Lamellar-to-Onion Transition with Increasing Temperature under Shear Flow In Nonionic Surfactant Systems

Tadashi Kato

Department of Chemistry
Tokyo Metropolitan University

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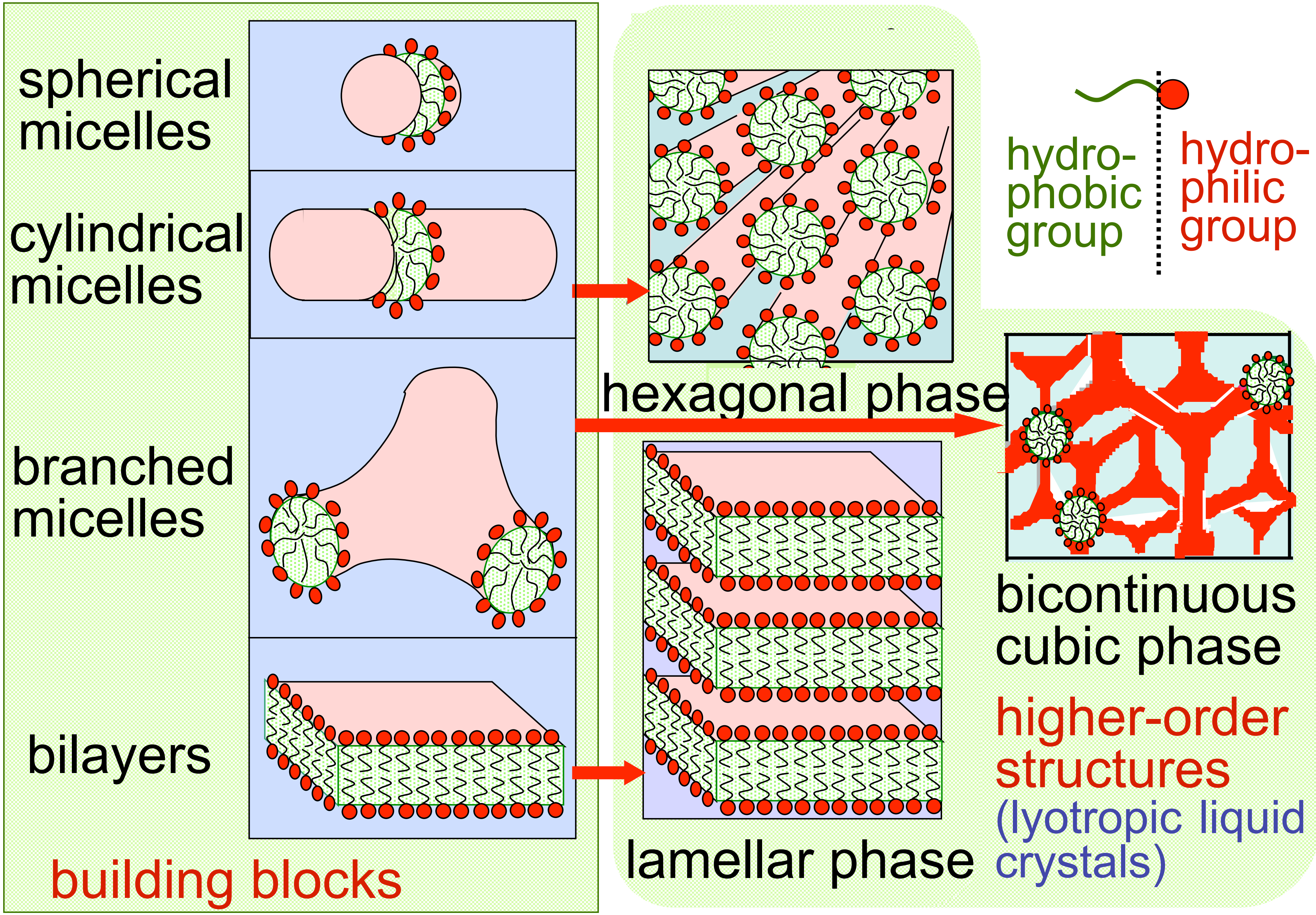
Coworkers:

Rheo-SALS and Rheo-SAXS
Yuriko Kosaka (Graduate Student)
Makiko Ito (Graduate Student)
Daijiro Sato (Graduate Student)

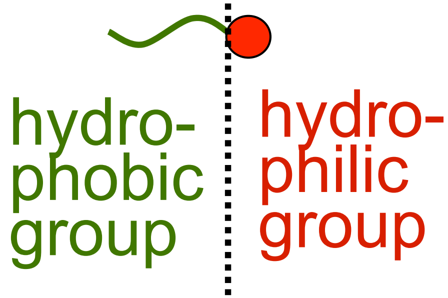
Phase Behaviors and Viscosity
Michiko Matsu-ura (Under Graduate Student)
Mari Okamoto (Under Graduate Student of Kitasato Univ.)
Kahoru Obara (Under Graduate Student of Kitasato Univ.)

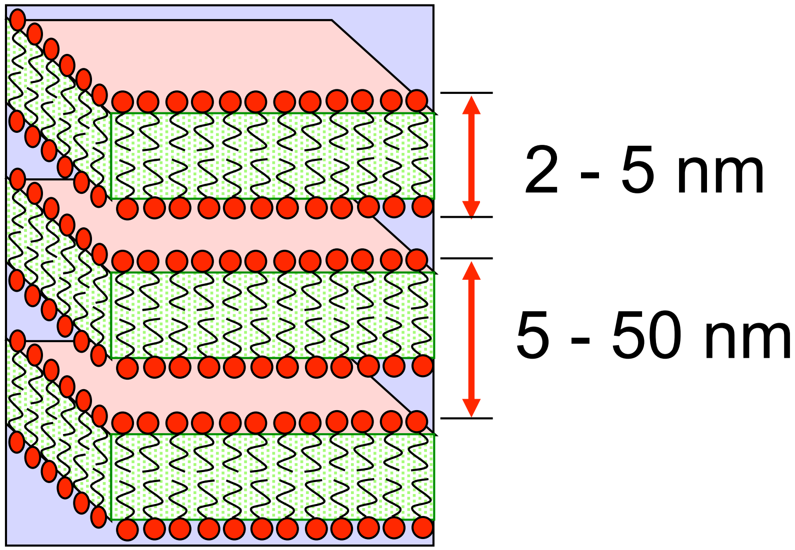
Dr. Youhei Kawabata (Assistant Professor)

Surfactant Self-Assemblies in Water



Surfactant Self-Assemblies in Water





lamellar phase

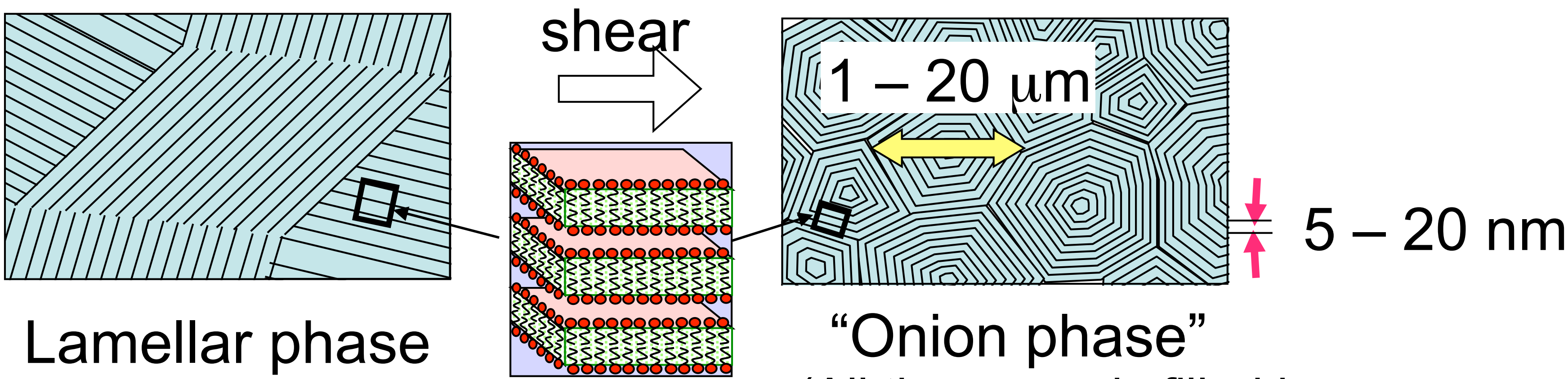
Effects of Shear Flow on Structures of Surfactant Lamellar Phase

- small-angle light, X-ray, and neutron scattering studies -

- Lamellar→ Onion transition
  O. Diat et al. *J. Phys II France* **3**, 1427 (1993),.
- Sponge→lamellar transition
  J. Yamamoto and H. Tanaka, *Phys. Rev. Lett*. **77**, 4390 (1996).
  L. Porcar et al. *Langmuir* **19**, 10779 (2003).
- Multi-lamellar vesicle→unilamellar vesicle trransition
  M. Bergmeier et al., *J. Phys. Chem. B* **102**, 2837 (1998).
- Collapse of membranes
  A. Al kahwaji et al., *Phys. Rev. Lett*. **84**, 3073 (2000).
  L. Porcar et al. *Phys. Rev. Lett*. **95**, 078302 (2005).
- Formation of multi-lamellar cylinders as inter-mediate structures between lamellae and onions.
  J. Zipfel et al., *Europhys. Lett*. **53**, 335 (2001).
- Anomalous Decrease in Lamellar Spacing
  T. Kato et al. *Langmuir*, **20**, 3504 (2004).

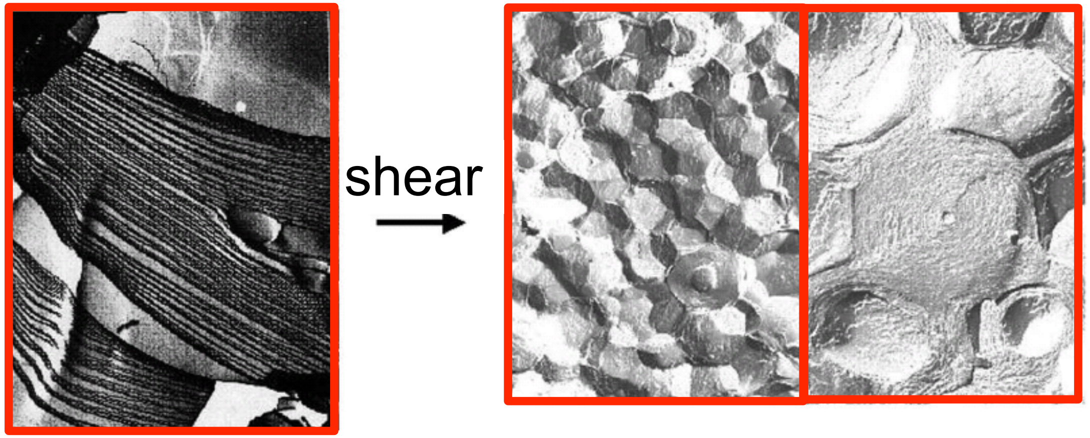
Transition from Lamellar to Onion Phase by Shear Flow

O. Diat, D. Roux, and F. Nallet, *J. Phys. II (France)* **3**, 1427 (1993).



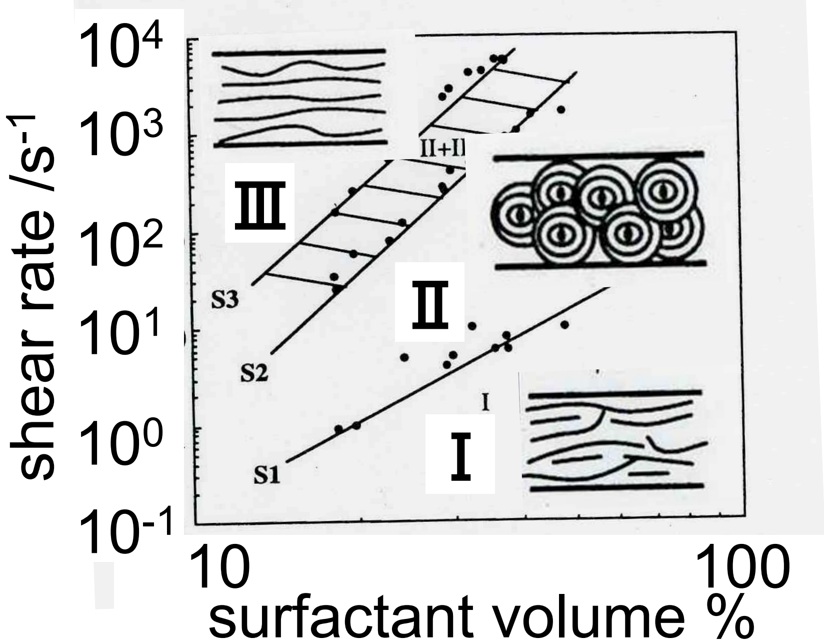
Lamellar phase

"Onion phase"
(All the space is filled by multilamellar vesicles alone)



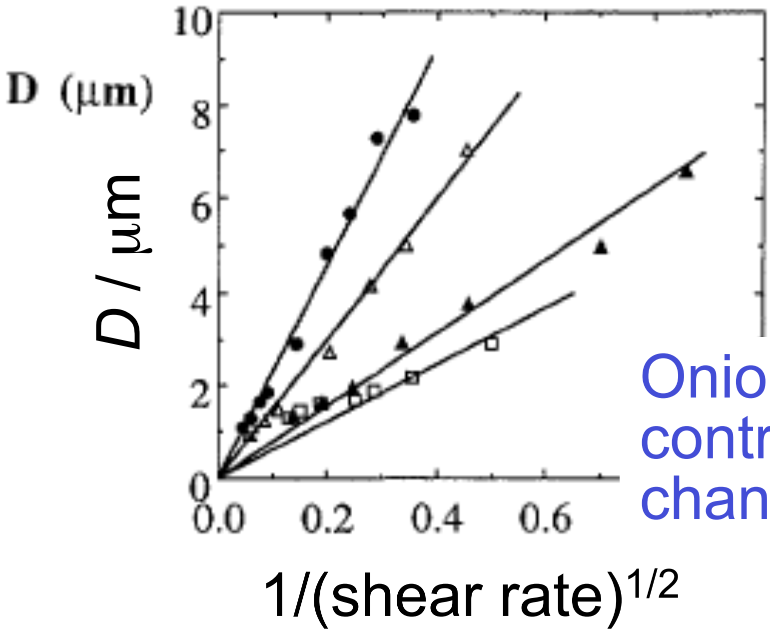
Electron microscope image
(T. Gulik-Krzywicki et al. *Langmuir* **12**, 4668 (1996).)

Transition from Lamellar to Onion Phase by Shear Flow



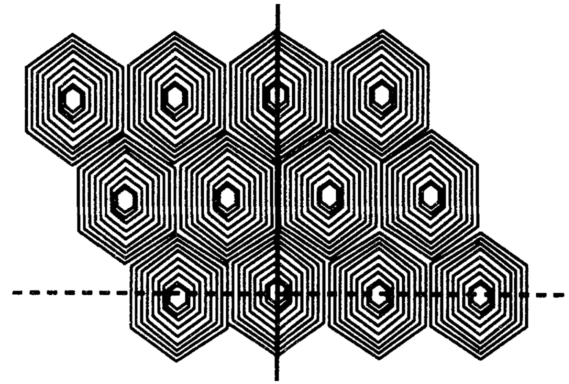
Dynamic phase diagram

O. Diat, D. Roux, and F. Nallet,
J. Phys. II (France) **3**, 1427 (1993),
Phys. Rev. E **51**, 3296 (1995).
P. Sierro and D. Roux
Phys. Rev. Lett. **78**, 1496 (1997).



Onion size can be controlled by changing shear rate

Long-range order In orientation above a critical shear rate



Transition from Lamellar to Onion Phase by Shear Flow

Experiments

- SDS/Pentanol/Water/Decane (Diat et al.,1993)
- SDS/Pentanol/Water/Dodecane (Courbin et al.,2002)
- SDS/Octanol/Brine (Sierro and Roux, 1997)
- AOT/Brine (Bergenholtz & Wagner, 1996, Courbin & Panniza, 2004)
- TDMAO/hexanol/water (Escalante et al., 2000).
- $C_{10}E_3$/Water, $C_{12}E_4$/Water (Müller et al, 1999, Zipfel et al., 2001, Lee et al., 2001, Nettesheim et al., 2003)

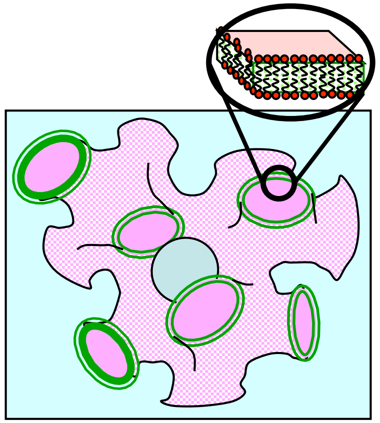
Theories

- O. Diat et al. *J. Phys. II (France)* **3**, 1427 (1993),
- E.van der Linden et al, *Langmuir* **12**, 3127 (1996)
- A.G. Zilman and R. Granek, *Eur. Phys. J. B* **11**, 593 (1999).
- S. W. Marlow and P. D. Olmsted, *Eur. Phys. J. E* **8**, 485 (2002).

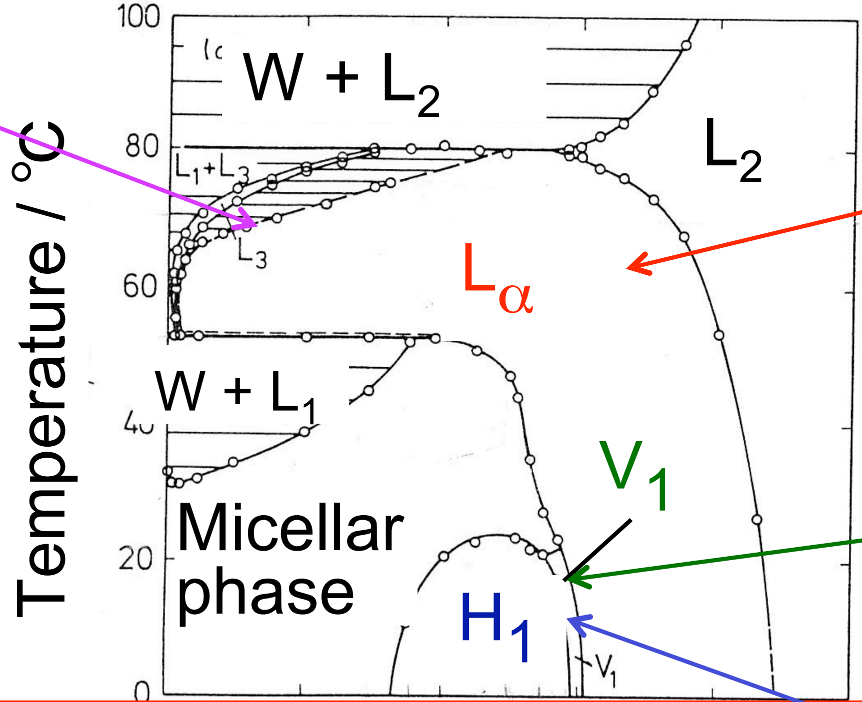
Conditions necessary for onion formation and transition mechanism remain still unclear. .

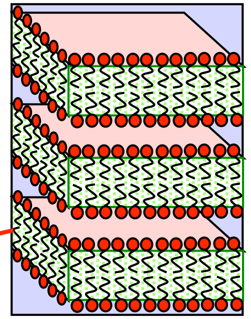
Typical Phase Behaviors of C_nE_m /Water Systems at Rest

C_nE_m : $C_nH_{2n+1}(OC_2H_4)_mOH$

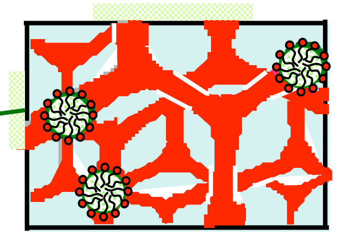


Sponge (L_3) phase

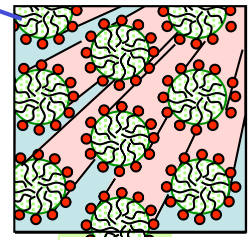




lamellar (L_α) phase



bicontinuous cubic (V_1) phase



hexagonal (H_1) phase

(1) Composed of only surfactant and water

(2) No electrostatic interaction.

(3) A variety of phases can be observed just by changing temperature

→ Useful for studying transition mechanism not only at rest but also under shear

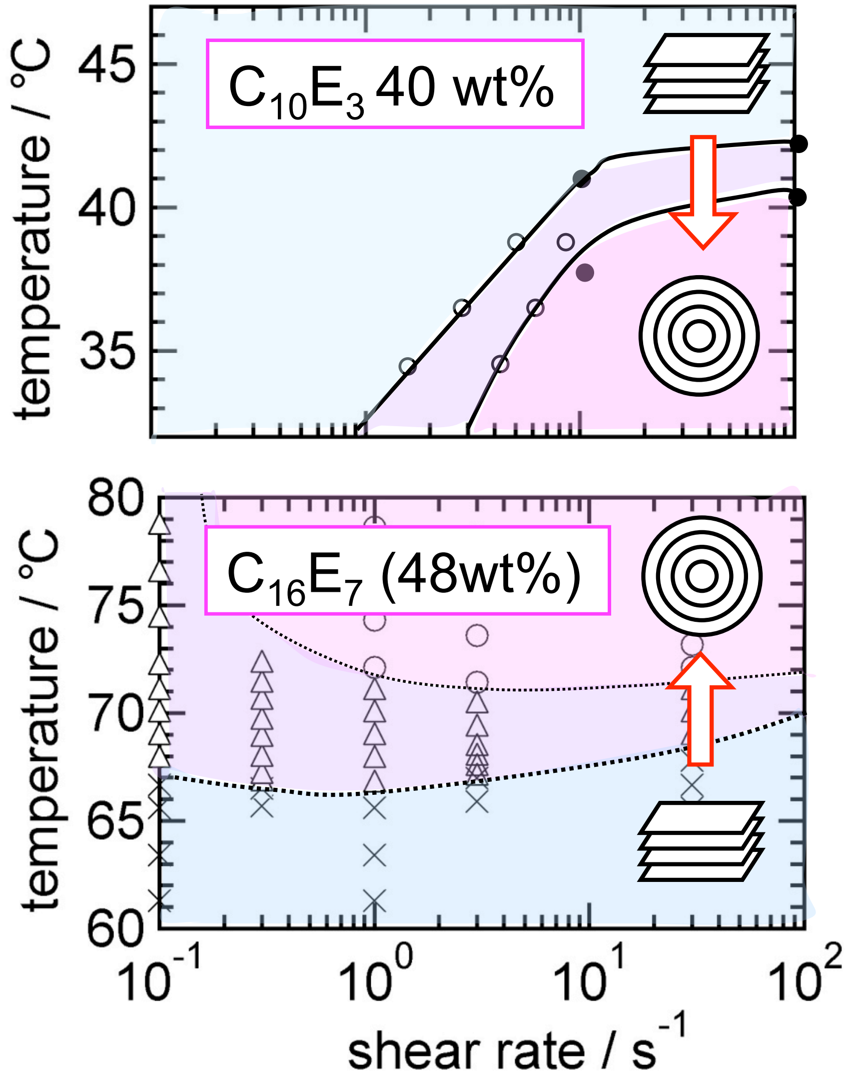
Lamellar-to-Onion Transition under Shear Flow in Nonionic Surfactant (C_nE_m) Systems

$C_{10}E_3$ /water, $C_{12}E_4$ /water

C_nE_m : $C_nH_{2n+1}(OC_2H_4)_mOH$

- T. D. Le et al., *Langmuir* **17**, 999 (2001), *Phys. Chem. Chem. Phys.* **3**, 1310 (2001).
- C. Oliviero et al., *Col. Surf. A* **228**, 85 (2003).

Lamellar-to-onion transition with decreasing temperature



$C_{16}E_7$ /water

- Y. Kosaka et al., *Langmuir,* **26**, 3835 (2010).

Lamellar-to-onion transition with Increasing temperature

Outline of the Present Talk

1. Lamellar-to-onion Transition with increasing temperature at a constant shear rate in $C_{16}E_7$/water System

   (1) Results of simultaneous measurements of

   - Shear stress / small-angle light scattering (Rheo-SALS)
   - Shear stress / small-angle X-ray scattering (Rheo-SAXS)

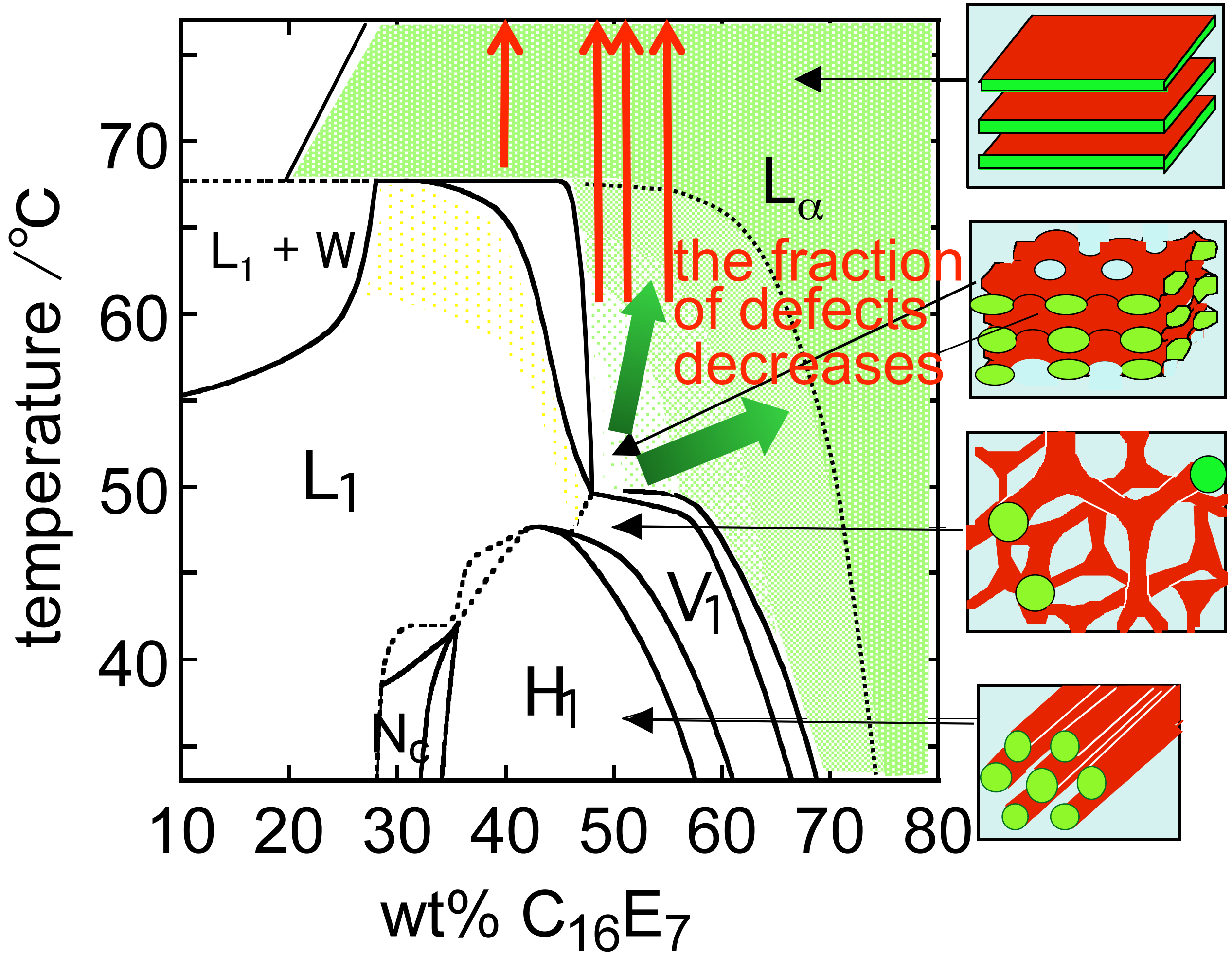
   (2) Conditions necessary for the onion formation

   - Temperature-shear rate diagram
   - Temperature-concentration diagram

   (3) Transition mechanism based on rheo-SAXS experiments

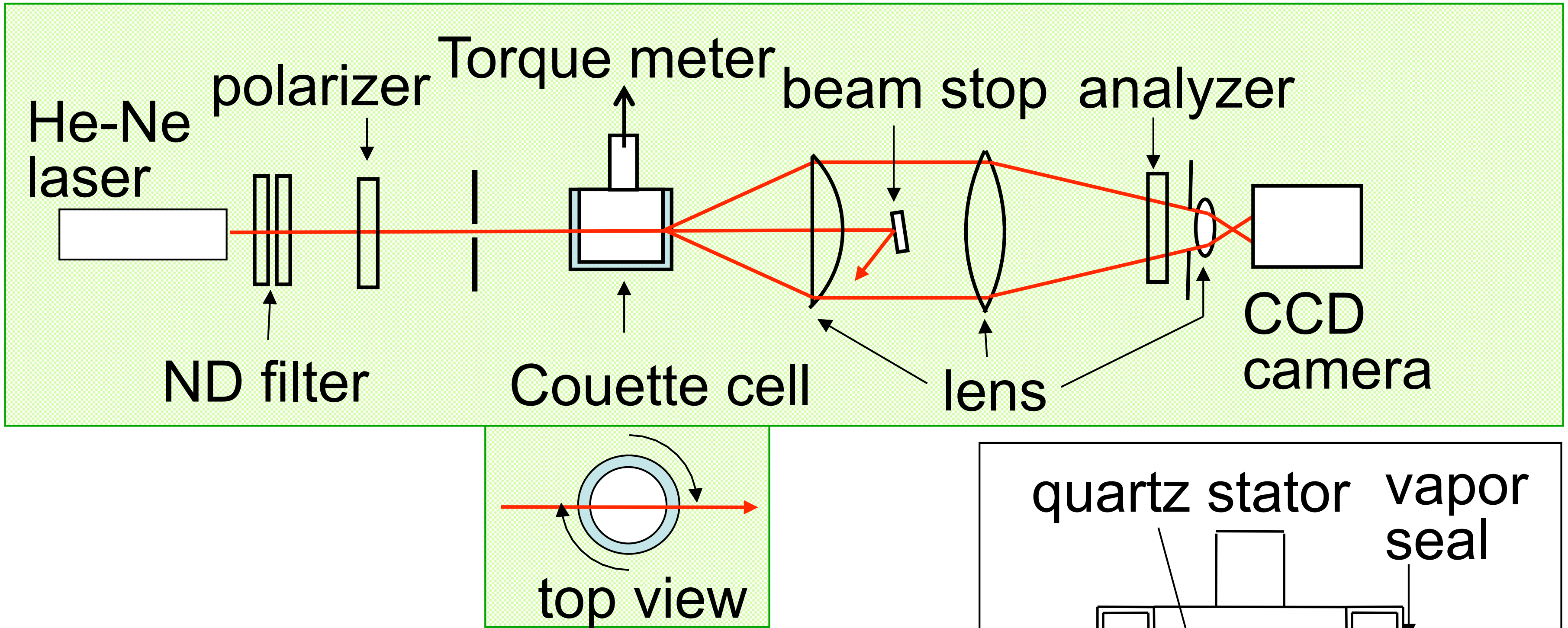
2. Reentrant lamellar-onion transition with varying temperature at a constant shear rate in $C_{14}E_5$/water System

Phase Diagram of $C_{16}E_7$ / D_2O System at Rest[1)]



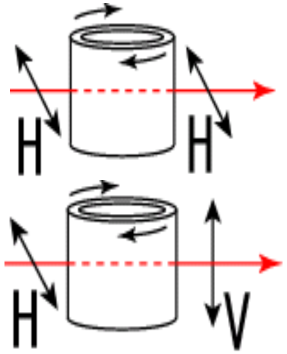
1) K. Minewaki, T. Kato, H. Yoshida, and M. Imai, *Langmuir* **17**, 1864 (2001).

