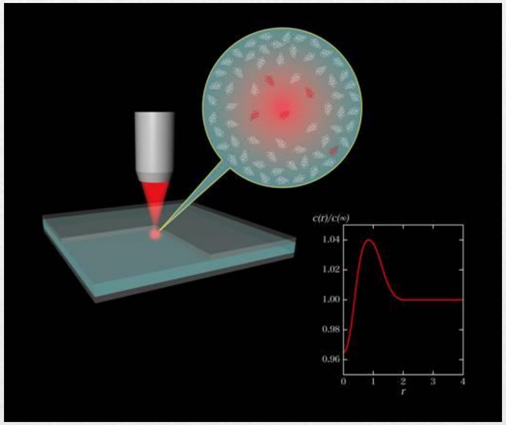
MIMS/CMMA Seminar

Minisymposium on active matter

明治大学 MEIJI UNIVERSITY

MIMS

Ring formation by competition between entropic effects and thermophoresis



Kenta Odagiri

Meiji Institute for Advanced Study of Mathematical Sciences (MIMS)

2013.10.18 (Fri)

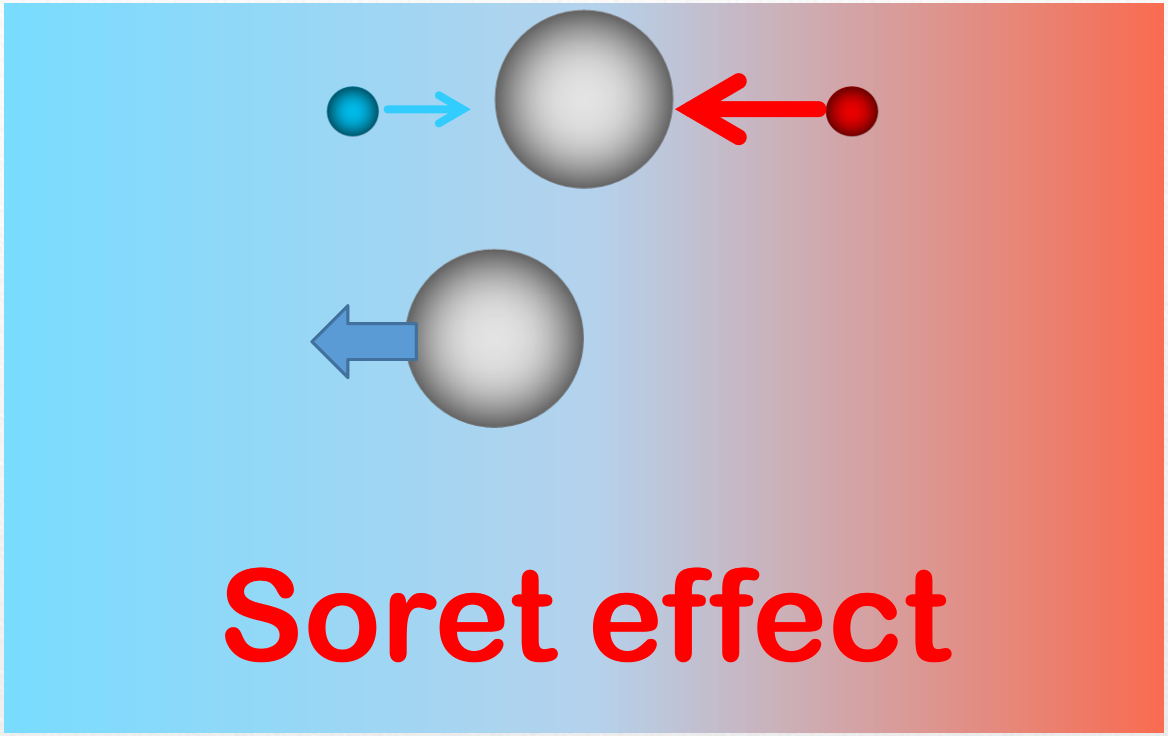
Collaboration with

K. Seki (AIST)

K. Kudo (Ochanomizu University)

Thermopheresis

Cold



Hot

Particle motion induced by temperature gradients

diffusion

