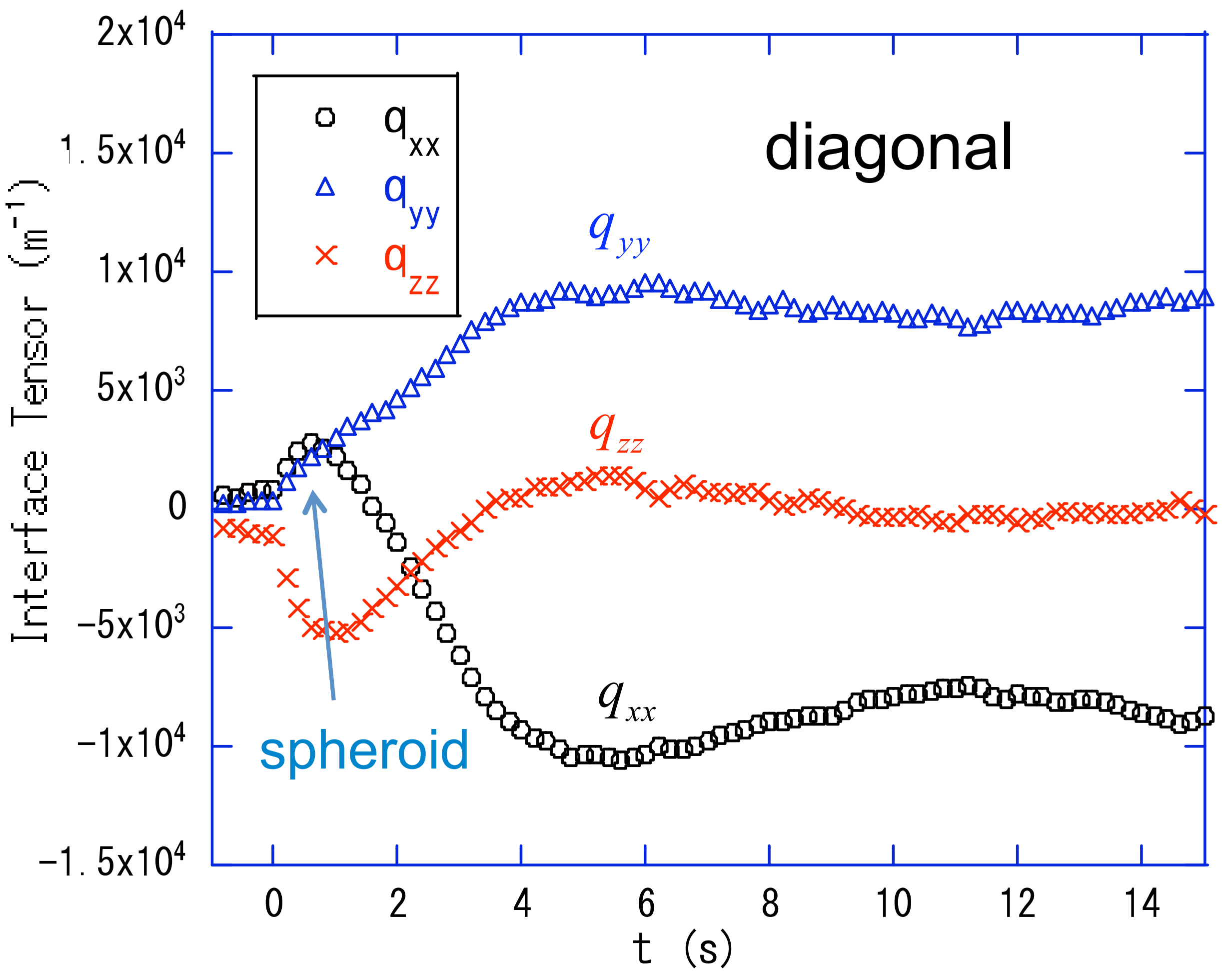


Slant ellipsoid

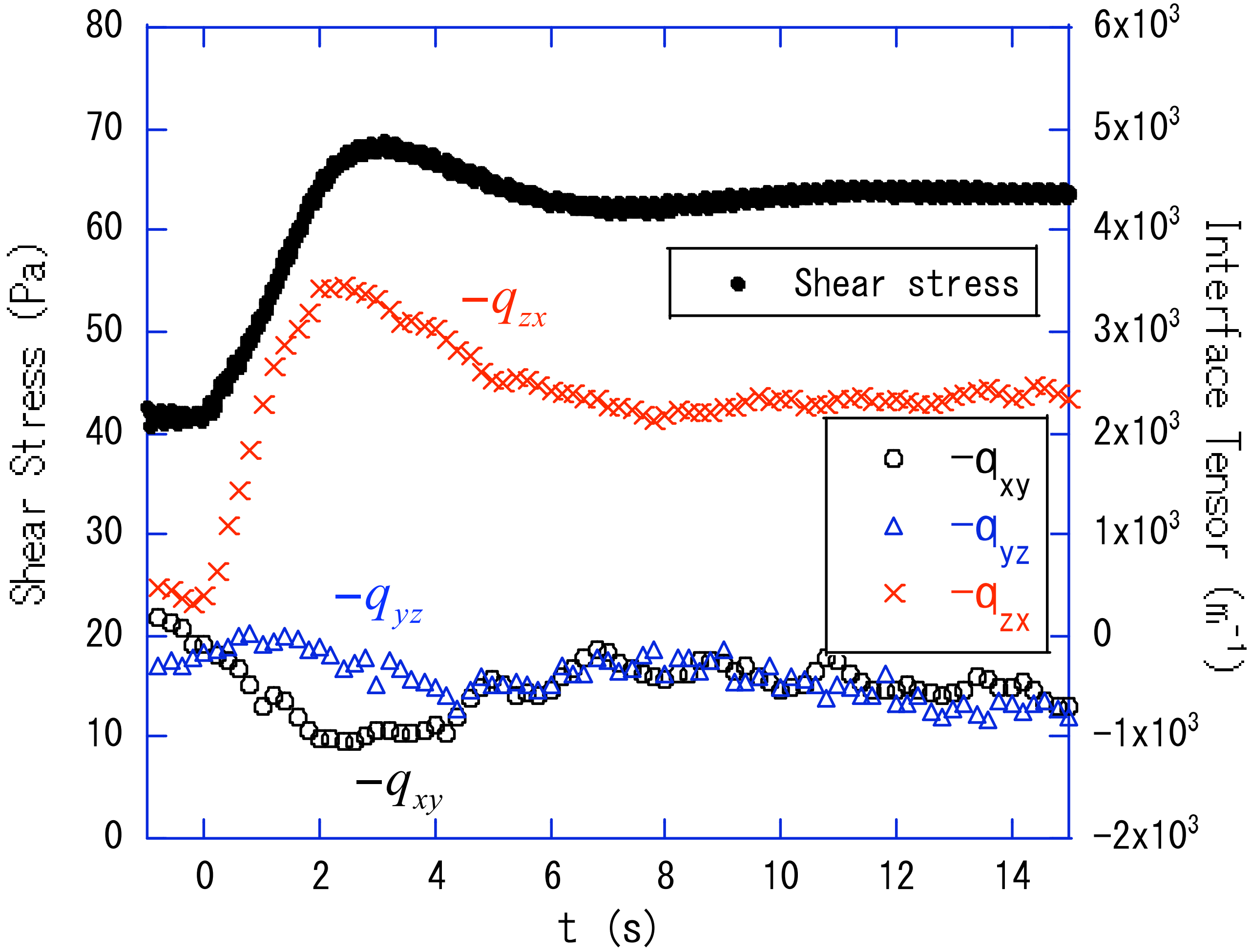
$$\begin{pmatrix} q_{xx} & 0 & q_{zx} \\ 0 & q_{yy} & 0 \\ q_{zx} & 0 & q_{zz} \end{pmatrix}$$