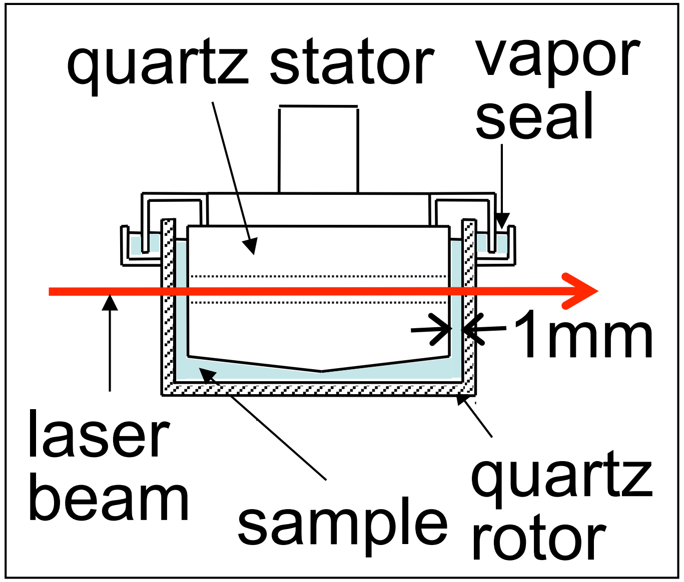
Apparatus for Rheo-SALS[1)]



Polarized scattering H_h

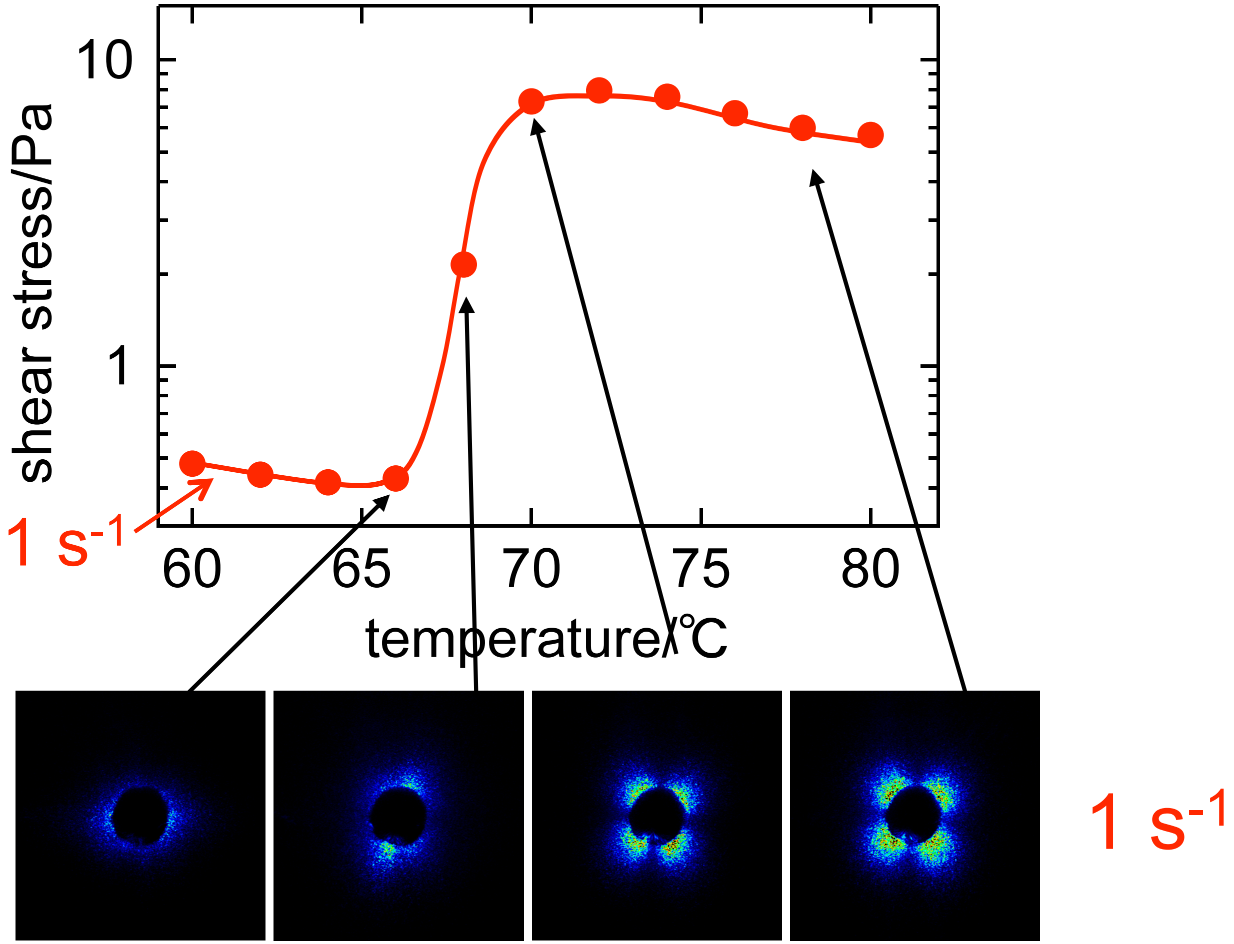
Depolarized scattering V_h



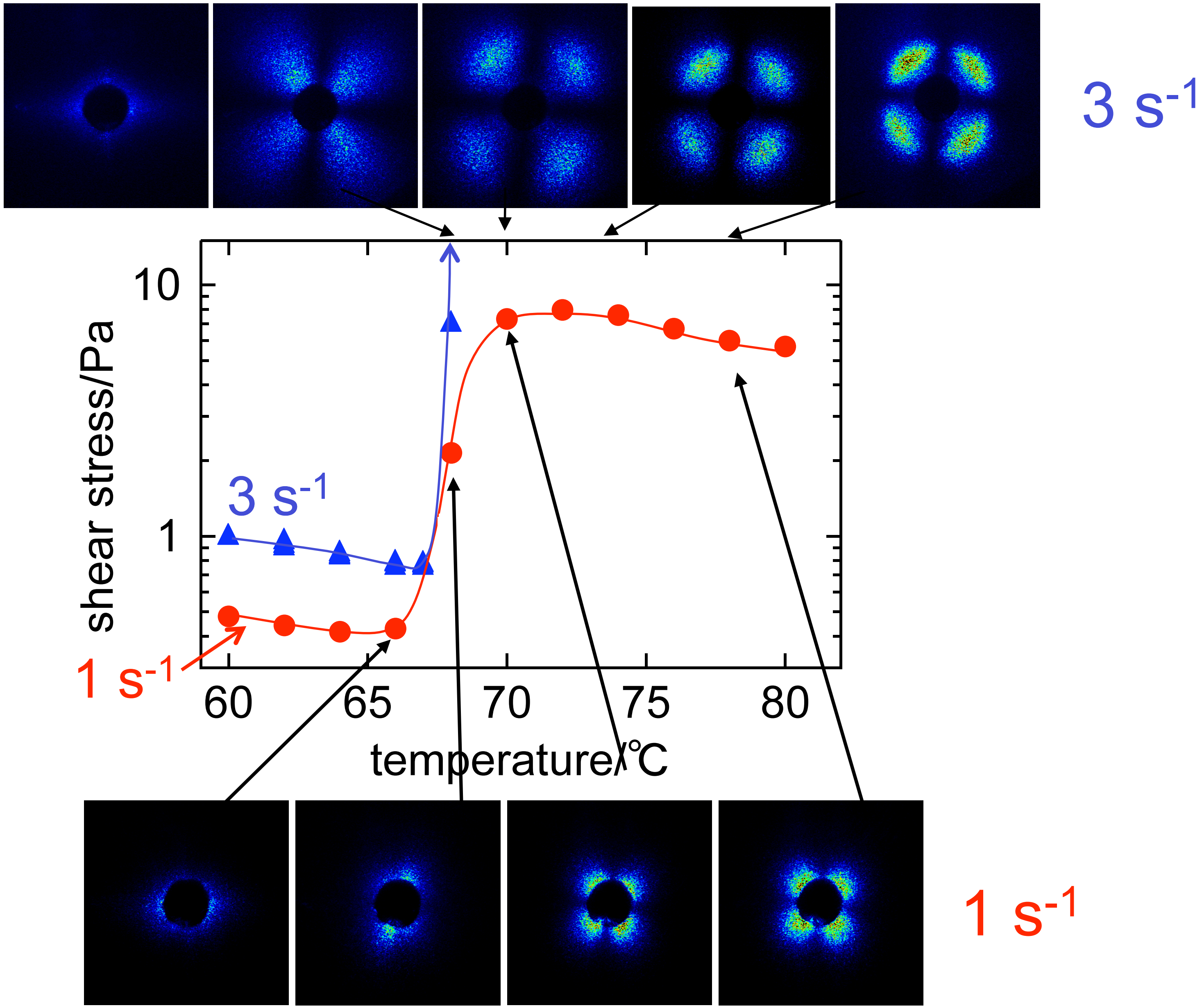


1) T. Kato et al., *Prog. Colloid Polym. Sci.*, **129**, 9-15 (2004), *J. Phys. Condens. Matter* **17**, S2923 (2005).

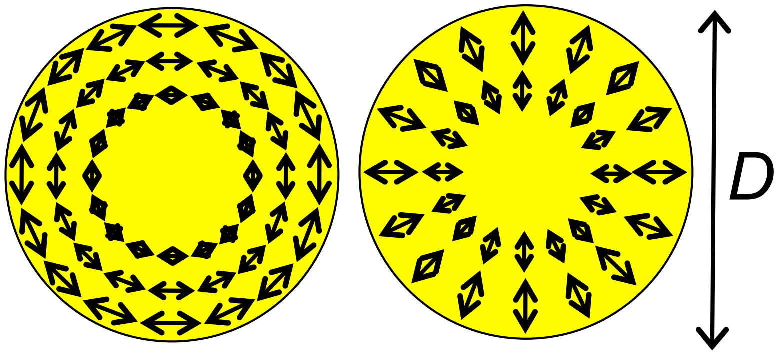
Temperature Dependences of Shear Stress and Depolarized SALS Patterns (48 wt%)



Temperature Dependences of Shear Stress and Depolarized SALS Patterns (48 wt%)

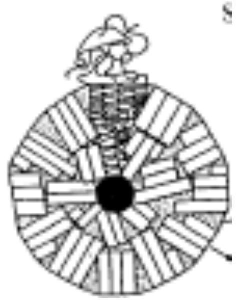


Depolarized SALS from optically anisotropic spheres

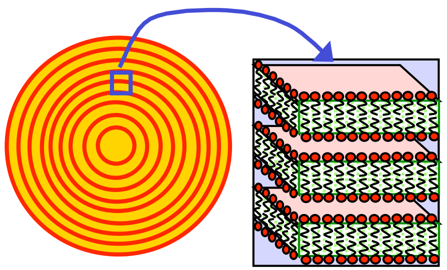


↔: direction of polarization

R.J.Samuels, *J.Polymer Sci.*, **9**, 2165 (1971)



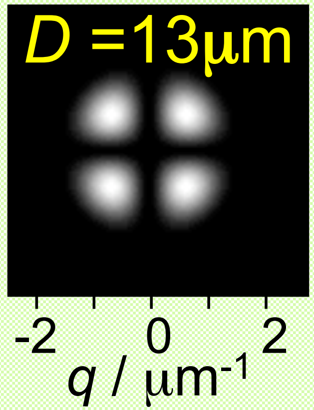
polymer spherulites

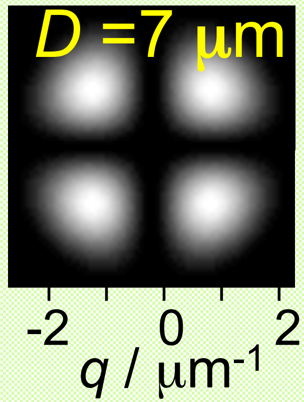


multilamellar vesicles (onions)

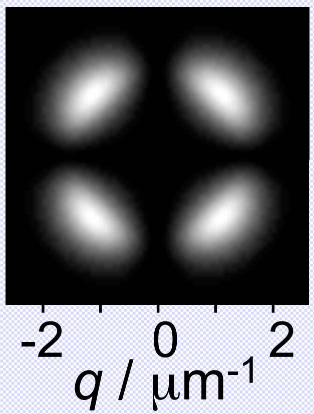
Calculated patterns

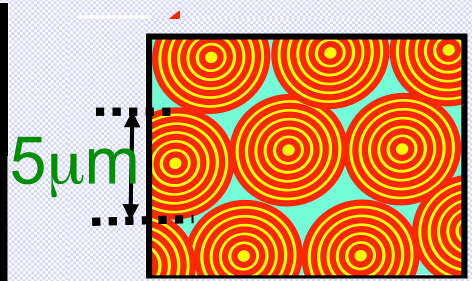
Isolated onions



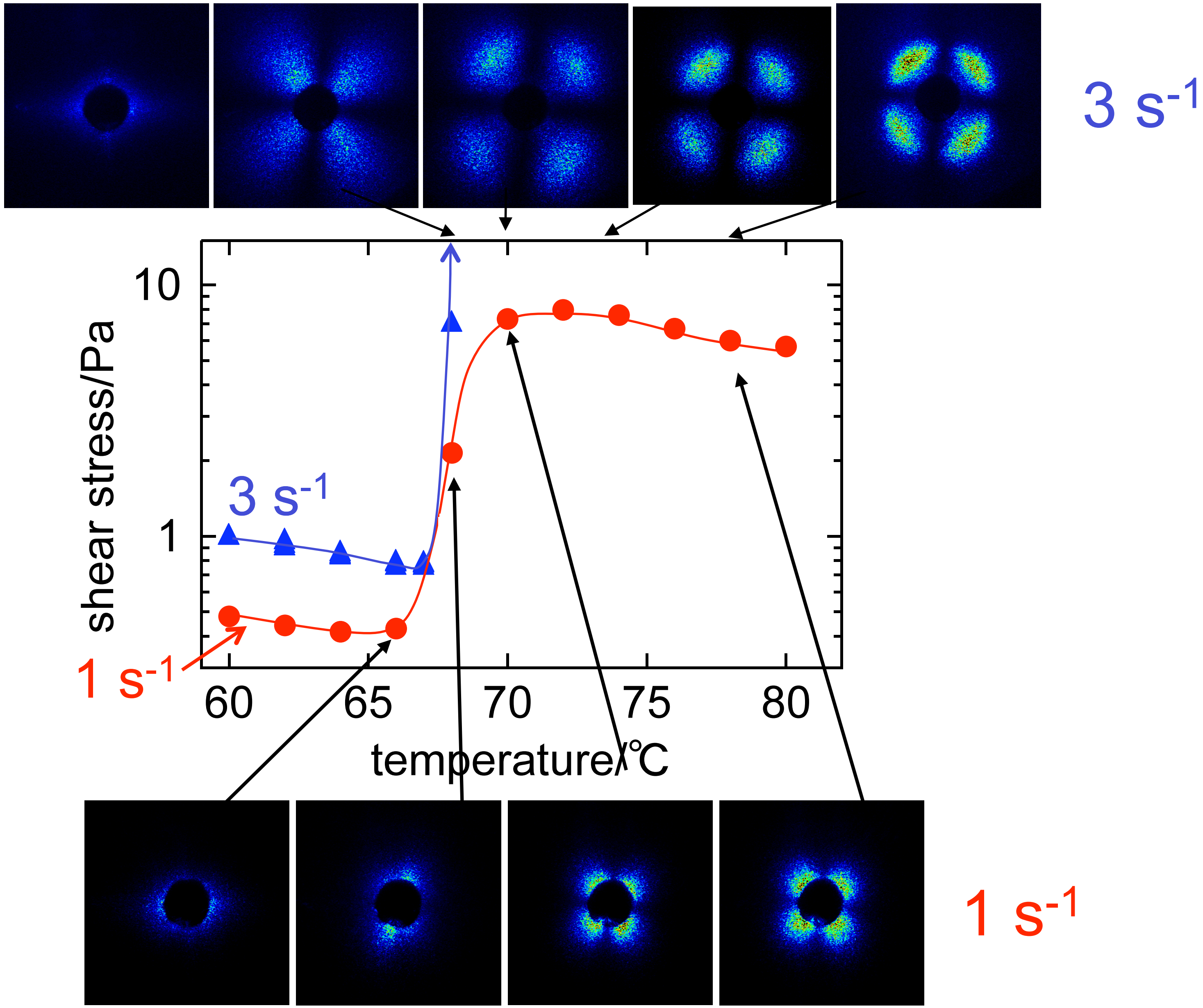


Randomly close-packed onions

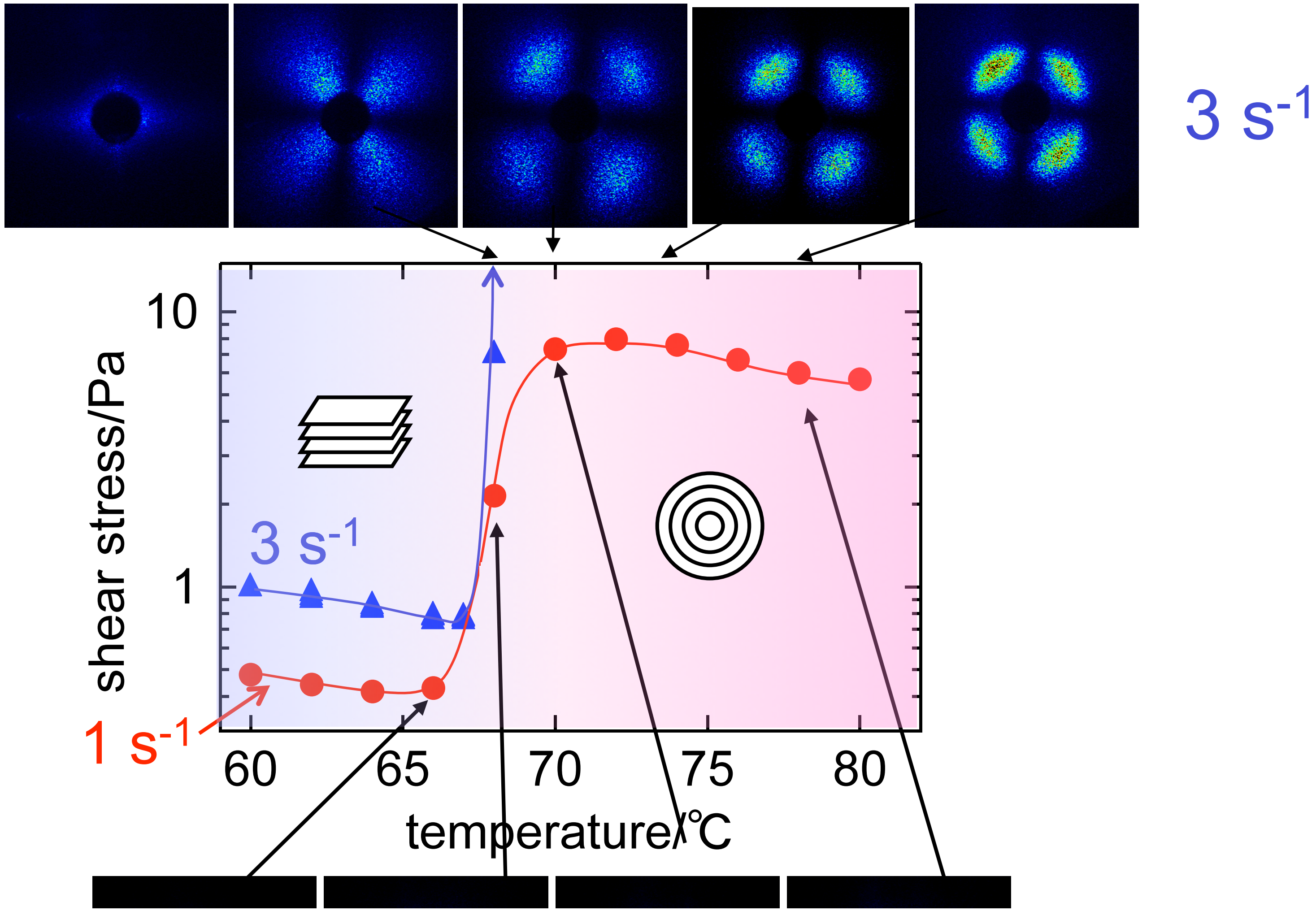




Temperature Dependences of Shear Stress and Depolarized SALS Patterns (48 wt%)

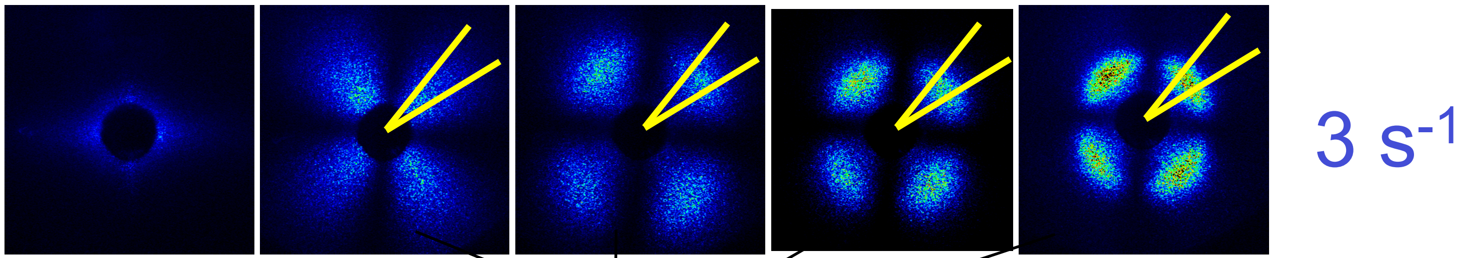


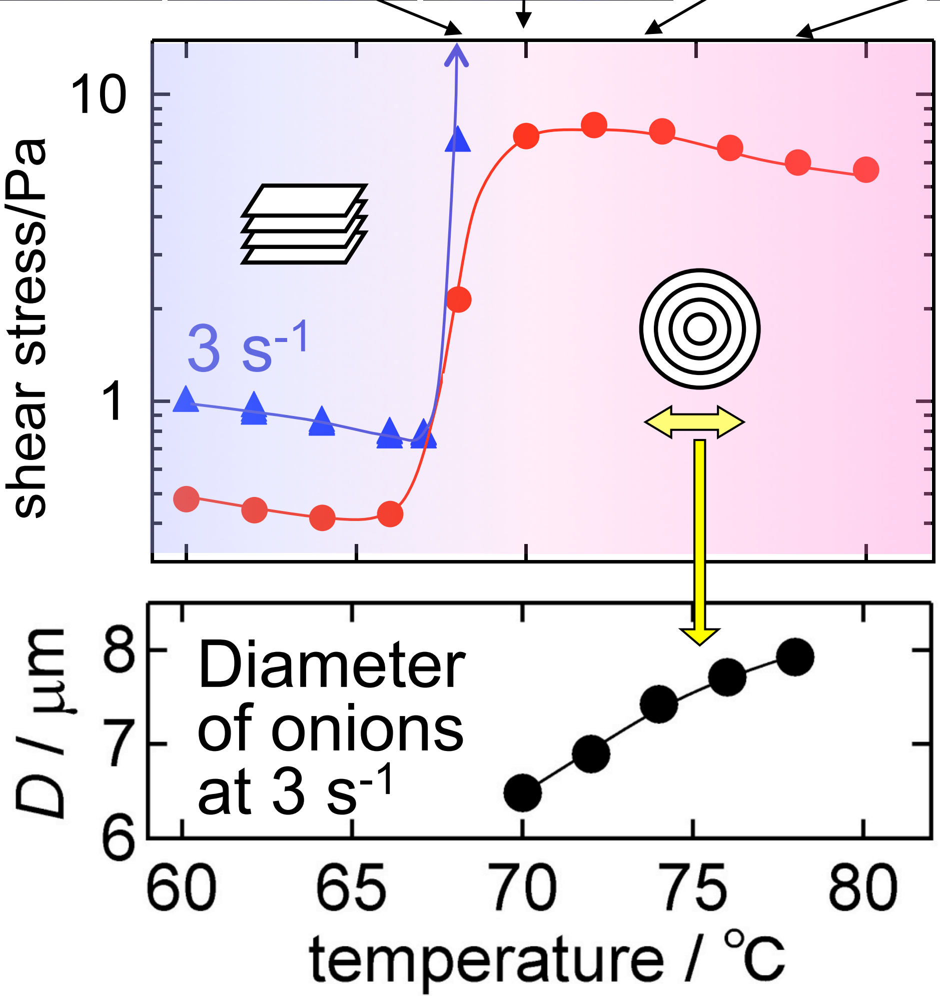
Temperature Dependences of Shear Stress and Depolarized SALS Patterns (48 wt%)

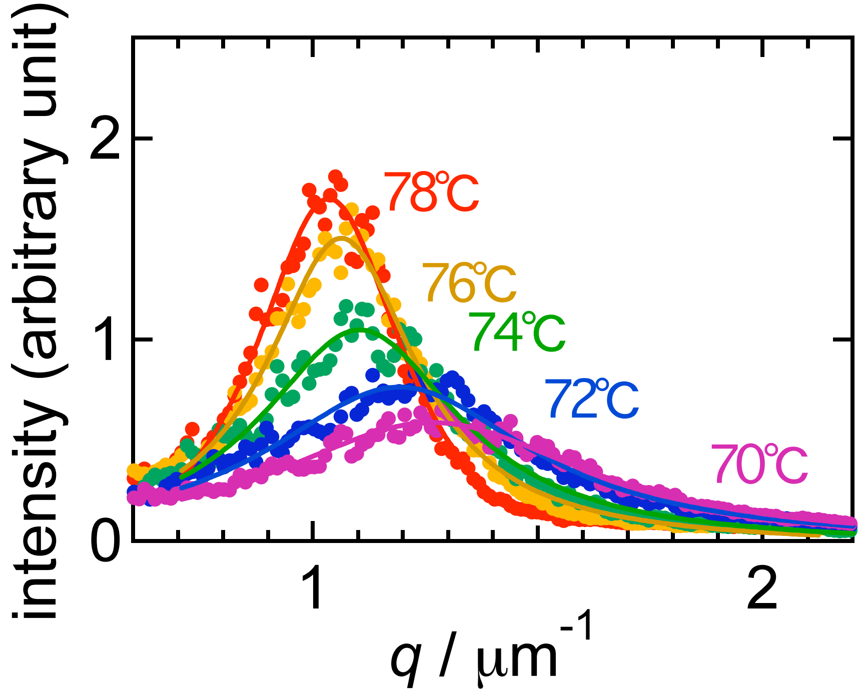


It is well known that the transition to the onion accompanies significant increase in shear stress. But in this case such an increment is observed when the temperature is increased !

Temperature Dependences of Shear Stress and Depolarized SALS Patterns (48 wt%)

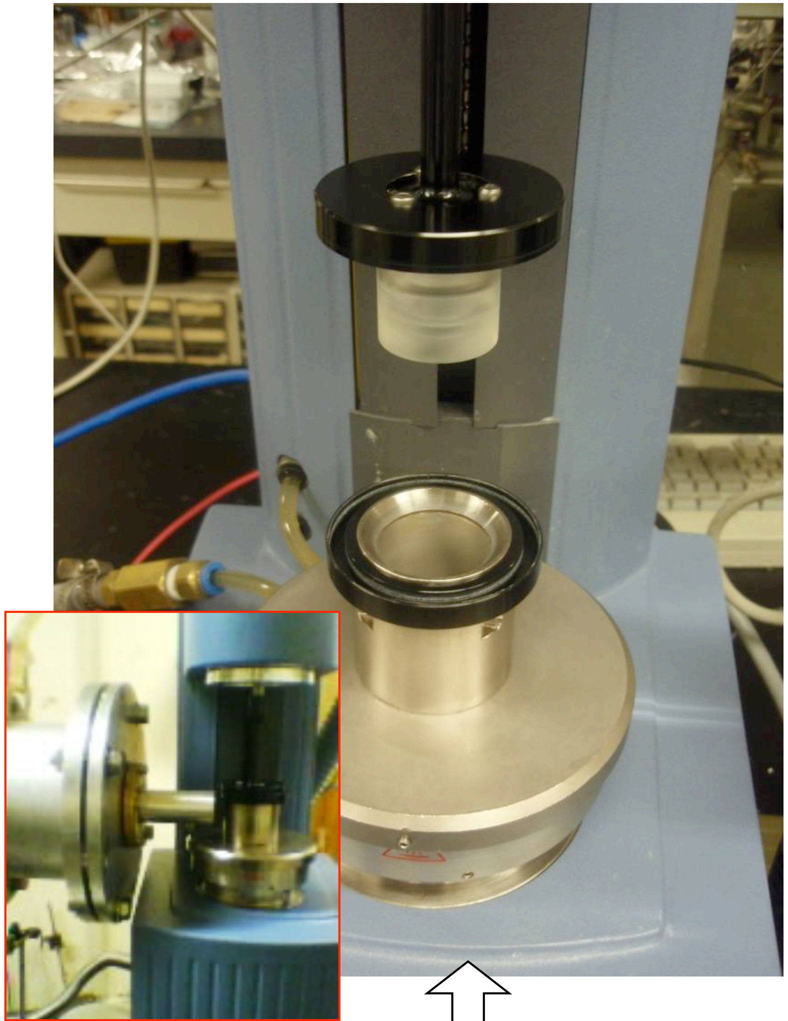




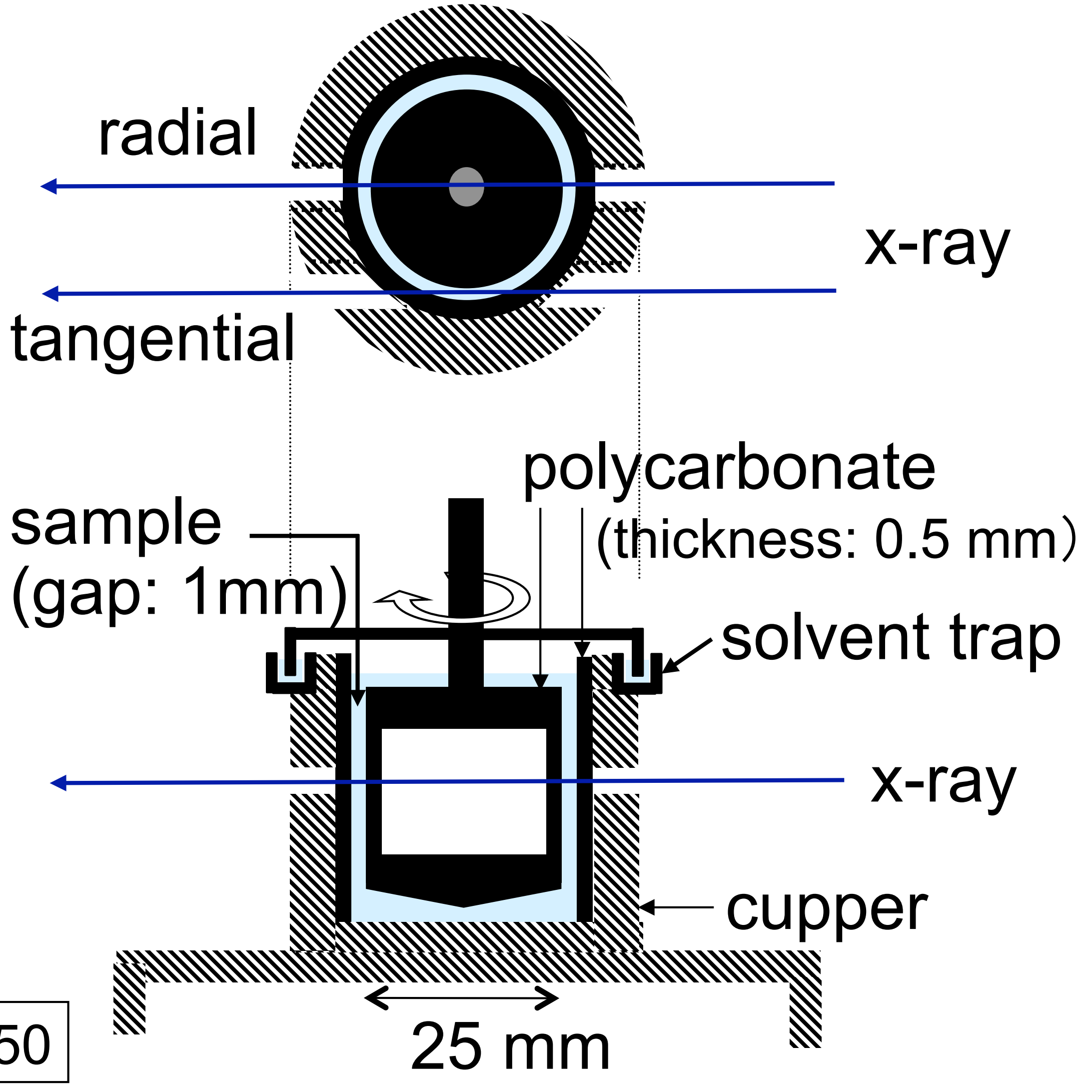


The onion size increases and size distribution becomes narrow with T

Apparatus for Rheo-SAXS[1)]