flow $\vec{j} = -D_B\left(\vec{\nabla}c + cS_T\vec{\nabla}T\right)$

thermophoresis

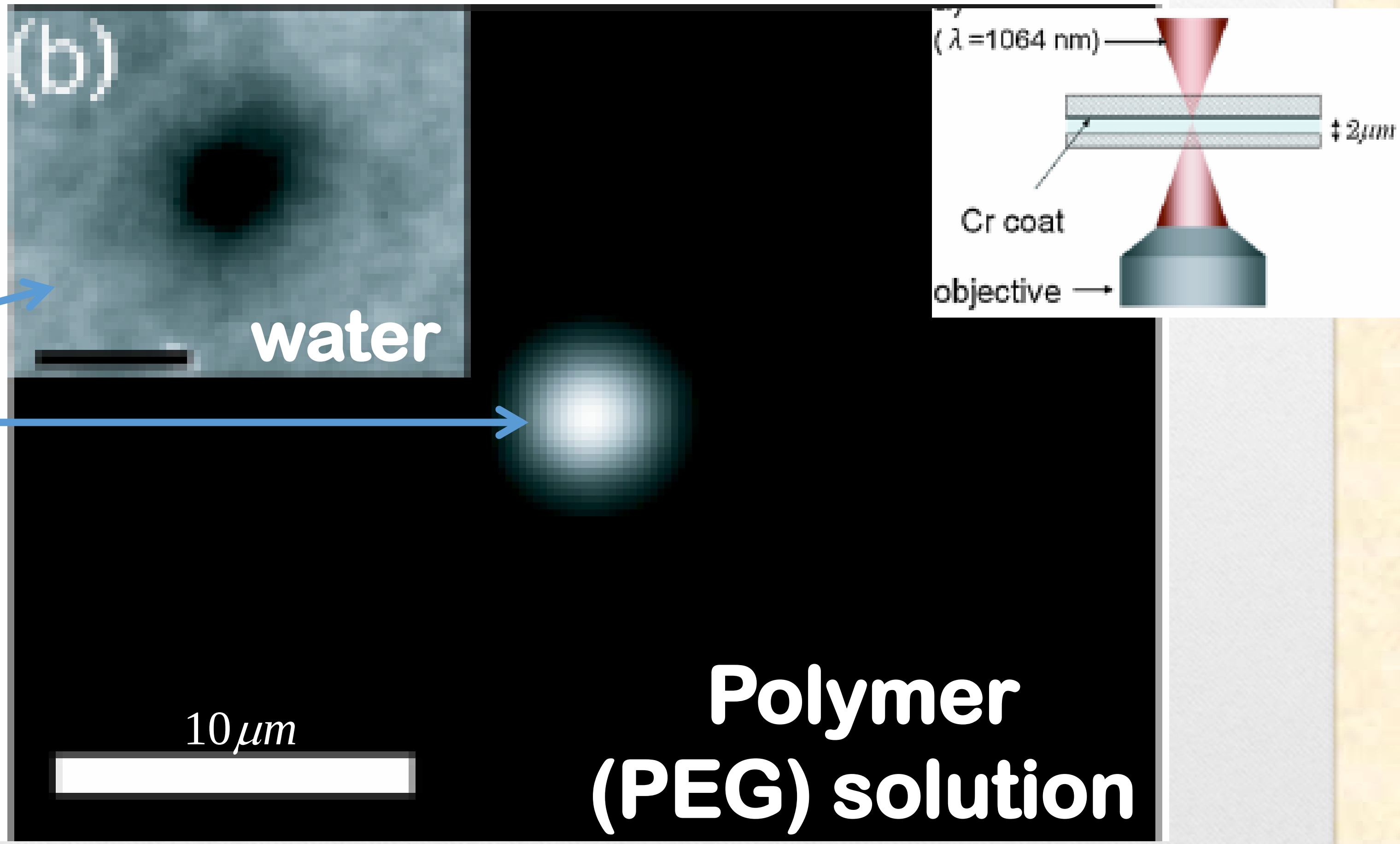
$$S_T \equiv \frac{D_T}{D_B}$$

Soret coefficient

D_B : Diffusion constant D_T : Thermal diffusion constant

Colloid aggregation in PEG solution under temperature gradient

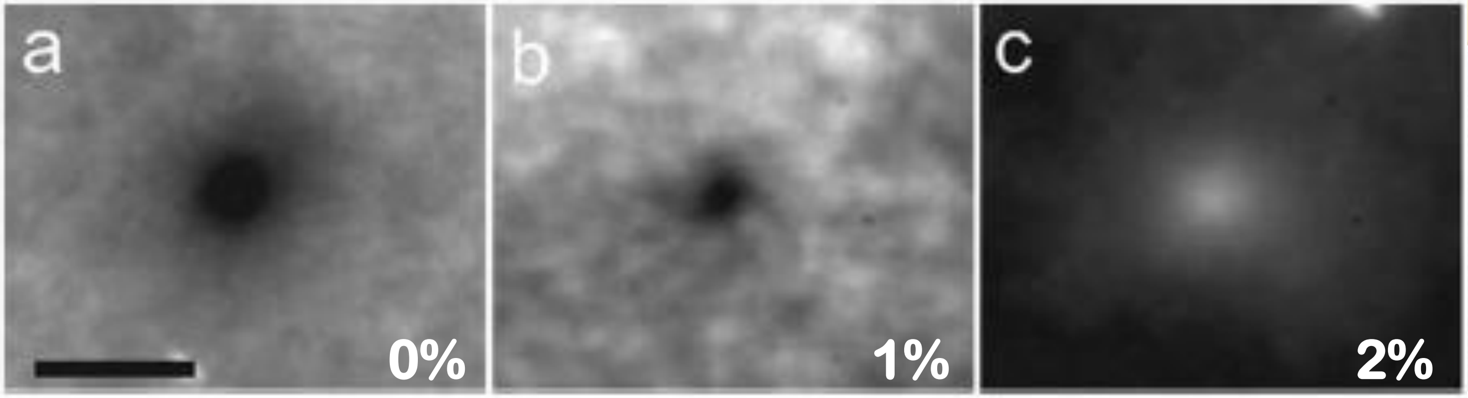
Polystyrene beads (100 nm)

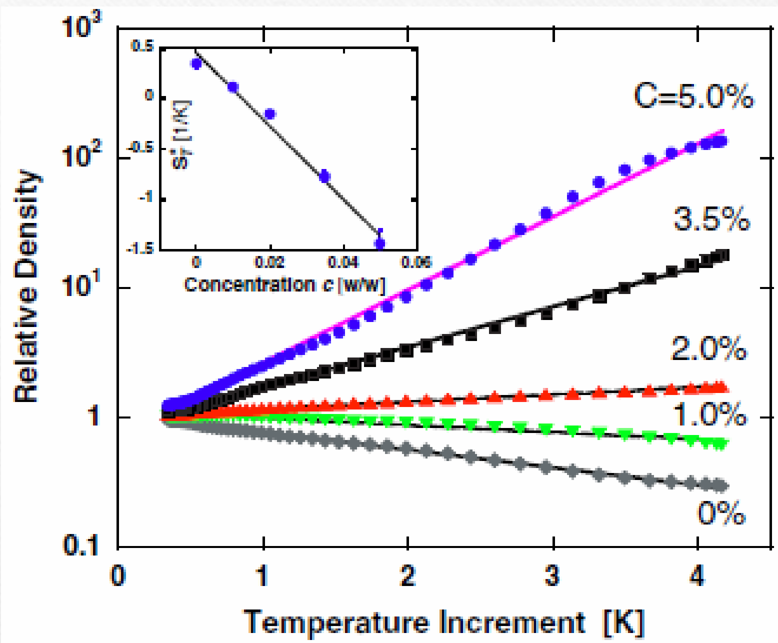


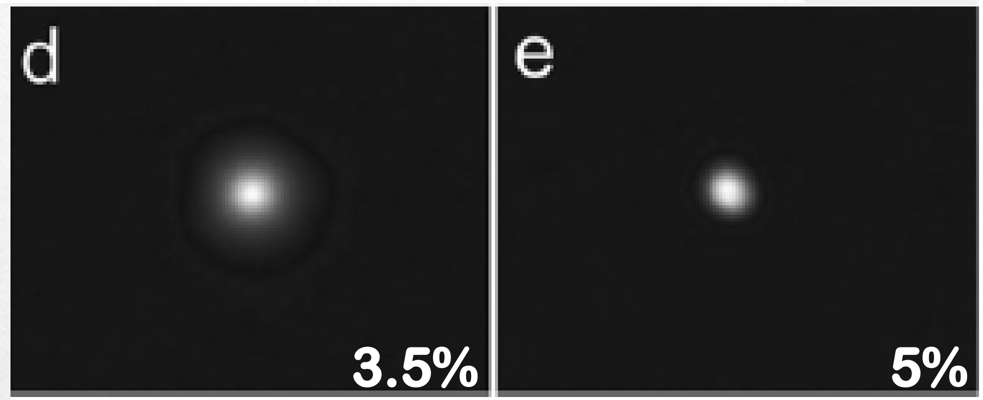
PEG= PolyEthylen Glycol

Aggregation of colloids driven by temperature gradient induced by laser radiation