$q_{zx} < 0$

Time evolution of interface tensor



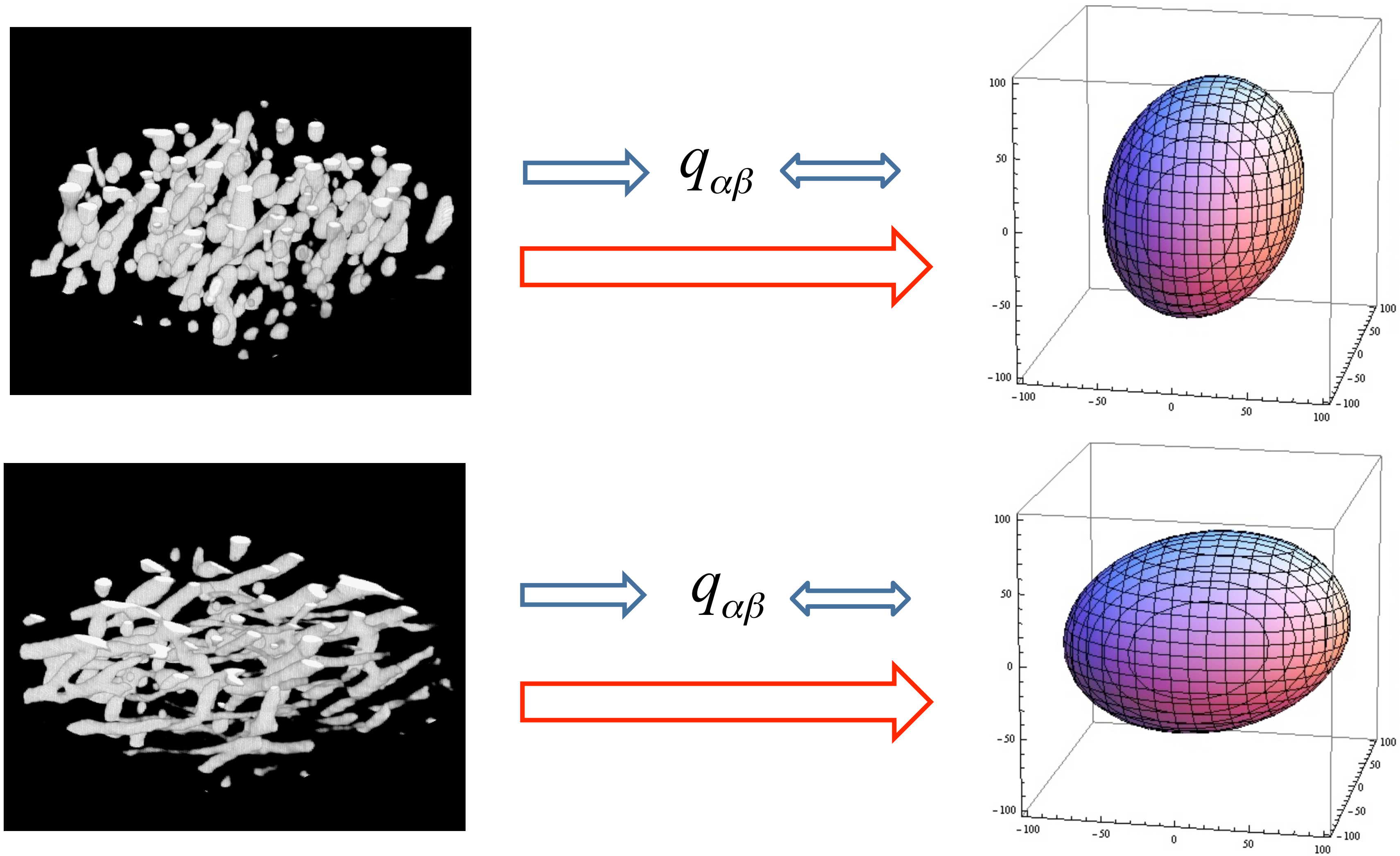
Off-diagonal elements



shear stress ⟺ $-q_{zx}$

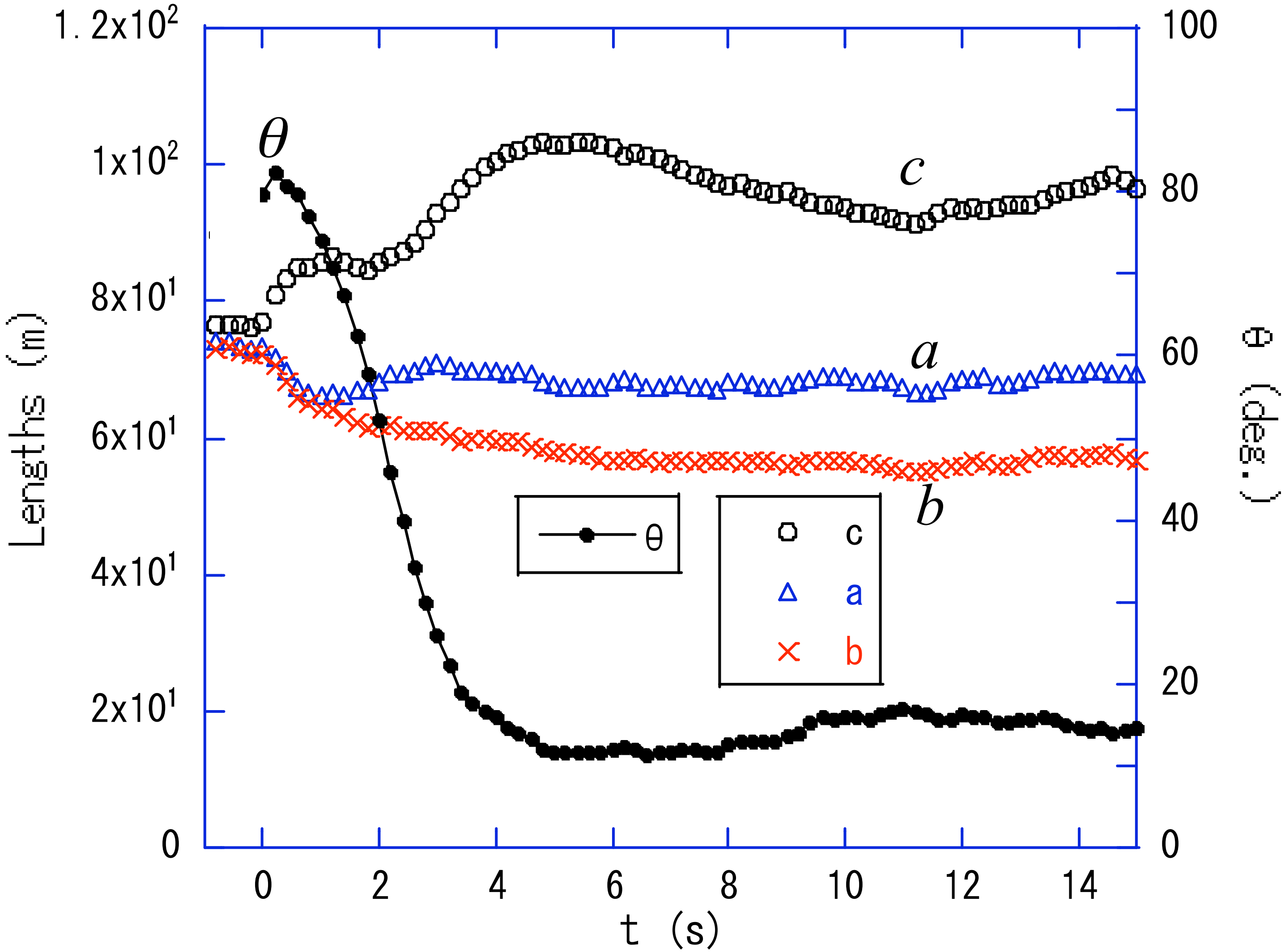
close relation

Mapping from structure to ellipsoid

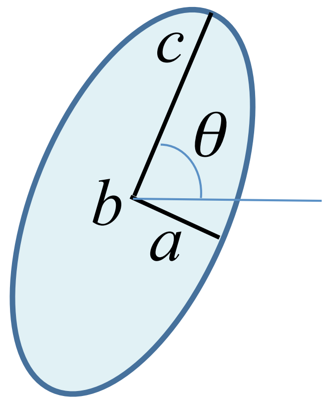


Structure

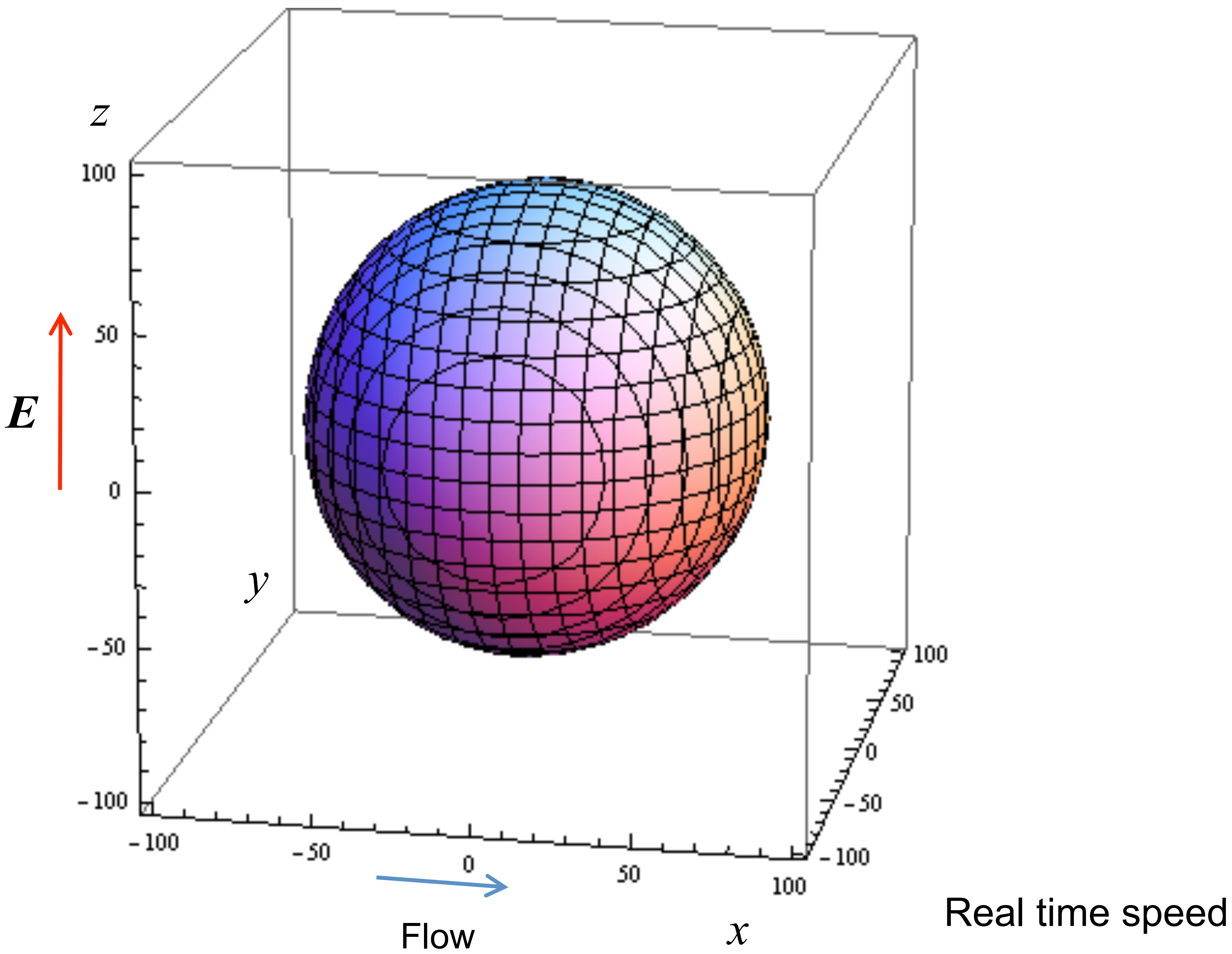
Ellipsoid



1. 2x10²
1x10²
8x10¹
6x10¹
4x10¹
2x10¹
0
Lengths (m)
θ
c
a
b
θ
c
a
b
0
2
4
6
8
10
12
14
t (s)
100
80
60
40
20
0
θ (deg.)



c
θ
b
a


z
100
50
0
- 50
- 100
E
y
- 100
- 50
0
50
100
x
Flow
100
50
0
- 50
- 100
Real time speed

σ : total shear stress

$$\sigma = \sigma_{\text{viscous}} + \sigma_{\text{interfacial}} + \sigma_{\text{electric}}$$

$\sigma_{\text{viscous}} = \eta\dot{\gamma}$ $\quad$ η: viscosity, $\dot{\gamma}$: shear rate

$\sigma_{\text{interfacial}} = -\Gamma q_{zx}$ $\quad$ Γ: interfacial tenson

(Batchelor 1970, Doi 1987, Onuki 1987)

σ_{electric} ?