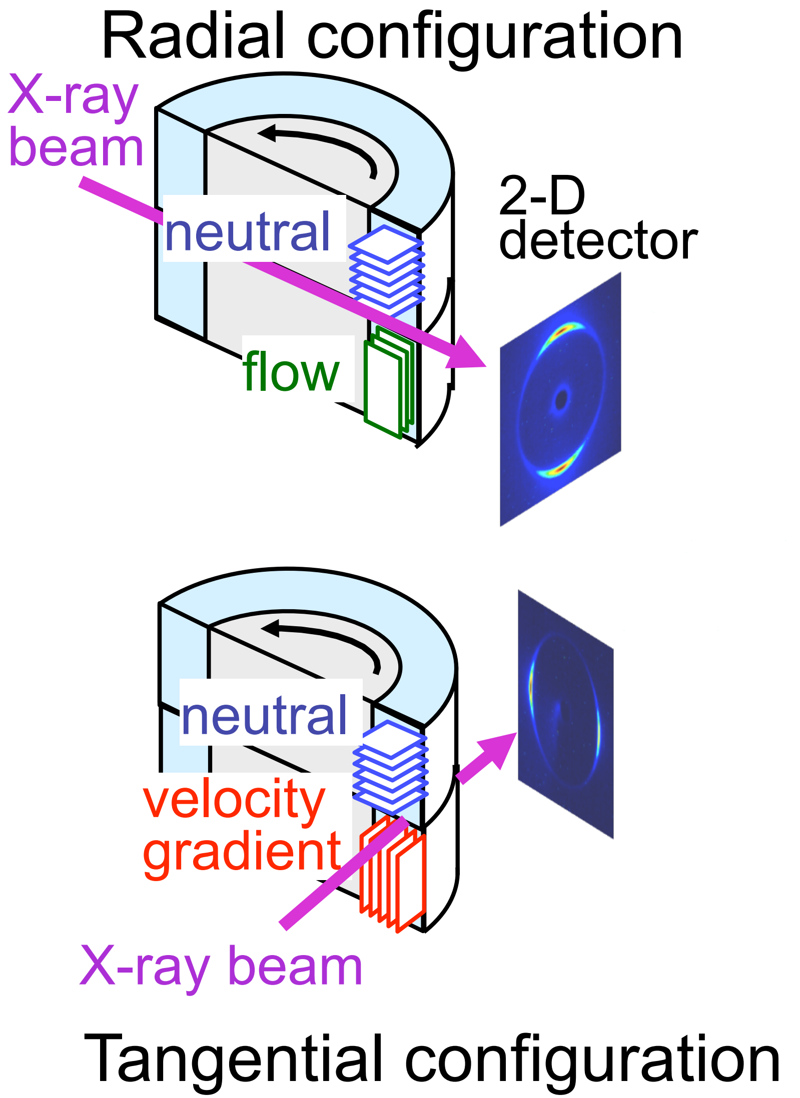


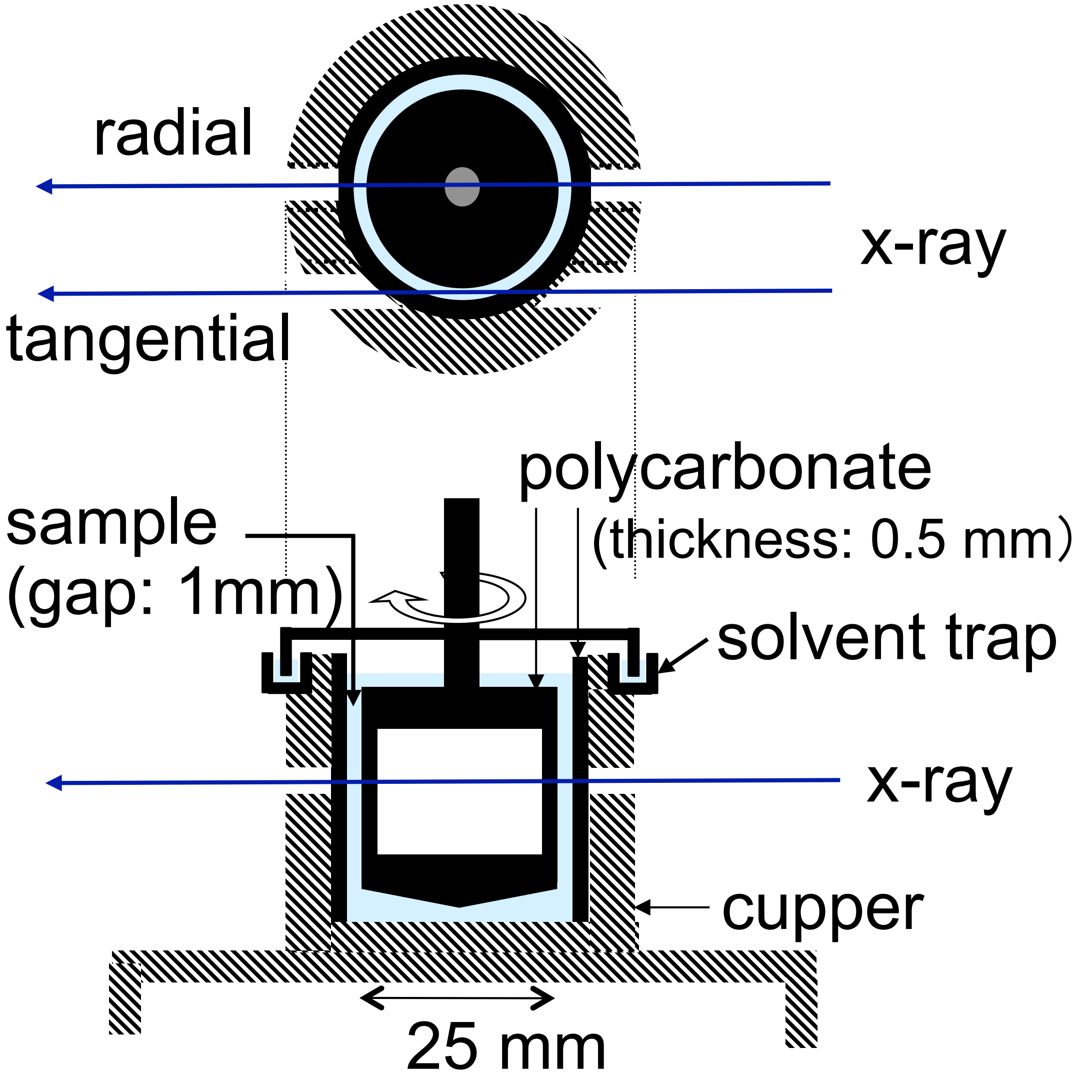
Rheometer: TA Instruments AR550



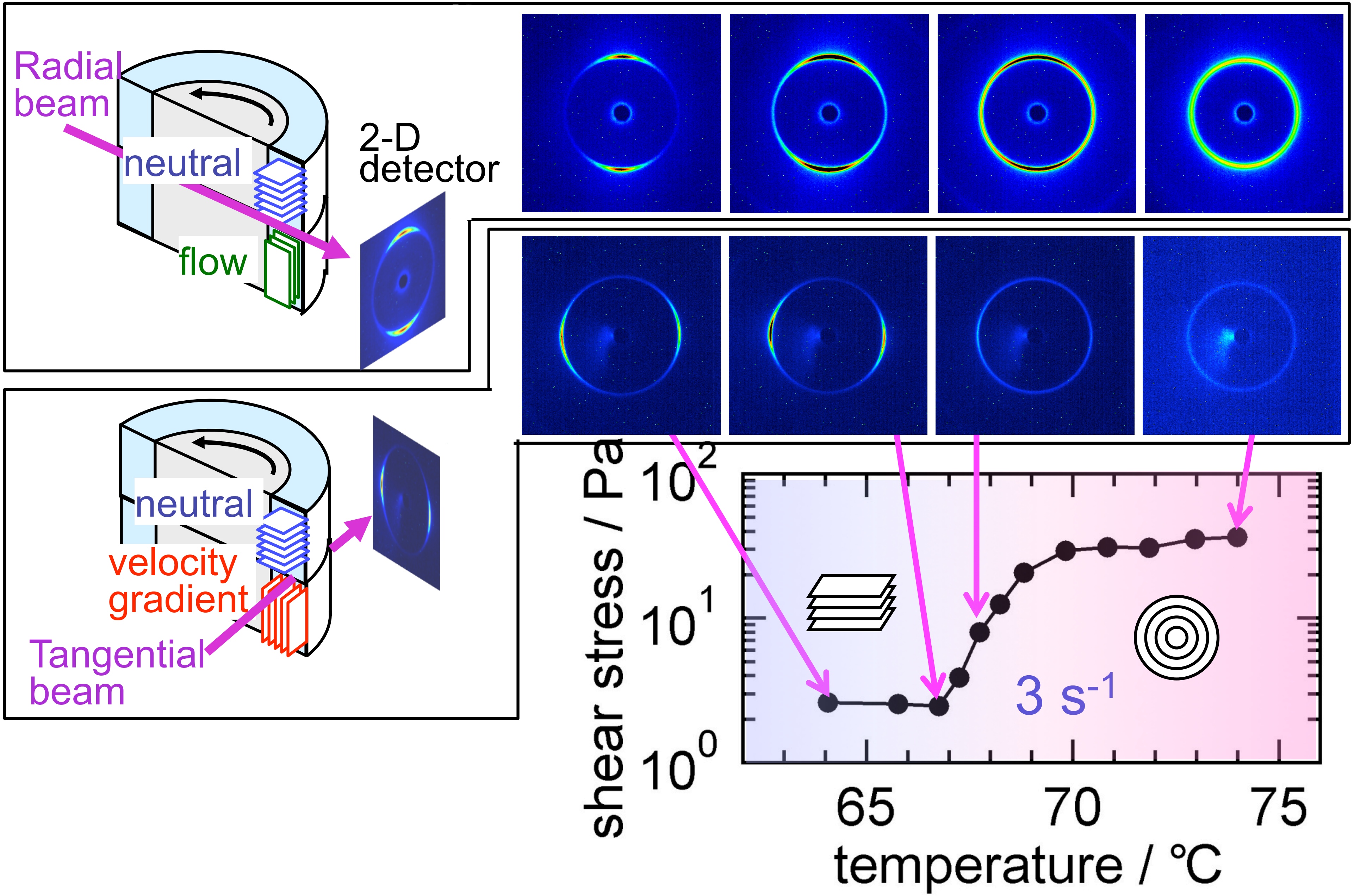
1) T. Kato et al. *Photon Factory Activity Report 2005* #23 Part B (2006).
Y. Kosaka, M. Ito, Y. Kawabata, and T. Kato, *Langmuir,* **26**, 3835 (2010).

Apparatus for Rheo-SAXS





Temperature Dependences of Shear Stress and 2-D SAXS Patterns at 3 s^{-1} (48wt%)



Outline of the Present Talk

1. Lamellar-to-onion Transition with increasing temperature at a constant shear rate in $C_{16}E_7$/water System

   (1) Results of simultaneous measurements of

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   - Shear stress / small-angle X-ray scattering (Rheo-SAXS)

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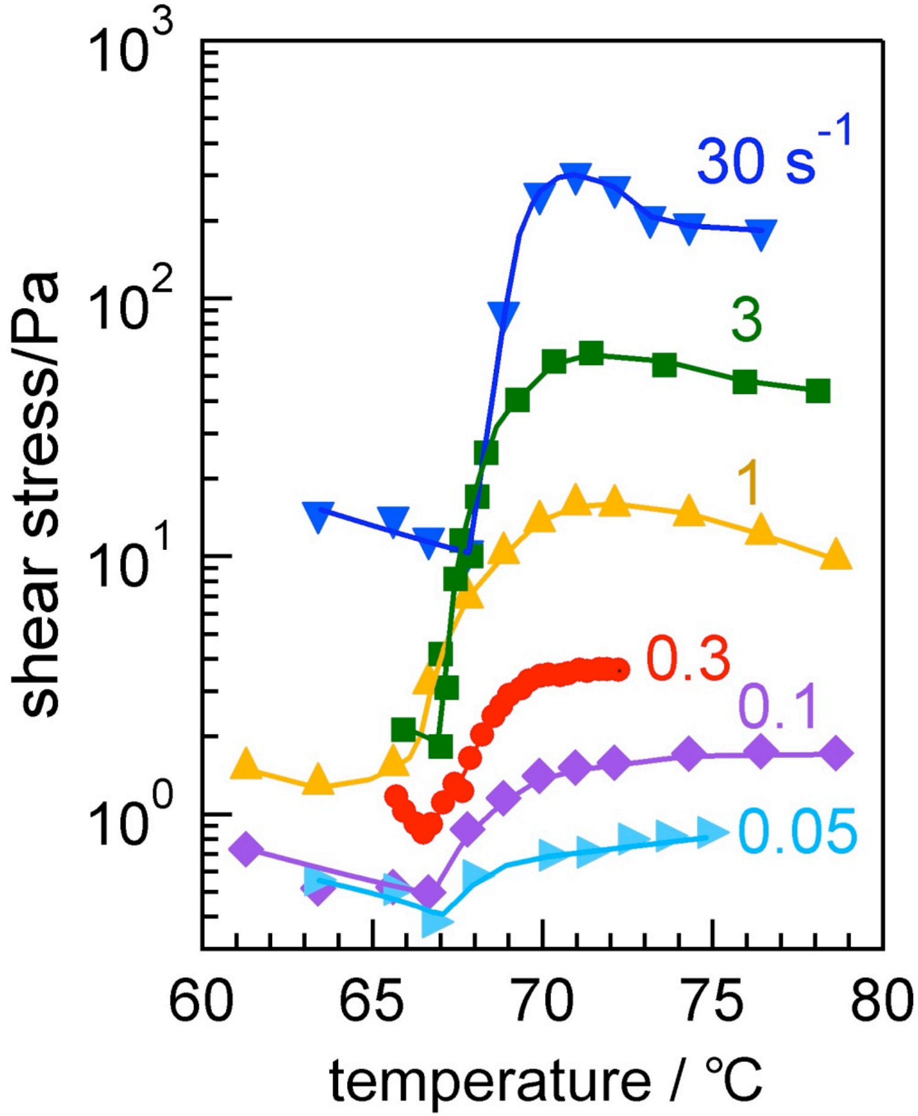
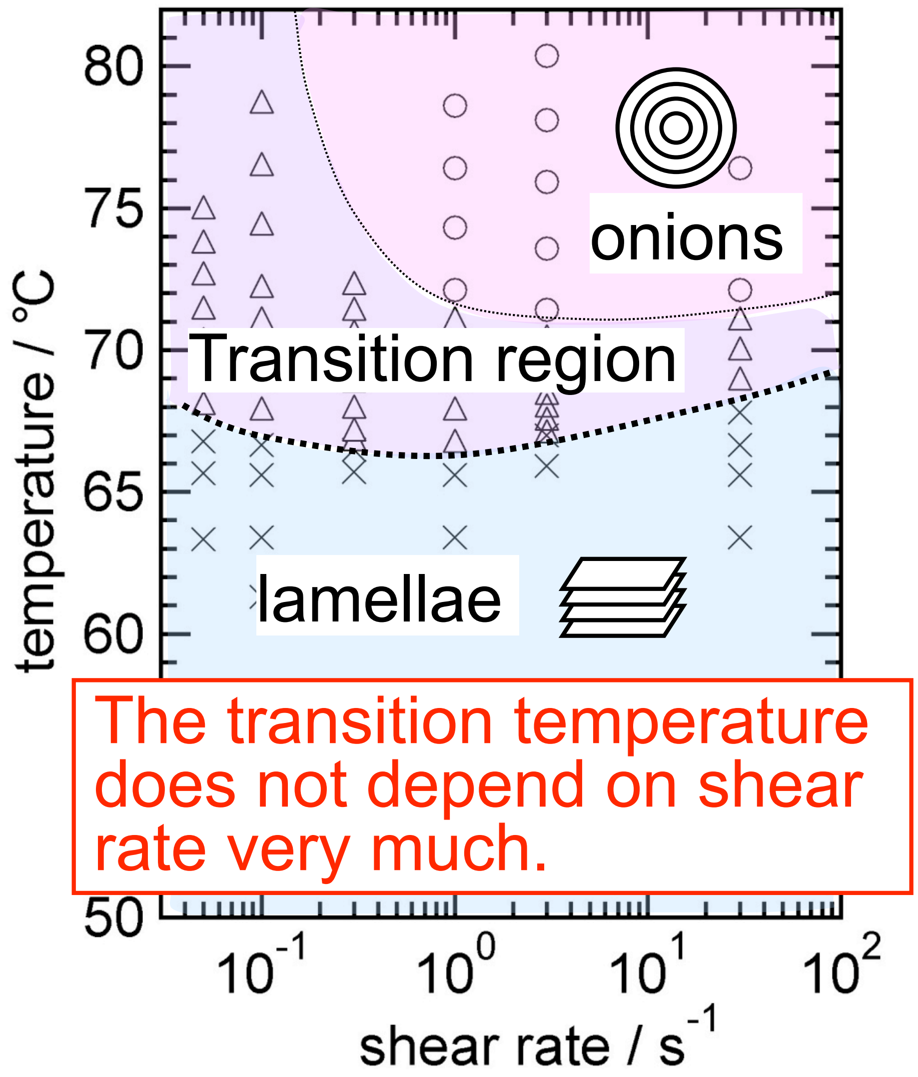
Temperature Dependences of Shear Stress (48wt%)

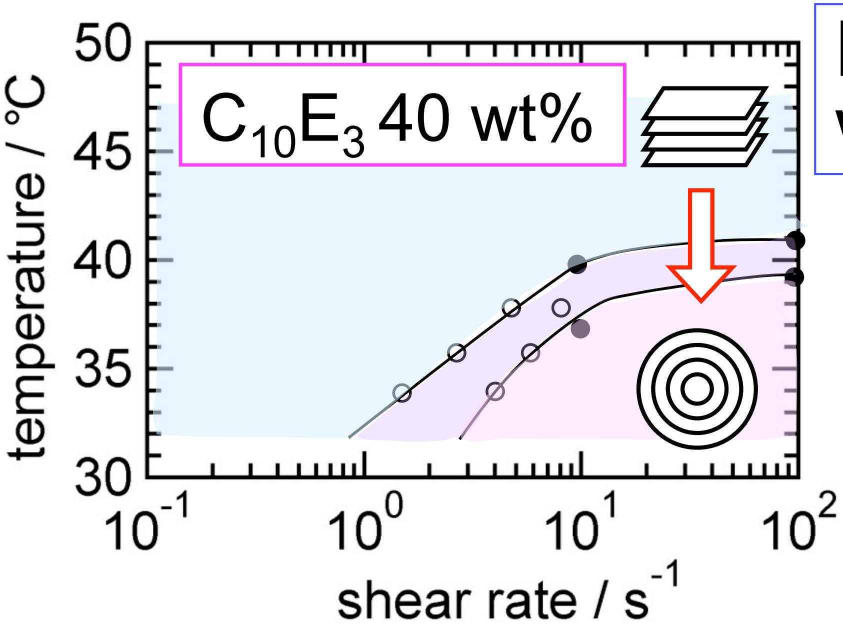


Temperature - Shear Rate Diagram (48wt%)



The transition temperature does not depend on shear rate very much.

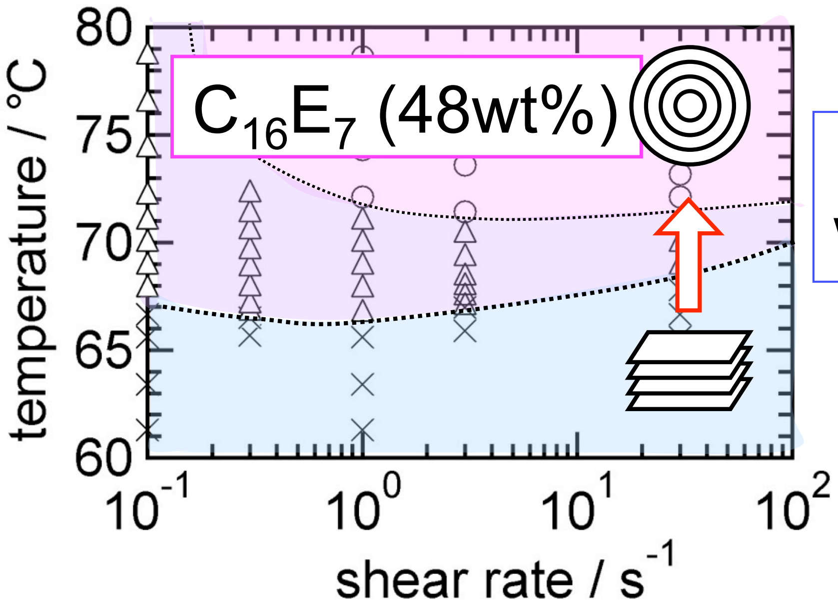
Comparison with Other Homologous Systems



Lamellar-to-onion transition with decreasing temperature

T. D. Le et al., *Langmuir* **17**, 999 (2001), C. Oliviero et al., *Col. Surf. A* **228**, 85 (2003).

Temperature dependence of elastic properties of isolated membranes



Lamellar-to-onion transition with increasing temperature

Y. Kosaka et al., *Langmuir,* **26**, 3835 (2010).

Elastic Properties of Isolated Membranes

Elastic free energy of bilayer relative to a flat state (L_α)

$$\frac{F - F(L_\alpha)}{A} = 2\kappa\langle H^2\rangle + \bar{\kappa}\langle G\rangle \qquad H \equiv \frac{1}{2}\left(\frac{1}{R_1} + \frac{1}{R_2}\right) \qquad G \equiv \frac{1}{R_1}\frac{1}{R_2}$$

κ : bending modulus of a bilayer

$\bar{\kappa}$: saddle splay modulus of a bilayer

L_3 phase

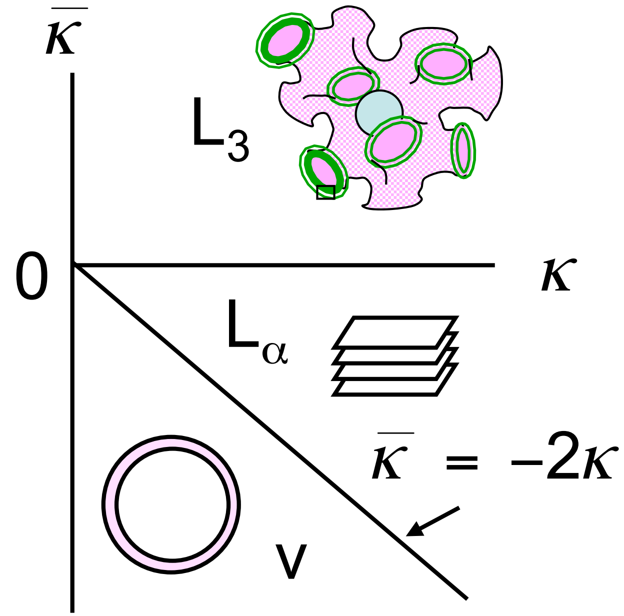
$$\frac{F(L_3) - F(L_\alpha)}{A} = \bar{\kappa}\langle G\rangle \qquad \langle G\rangle < 0$$

$$\bar{\kappa} > 0 \quad \rightarrow \quad F(L_3) < F(L_\alpha)$$

A vesicle of radius R

$$\frac{F(V) - F(L_\alpha)}{A} = (2\kappa + \bar{\kappa})\frac{1}{R^2}$$

$$2\kappa + \bar{\kappa} < 0 \quad (\bar{\kappa} < -2\kappa < 0) \quad \rightarrow \quad F(V) < F(L_\alpha)$$



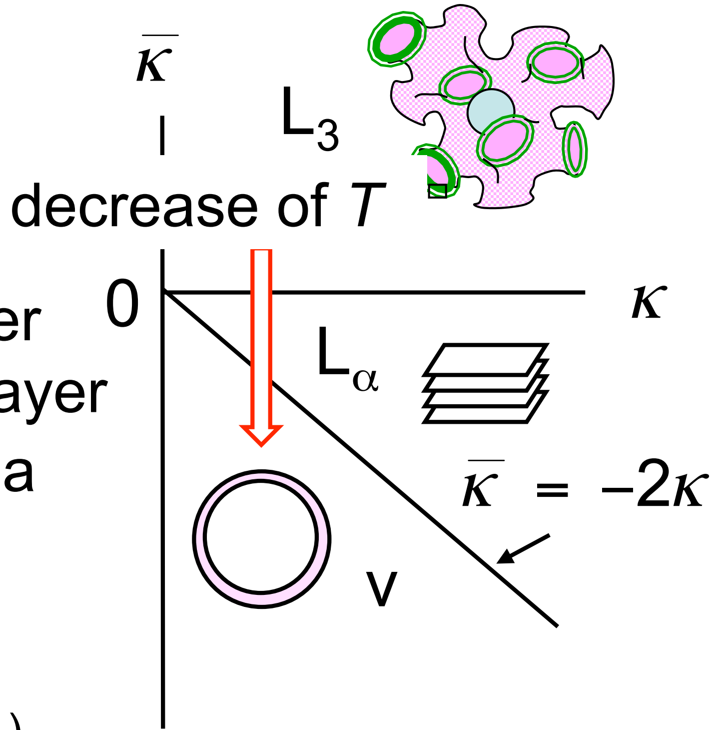
W. Helfrich, *J. Phys. Condens. Matter* **6**, A79 (1994).

Elastic Properties of Isolated Membranes

Saddle splay modulus of a bilayer

$$\bar{\kappa} = 2\bar{\kappa}_m - 4H_{0m}\delta_{hc}\kappa_m$$

$\bar{\kappa}_m$: saddle splay modulus of a monolayer
H_{0m} : spontaneous curvature of a monolayer
δ_{hc}: thickness of a hydrophobic part of a monolayer



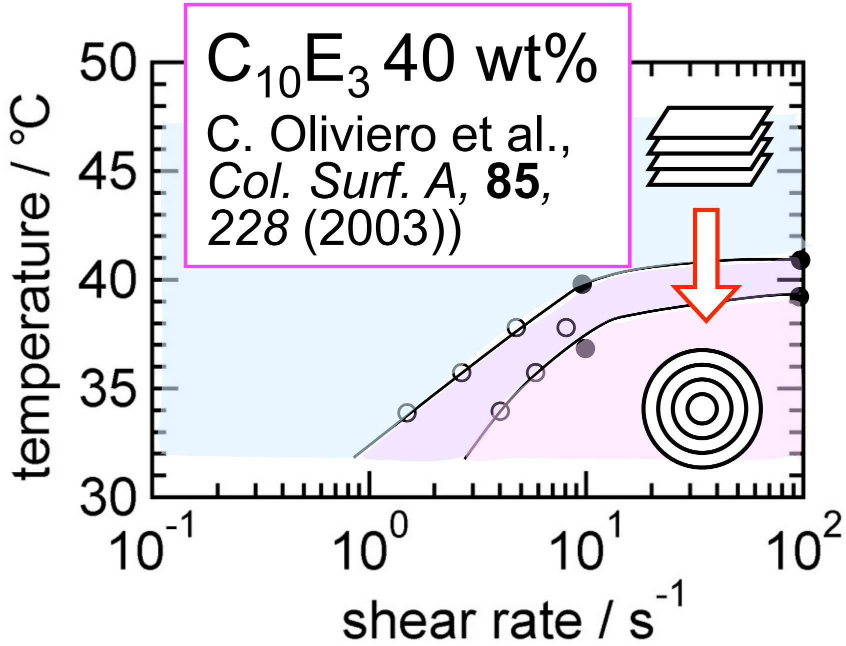
Nonionic surfactants of the C_nE_m type

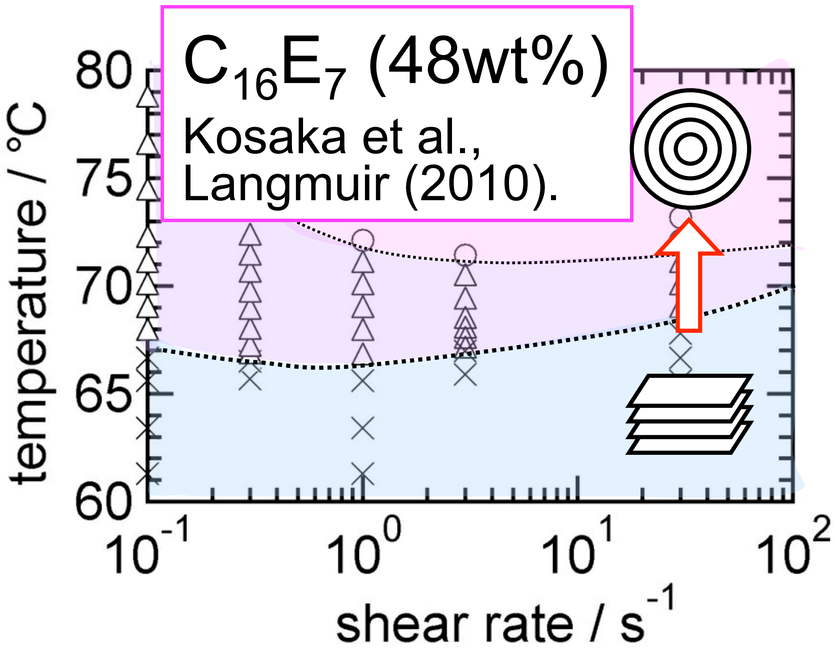
→ H_{0m} increases with decreasing T [1)]

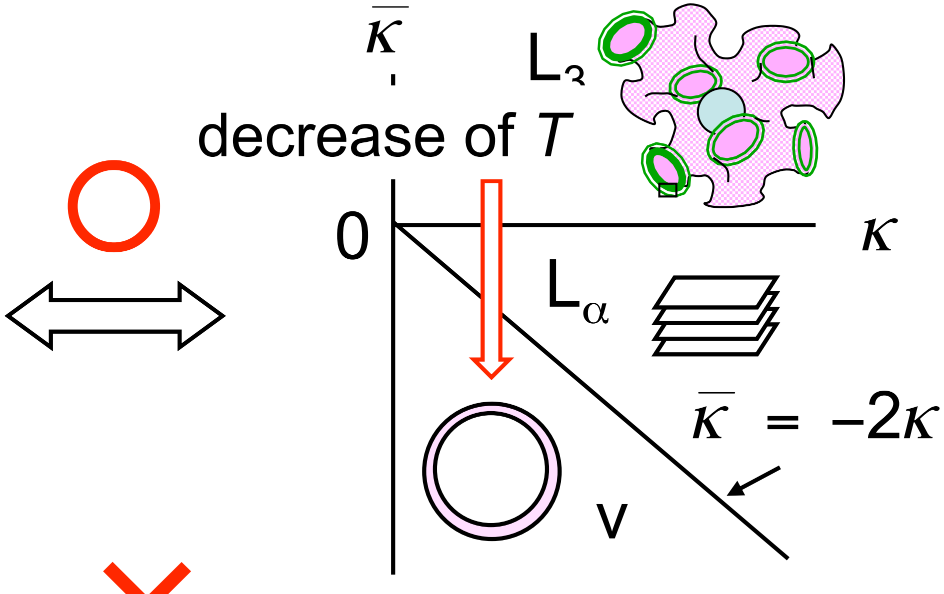
→ $\bar{\kappa}$ decreases with decreasing T [2)]
→ Vesicles become more stable than lamellae in the lower temperature range [2)]

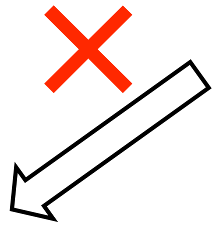
1) R. Strey, *Colloid Polym. Sci*. **272**, 1005 (1994).
2) T. D. Le et al. *Langmuir* **17**, 999 (2001).