H. Jiang, H. Wada, N. Yoshinaga, and M. Sano, PRL **102**, 208301 (2009).







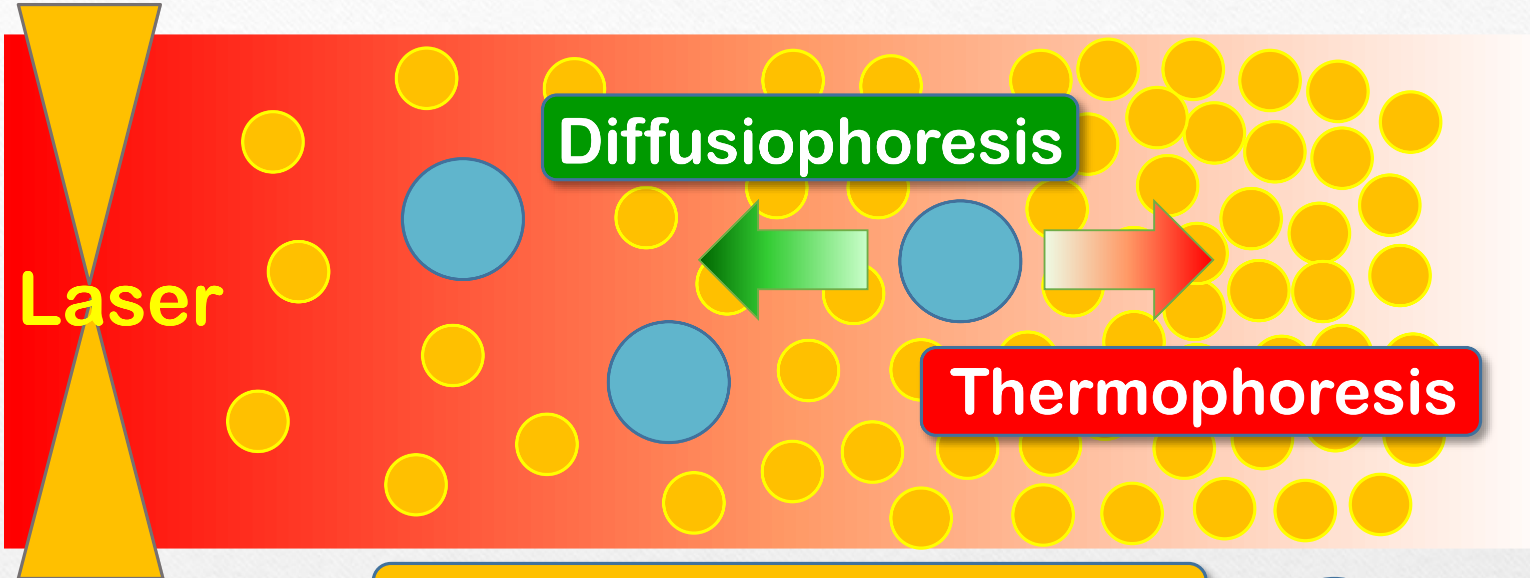
Steady state

$$\vec{\nabla} c = -c \mathbf{S_T} \vec{\nabla} T$$

The Soret coefficient can be controlled by changing PEG concentration

H. Jiang, H. Wada,N. Yoshinaga, and M. Sano, PRL **102**, 208301 (2009).

Mechanism of colloid aggregation



Temperature gradient

PEG's thermophoresis

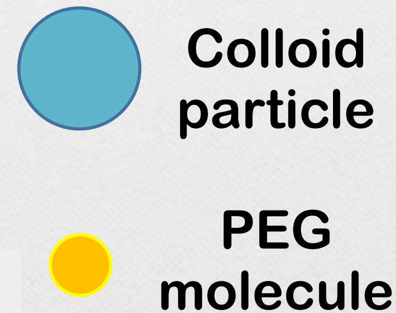