Maxwell stress tensor $T_{\alpha\beta} = \varepsilon\left(E_\alpha E_\beta - \frac{1}{2}\delta_{\alpha\beta}E^2\right)$

$\sigma_{\text{electric}} \propto E^2$

$E \to 0 \Rightarrow \sigma_{\text{electric}} \to 0$

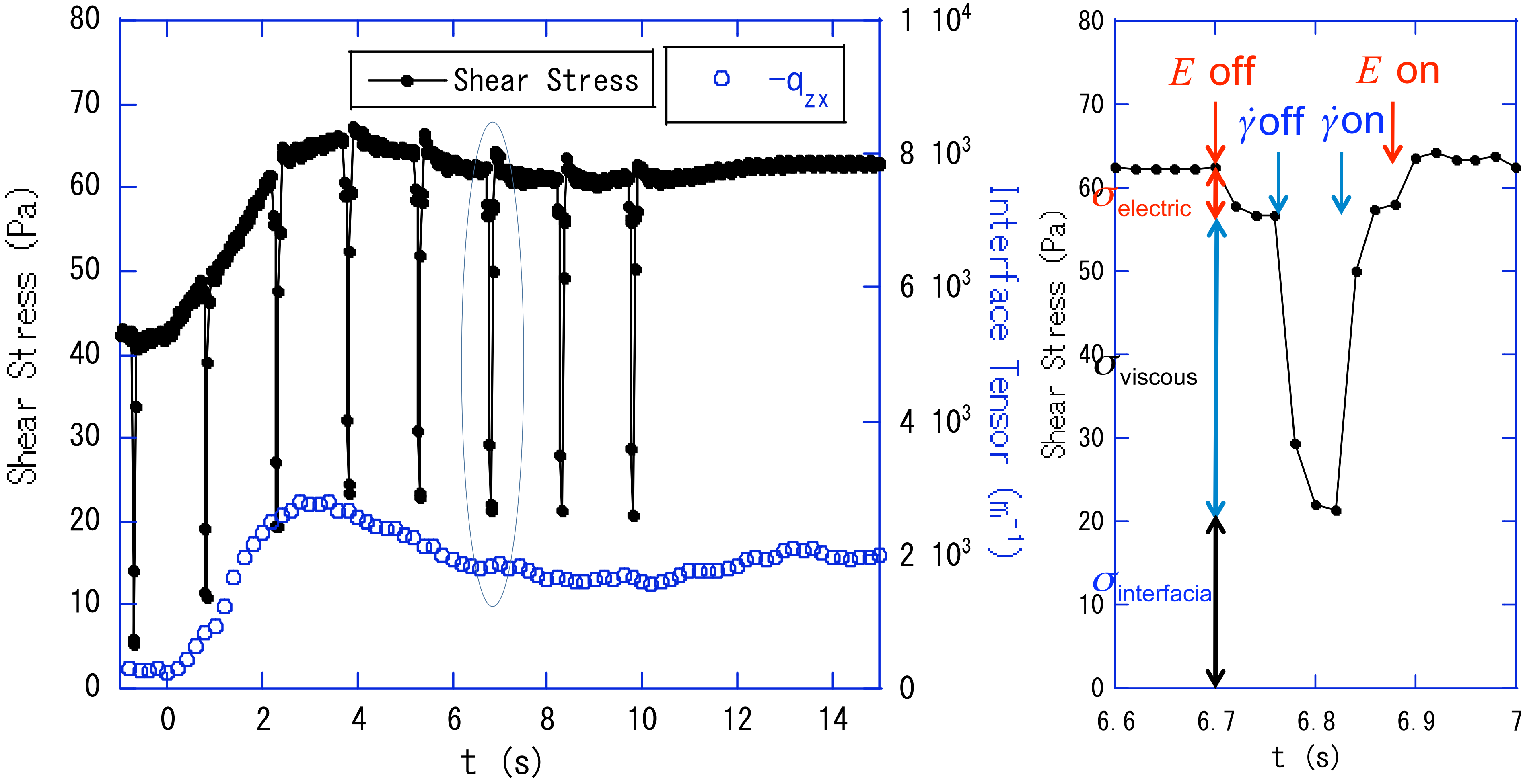
$\sigma_{\text{viscous}} = \eta\dot{\gamma}$

$\dot{\gamma} \to 0 \Rightarrow \sigma_{\text{viscous}} \to 0$

⇩

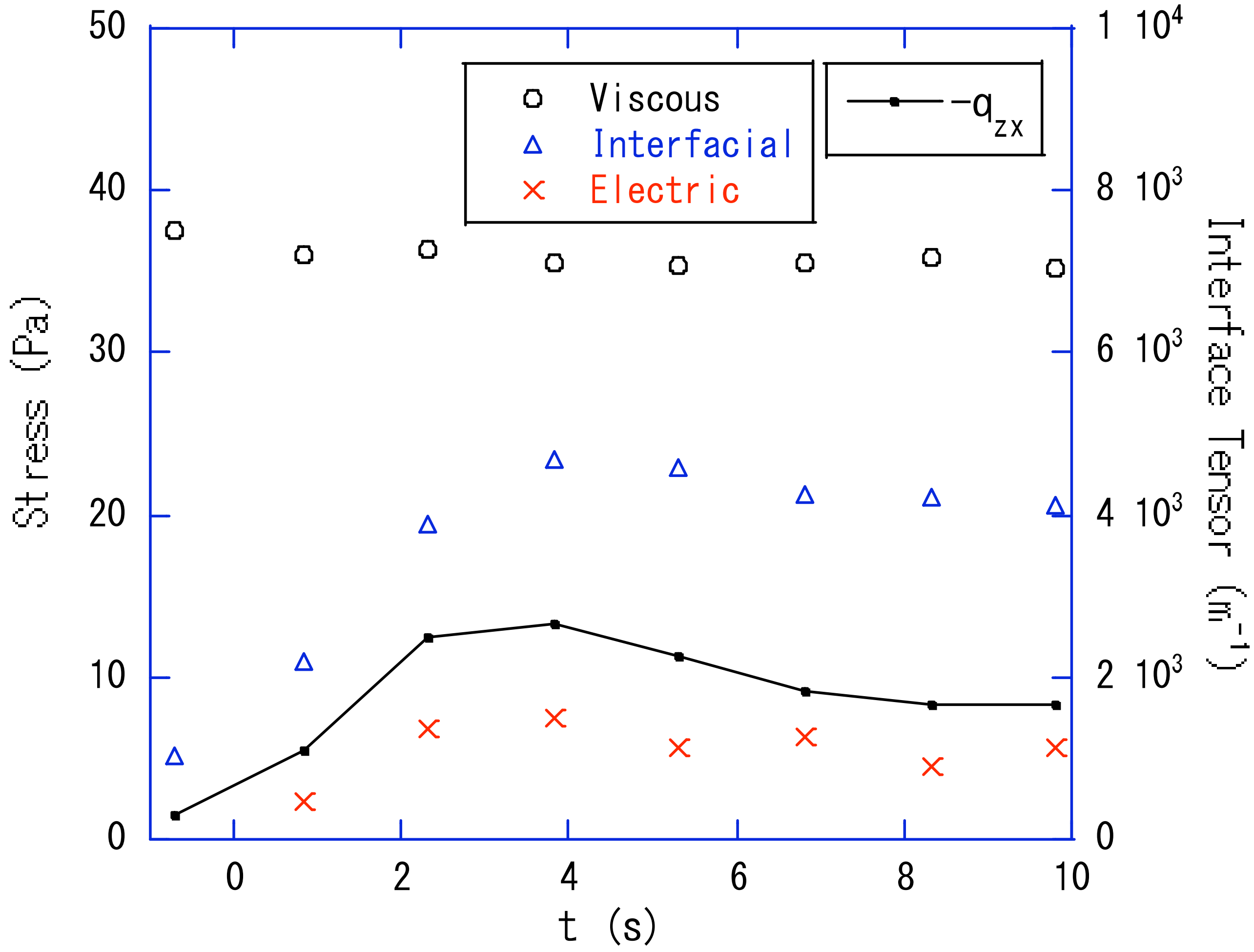
Separation of σ_{electric}, $\sigma_{\text{interfacial}}$, σ_{viscous}

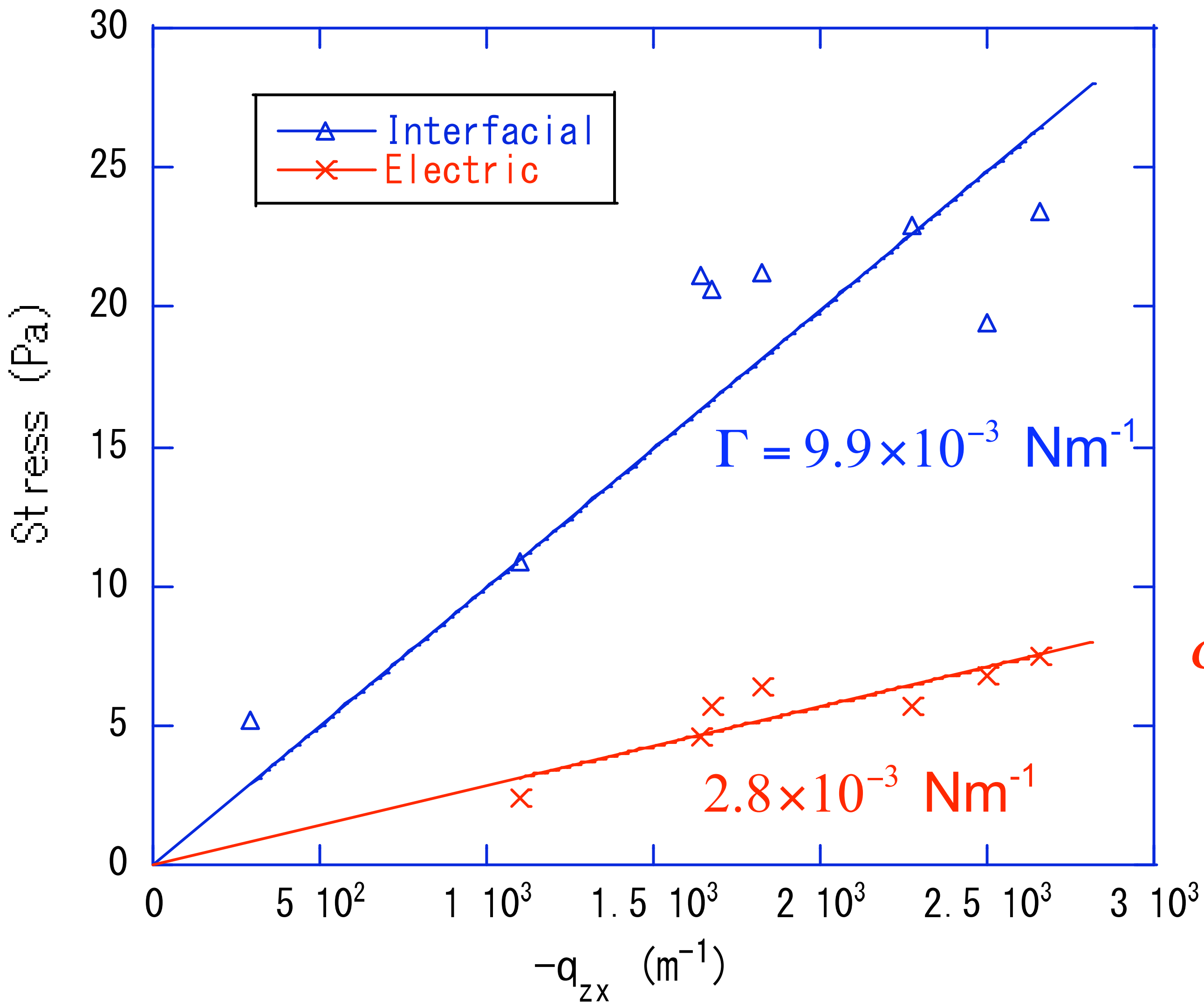
Separation of $\sigma_{electric}$, $\sigma_{interfacial}$, $\sigma_{viscous}$



$\eta = 33.5$ Pa s

$\dot{\gamma} = 1$ s^{-1}





$$\sigma_{electric} = c(-q_{zx})$$

c ?