Comparison with Other Homologous Systems









κ : bending modulus of a bilayer

$\bar{\kappa}$: saddle splay modulus of a bilayer

Our results cannot be explained by properties of isolated membranes

The transition should be dominated by other factors

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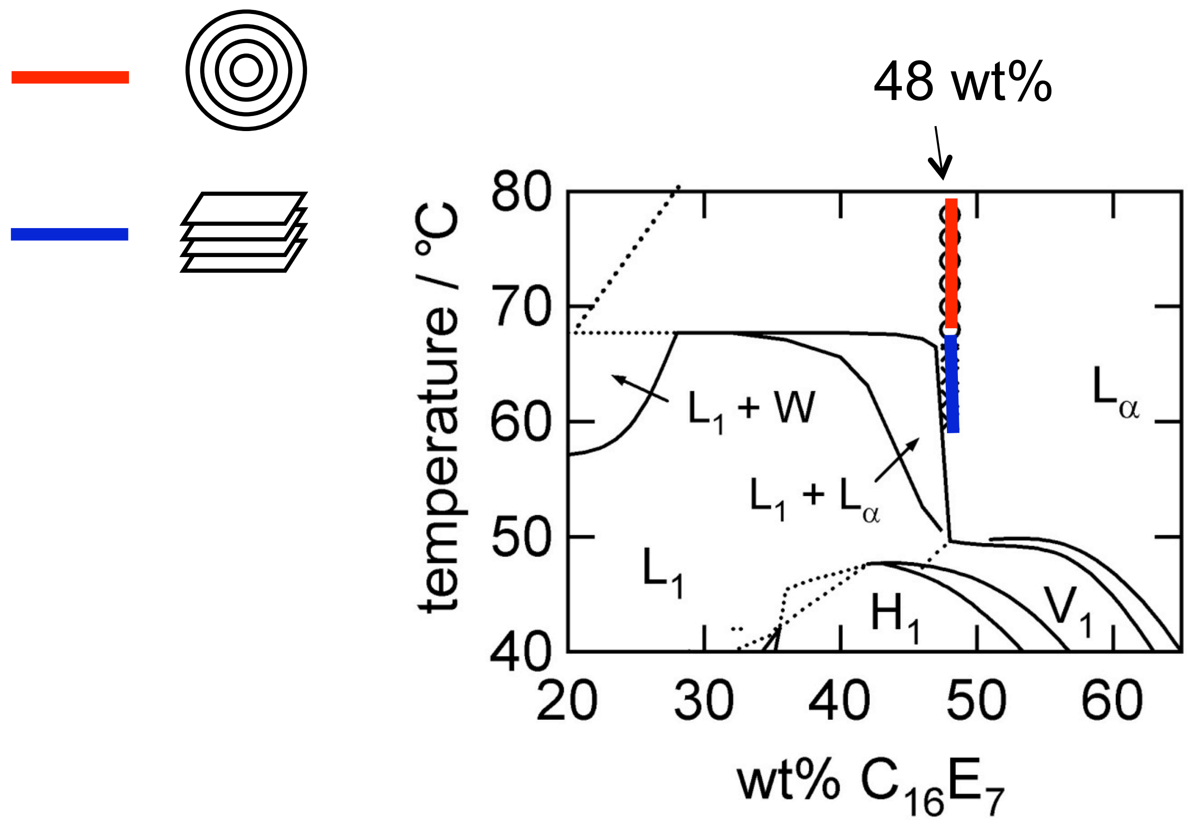
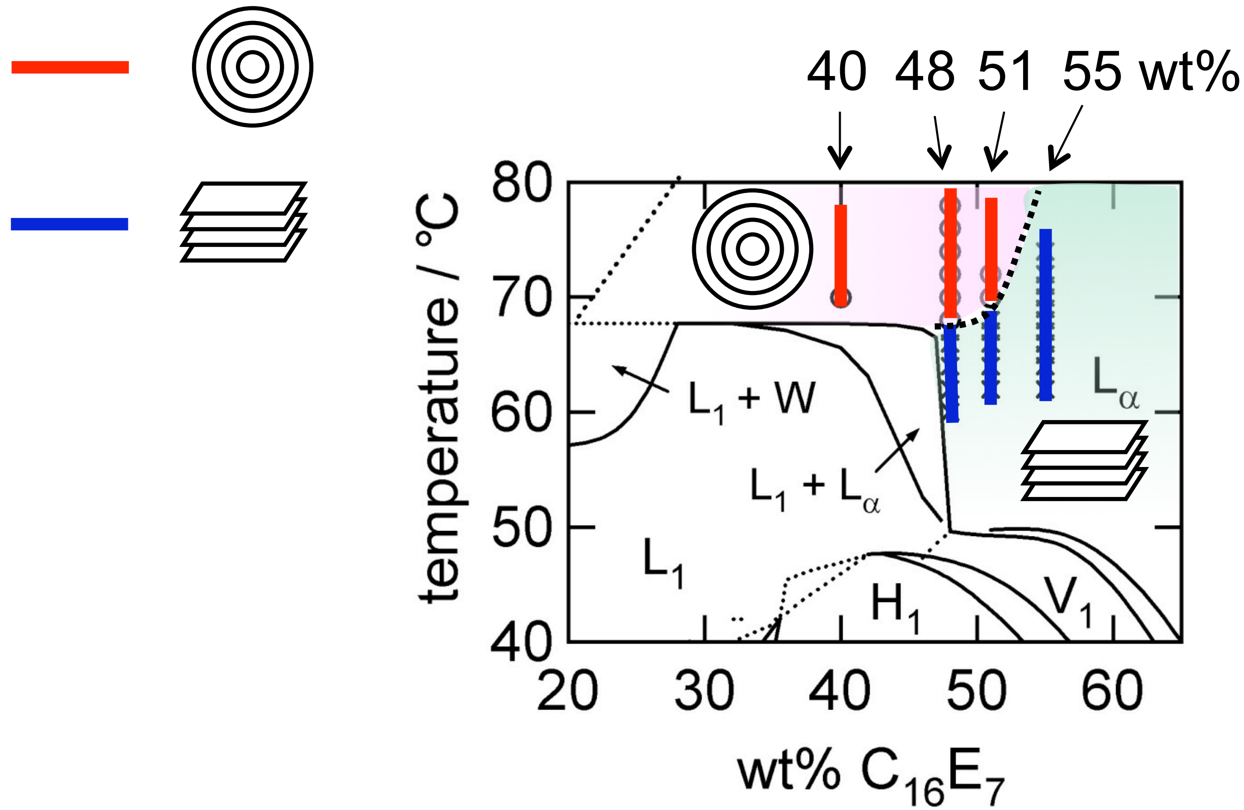
2. Reentrant lamellar-onion transition with varying temperature at a constant shear rate in $C_{14}E_5$/water System

Phase Behaviors of $C_{16}E_7$ / D_2O System at Rest[1] and the Lamellar-to-Onion Transition Temperature at 3 s^{-1}



1) K. Minewaki, T. Kato, H. Yoshida, and M. Imai, *Langmuir* **17**, 1864 (2001).

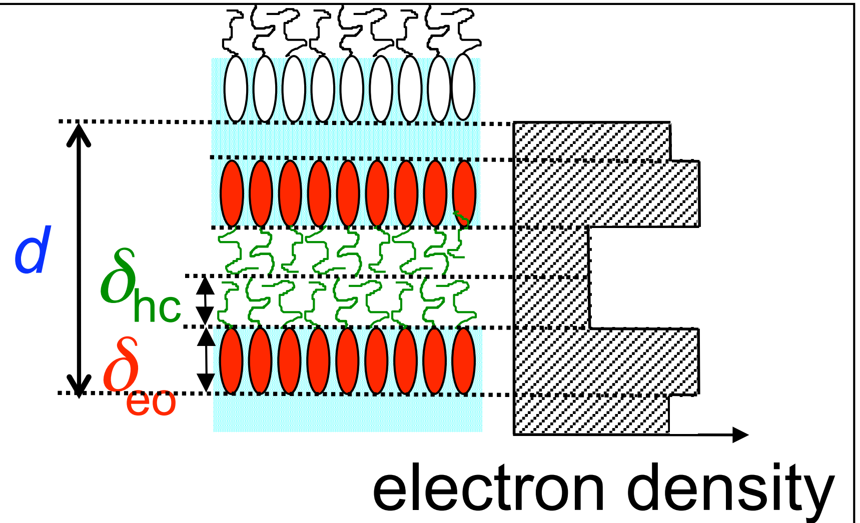
Phase Behaviors of $C_{16}E_7$ / D_2O System at Rest[1)] and the Lamellar-to-Onion Transition Temperature at 3 s^{-1}

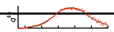


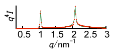
The transition temperature increases with increasing surfactant concentration

1) K. Minewaki, T. Kato, H. Yoshida, and M. Imai, *Langmuir* **17**, 1864 (2001).

SAXS Study on the Lamellar Phase of $C_{16}E_7$ System at Rest[1)]







$$I(q) = \frac{2\pi}{d}\frac{P(q)S(q)}{q^2}$$

$P(q)$: form factor of bilayers*

$\Leftrightarrow \delta_{hc}, \delta_{eo}$

$S(q)$: structure factor*

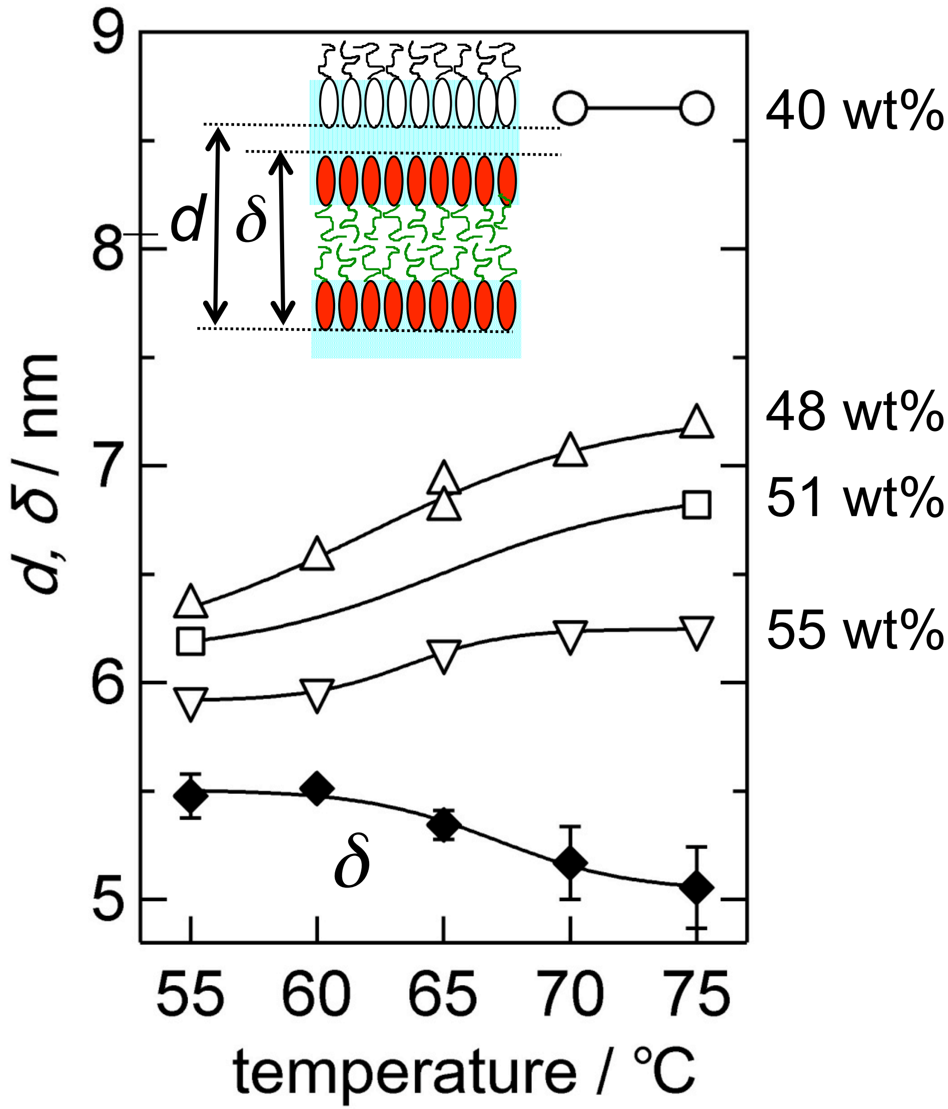
$\Leftrightarrow d, \eta$

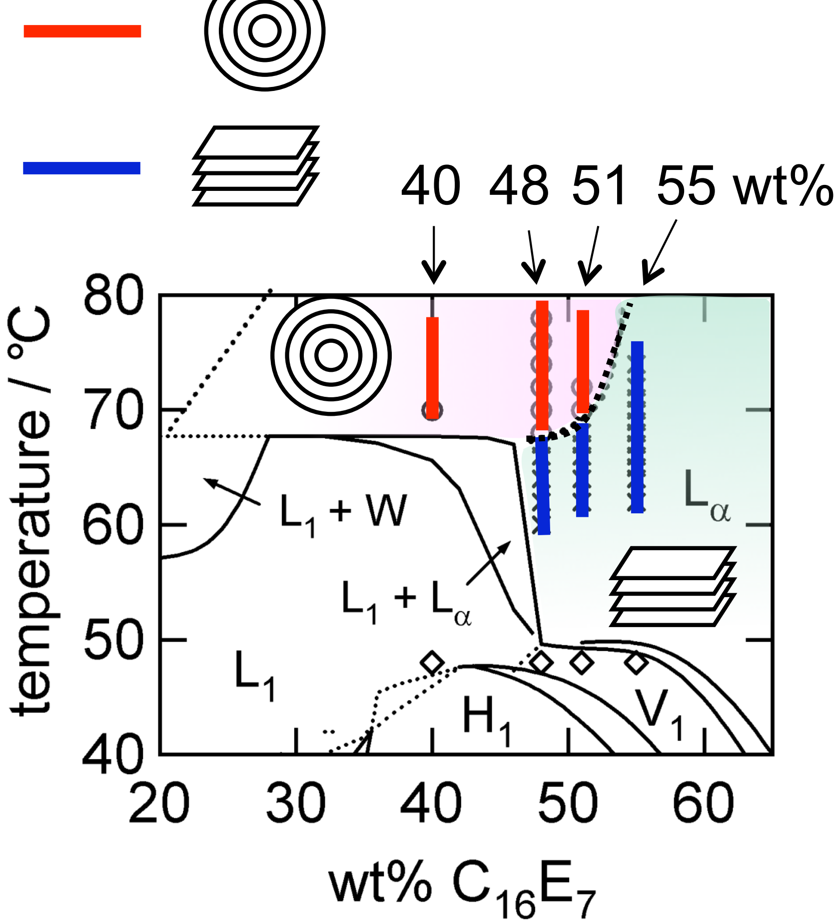
$\eta \Leftrightarrow$ fluctuations of d

* F. Nallet, R. Laversanne, and D. Roux, *J. Phys. II France*, **3**, 487 (1993) (applied to AOT-water and DDAB-water)

1) K. Minewaki, T. Kato, H. Yoshida, and M. Imai, *Langmuir* **17**, 1864 (2001).

Comparison with Temperature Dependence of Repeat Distance at Rest[1)]





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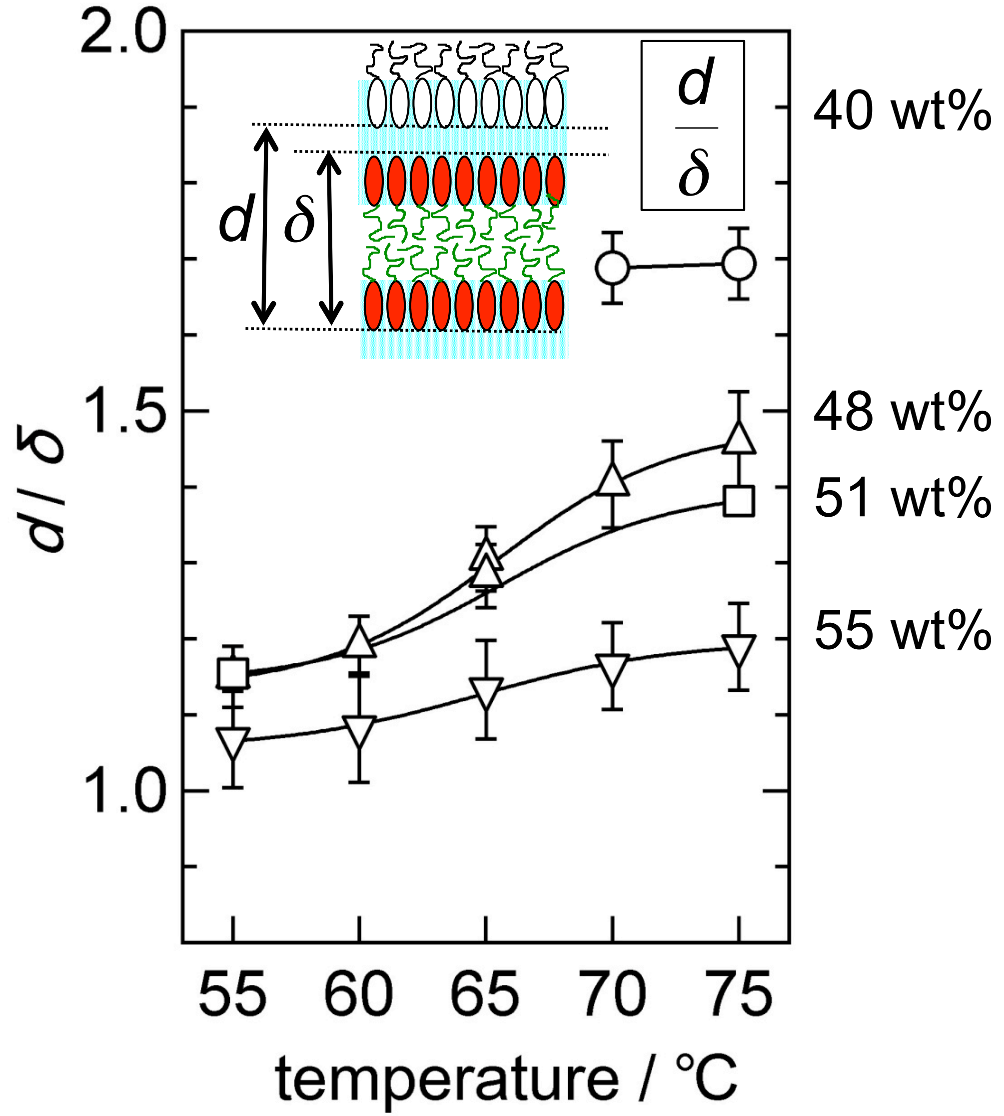

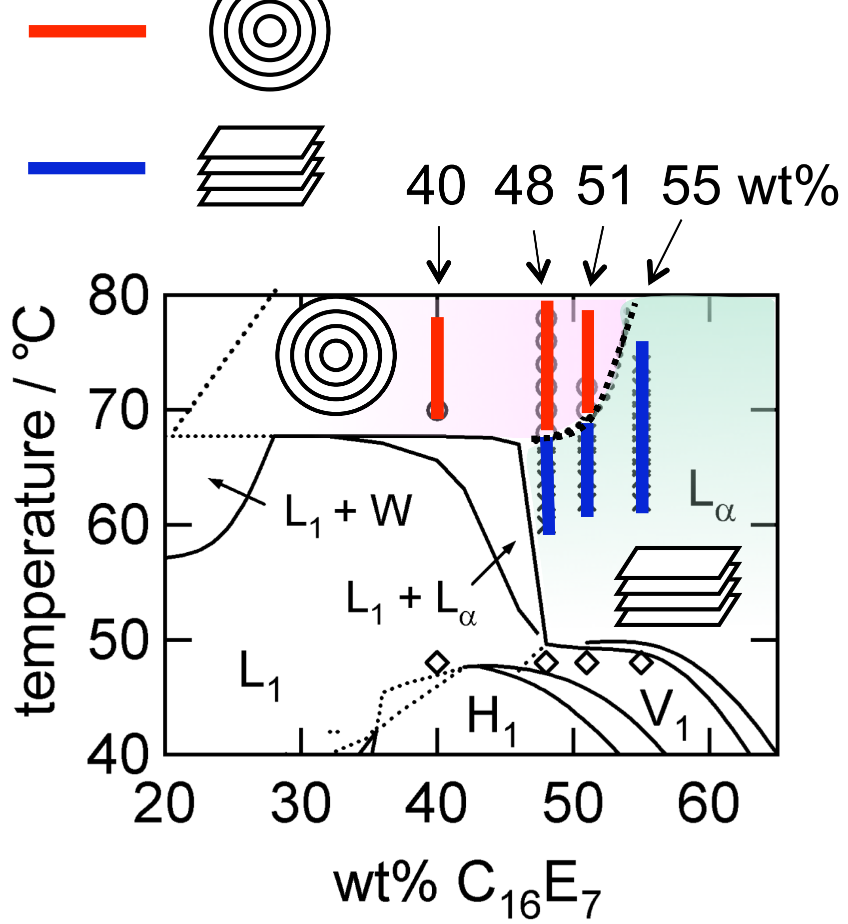

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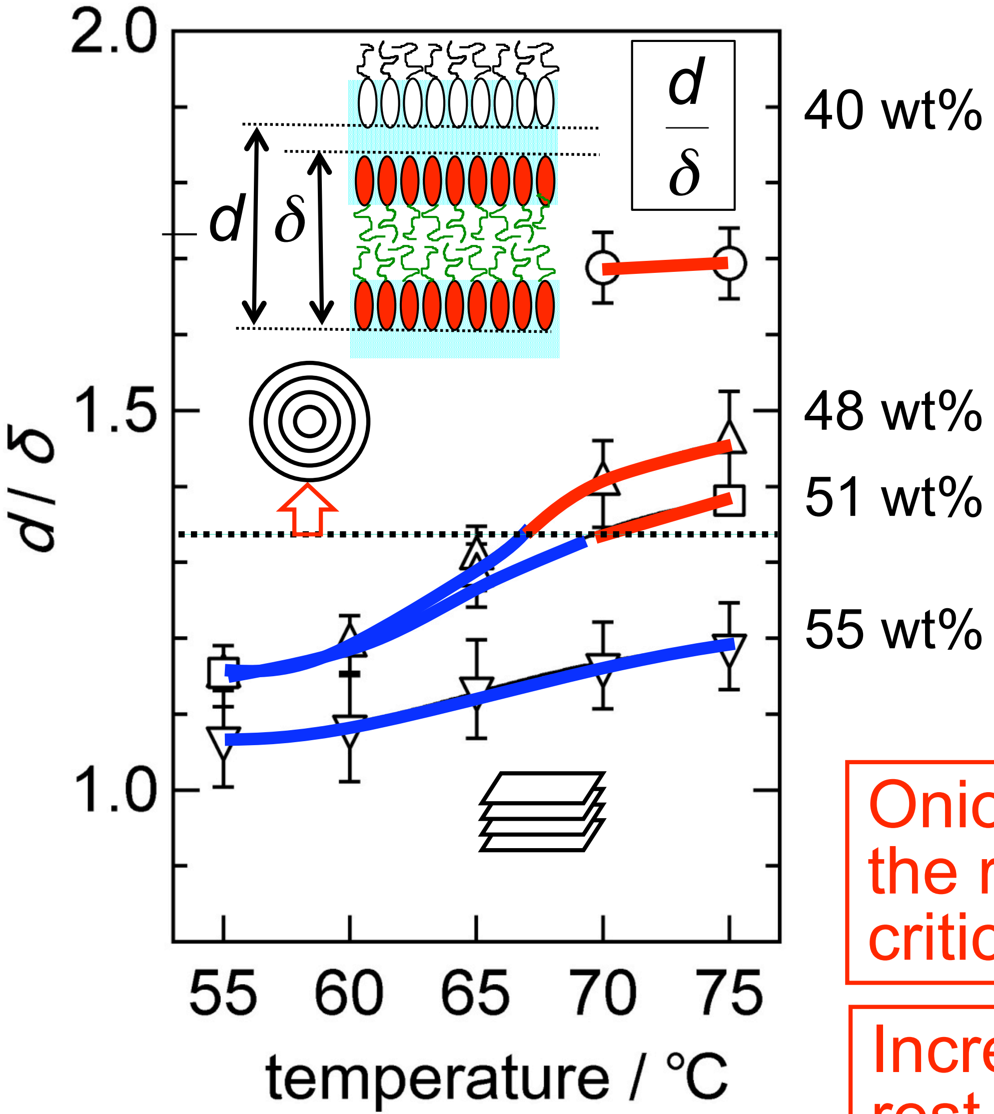
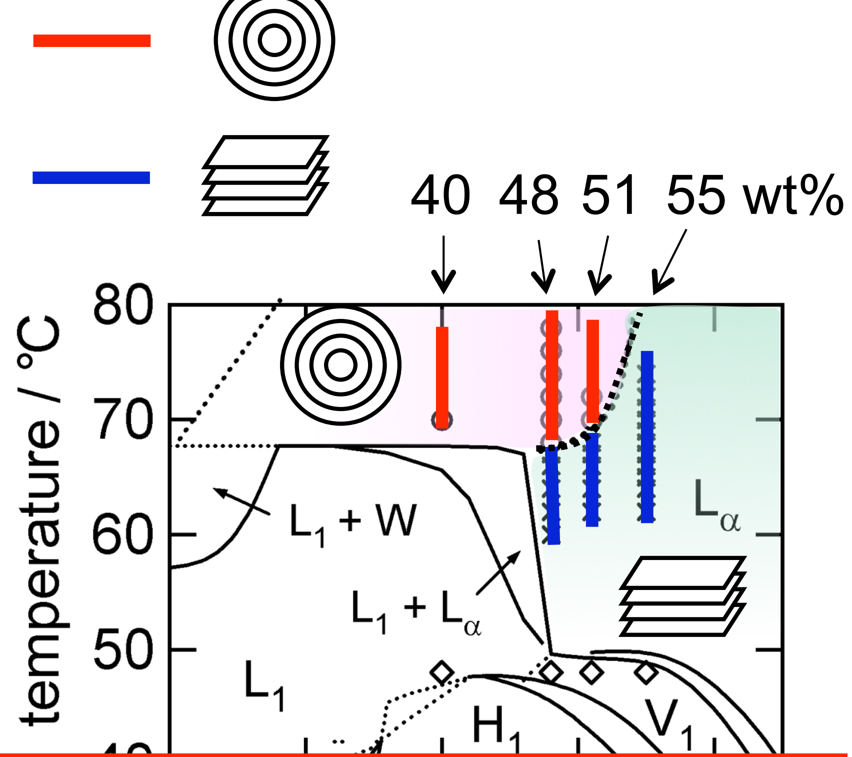


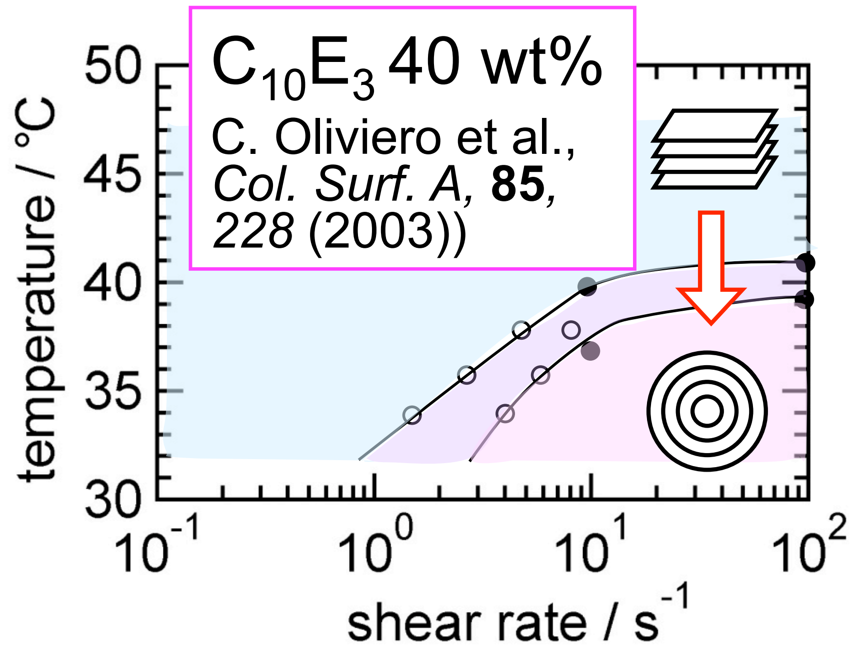


Onions can be formed only when the ratio d/δ exceeds a certain critical value

Increase in the repeat distance at rest may be necessary for the transition

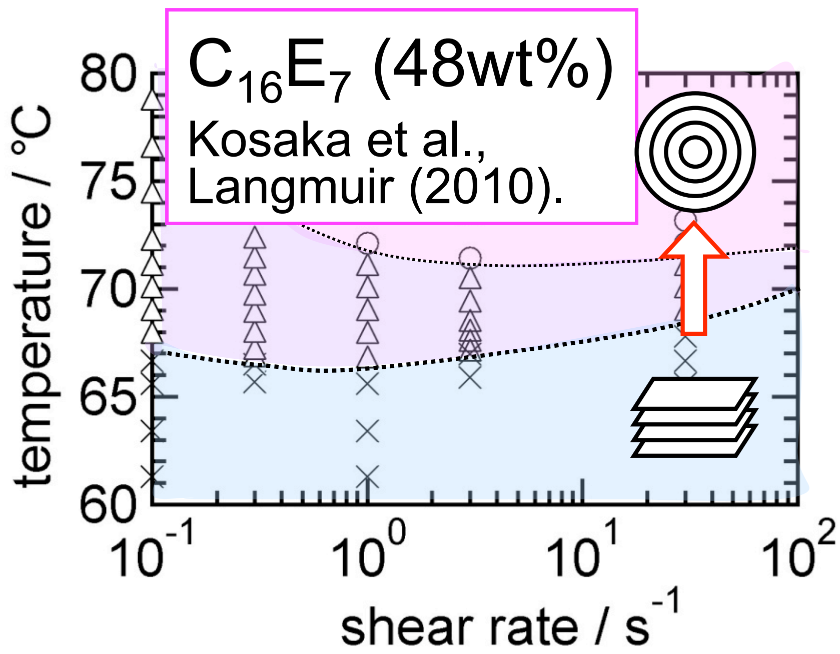
1) K. Minewaki, T. Kato, H. Yosh … 1).

Comparison with Other Homologous Systems



Lamellar-to-onion transition with decreasing temperature

Decrease in the saddle splay modulus of a bilayer with decreasing temperature ?



Lamellar-to-onion transition with increasing temperature

Increase in the repeat distance with increasing temperature at rest

Outline of the Present Talk

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   (1) Results of simultaneous measurements of

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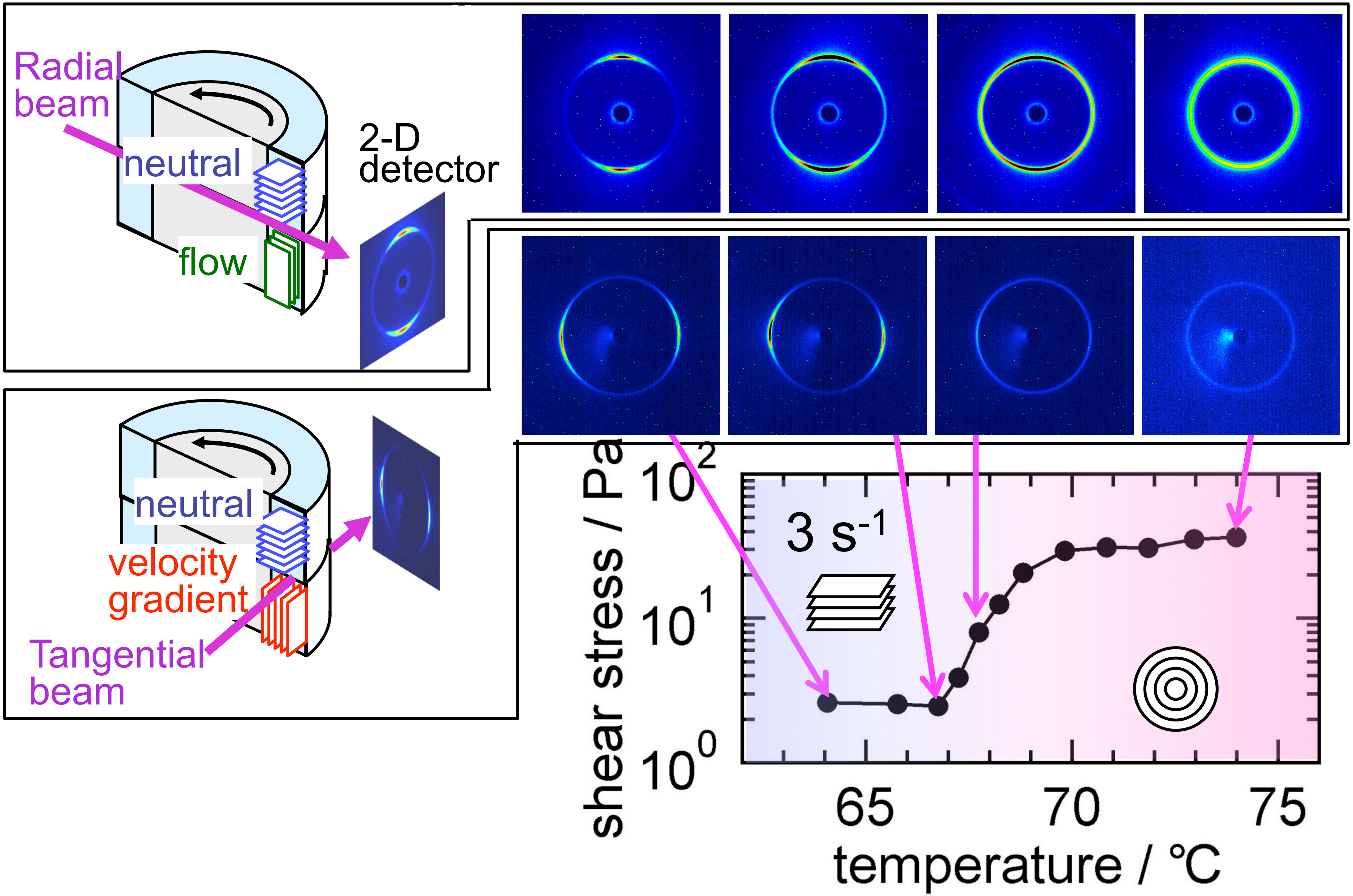
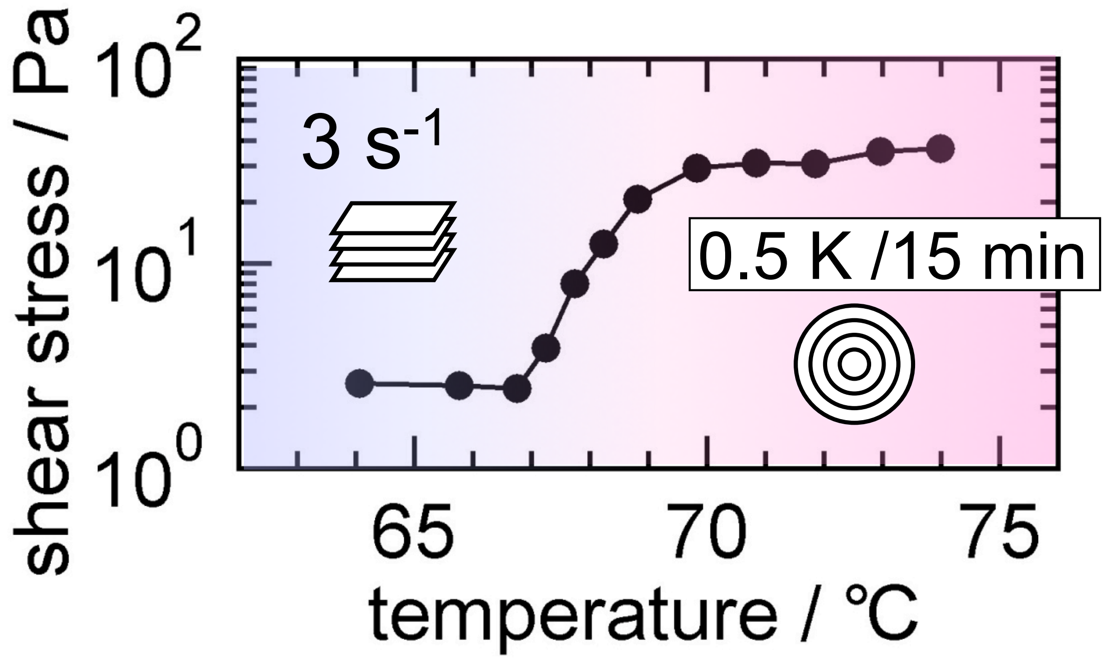
Temperature Dependences of Shear Stress and 2-D SAXS Patterns at 3 s^{-1} (48wt%)