PEG's concentration gradient

Hydrodynamic interaction

Colloid's diffusiophoresis

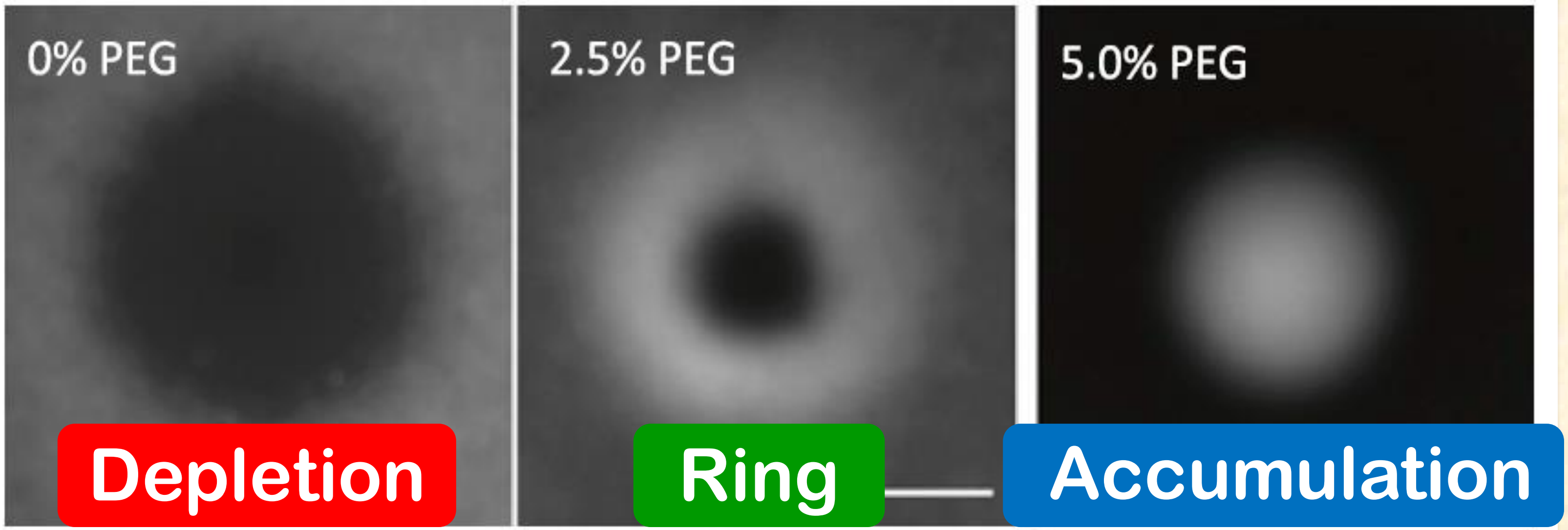
Excluded volume interaction

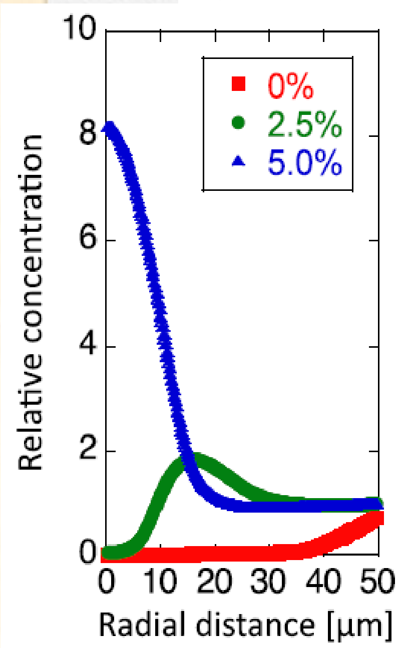
Colloid aggregation

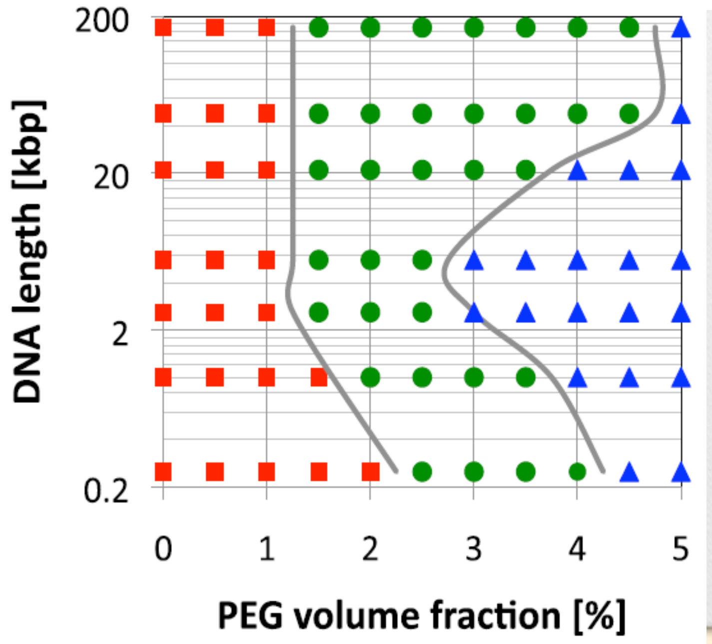


Three different localized patterns

T4DNA (166kbp)



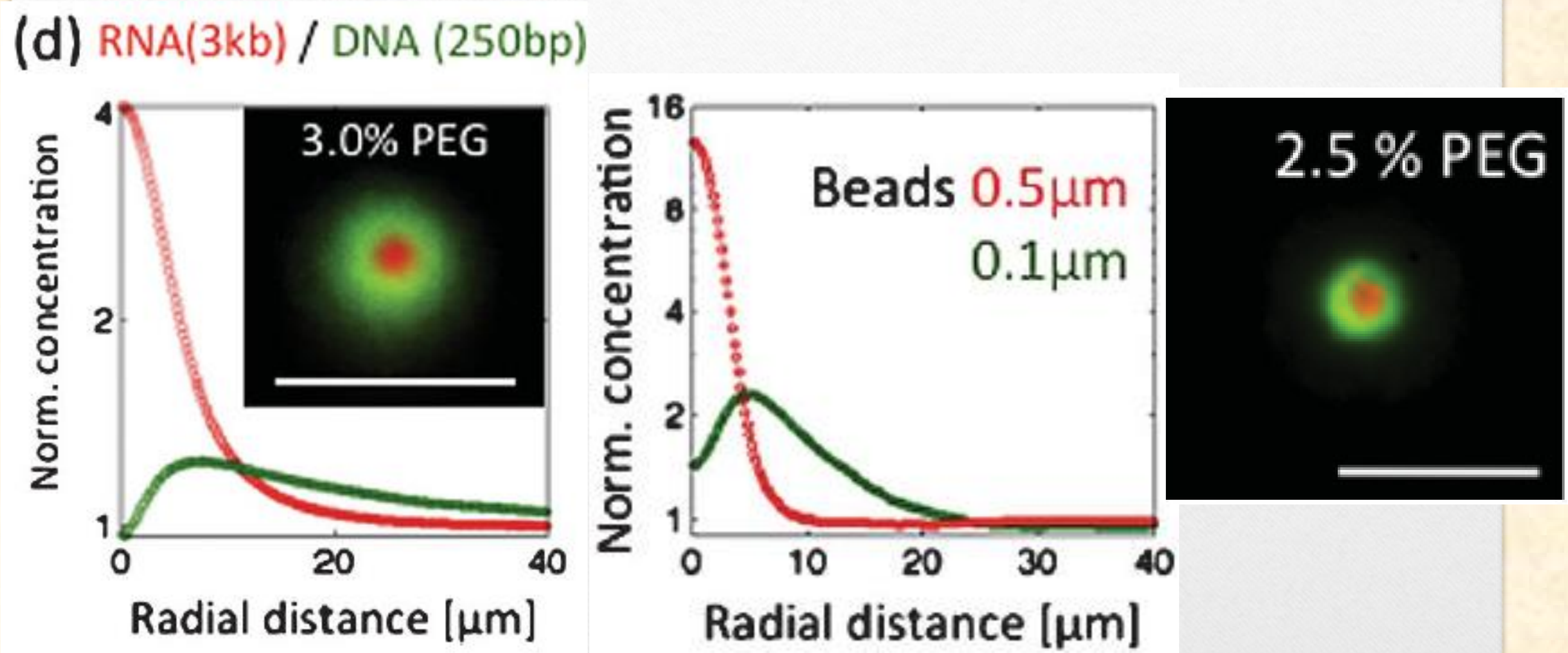




Three different phases appear depending on **PEG concentration** and **DNA length**