Electric stress

Electric torque on ellipsoid

$$\boldsymbol{K}^{(e)} = \boldsymbol{p} \times \boldsymbol{E}$$

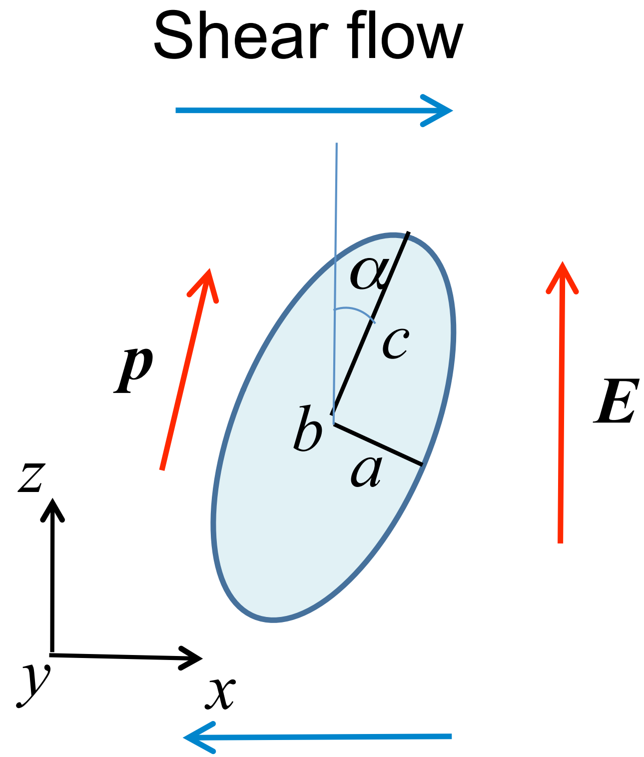
⇩

Electric stress (Halsey et al., 1992)

$$\sigma_{electric} = -K_y^{(e)} / v \cdot \phi$$

v: ellipsoid volume

ϕ: volume fraction



$\boldsymbol{p}$: dipole moment

$$\sigma_{electric} = \varepsilon_2 \frac{(\varepsilon_1 - \varepsilon_2)\left(n^{(a)} - n^{(c)}\right)}{\left\{(\varepsilon_1 - \varepsilon_2)n^{(a)} + \varepsilon_2\right\}\left\{(\varepsilon_1 - \varepsilon_2)n^{(c)} + \varepsilon_2\right\}} \phi E^2 \sin\alpha \cos\alpha$$

$n^{(a)}, n^{(c)}$: depolarization factor

⇩ $a \sim c$

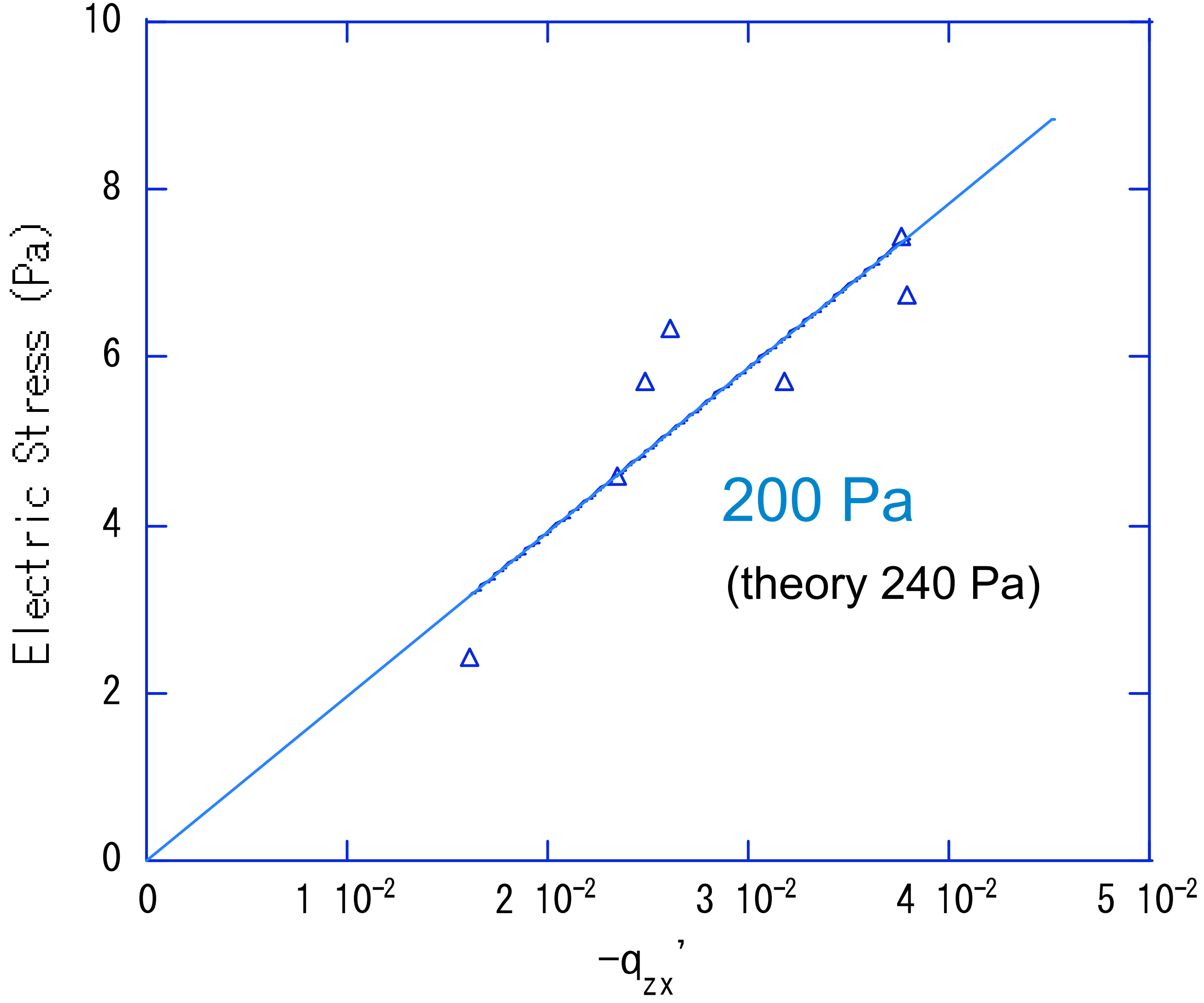
$$\sigma_{electric} = -9\varepsilon_2 \frac{(\varepsilon_1 - \varepsilon_2)^2}{(\varepsilon_1 + 2\varepsilon_2)^2} E^2 \phi \left(n^{(c)} - n^{(a)}\right) \sin\alpha \cos\alpha$$

⇩ approximation

$$\sigma_{electric} = -9\varepsilon_2 \frac{(\varepsilon_1 - \varepsilon_2)^2}{(\varepsilon_1 + 2\varepsilon_2)^2} E^2 \phi q_{zx}' \qquad q_{zx}' \equiv \frac{q_{zx}}{Q} = \frac{\int_S n_z n_x dS}{\int_S dS} = \langle n_z n_x \rangle$$

$\|$

240 Pa



Electric Stress (Pa)
10
8
6
4
2
0
0
1 10^-2
2 10^-2
3 10^-2
4 10^-2
5 10^-2
−q_zx'
200 Pa
(theory 240 Pa)

$$\sigma_{electric} = -9\varepsilon_2 \frac{(\varepsilon_1 - \varepsilon_2)^2}{(\varepsilon_1 + 2\varepsilon_2)^2} E^2 \phi q_{zx}'$$

$$q_{zx}' \equiv \frac{q_{zx}}{Q} = \frac{q_{zx}}{S/V}$$

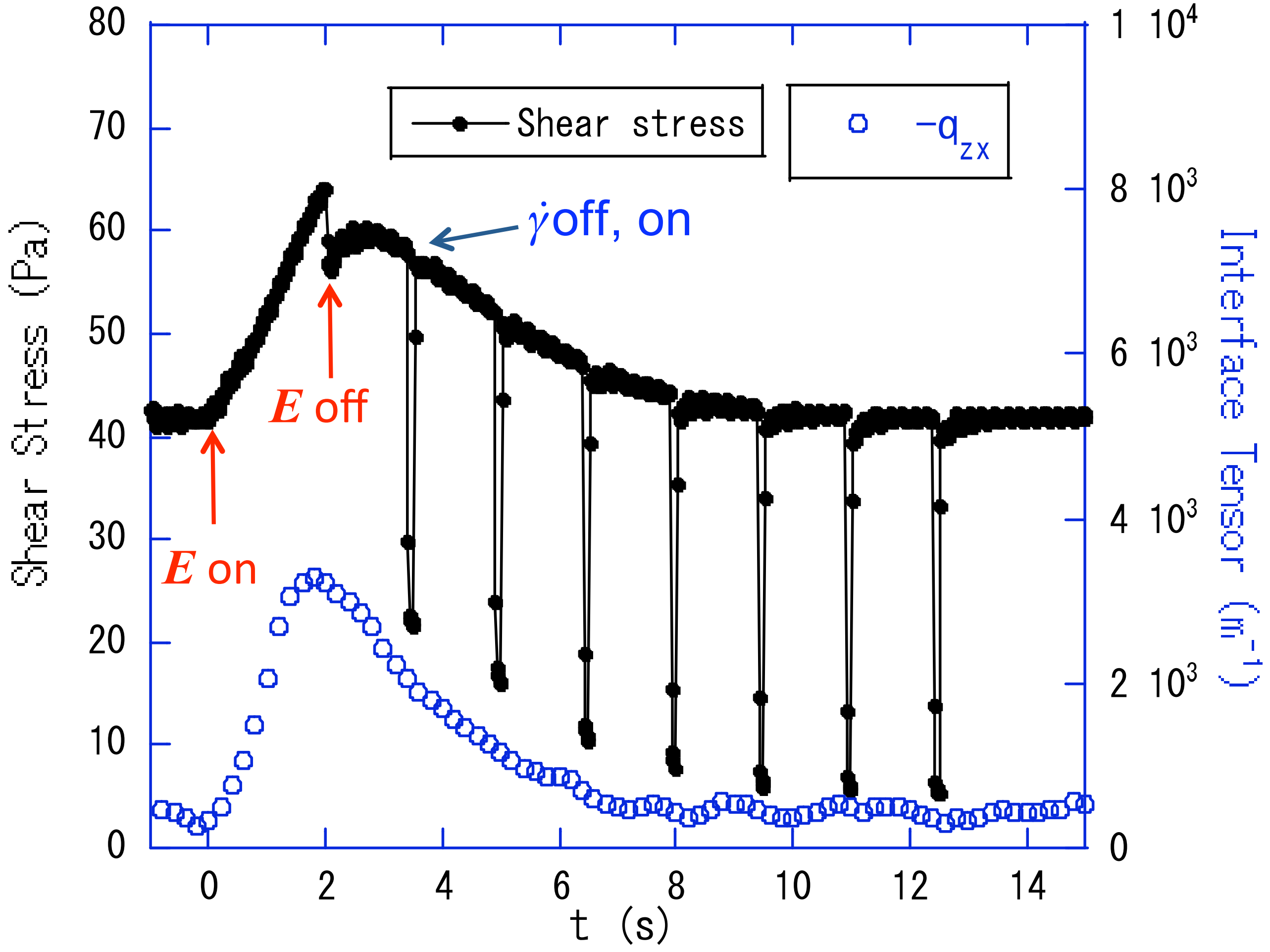
$$\sigma_{electric} = -\Gamma_{electric} q_{zx}$$