Temperature Dependences of Shear Stress and 2-D SAXS Patterns at 3 s^{-1} (48wt%)



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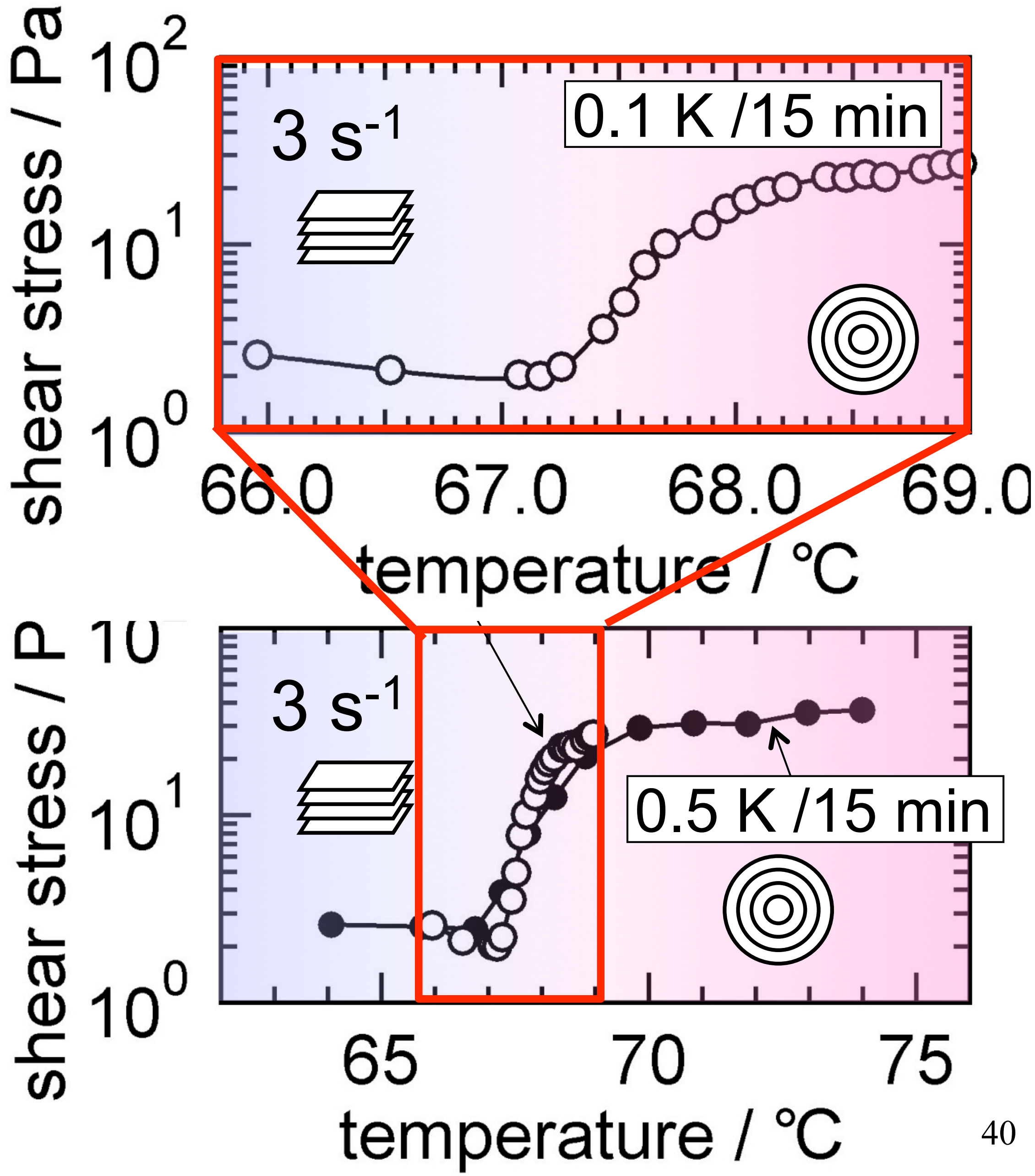

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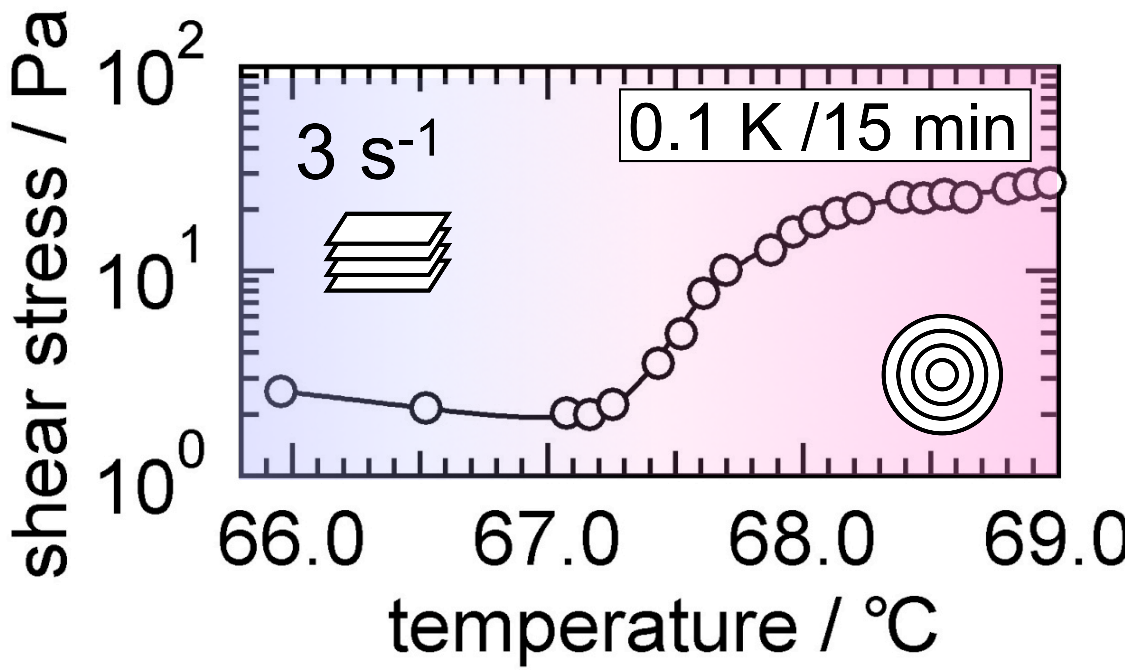

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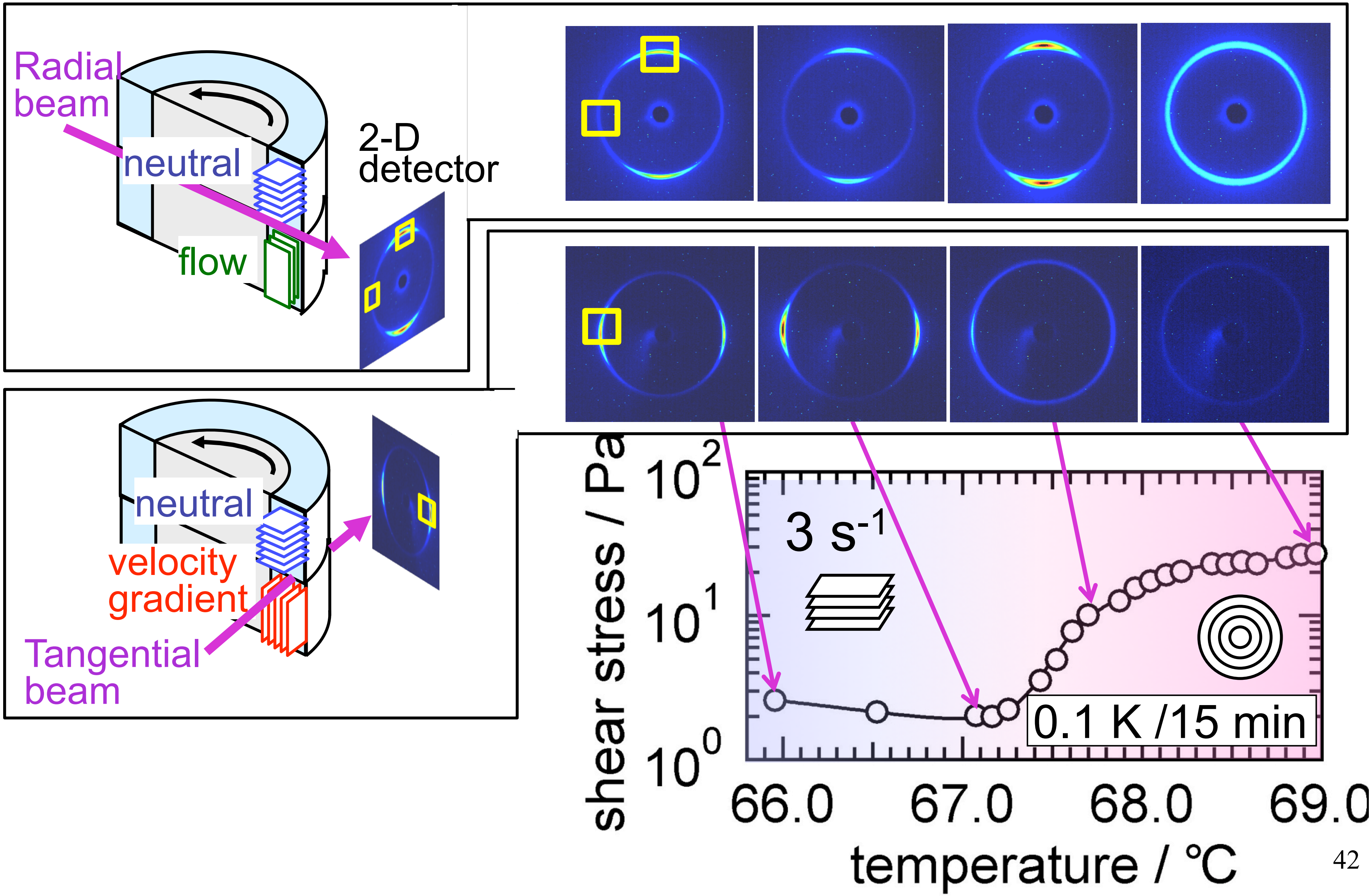
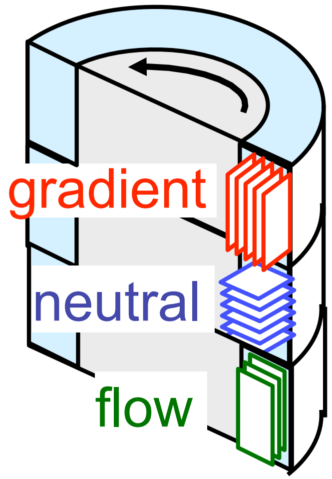
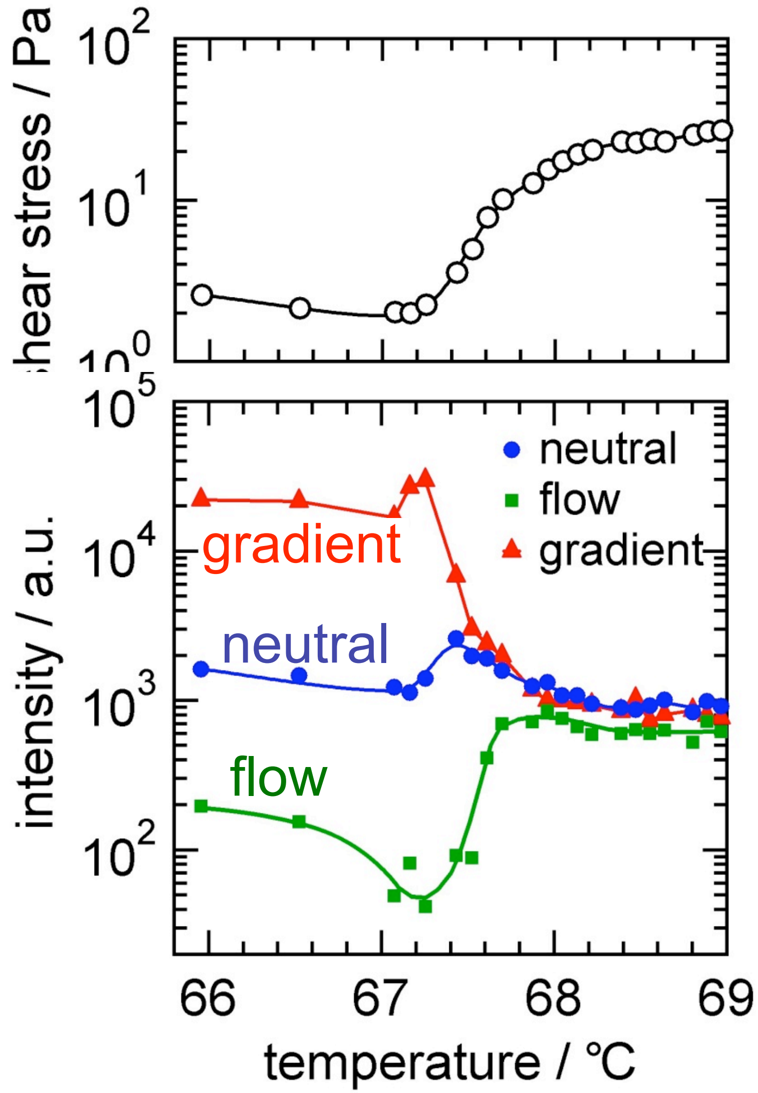


Temperature Dependence of SAXS Peak Intensity





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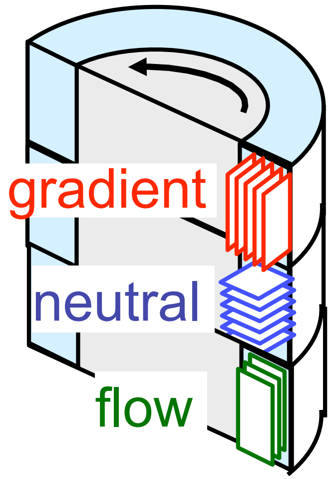
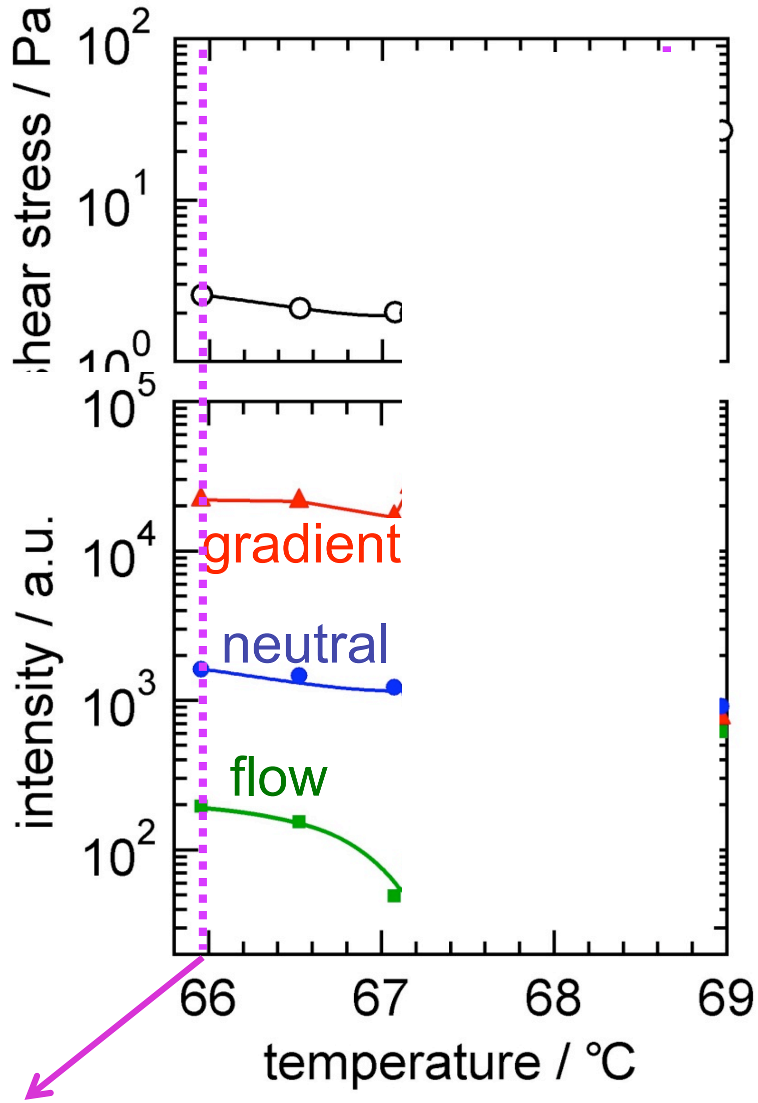
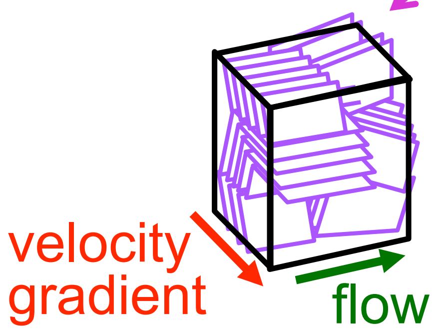
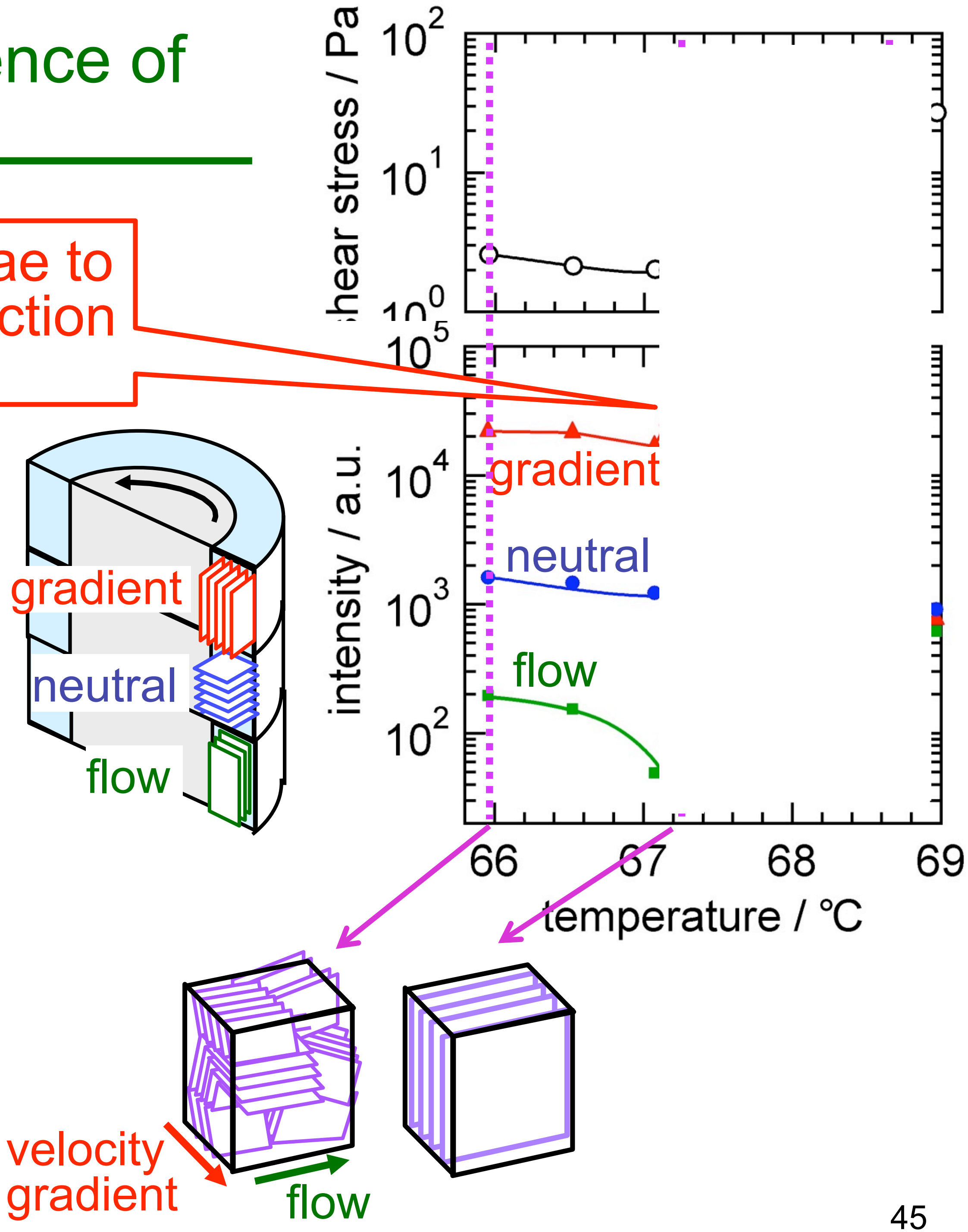






Temperature Dependence of SAXS Peak Intensity

The orientation of lamellae to the velocity gradient direction is suddenly enhanced



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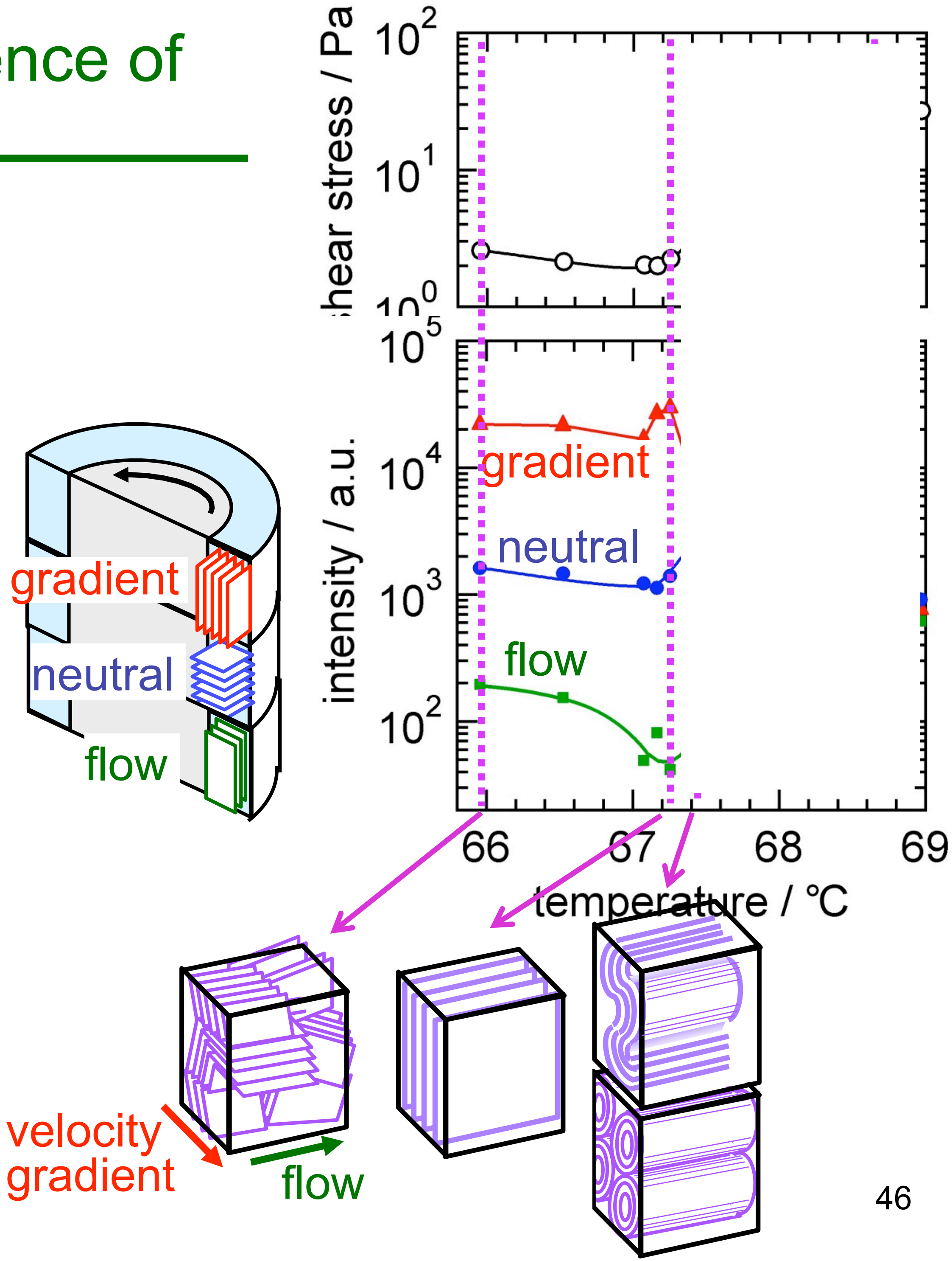

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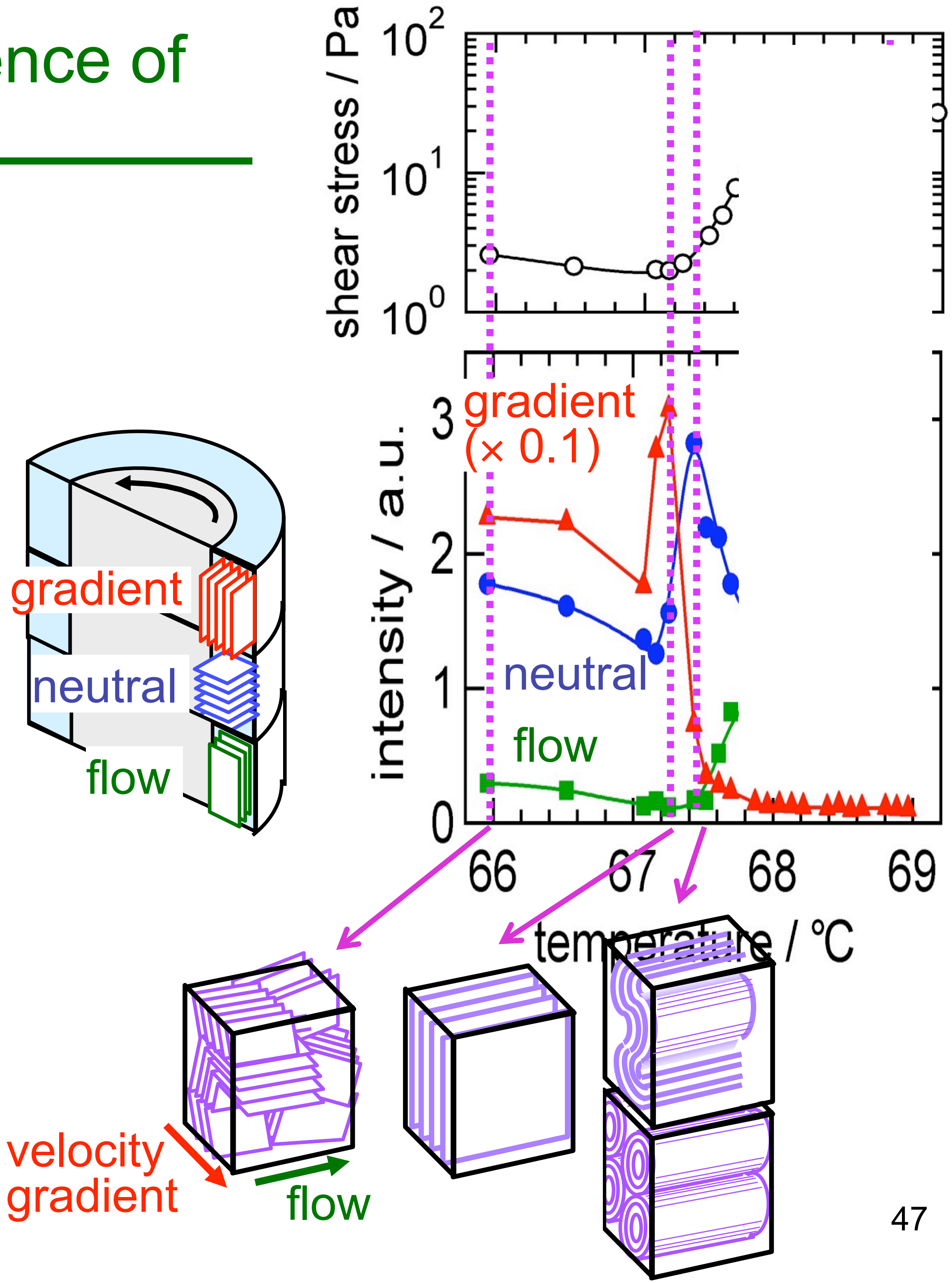

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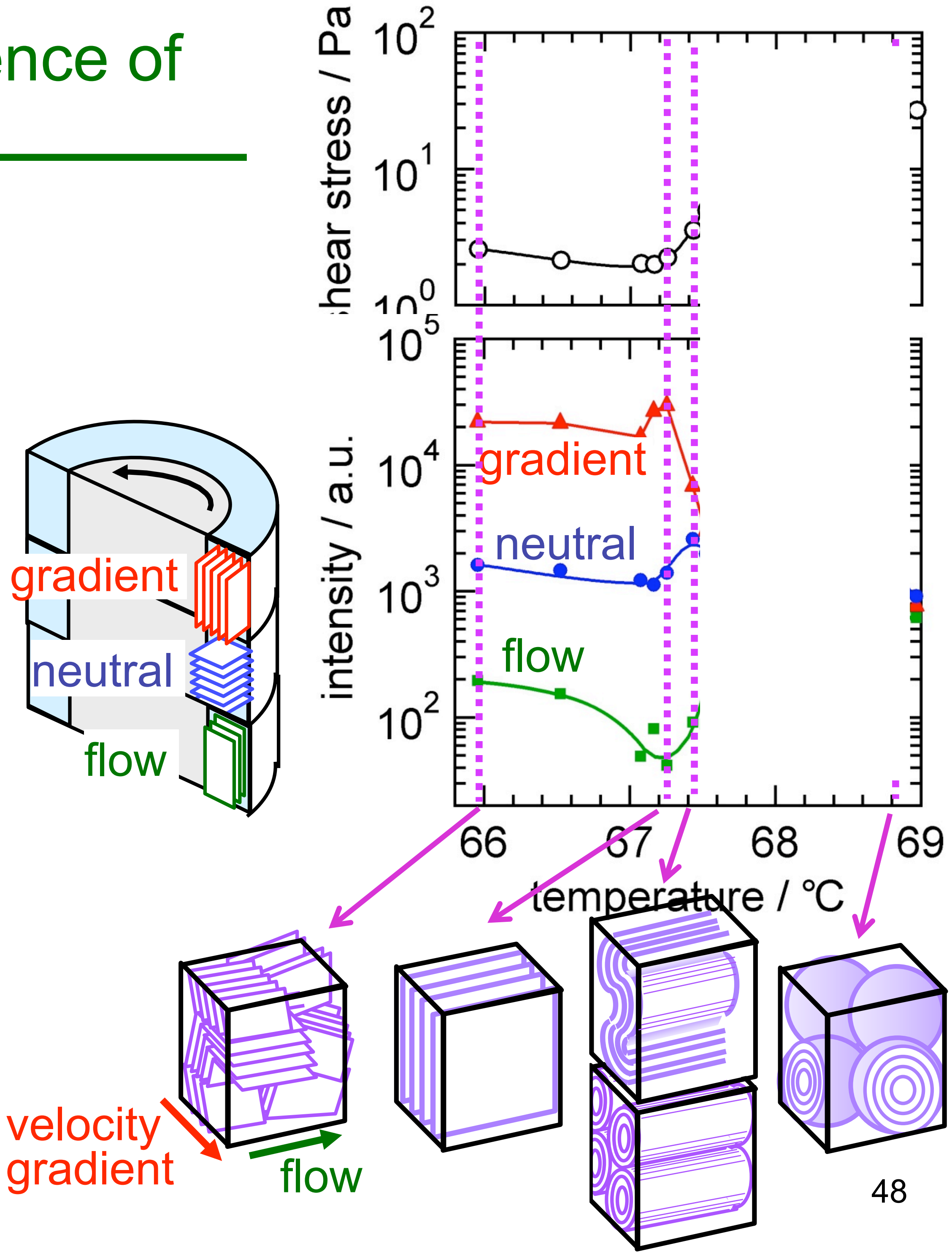
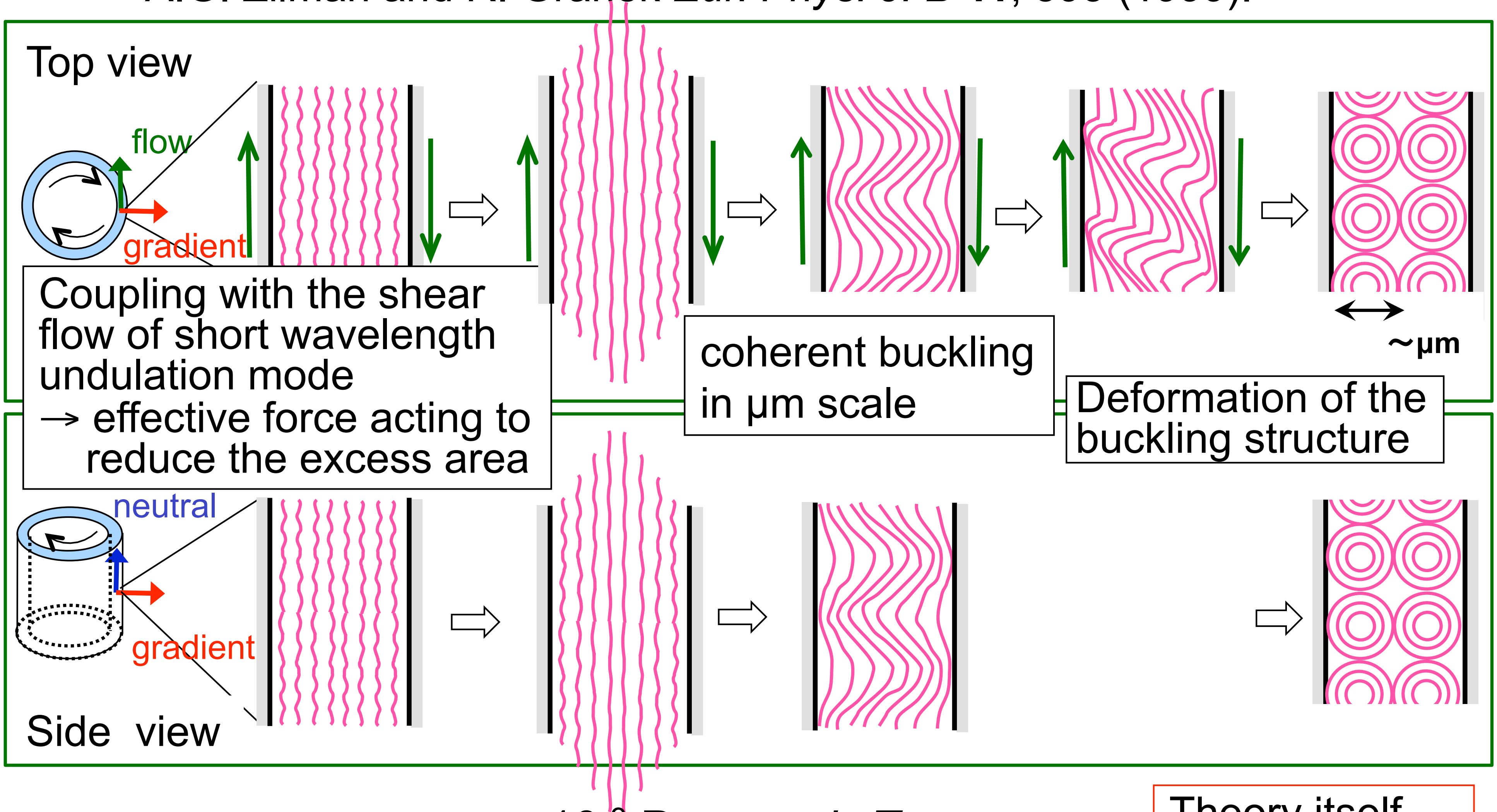