Y. T. Maeda, T.Tlusty, and A. Libchaber, PNAS **109**, 17972-77 (2012).

Size-dependent localized patterns



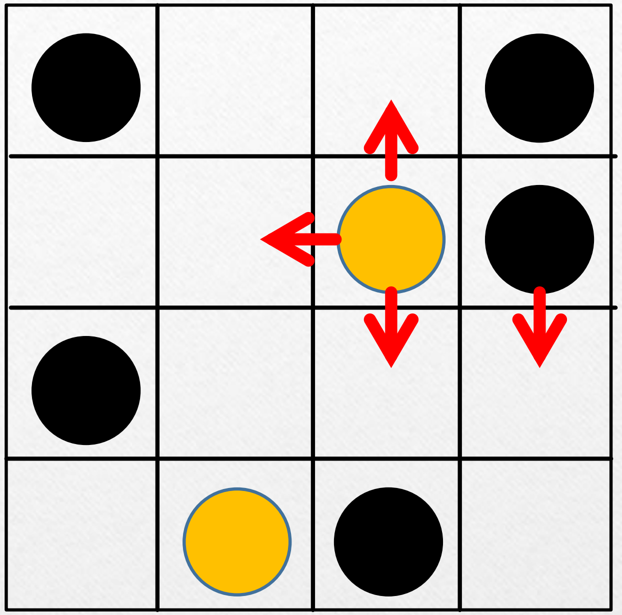
Larger colloid particles (Longer DNA chains) tend to accumulate at the center(hot) area

Mixture of different size of colloid particles can be separated

Y. T. Maeda, A. Buguin, and A. Libchaber, PRL **107**, 038301 (2011).

Model

Diffusion in the presence of excluded volume effect



concentration

Colloidal particle $c(\vec{r},t)$

Polymer molecule $p(\vec{r},t)$

Excluded volume effect

Mixing Entropy

$$W = \frac{N_{tot}!}{N_c!N_p!\left(N_{tot}-N_c-N_p\right)!}$$

$$\ln N! \simeq N\ln N - N$$

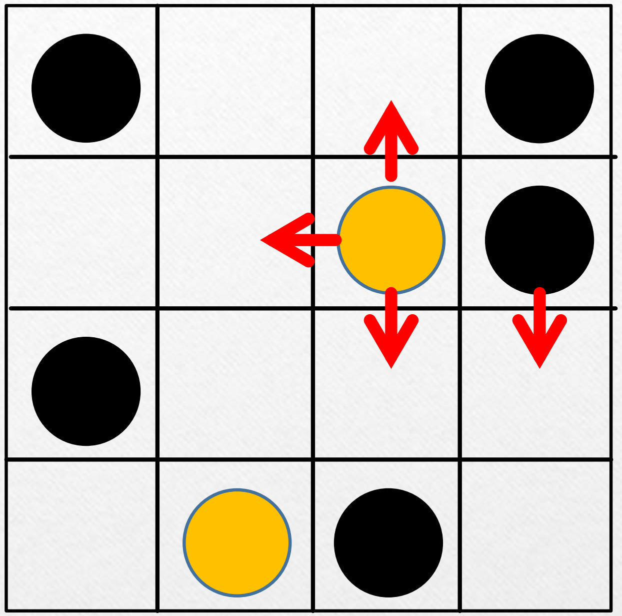
$$c = \frac{N_c}{N_{tot}}, \quad p = \frac{N_p}{N_{tot}}$$

$$S = \int d\vec{r}\, k_B \ln W$$

$$= \int k_B d\vec{r}\left[-c\ln c - p\ln p - (1-c-p)\ln(1-c-p)\right]$$

Model

Diffusion in the presence of excluded volume effect



concentration

Colloidal particle $c(\vec{r},t)$

Polymer molecule $p(\vec{r},t)$

Excluded volume effect

Mixing Entropy

$$S=\int k_B d\vec{r}\left[-c\ln c-p\ln p-(1-c-p)\ln(1-c-p)\right]$$

Chemical potential of colloids

$$\mu^c=\frac{\delta(-TS)}{\delta c}$$

Eq. of continuity

$$\frac{\partial c}{\partial t}+\vec{\nabla}\cdot\vec{j}_0^c=0$$

Current of colloids

$$\vec{j}_0^c=-L\vec{\nabla}\frac{\mu^c}{k_B T}$$

Onsager coefficient

$$L=D_B^c c(1-c-p)$$

$$\frac{\partial}{\partial t}c(\vec{r},t)=\vec{\nabla}\cdot D_B^c\left[\left(1-p(\vec{r},t)\right)\vec{\nabla}c(\vec{r},t)+c(\vec{r},t)\vec{\nabla}p(\vec{r},t)\right]$$

Model

Introduction of Soret effect

Current of colloidal particles without polymers

$$\vec{j}^{\,c} = -D_B^c \vec{\nabla} c - c D_T^c \vec{\nabla} T = -D_B^c \left(\vec{\nabla} c - c \boldsymbol{S_T^c} \vec{\nabla} T \right)$$

Soret coefficient of colloid

$$S_T^c \equiv \frac{D_T^c}{D_B^c}$$

T : Temperature

D_B^c : Diffusion constant of colloids

D_T^c : Thermal diffusion constant

Colloidal diffusion in the polymer solution under temperature gradient

$$\frac{\partial}{\partial t} c(\vec{r},t) = \vec{\nabla} \cdot D_B^c \left[\left(1 - p(\vec{r},t)\right) \left(\vec{\nabla} c(\vec{r},t) + c(\vec{r},t) S_T^c \vec{\nabla} T(\vec{r},t) \right) + c(\vec{r},t) \vec{\nabla} p(\vec{r},t) \right]$$

Steady-state distribution of colloids

In the steady state $\frac{\partial}{\partial t}c(r,t)=0$

$$\frac{c(r)}{c(\infty)}=\frac{1-p(r)}{1-p(\infty)}\exp\left[-S_T^c\Delta T(r)\right] \qquad \Delta T(r)=T(r)-T(\infty)$$

Influence of colloids (minor species) on the concentration of polymers (major species) can be ignored

$$p(r)=p(\infty)\exp\left[-S_T^p\Delta T(r)\right]$$

Steady-state distribution of colloids

$$\frac{c(r)}{c(\infty)}=\exp\left[-S_T^c\Delta T(r)\right]\frac{1-p(\infty)\exp\left[-S_T^p\Delta T(r)\right]}{1-p(\infty)}$$