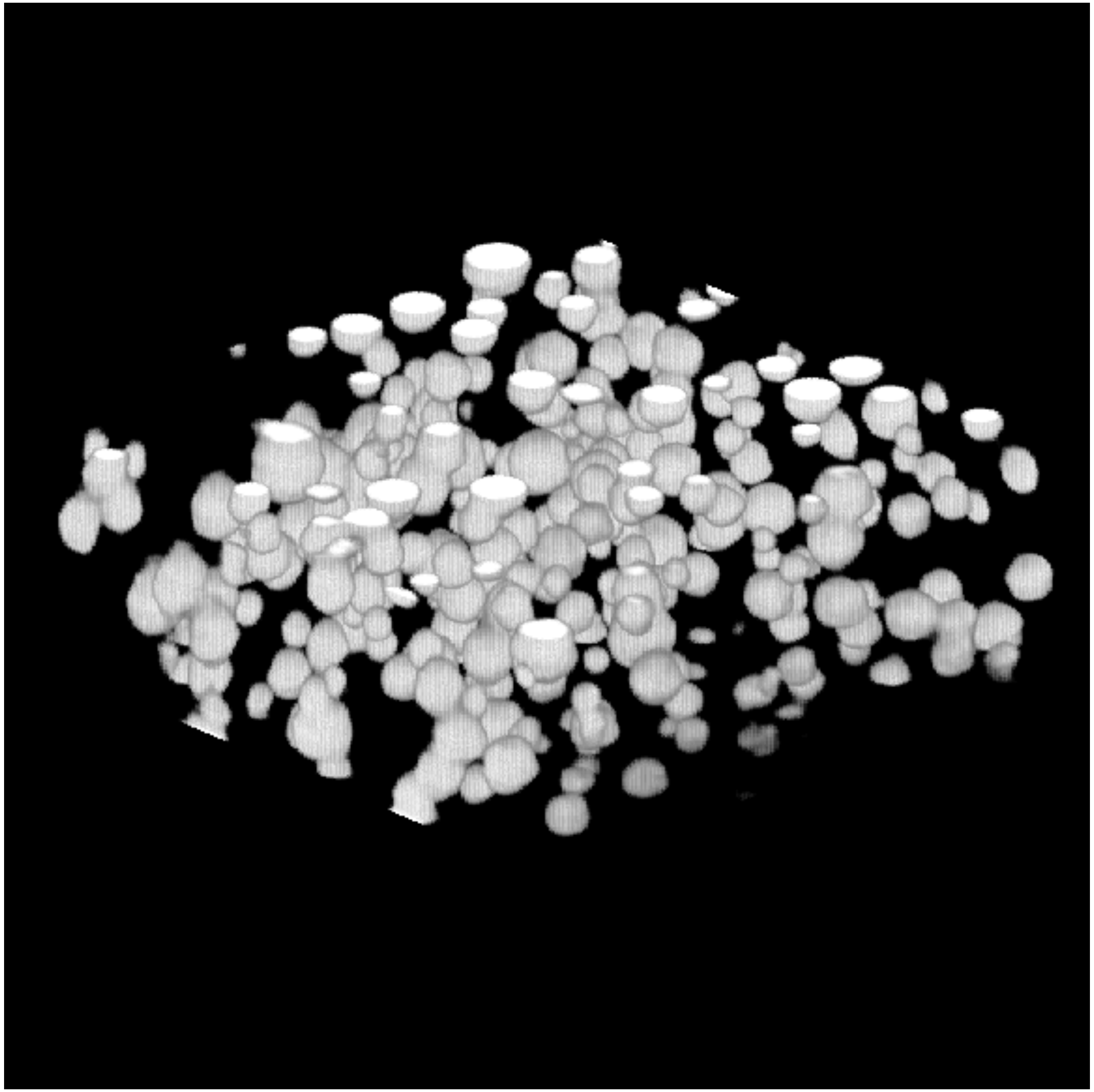
$$\Gamma_{electric} \equiv 9\varepsilon_2 \frac{(\varepsilon_1 - \varepsilon_2)^2}{(\varepsilon_1 + 2\varepsilon_2)^2} E^2 V_d / S$$

V_d : total volume of droplets (LCP)

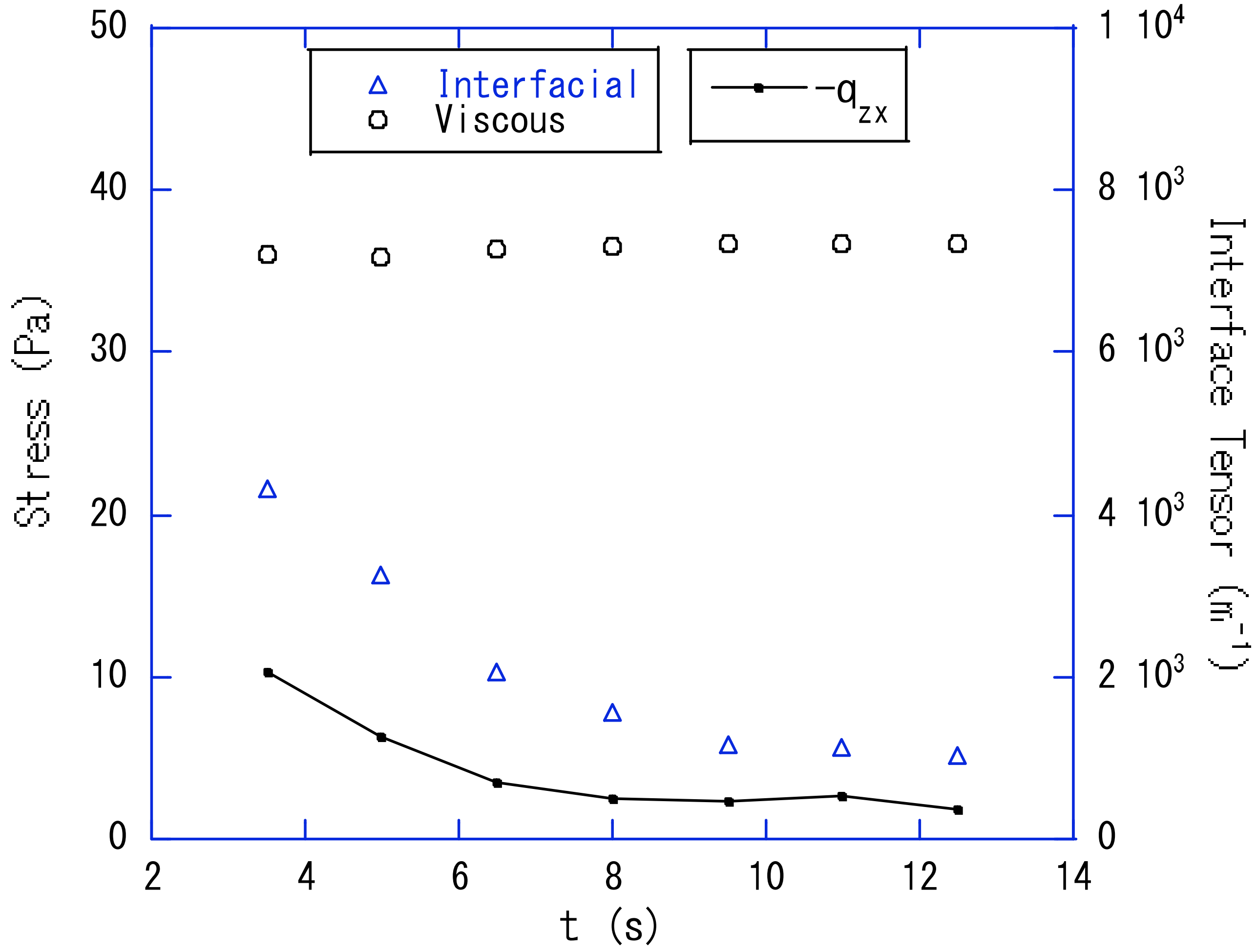
Relaxation process to droplets after removing E