Theory for Onion Formation

A.G. Zilman and R. Granek *Eur. Phys. J. B* **11**, 593 (1999).



$$\dot{\gamma}_c \cong C \frac{(k_B T / \kappa) k_B T}{\eta\, d^{5/2} D^{1/2}}$$

$\eta \sim 10^{-3}$ Pa s $\kappa \sim k_B T$

$d \sim 10$ nm D ~ 1mm

$$\dot{\gamma}_c \cong 10^6 \mathrm{s}^{-1} >>> \dot{\gamma}_c^{obsd}$$

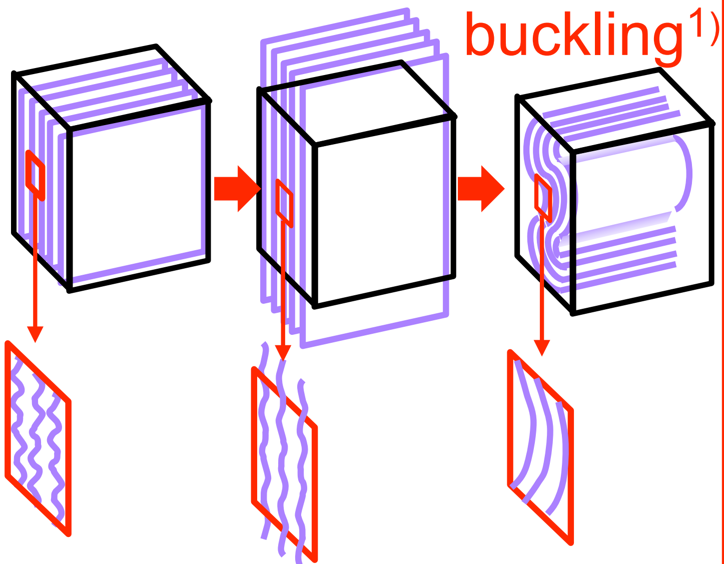
Theory itself may be wrong

Temperature Dependence of SAXS Peak Intensity

The orientation of lamellae to the velocity gradient direction is suddenly enhanced

Consistent with our results

coherent buckling[1)]



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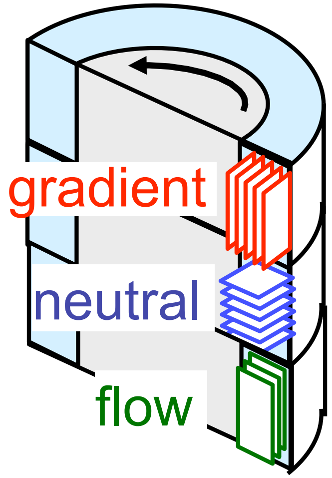
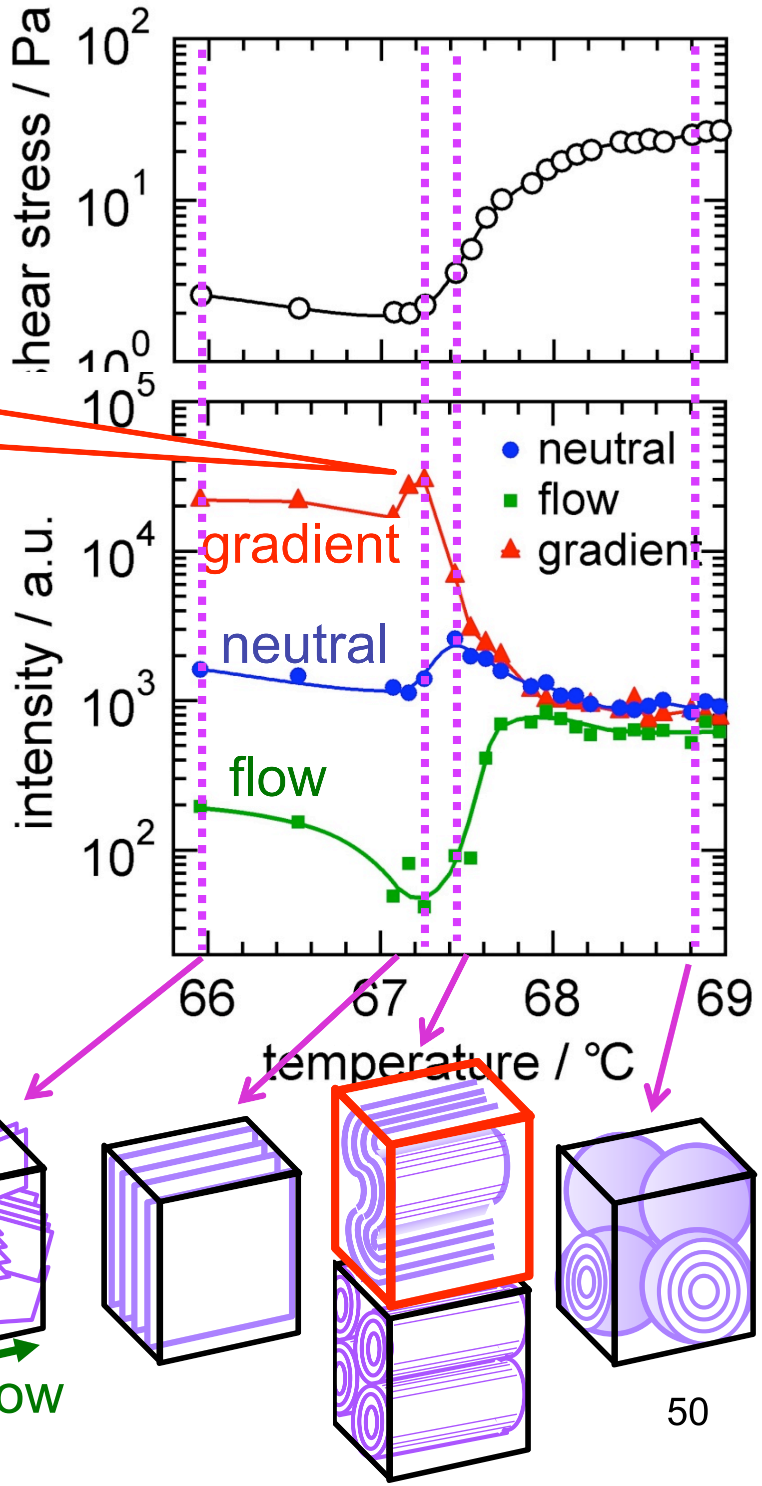
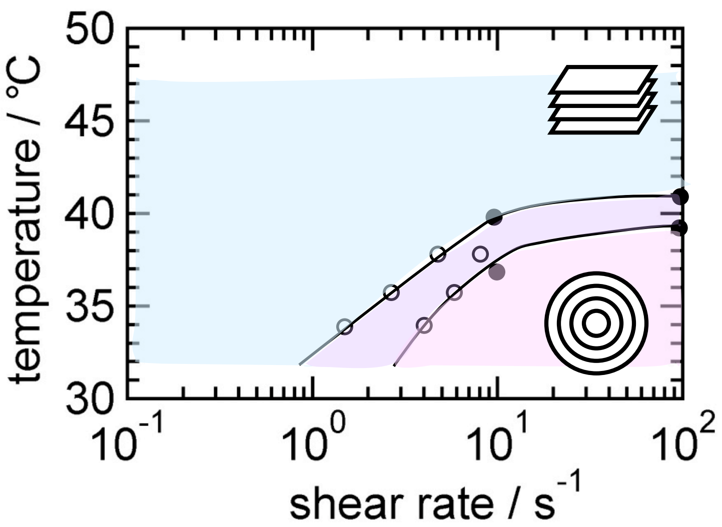
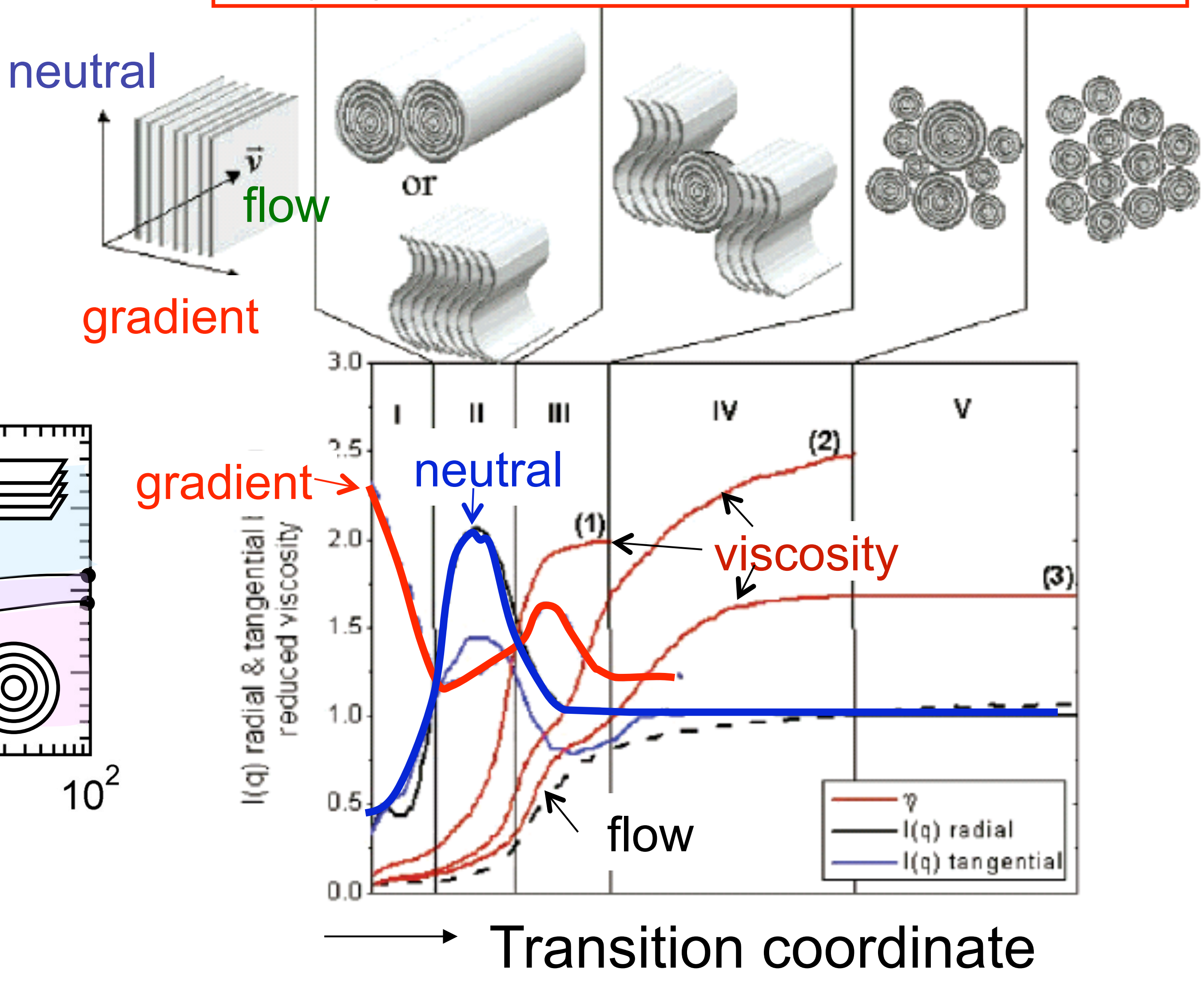




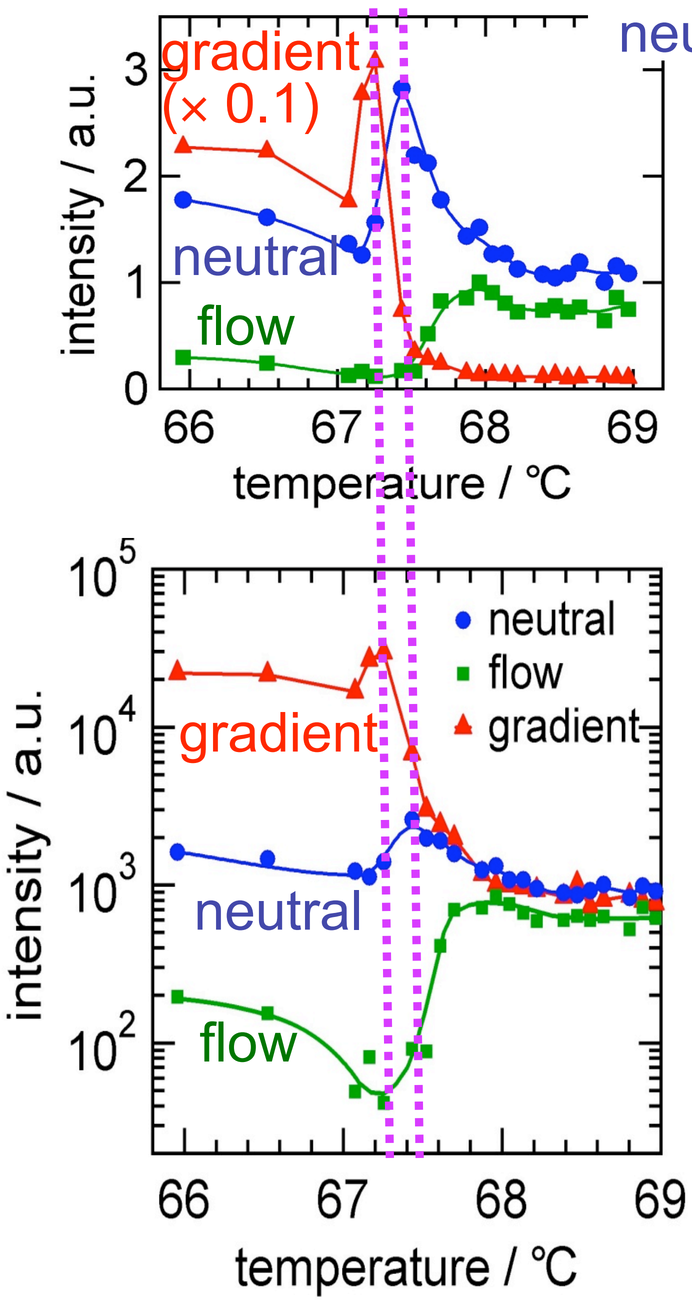
$C_{10}E_3$ at 25°C at 10 s^{-1} (SANS)



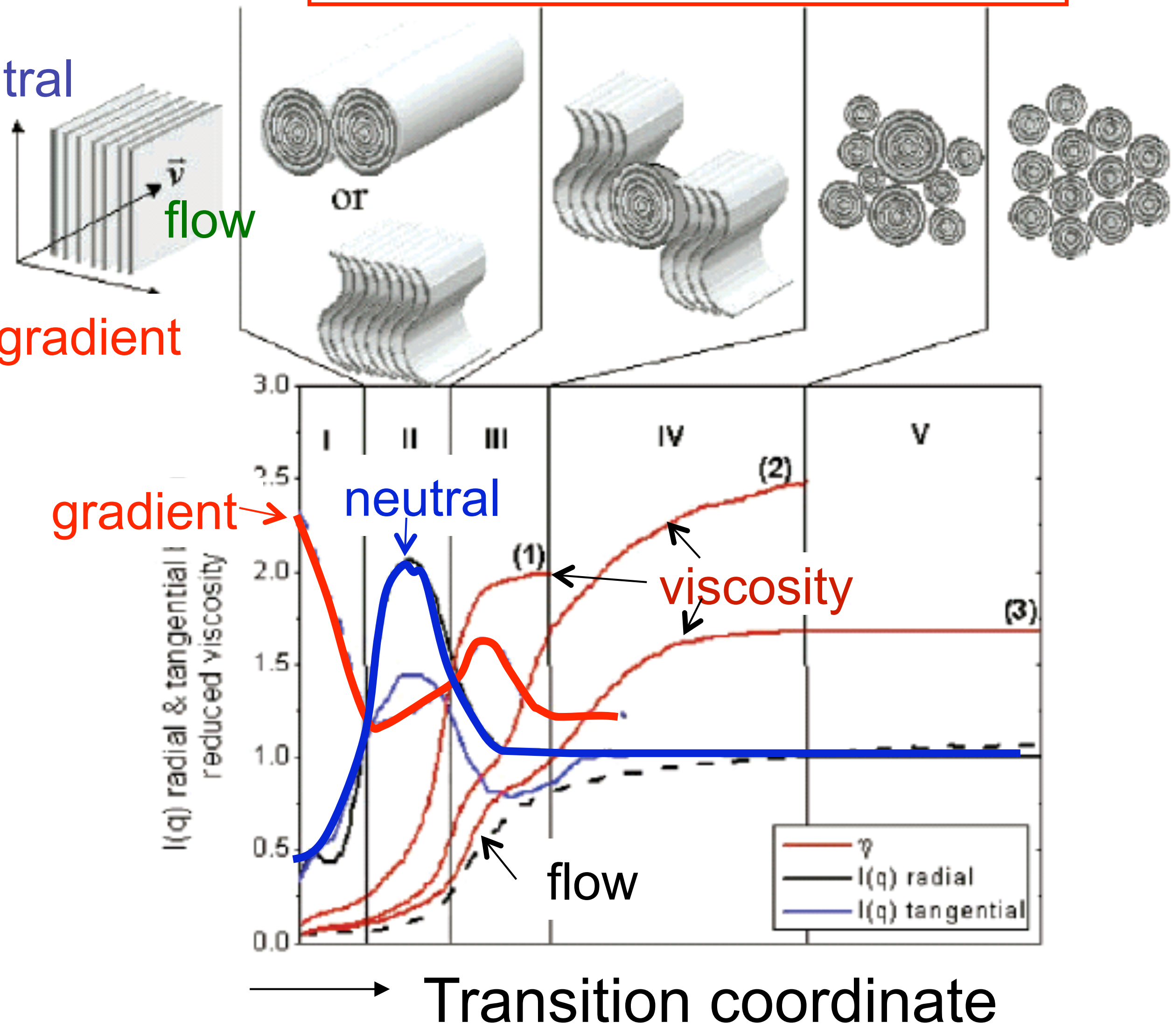


F. Nettesheim, J. Zipfel, U. Olsson, F. Renth, P. Linder, and W. Richtering, *Langmuir*, **19**, 3618 (2003).

$C_{16}E_7$ at 3 s^{-1}



$C_{10}E_3$ at 25℃ at 10 s^{-1}



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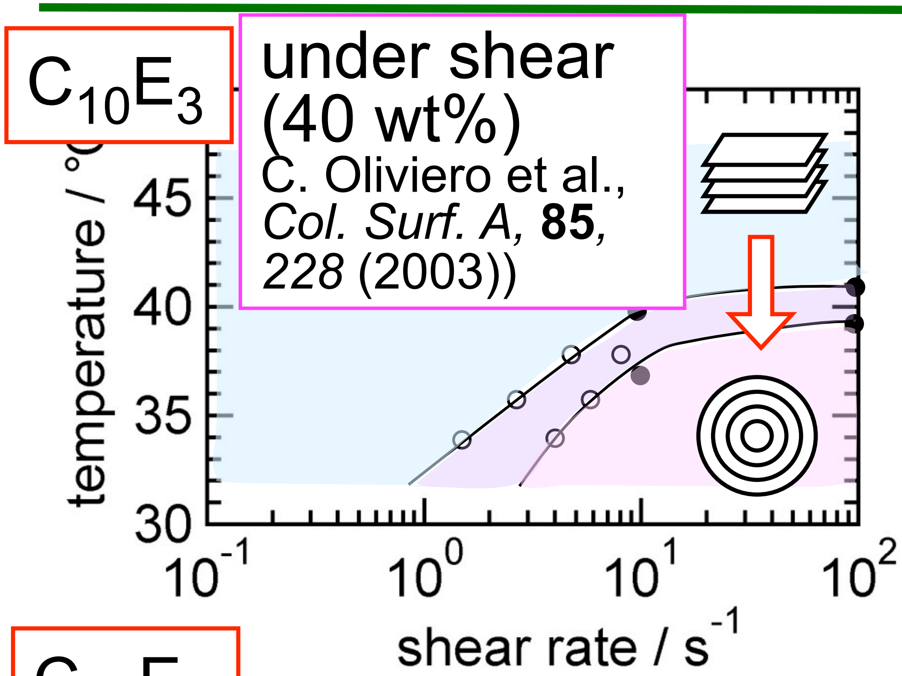
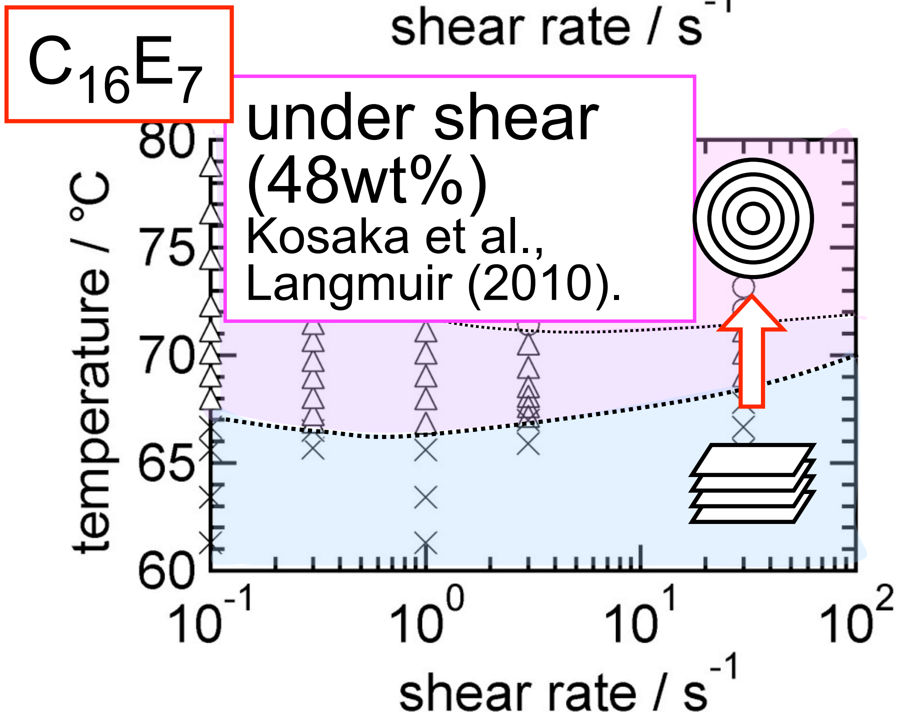




Lamellar-to-onion transition with decreasing temperature

⇕

Decrease in the saddle splay modulus of a bilayer

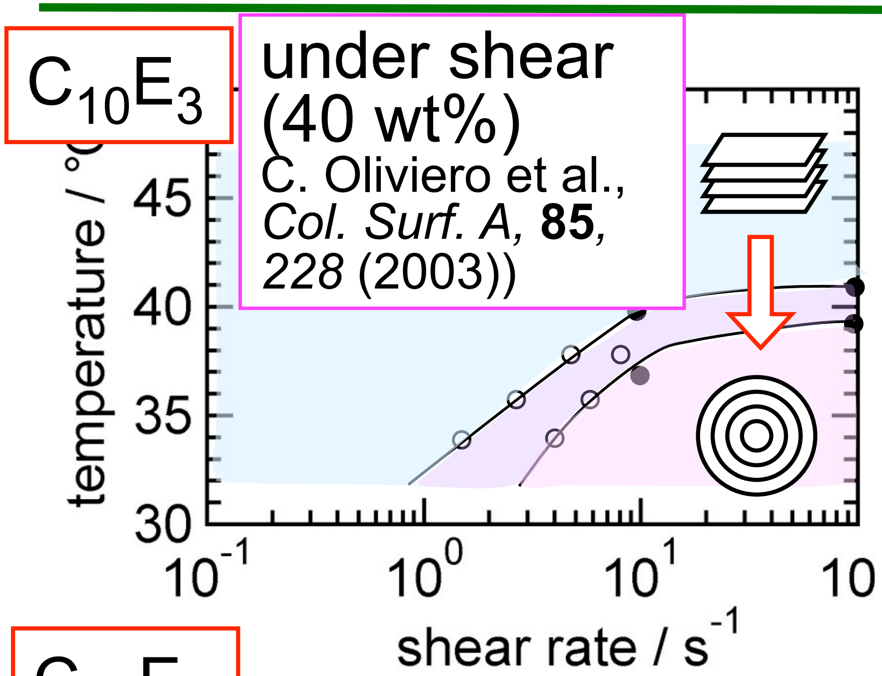
Is there any system which exhibits both types of transition ?

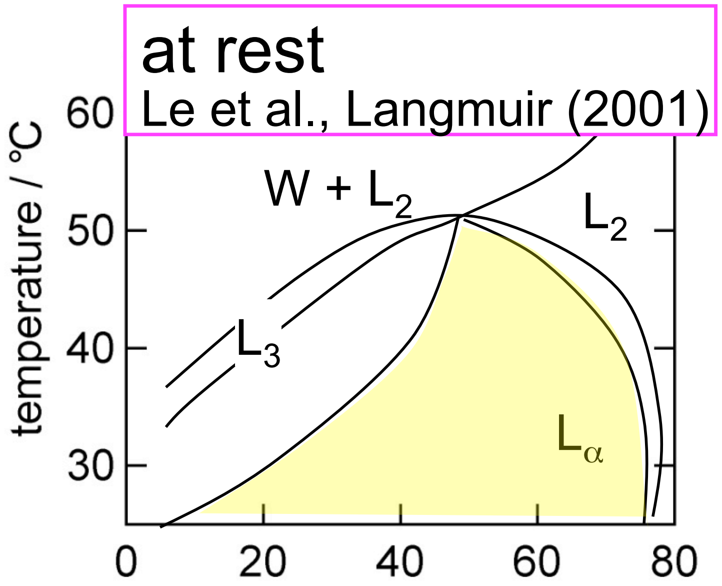
Lamellar-to-onion transition with increasing temperature