Effective Soret coefficient

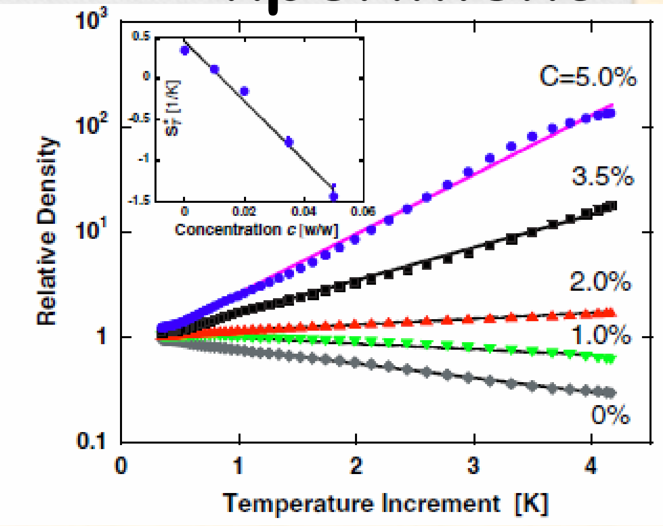
When $S_T^p \Delta T \ll 1$

$$\frac{c(r)}{c(\infty)} \approx \exp\left[-\left(S_T^c - \frac{p(\infty)}{1-p(\infty)} S_T^p\right)\Delta T(r)\right]$$

Effective Soret coefficient

$$S_T^{c*} \equiv S_T^c - \frac{p(\infty)}{1-p(\infty)} S_T^p$$

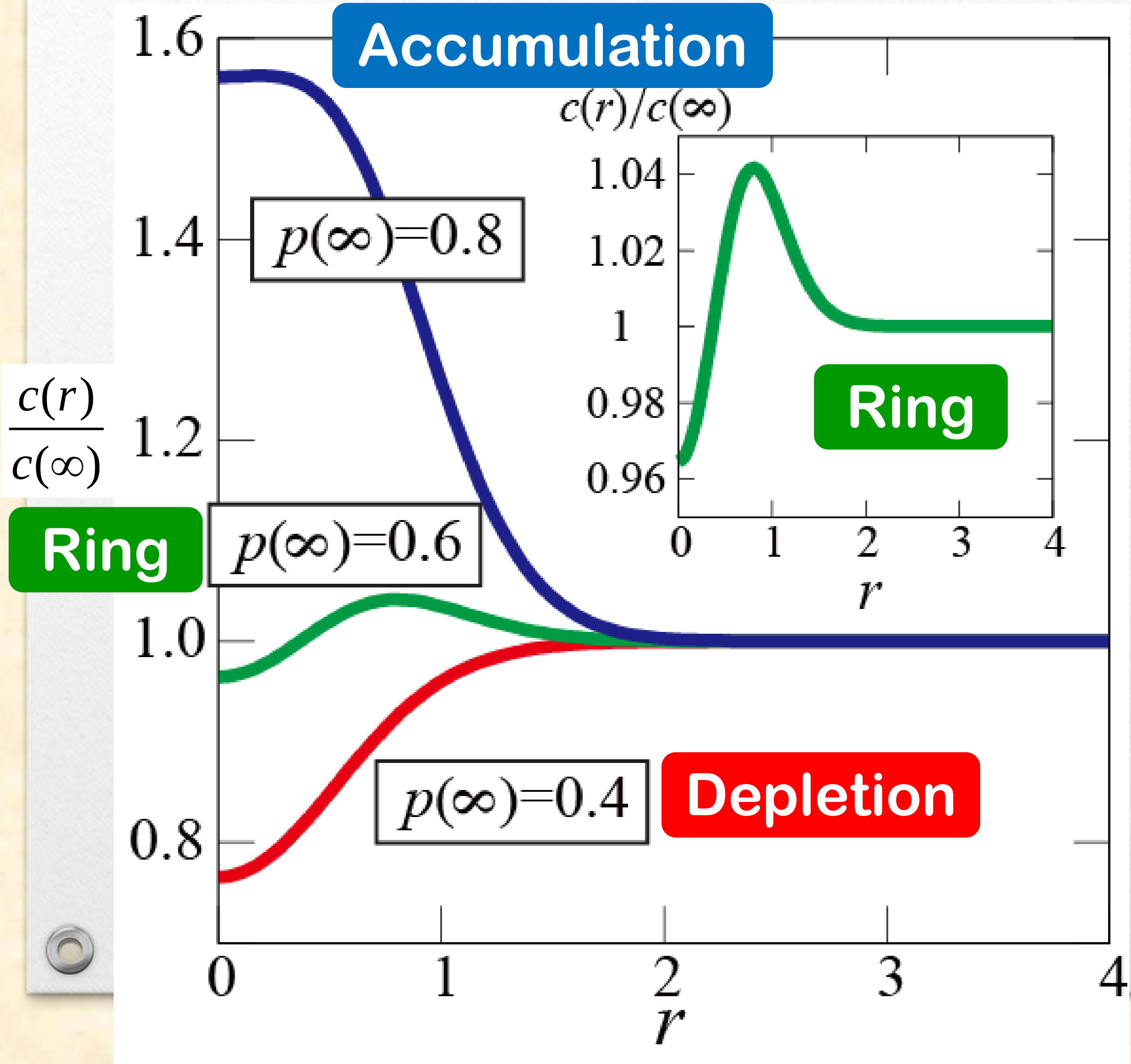
Experiment



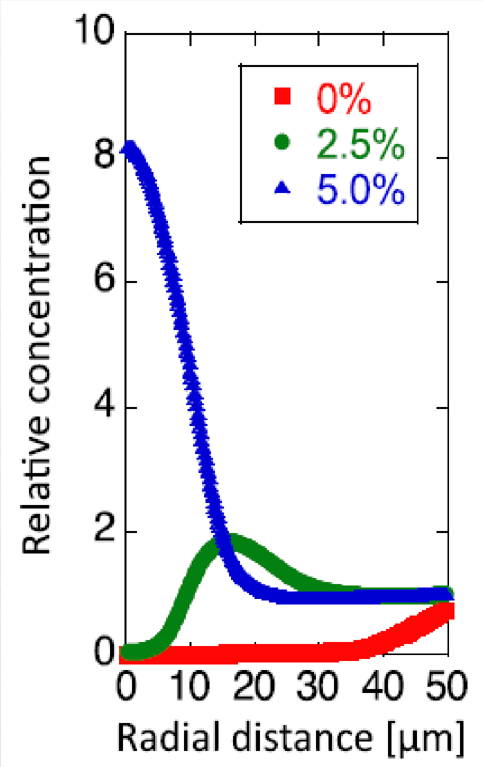
The effective Soret coefficient decreases as the concentration of polymers increases.