From columnar structure

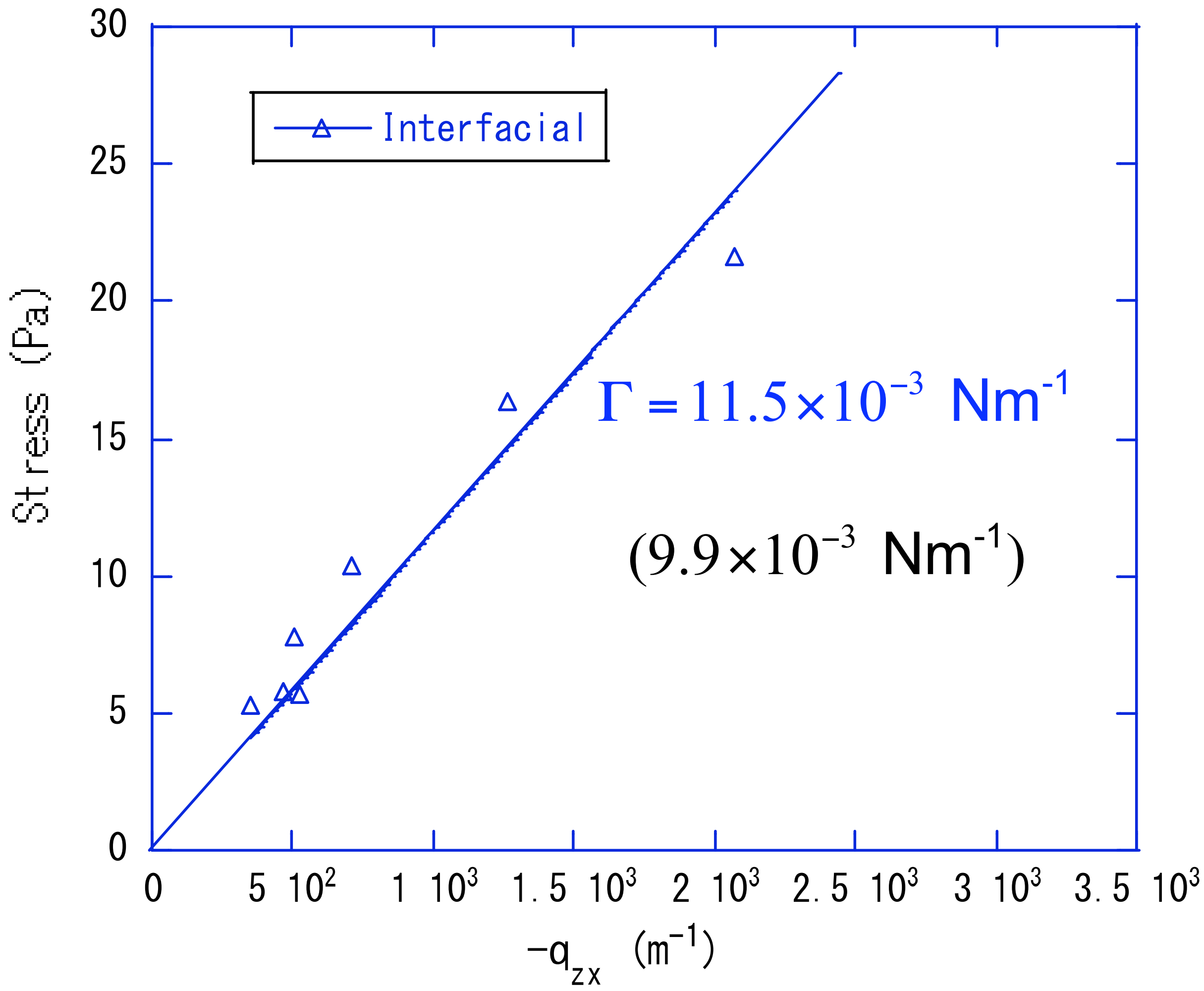




Real time speed

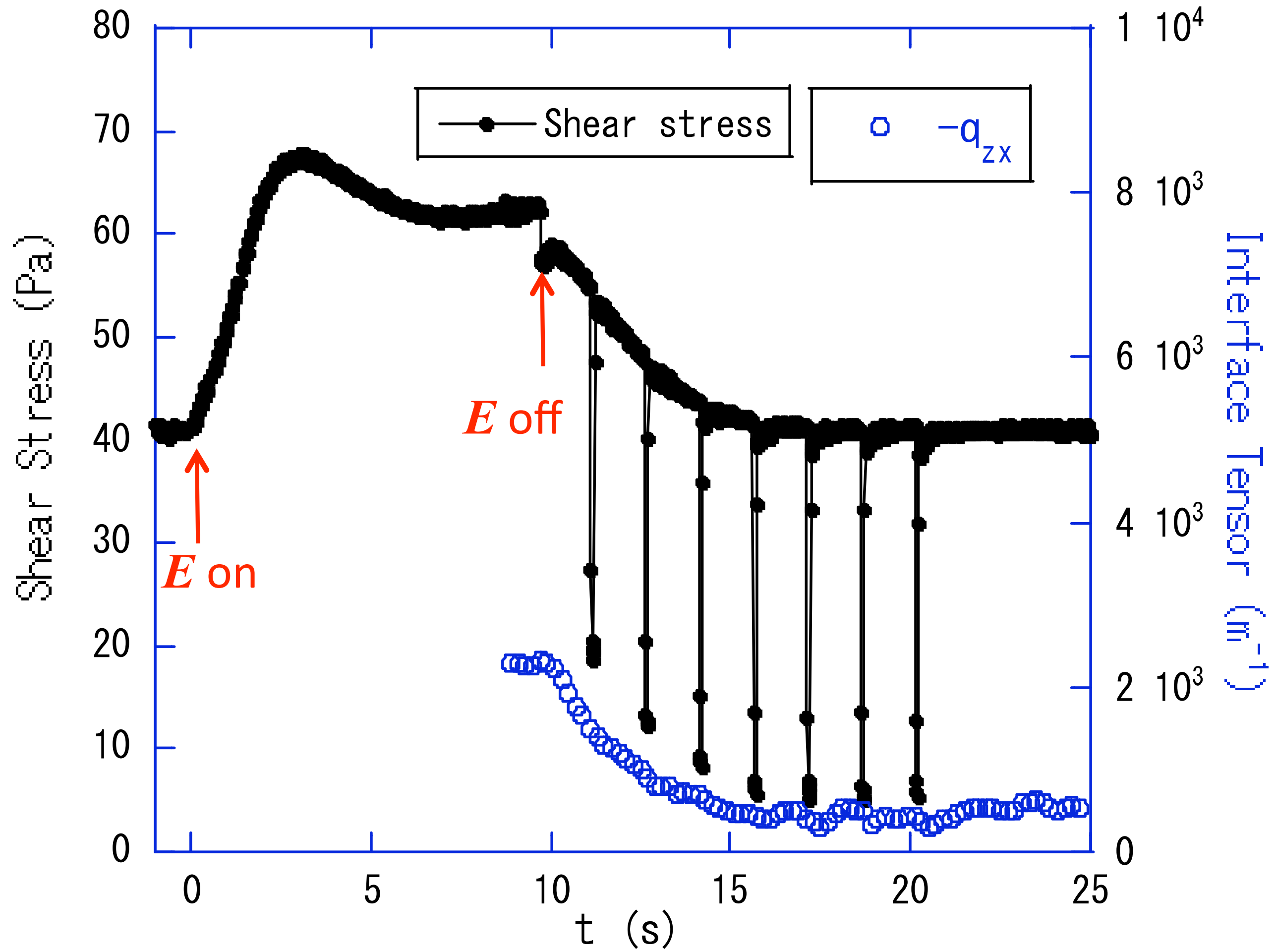


Interfacial
Viscous
$-q_{zx}$
Stress (Pa)
Interface Tensor (m^{-1})
t (s)
0
10
20
30
40
50
2
4
6
8
10
12
14
0
2 10^3
4 10^3
6 10^3
8 10^3
1 10^4

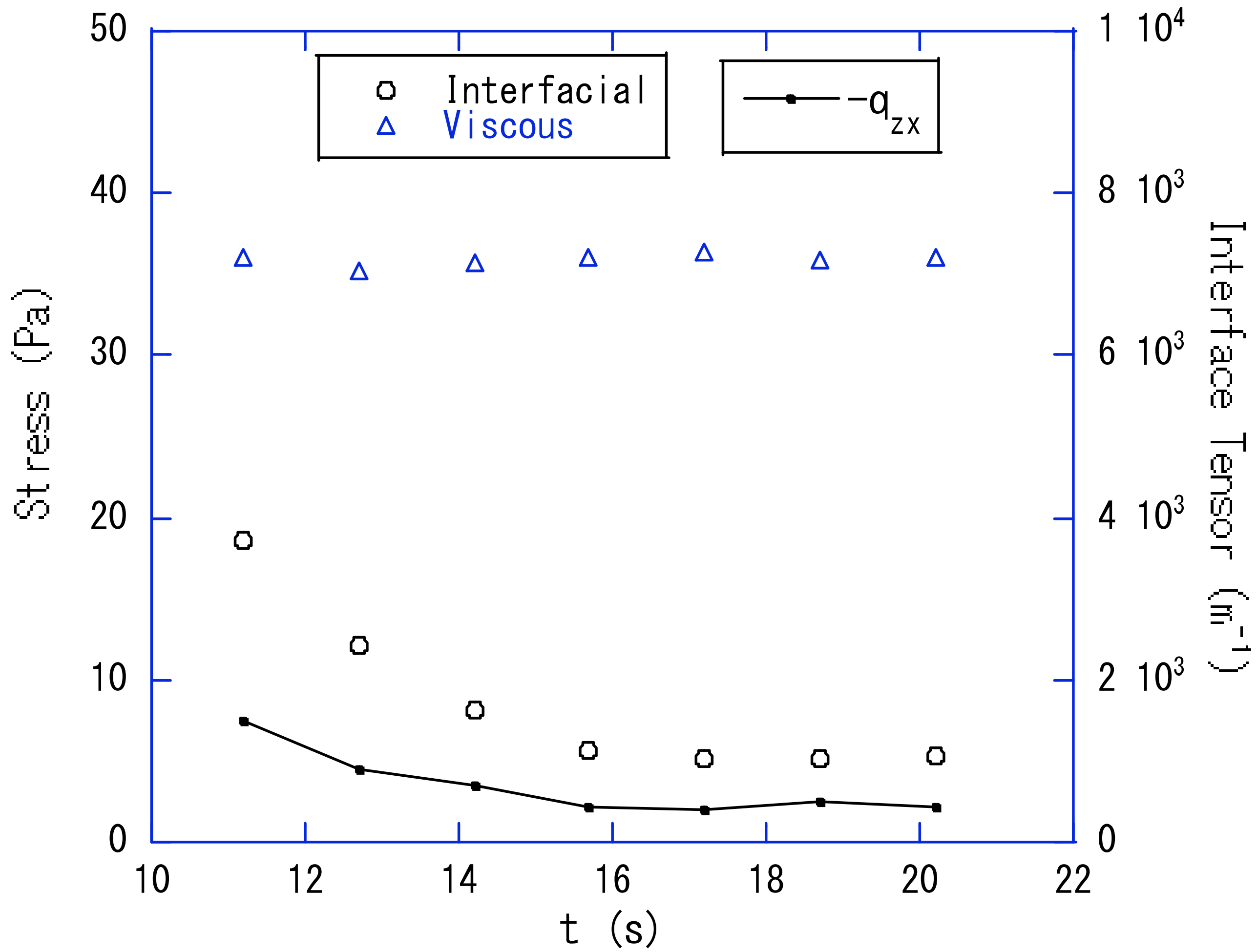


Interfacial
$\Gamma = 11.5\times10^{-3}$ Nm^{-1}
(9.9×10^{-3} Nm^{-1})
Stress (Pa)
0
5
10
15
20
25
30
0
5 10^{2}
1 10^{3}
1.5 10^{3}
2 10^{3}
2.5 10^{3}
3 10^{3}
3.5 10^{3}
$-q_{zx}$ (m^{-1})