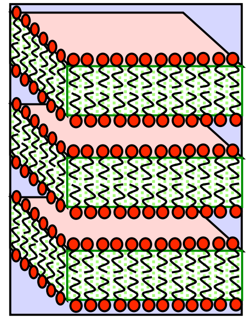
⇕

Increase in the repeat distance at rest

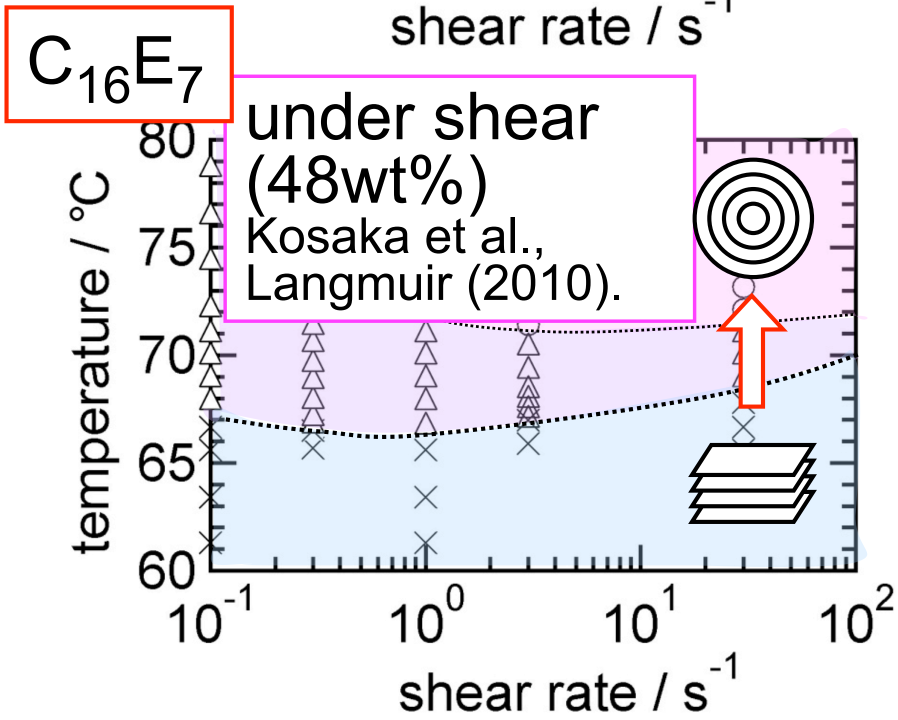
Comparison with Phase Behaviors at Rest

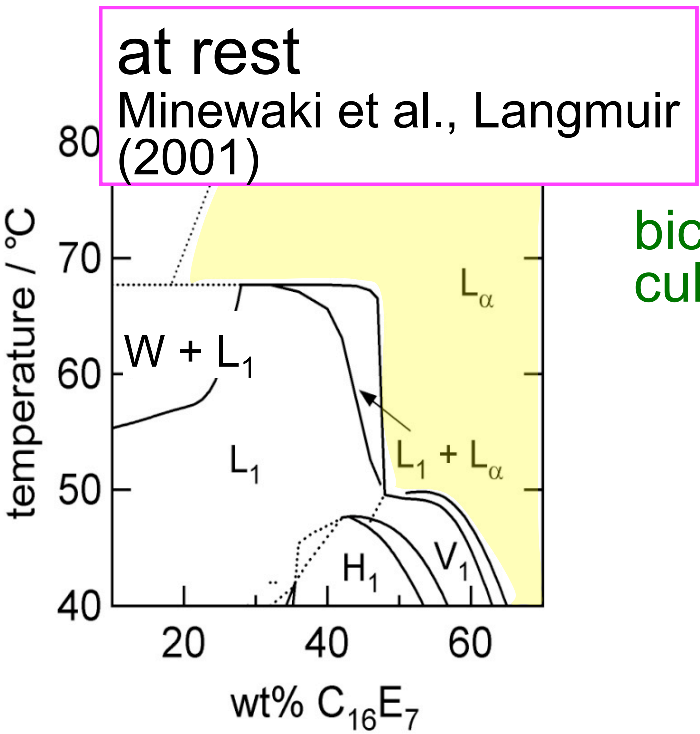


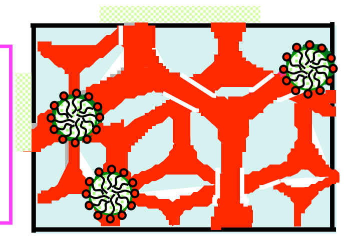




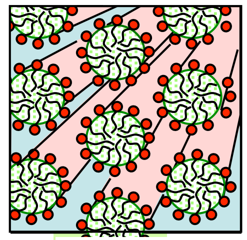
lamellar (L_α) phase





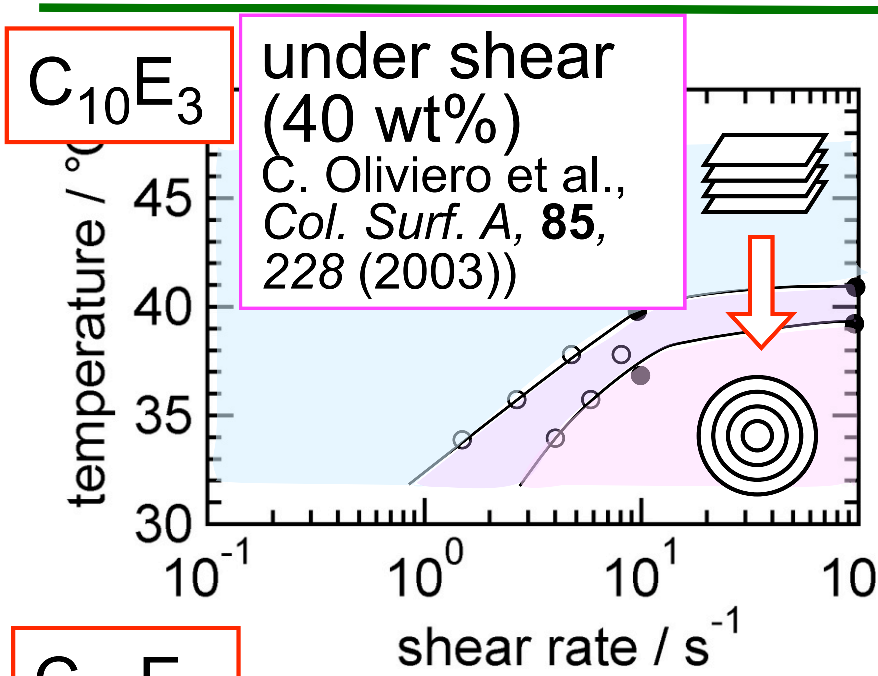


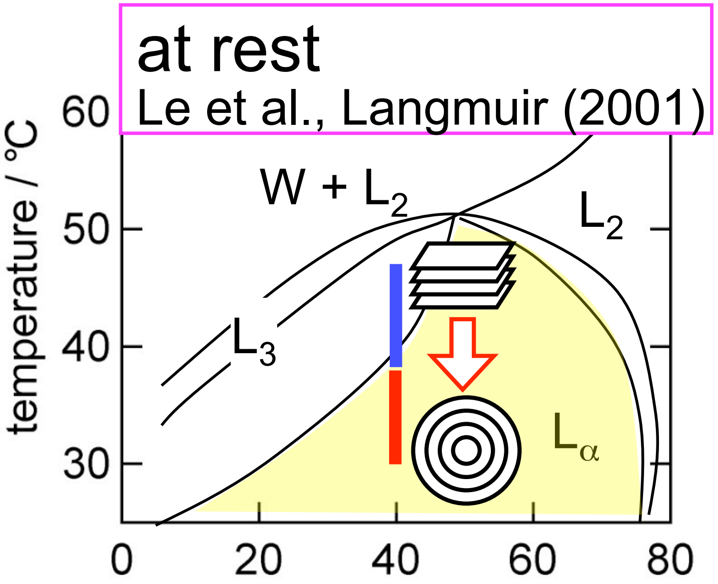
bicontinuous cubic (V_1) phase

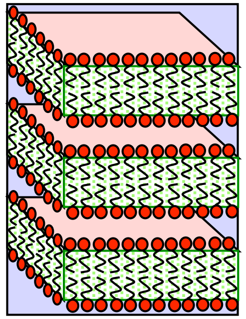


hexagonal (H_1) phase

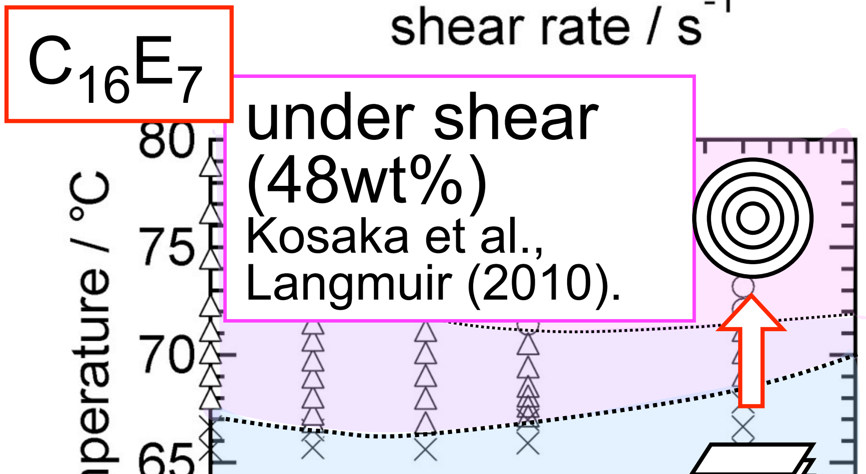
Comparison with Phase Behaviors at Rest

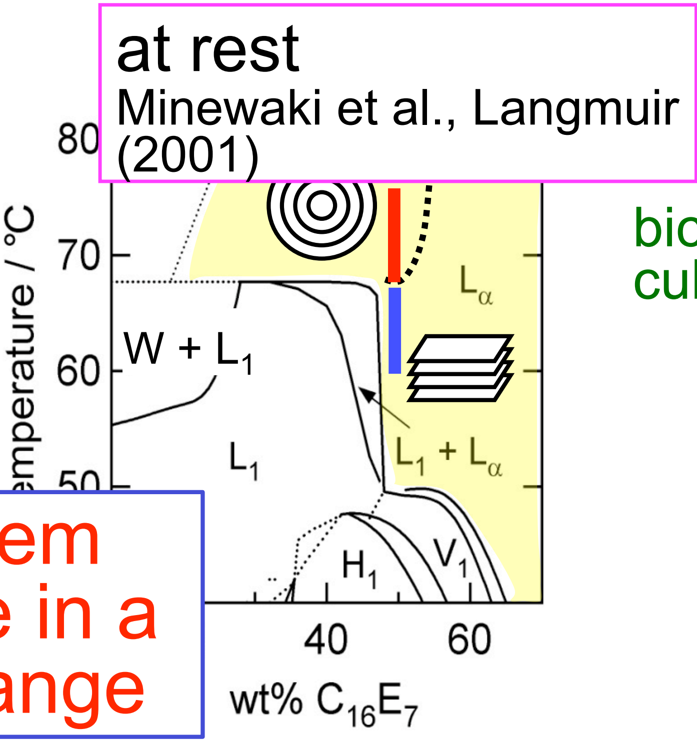


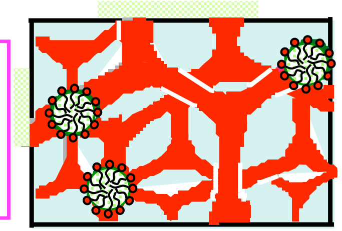




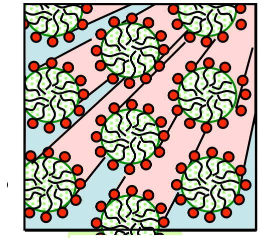
lamellar (L_α) phase







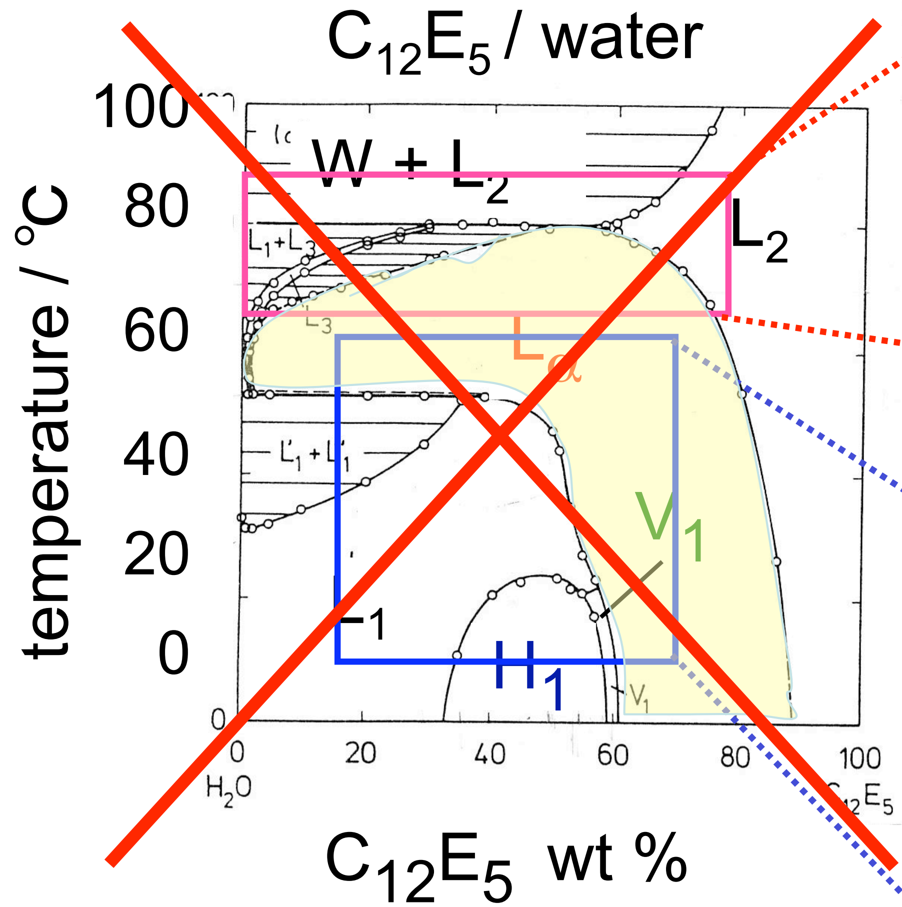
bicontinuous cubic (V_1) phase

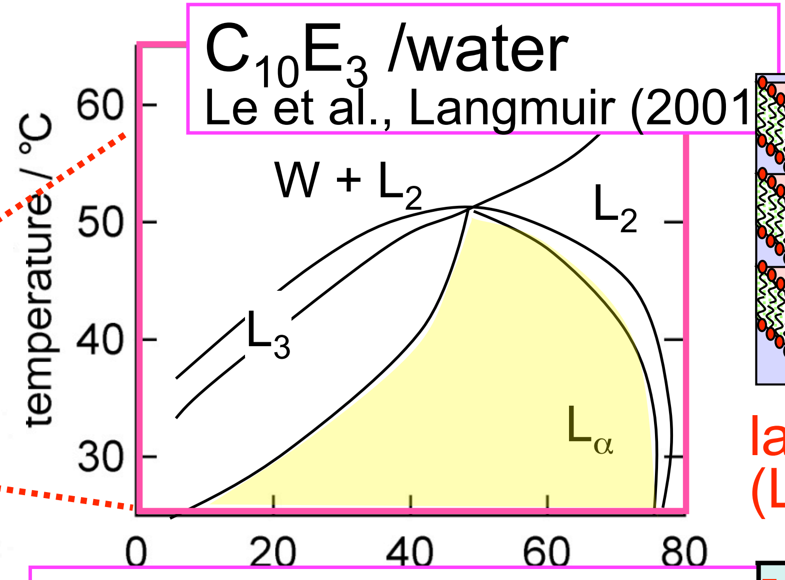


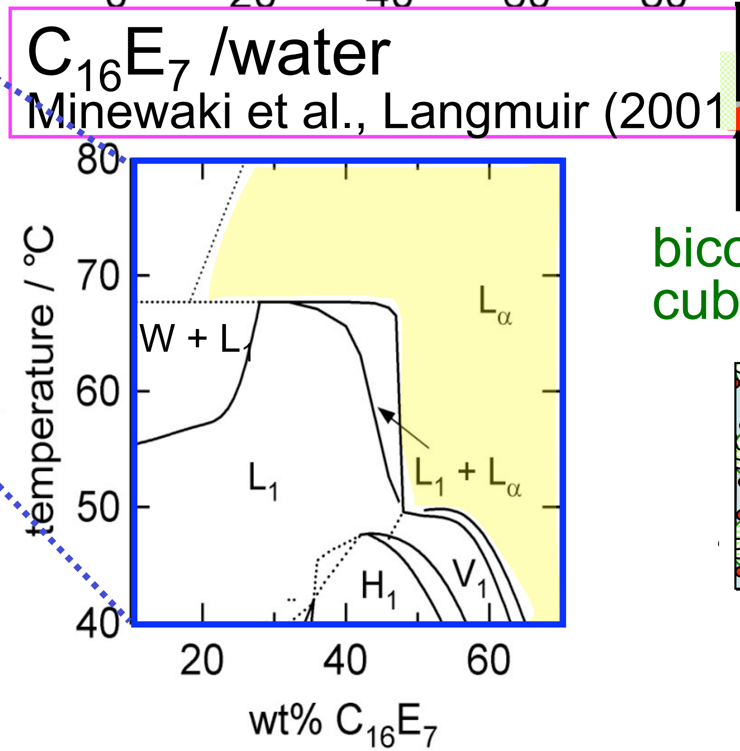
hexagonal (H_1) phase

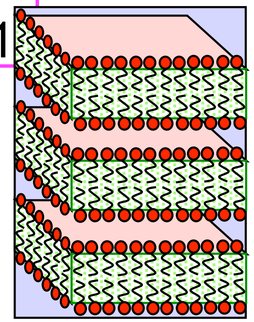
We should look for a system having the lamellar phase in a more wide temperature range

Phase Behaviors at Rest

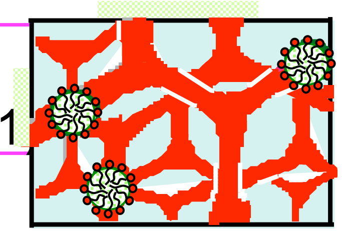




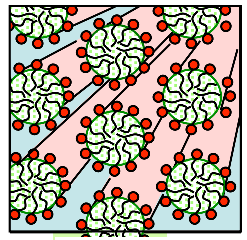




lamellar (L_α) phase



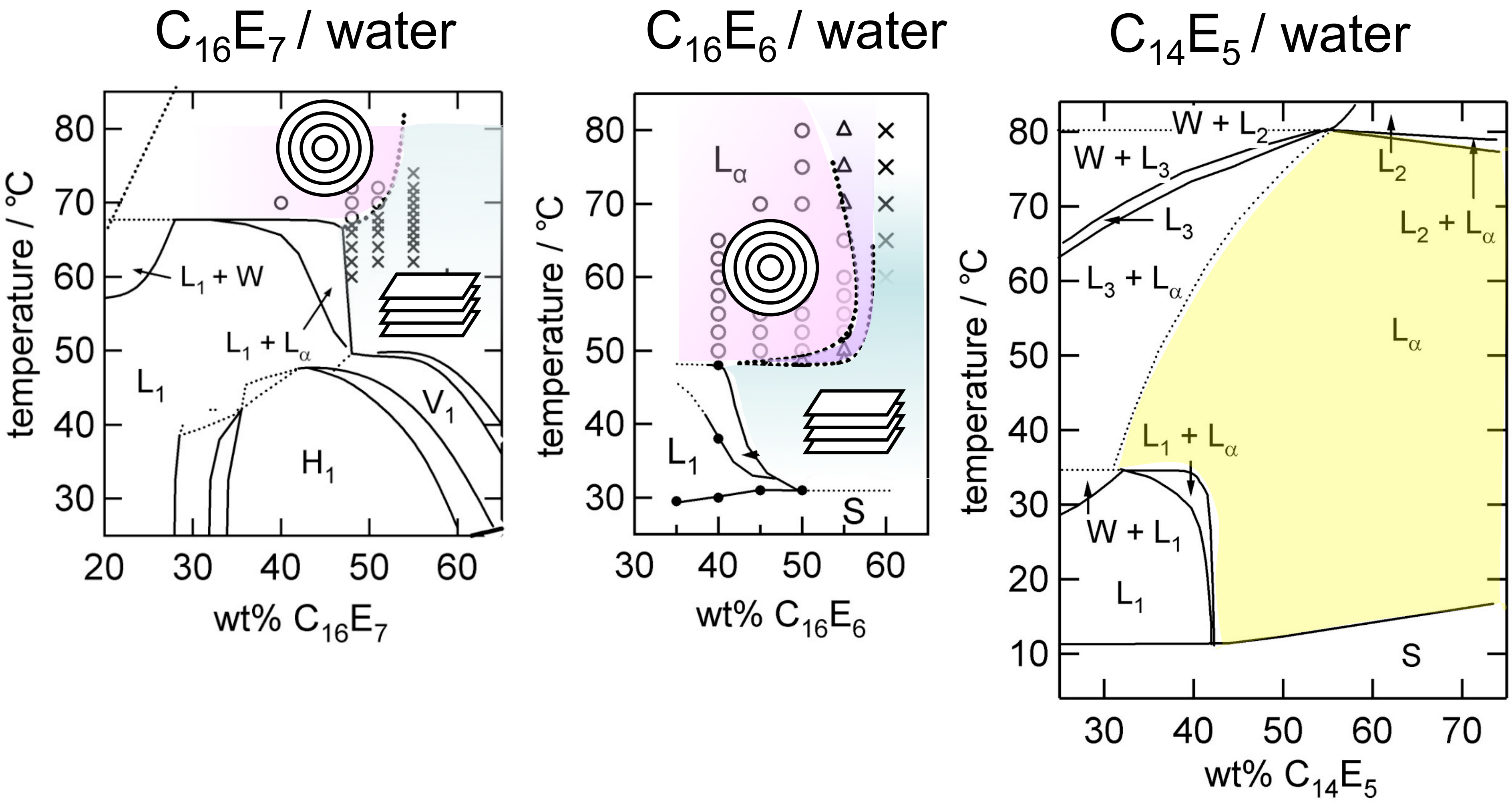
bicontinuous cubic (V_1) phase



hexagonal (H_1) phase

C_nE_m : $C_nH_{2n+1}(OC_2H_4)_mOH$

Temperature - Concentration Diagrams at 3 s^{-1}



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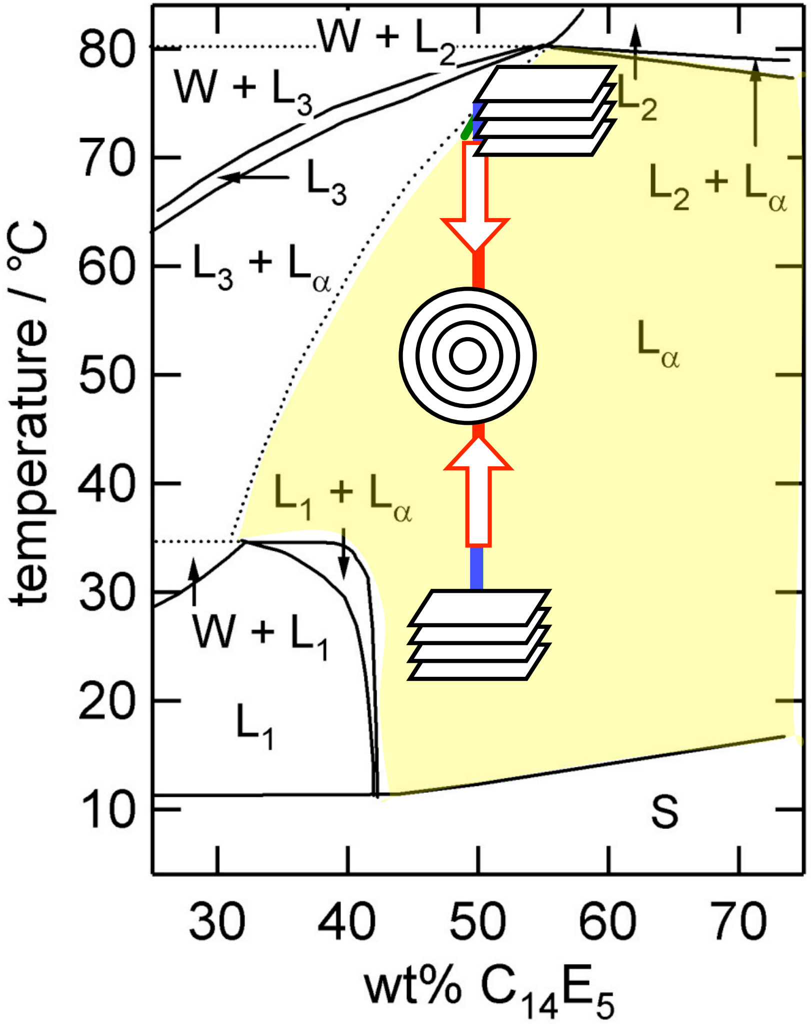
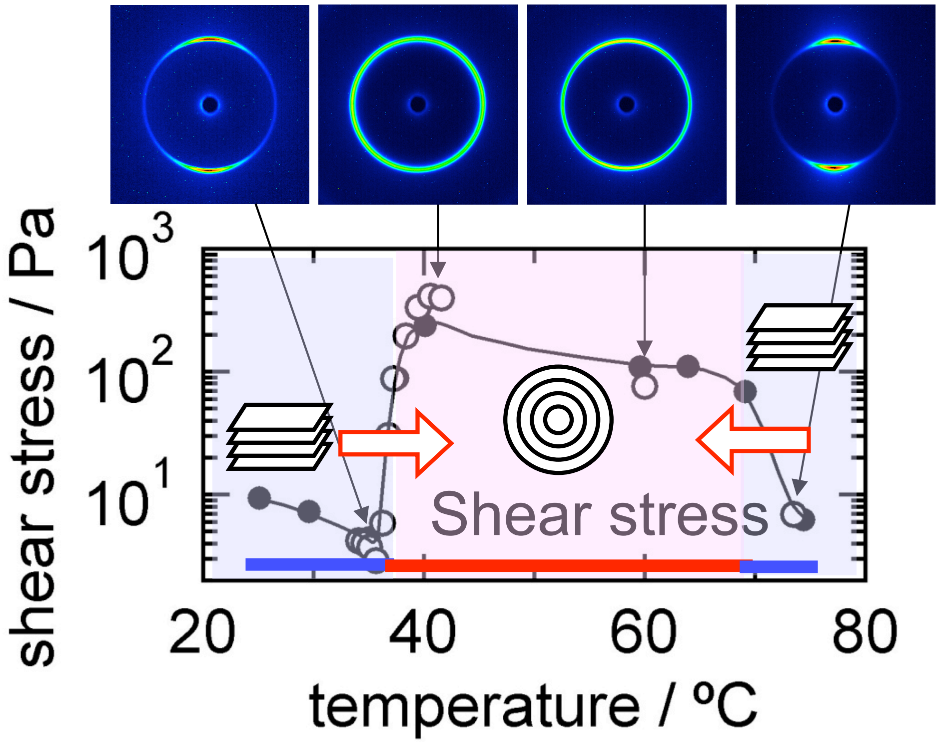
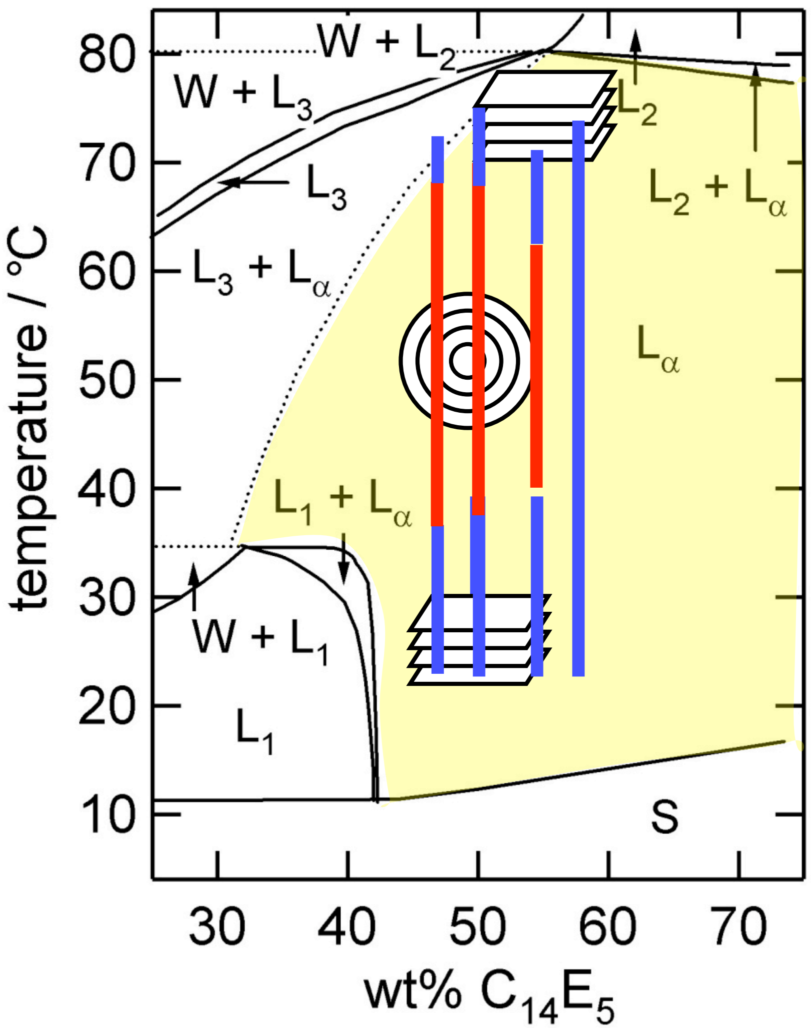
Temperature Dependence of Shear Stress and 2-D SAXS Patterns for $C_{14}E_5$/Water System at 3 s^{-1}

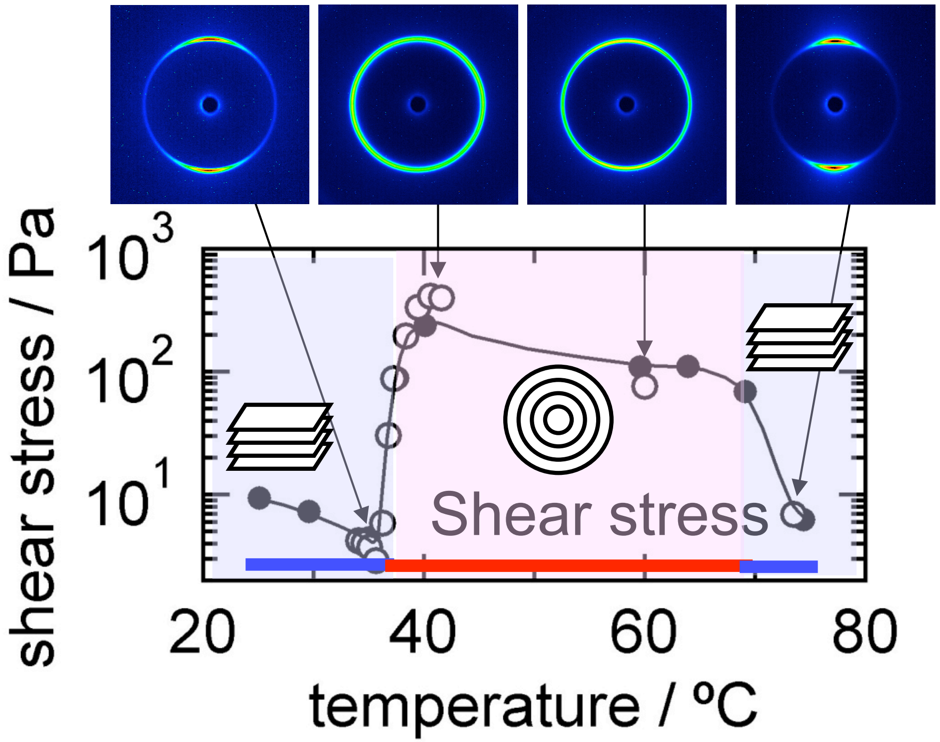




Lamellar-onion-lamellar transition (Reentrant lamellar-onion transition) with varying temperature

Temperature Dependence of Shear Stress and 2-D SAXS Patterns for $C_{14}E_5$ /Water System at 3 s^{-1}





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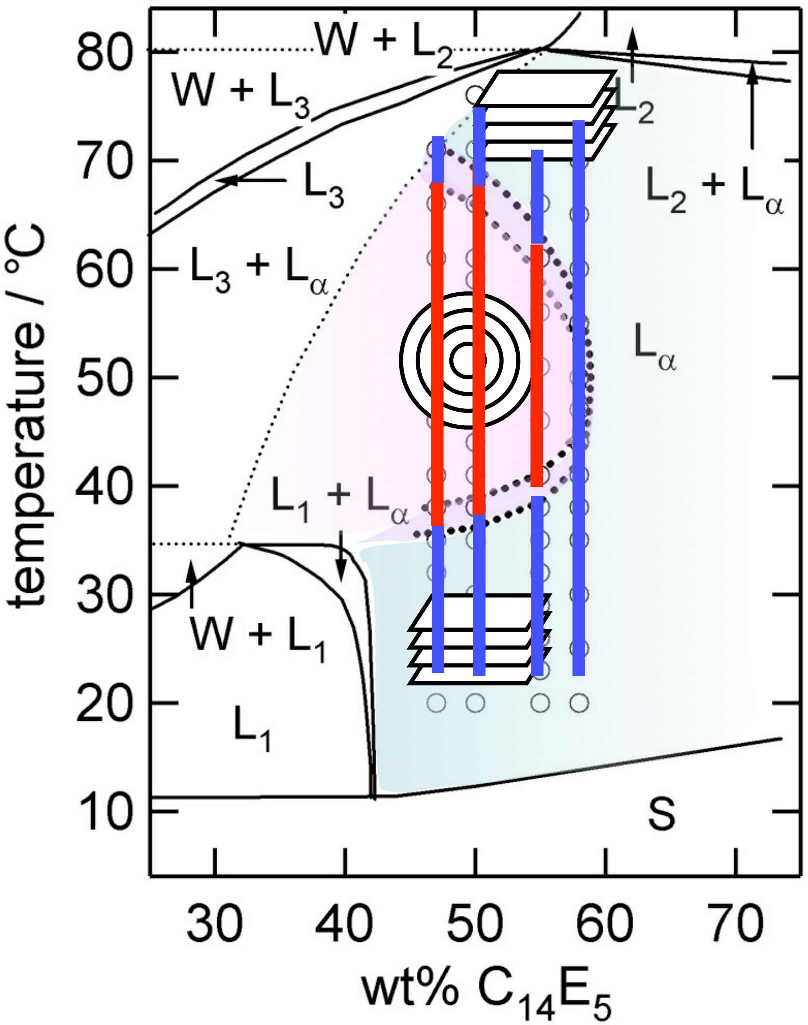