Three different phases

$\Delta T(r)$ can be well approximated by $\Delta T(r) = T(0)\exp\left[-r^2/(2\sigma^2)\right]$



Experiment



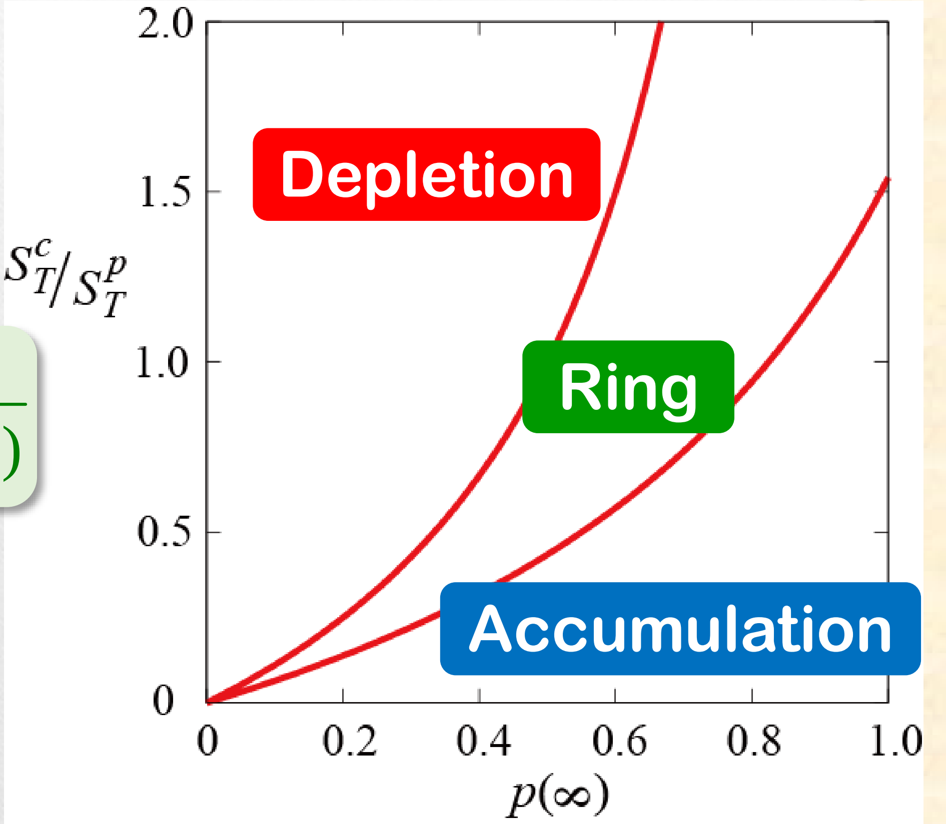
Phase diagram

$$\frac{\partial}{\partial r}c(r) = \left(-S_T^c + \frac{p(r)}{1-p(r)}S_T^p\right)c(r)\frac{\partial \Delta T(r)}{\partial r} \qquad c(r) \geq 0 \qquad \frac{\partial \Delta T(r)}{\partial r} < 0$$

Accumulation $\frac{S_T^c}{S_T^p} < \frac{p(0)}{1-p(0)}$

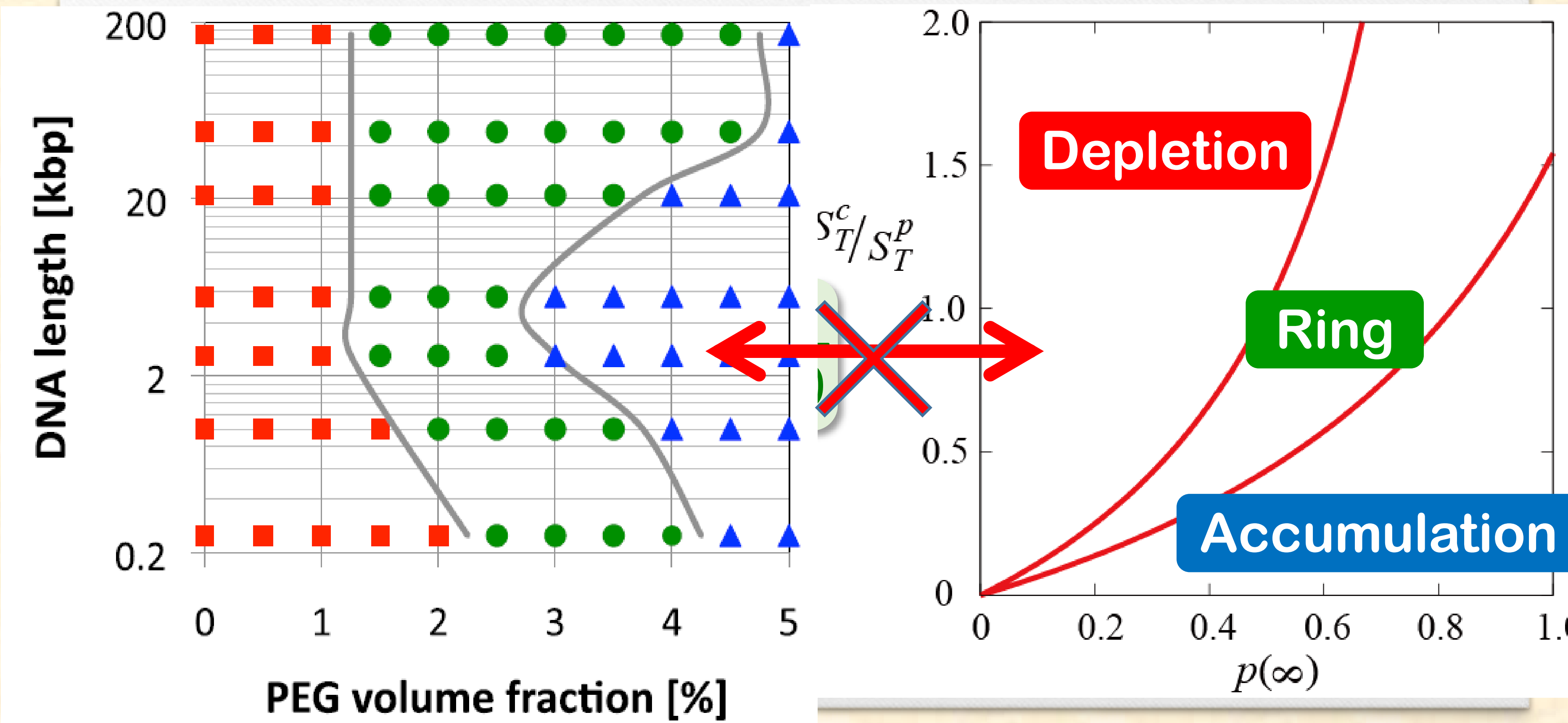
Ring $\frac{p(0)}{1-p(0)} < \frac{S_T^c}{S_T^p} < \frac{p(\infty)}{1-p(\infty)}$