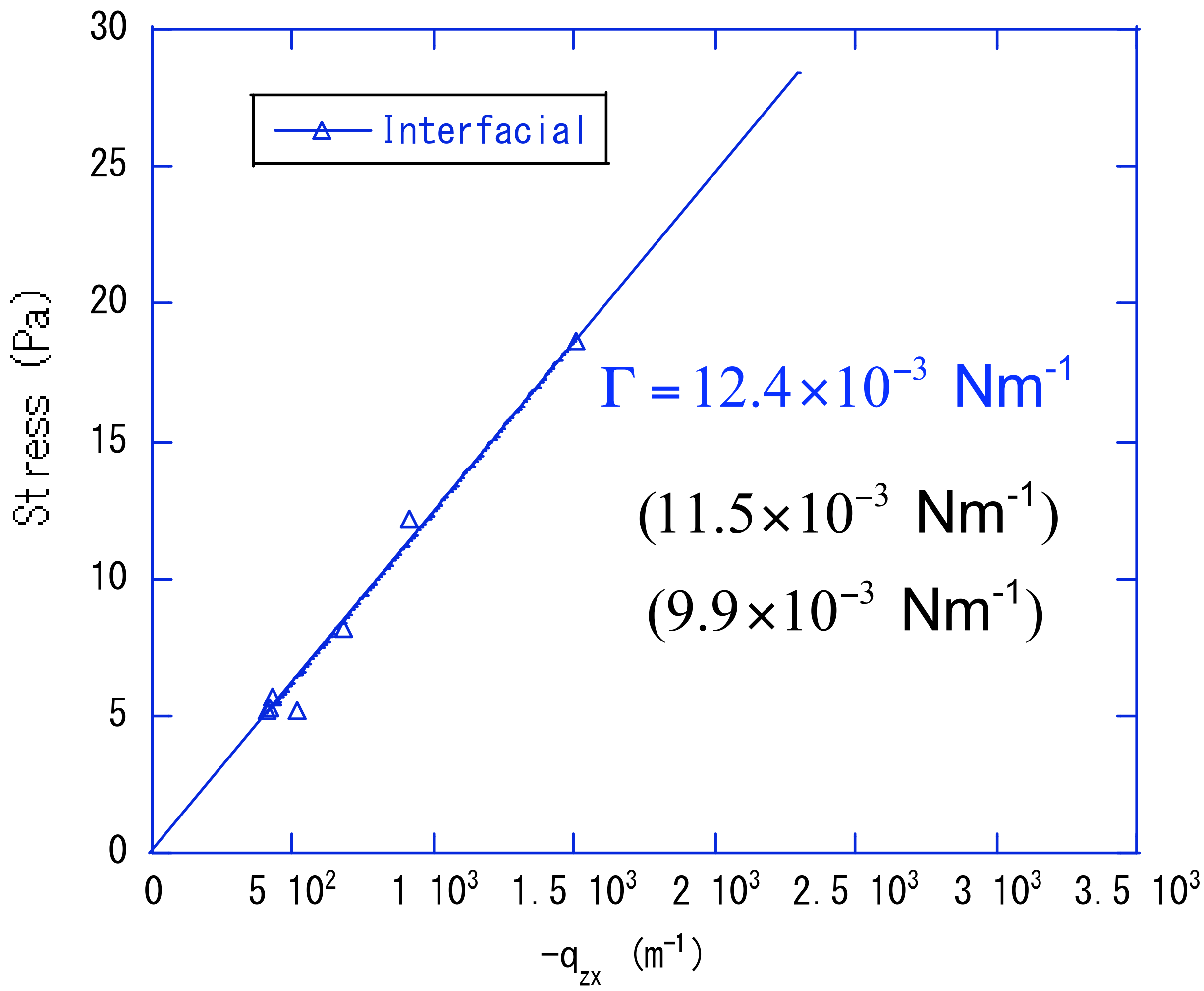
From network structure



Real time speed

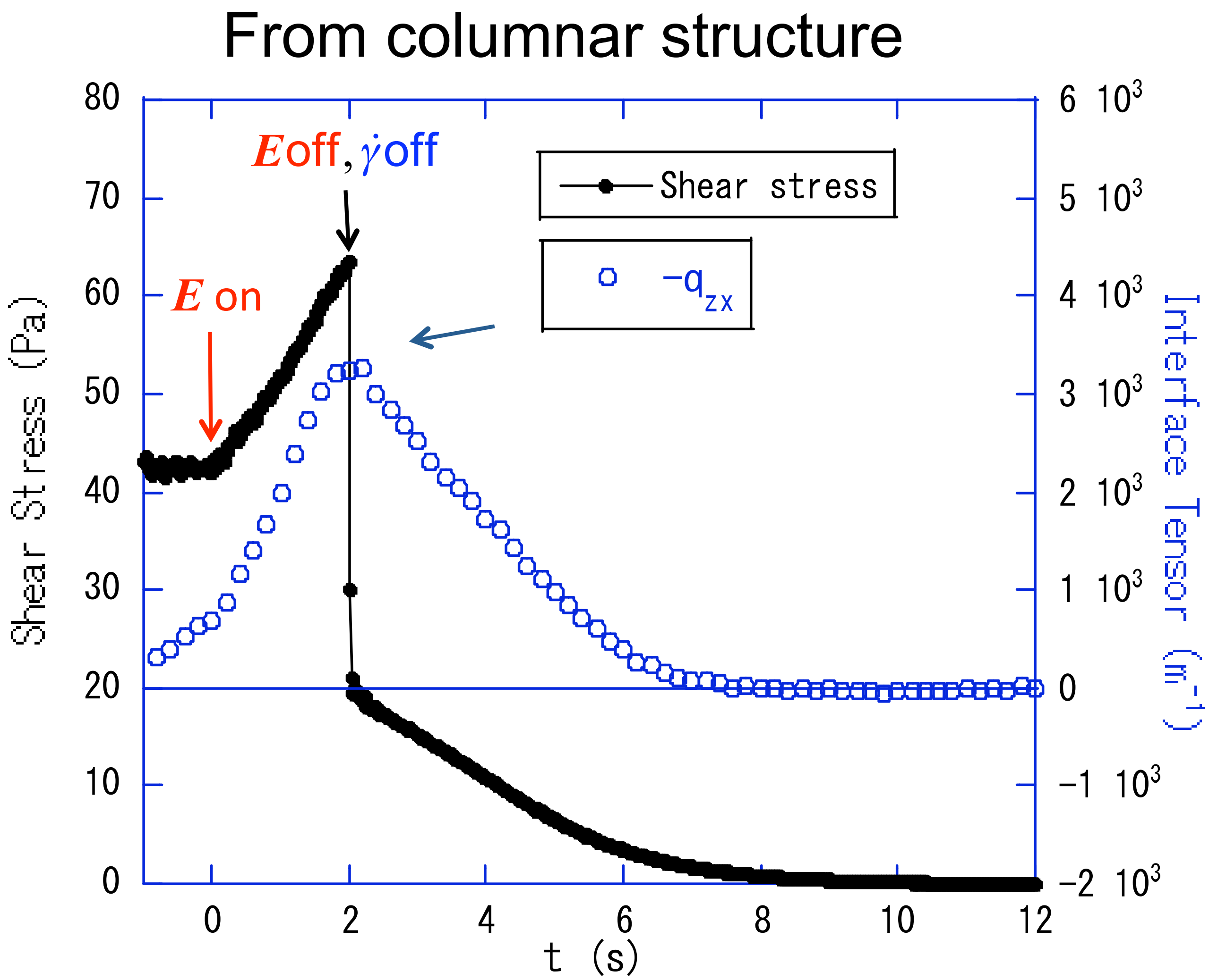


Interfacial
Viscous
$-q_{zx}$
Stress (Pa)
Interface Tensor (m^{-1})
t (s)
50
40
30
20
10
0
10
12
14
16
18
20
22
$1\ 10^4$
$8\ 10^3$
$6\ 10^3$
$4\ 10^3$
$2\ 10^3$
0

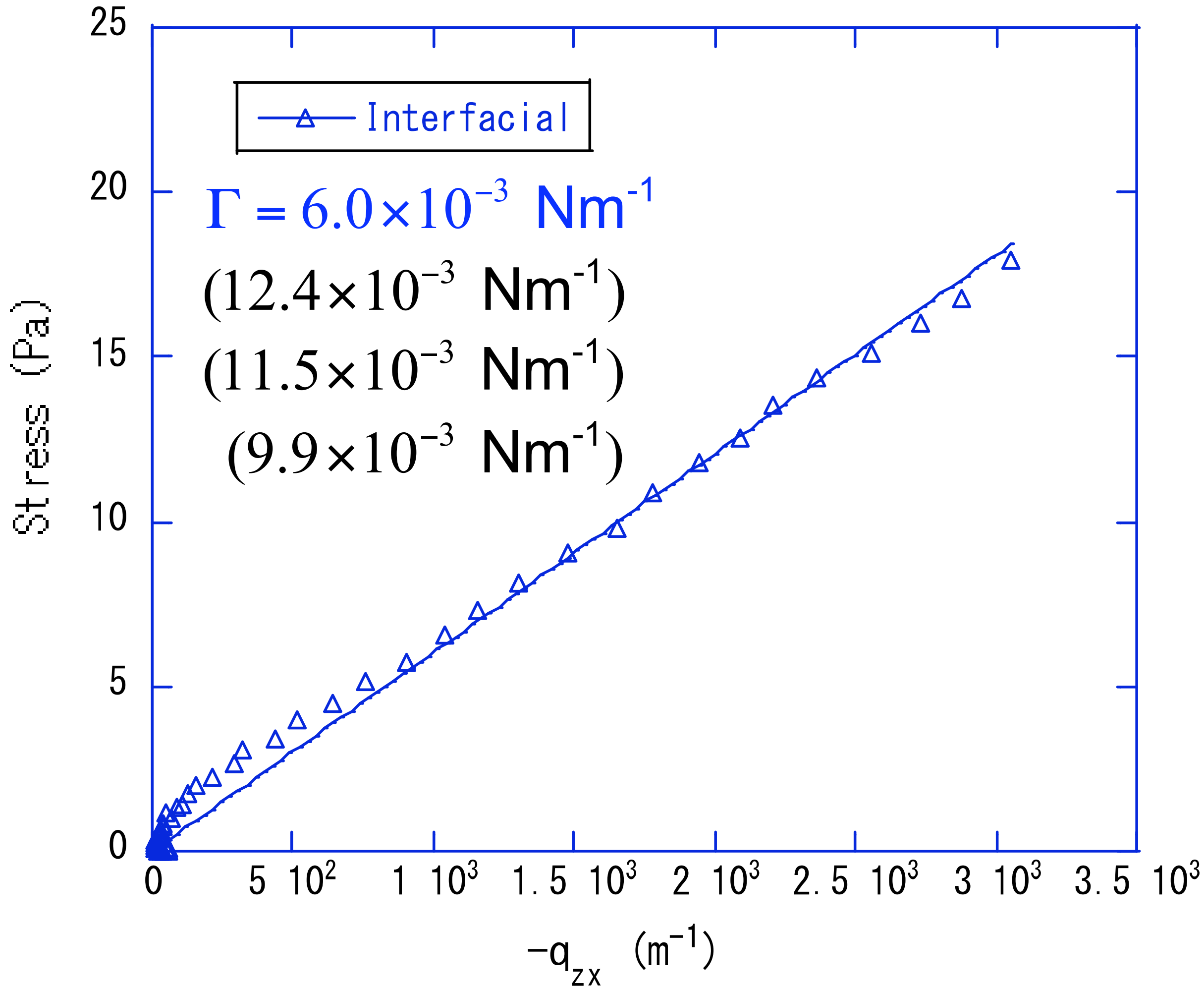


Interfacial
Stress (Pa)
$-q_{zx}$ (m^{-1})
0
5
10
15
20
25
30
0
5 10^2
1 10^3
1.5 10^3
2 10^3
2.5 10^3
3 10^3
3.5 10^3
$\Gamma = 12.4\times10^{-3}$ Nm^{-1}
(11.5×10^{-3} Nm^{-1})
(9.9×10^{-3} Nm^{-1})