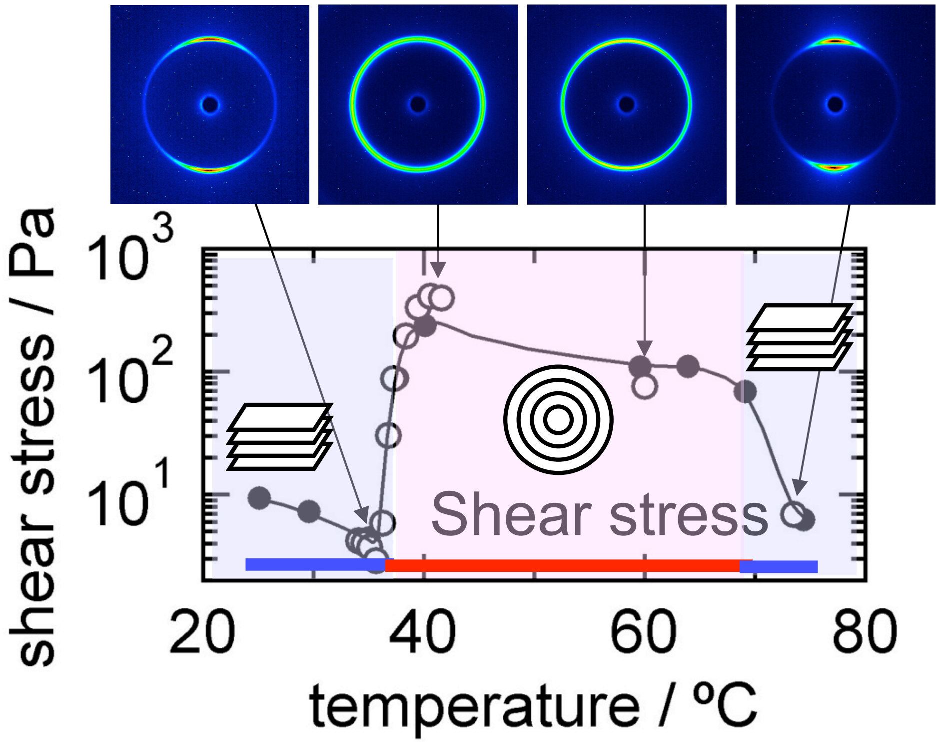

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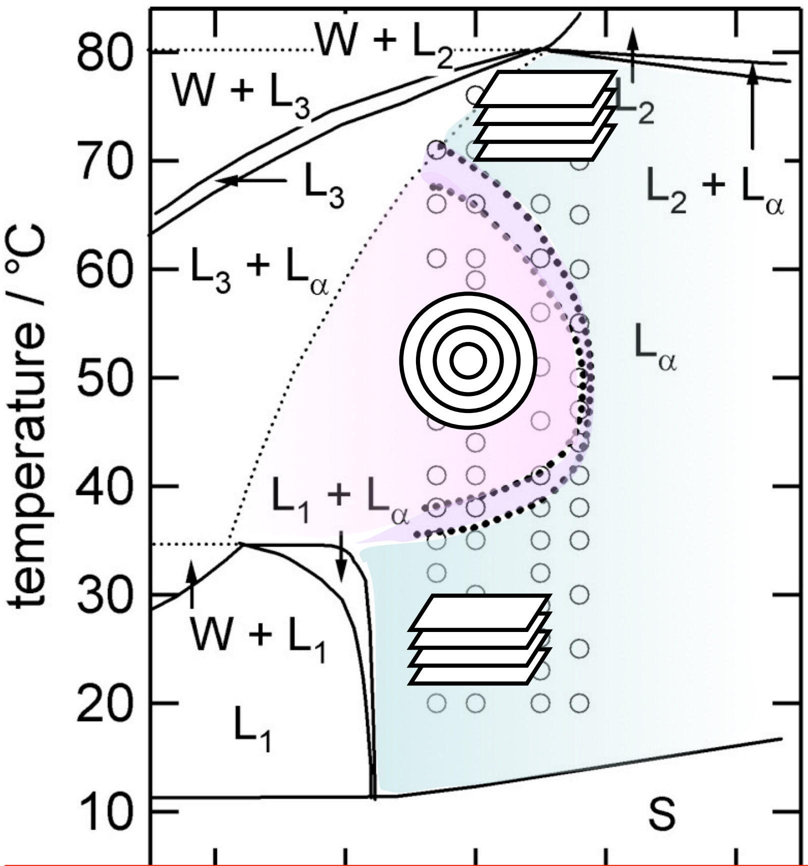
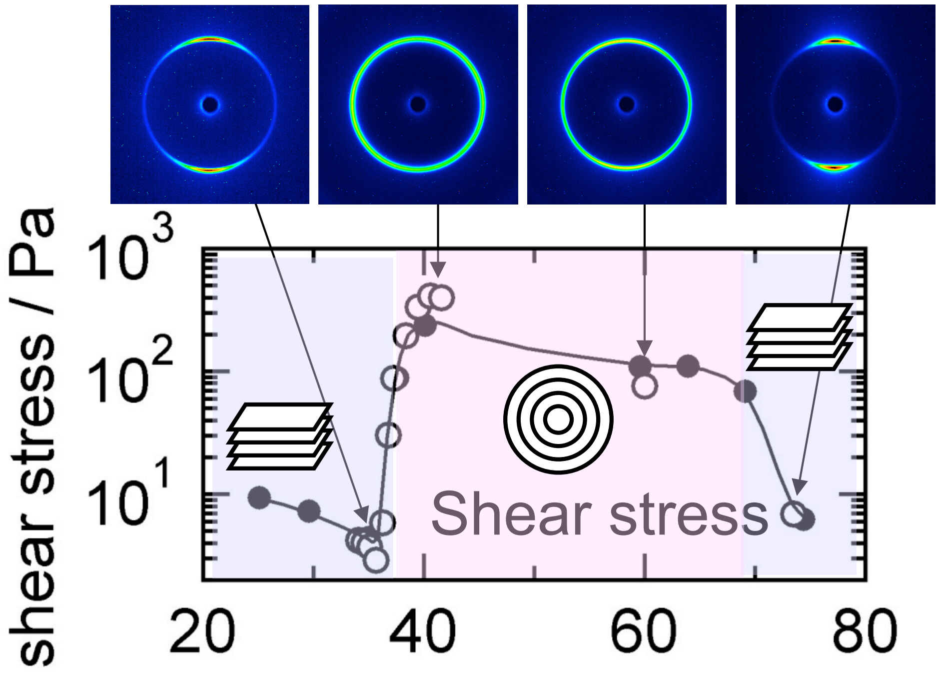


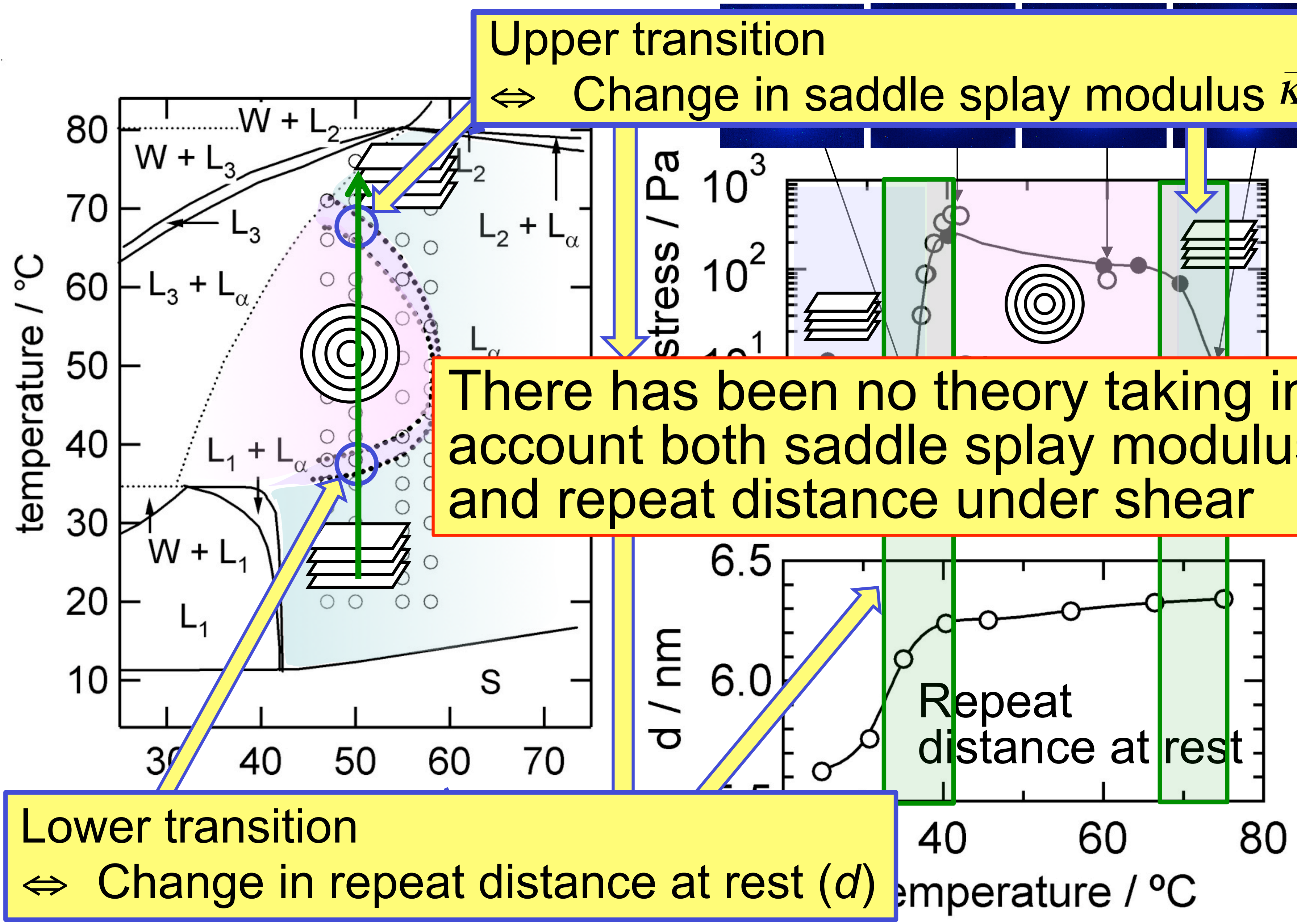


Lamellar-onion-lamellar transition (Reentrant lamellar-onion transition) with varying temperature

Closed region of the onion phase !

Useful system for clarifying mechanism of onion formation

Temperature Dependence of Shear Stress and 2-D SAXS Patterns for $C_{14}E_5$/Water System at 3 s^{-1}



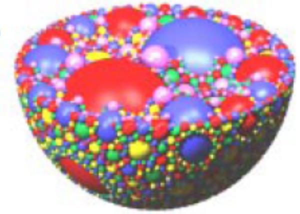
Upper transition
⇔ Change in saddle splay modulus $\bar{\kappa}$?

There has been no theory taking into account both saddle splay modulus and repeat distance under shear

Lower transition
⇔ Change in repeat distance at rest (d)

Theory for Stable Equilibrium Onion Phase

c)



L. Ramos et al., *Europhys. Lett.* **66**, 888 (2004).

Free energy of a symmetric bilayer
(relative to a flat state)

$$\frac{F}{A} = 2\kappa H^2 + \bar{\kappa} G + \frac{1}{4} c_1 H^4 + \frac{1}{4} c_2 G^2 + 2c_3 G H^2$$

A vesicle of radius r

$$F_{\text{shell}}(r) = 4\pi\tilde{\kappa} + \frac{\pi\tilde{c}}{r^2}$$

$$\tilde{\kappa} \equiv 2\kappa + \bar{\kappa}$$

$$\tilde{c} \equiv c_1 + c_2 + 8c_3$$

$F_{\text{onion}}(k)$ (an onion of raidus $R = kd$)

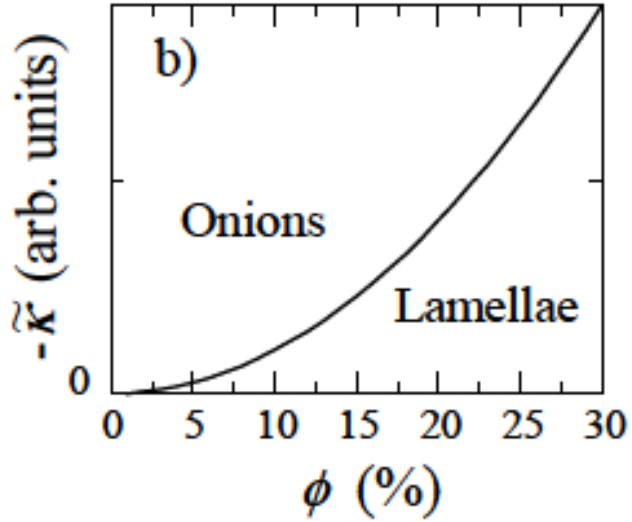
$$= \sum_{j=1}^{k} F_{\text{shell}}(r_j = jd) = \frac{4\pi\tilde{c}}{d^2}\left(k\frac{\tilde{\kappa}d^2}{\tilde{c}} + \sum_{j=1}^{k}\frac{1}{j^2}\right)$$

$$\frac{F_{\text{tot}}}{V} = \frac{1}{V}\sum_{k=1}^{k_{\max}} \bar{n}(k) F_{\text{onion}}(k) \rightarrow \text{Minimized over } k_{\max}$$

Apollonian distribution

Condition for the stable onion phase

$$-\tilde{\kappa} > \frac{0.86\,\tilde{c}}{d^2}$$



Theory for Stable Equilibrium Onion Phase (at Rest) [1)] and Reentrant Lamellar/Onion Transition under Shear

1) L. Ramos et al., *Europhys. Lett.* **66**, 888 (2004).

$$\tilde{\kappa} \equiv 2\kappa + \bar{\kappa}$$

κ : bending modulus of a bilayer
$\bar{\kappa}$: saddle splay modulus of a bilayer

$$\bar{\kappa} = 2\bar{\kappa}_m - 4H_{0m}\delta_{hc}\kappa_m$$

$\bar{\kappa}_m$: saddle splay modulus of a monolayer
H_{0m} : spontaneous curvature of a monolayer
δ_{hc} : thickness of a hydrophobic part of a monolayer

C_nE_m systems:

$$T\downarrow \;\Leftrightarrow\; H_0^m \uparrow \;\Leftrightarrow\; \tilde{\kappa}\downarrow \;\Leftrightarrow\; -\tilde{\kappa}\uparrow$$

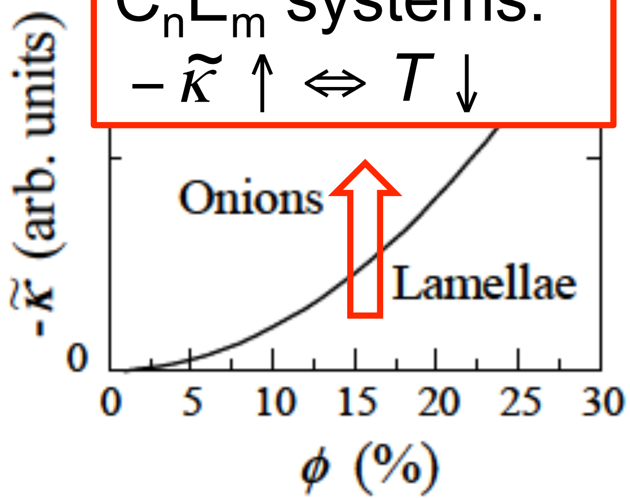
Condition for the stable onion phase

$$-\tilde{\kappa} > \frac{0.86\,\tilde{c}}{d^2} = \frac{0.86\,\tilde{c}}{\delta^2}\phi^2$$

$\phi = \dfrac{\delta}{d}$ volume fraction of bilayers

δ : thickess of a bilayer

C_nE_m systems:
$-\tilde{\kappa}\uparrow \Leftrightarrow T\downarrow$



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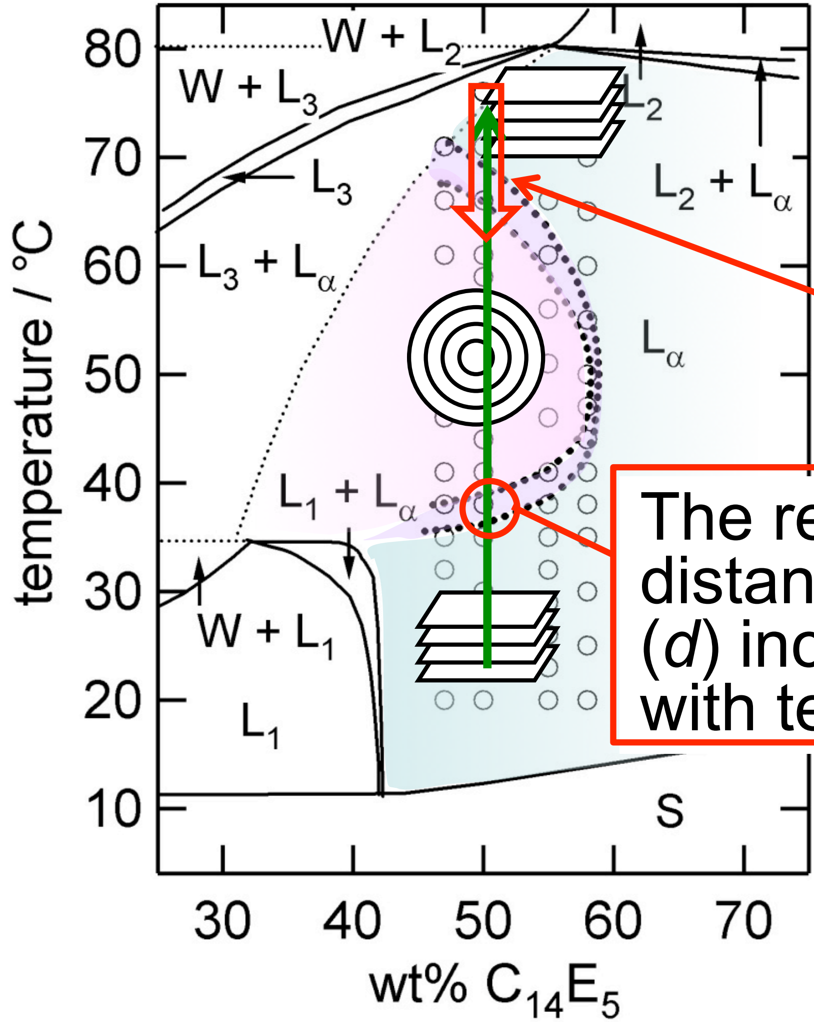

The repeat distance at rest (d) increases with temperature

Condition for the stable onion phase

$$-\tilde{\kappa} > \frac{0.86\,\tilde{c}}{d^2} = \frac{0.86\,\tilde{c}}{\delta^2}\phi^2$$

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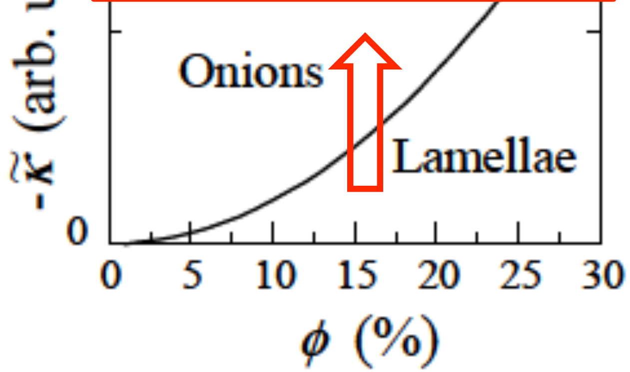


Theory for Stable Equilibrium Onion Phase (at Rest) and Reentrant Lamellar/Onion Transition under Shear

$$-\tilde{\kappa} > \frac{0.86\,\tilde{c}}{d^2}$$ ← L. Ramos et al. (2004)

$\tilde{c} \approx k_B T \delta^2$ δ : thickness of a bilayer

$$\frac{\tilde{\kappa}}{k_B T} < -c'\left(\frac{\delta}{d}\right)^2$$

c': numerical factor of order 1

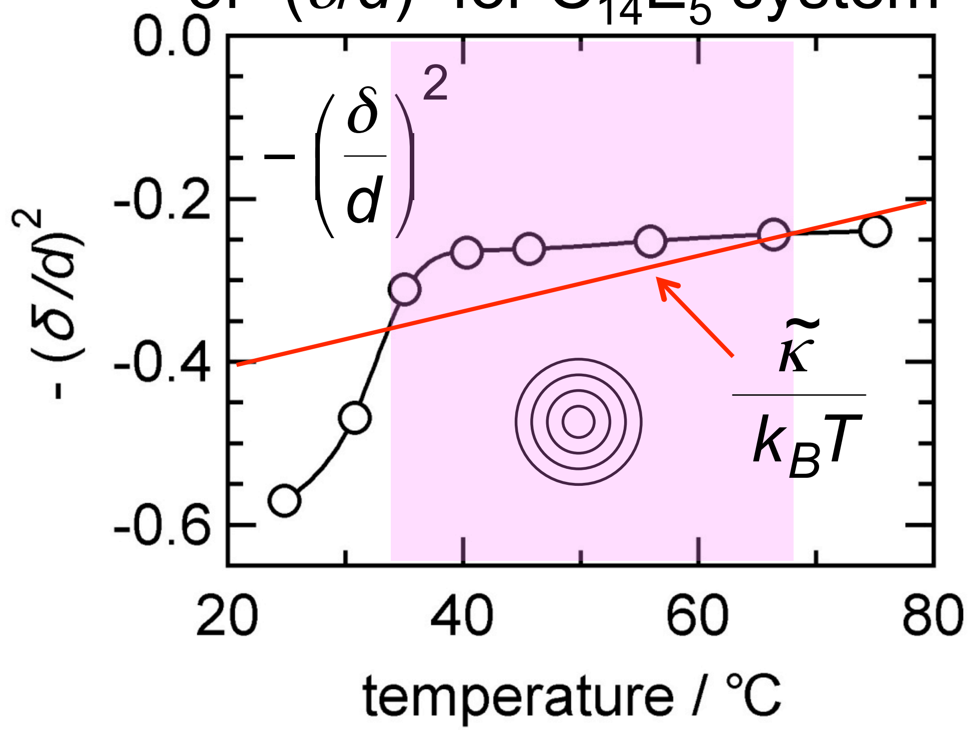
C_nE_m systems: $\tilde{\kappa} \downarrow \Leftrightarrow T \downarrow$

$\tilde{\kappa} \equiv 2\kappa + \bar{\kappa}$ $(\tilde{\kappa} < 0)$

κ : bending modulus of a bilayer

$\bar{\kappa}$: saddle spray modulus of a bilayer

Temperature dependence of $-(\delta/d)^2$ for $C_{14}E_5$ system



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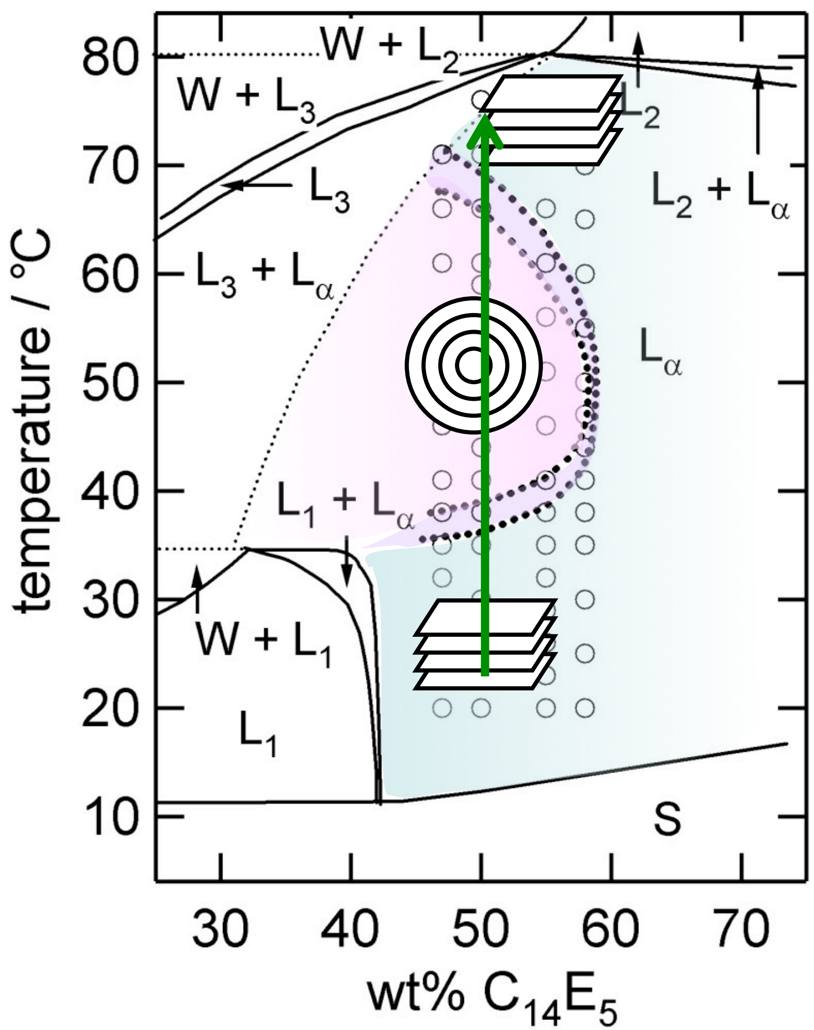

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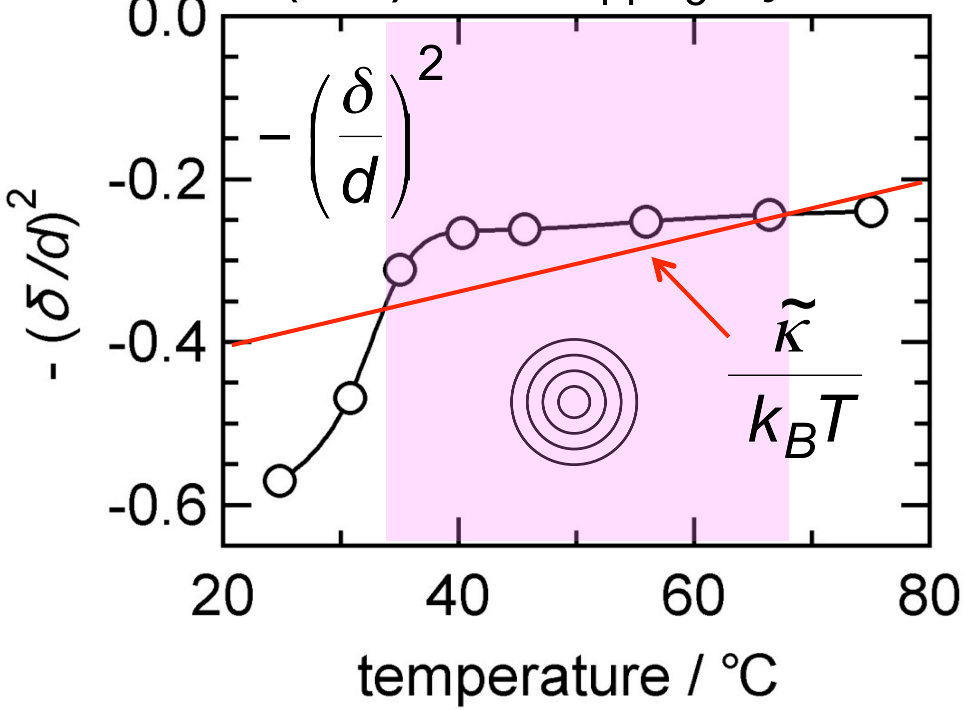

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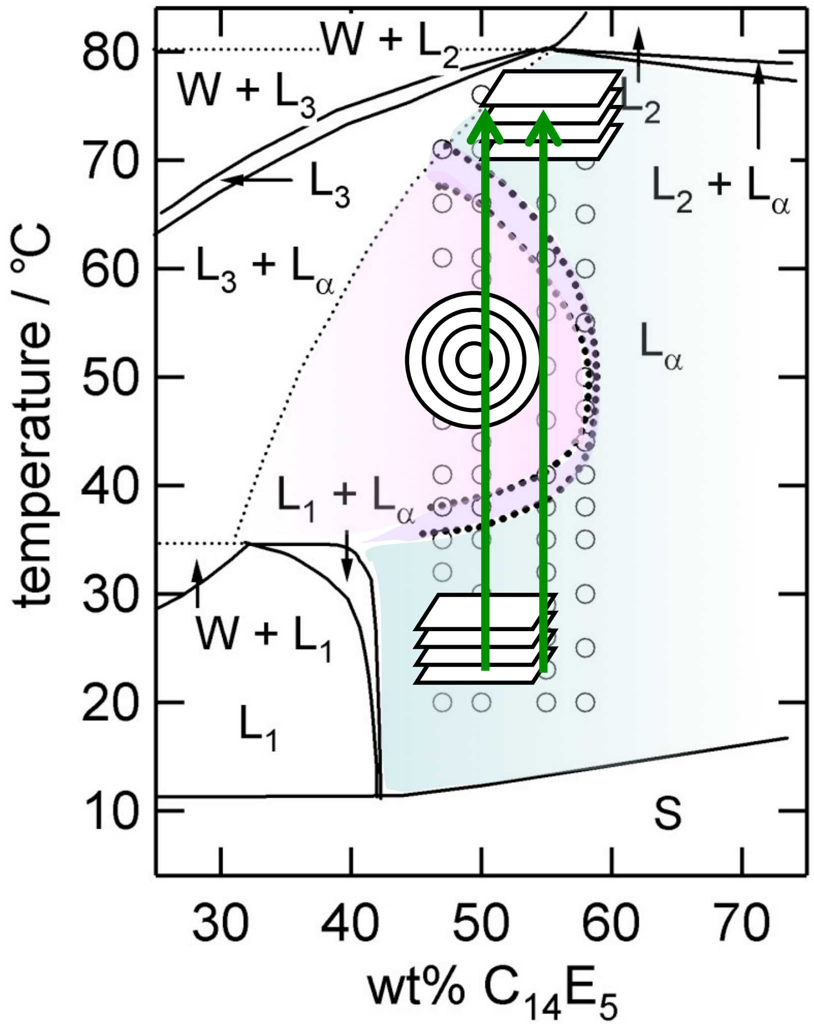

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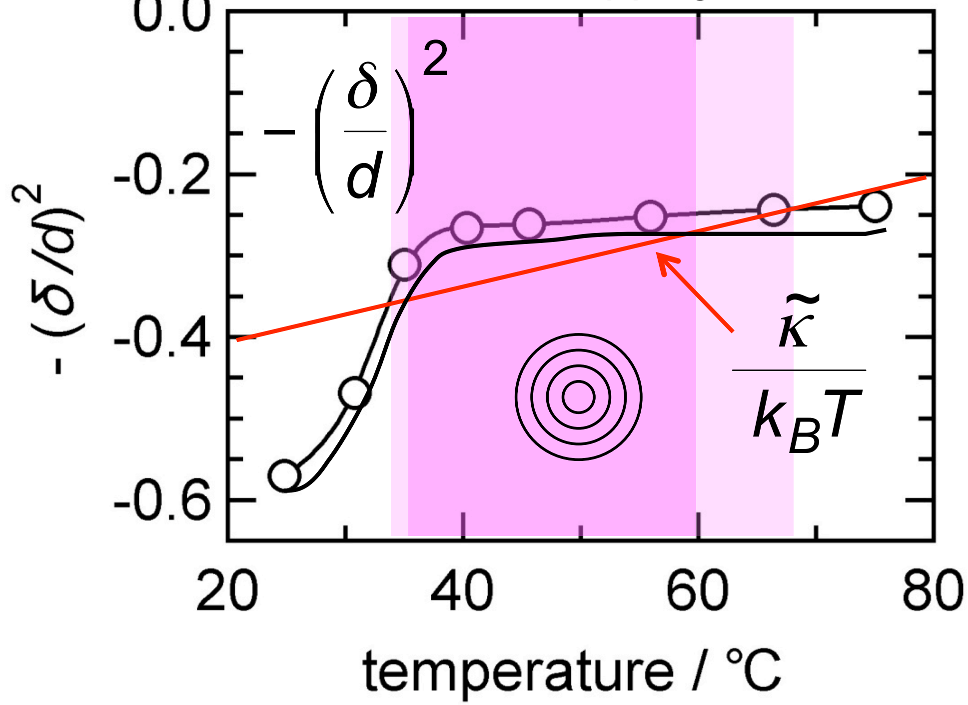
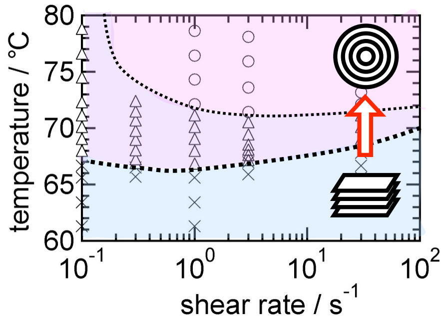
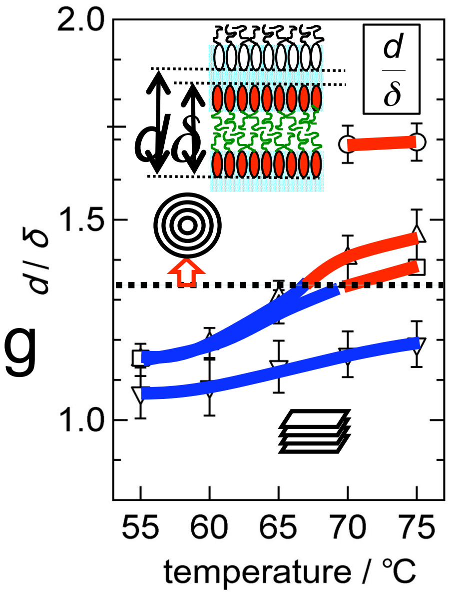


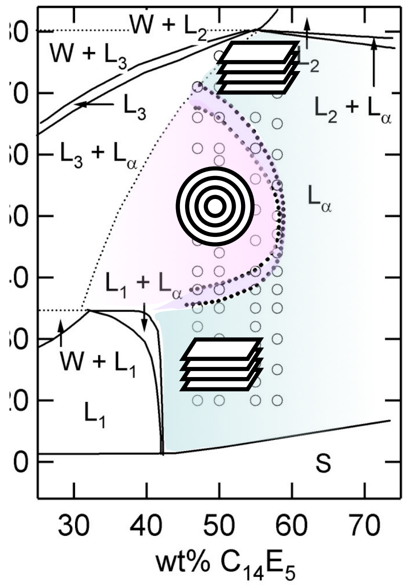
Summary

1. Lamellar-to-onion transition with increasing temperature has been found at a constant shear rate in nonionic surfactant $C_{16}E_7$/water system by using Rheo-SALS and Rheo-SAXS.



2. Increase in the repeat distance at rest is necessary for the lamellar-to-onion transition with increasing temperature.





3. The orientation of lamellae along the velocity gradient direction is suddenly enhanced just before the transition.

4. Reentrant lamellar-onion transition has been found in $C_{14}E_5$/water system. This system is considered to be useful to study the conditions and mechanism of onion formation.