Removal of both electric field and shear flow

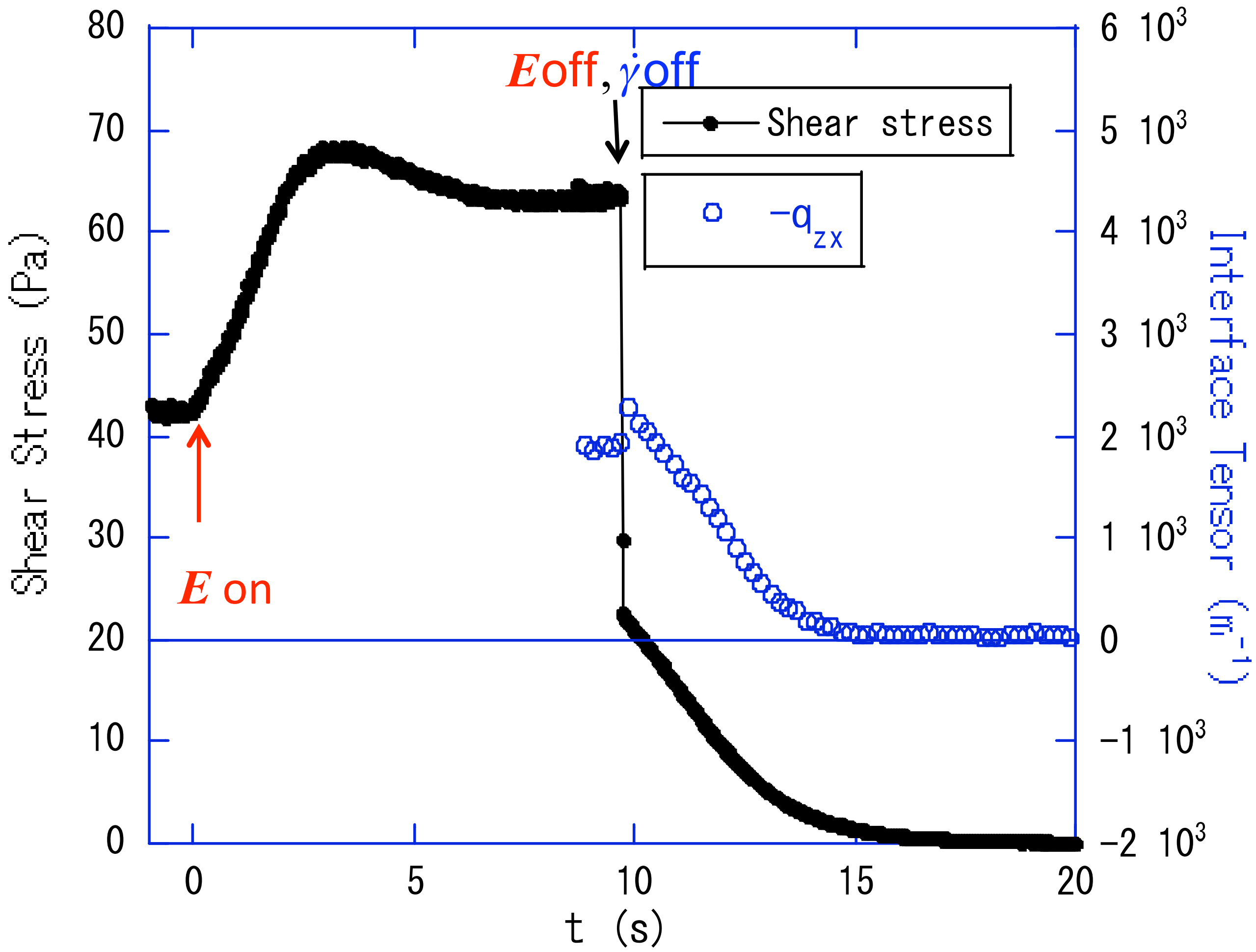


Real time speed

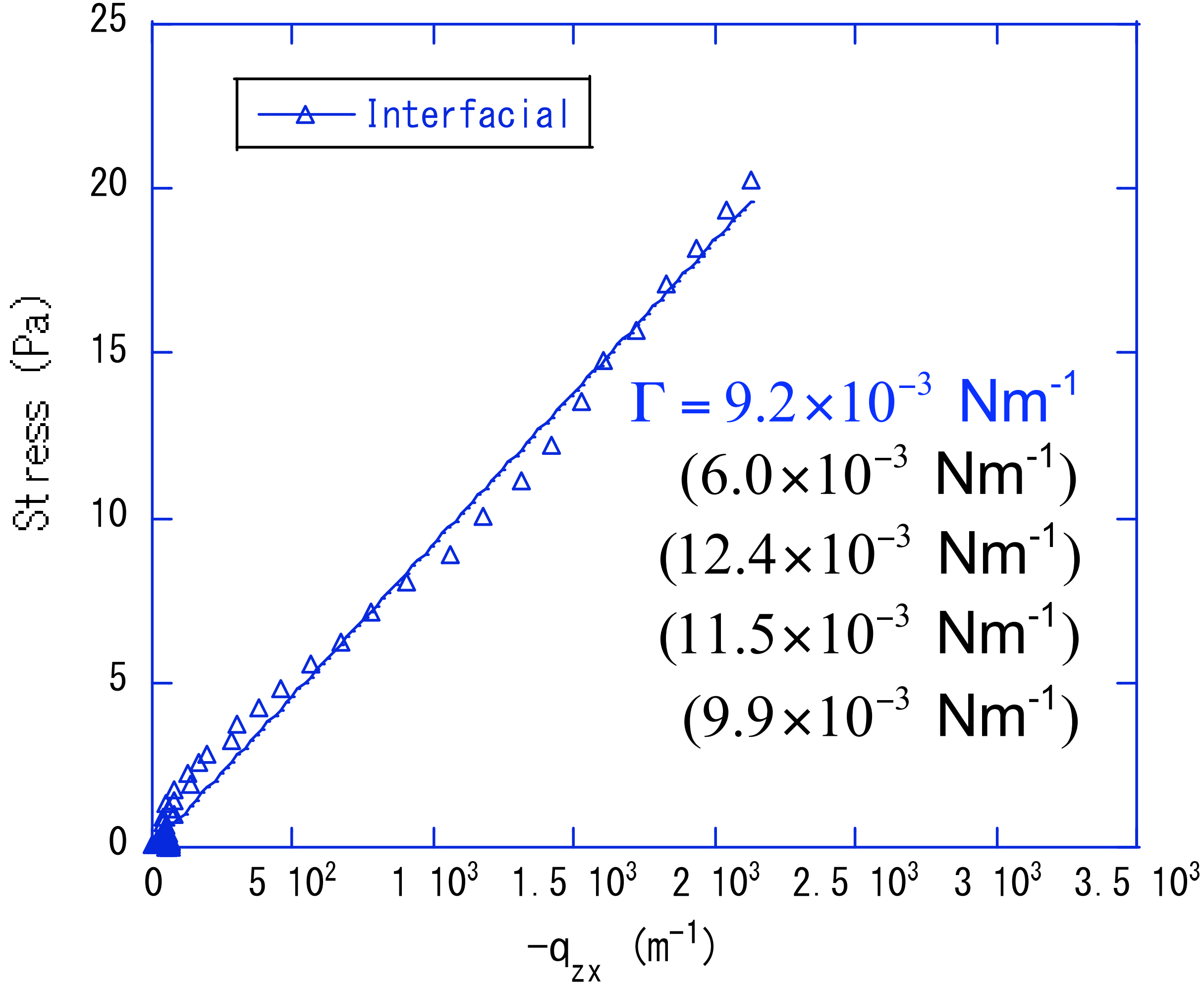


Interfacial
Γ = 6.0×10^-3 Nm^-1
(12.4×10^-3 Nm^-1)
(11.5×10^-3 Nm^-1)
(9.9×10^-3 Nm^-1)
Stress (Pa)
25
20
15
10
5
0
0
5 10^2
1 10^3
1.5 10^3
2 10^3
2.5 10^3
3 10^3
3.5 10^3
-q_zx (m^-1)

From network structure



Real time speed

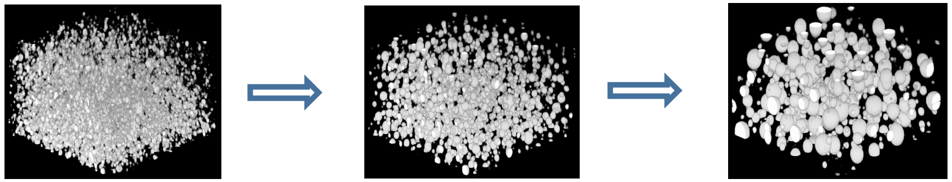


Interfacial
Stress (Pa)
25
20
15
10
5
0
0
5 10^2
1 10^3
1.5 10^3
2 10^3
2.5 10^3
3 10^3
3.5 10^3
$-q_{zx}$ (m^{-1})
$\Gamma = 9.2\times10^{-3}$ Nm^{-1}
(6.0×10^{-3} Nm^{-1})
(12.4×10^{-3} Nm^{-1})
(11.5×10^{-3} Nm^{-1})
(9.9×10^{-3} Nm^{-1})

Summary

Subjected to a step electric field without shear flow

1. Coalescence of droplets in electric filed

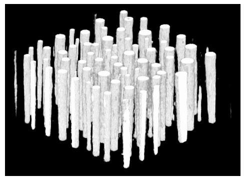


Hierarchical model is applicable

Exponential growth — Sphere

Non-exponential growth — Spheroid

2. Shear modulus of columnar structure

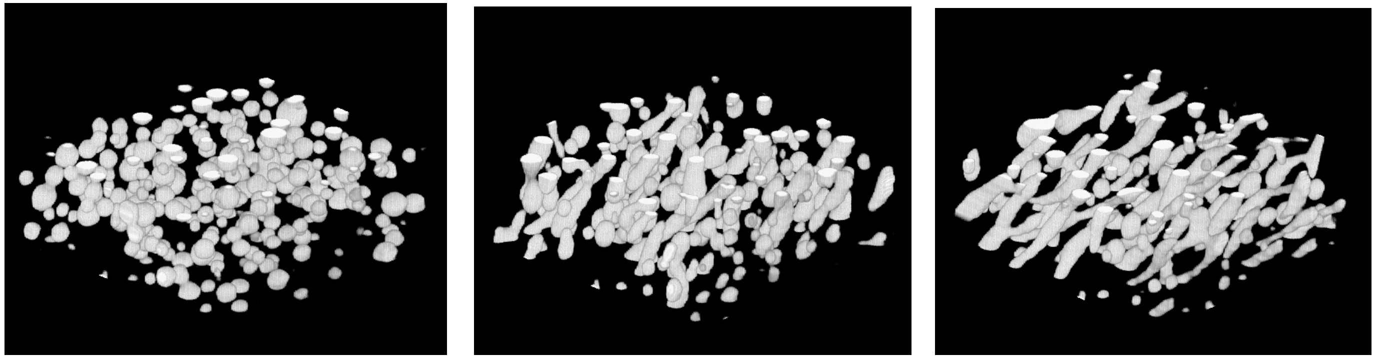


Emergence of elasticity under electric fields

Dependences of field strength and frequency

Subjected to a step electric field under shear flow

3. 3D images



4. Separation of viscous, interfacial and electric stresses

$$\sigma = \sigma_{\text{viscous}} + \sigma_{\text{interfacial}} + \sigma_{\text{electric}}$$

5. Interface tensor

$$\sigma_{\text{interfacial}} = -\Gamma q_{zx}$$

$$\sigma_{electric} = -9\varepsilon_2 \frac{(\varepsilon_1 - \varepsilon_2)^2}{(\varepsilon_1 + 2\varepsilon_2)^2} E^2 \phi q_{zx}' \left(= q_{zx}/Q\right)$$

Future subject

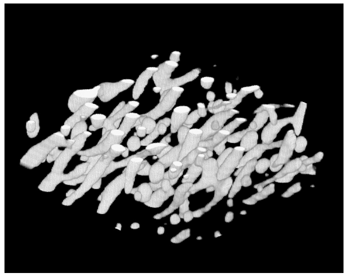
Structure $\Longrightarrow$ $q_{\alpha\beta}$, Q

$\Downarrow$

$$\sigma = \sigma_{\text{viscous}} + \sigma_{\text{interfacial}} + \sigma_{\text{electric}}$$

Can Doi-Ohta theory describe the change
from droplet-dispersed structure to network one?

$\Longrightarrow$



Topology changes!

$\bar{K} > 0$

$\bar{K} < 0$

Average Gaussian curvature $\bar{K}$

Constitutive equations of $q_{\alpha\beta}$, Q, $\bar{K}$???

Different viscosities

$$\sigma = \sigma_{\text{viscous}} + \sigma_{\text{interfacial}} + \sigma_{\text{electric}} + \sigma_{\text{interface velocity}}$$

$$\sigma_{\text{interface velocity}} = -\frac{(\eta_m - \eta_d)}{V}\int_S (u_z n_x + u_x n_z) dS$$

η_m : viscosity of matrix

η_d : viscosity of droplet

$\boldsymbol{u}$: local velocity on interface

(Batchelor, 1970)

Calculation of interface tensor