Depletion $\frac{S_T^c}{S_T^p} > \frac{p(\infty)}{1-p(\infty)}$

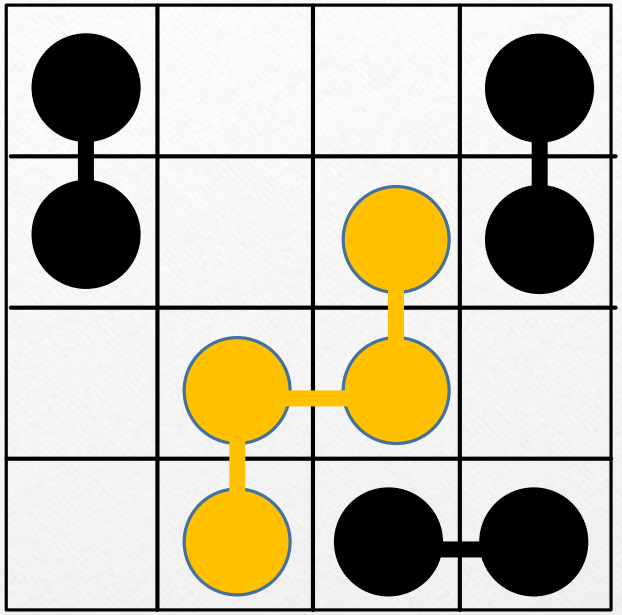


Phase diagram

$$\frac{\partial}{\partial r}c(r) = \left(-S_T^c + \frac{p(r)}{1-p(r)}S_T^p\right)c(r)\frac{\partial \Delta T(r)}{\partial r} \qquad c(r) \geq 0 \qquad \frac{\partial \Delta T(r)}{\partial r} < 0$$



Chain-like molecular model



	concentration	chain length
Colloidal particle	$c(\vec{r},t)$	m_c
Polymer molecule	$p(\vec{r},t)$	m_p

Entropy

$$S=\int k_B d\vec{r}\left[-c\ln(m_c c)-p\ln(m_p p)-\left(1-m_c c-m_p p\right)\ln\left(1-m_c c-m_p p\right)\right]$$

In the limit of $m_c{}^2 c(\vec{r},t)\ll m_p p(\vec{r},t)$

Colloidal diffusion with chain-like molecular model

$$\frac{\partial}{\partial t}c(\vec{r},t)=\vec{\nabla}\cdot D_B^c\left[\left(1-m_p p(\vec{r},t)\right)\left(\vec{\nabla}c(\vec{r},t)+c(\vec{r},t)S_T^c\vec{\nabla}T(\vec{r},t)\right)+m_c m_p c(\vec{r},t)\vec{\nabla}p(\vec{r},t)\right]$$

Steady-state distribution of colloids

In the steady state $\frac{\partial}{\partial t}c(r,t)=0$

$$\frac{c(r)}{c(\infty)}=\left[\frac{1-m_p p(r)}{1-m_p p(\infty)}\right]^{m_c}\exp\left[-S_T^c\Delta T(r)\right] \qquad \Delta T(r)=T(r)-T(\infty)$$

Influence of colloids (minor species) on the concentration of polymers (major species) can be ignored

$$p(r)=p(\infty)\exp\left[-S_T^p\Delta T(r)\right]$$

Steady-state distribution of colloids with chain-like molecular model

$$\frac{c(r)}{c(\infty)}=\exp\left[-S_T^c\Delta T(r)\right]\left(\frac{1-m_p p(\infty)\exp\left[-S_T^p\Delta T(r)\right]}{1-m_p p(\infty)}\right)^{m_c}$$

Effective Soret coefficient

In general, the Soret coefficient S_T^c and the chain length m_c depends on the radius of gyration R_g .

$$S_T^c \sim R_g^{\beta}$$

$$m_c \sim R_g^{\gamma}$$

$$\frac{1}{m_c}\frac{S_T^c}{S_T^p} = bR_g^{\beta-\gamma}$$

Effective Soret coefficient

$$S_T^{c*} \equiv S_T^c\left(1-\frac{m_p p(\infty)}{1-m_p p(\infty)}\frac{R_g^{\gamma-\beta}}{b}\right)$$

$$\frac{\partial}{\partial r}c(r) = \left(-S_T^c + m_c\frac{m_p p(r)}{1-m_p p(r)}S_T^p\right)c(r)\frac{\partial \Delta T(r)}{\partial r}$$

Accumulation

$$\frac{m_p p(0)}{1-m_p p(0)} < bR_g^{\beta-\gamma}$$

Ring

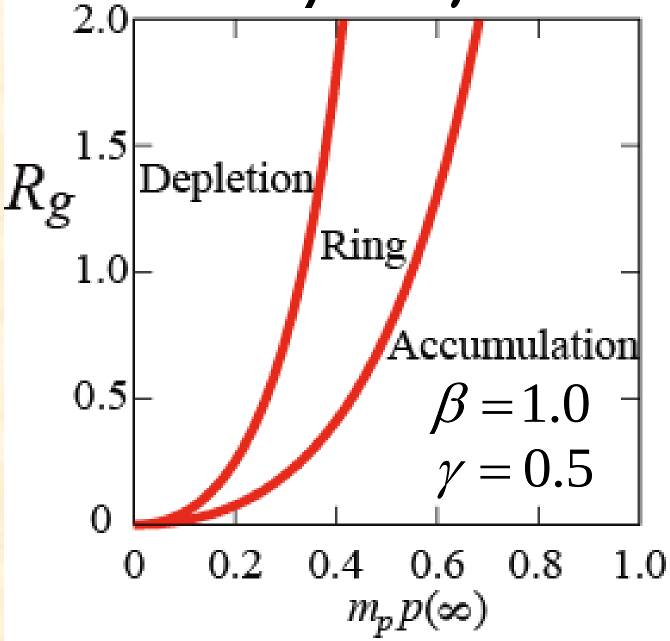
$$\frac{m_p p(0)}{1-m_p p(0)} < bR_g^{\beta-\gamma} < \frac{m_p p(\infty)}{1-m_p p(\infty)}$$

Depletion

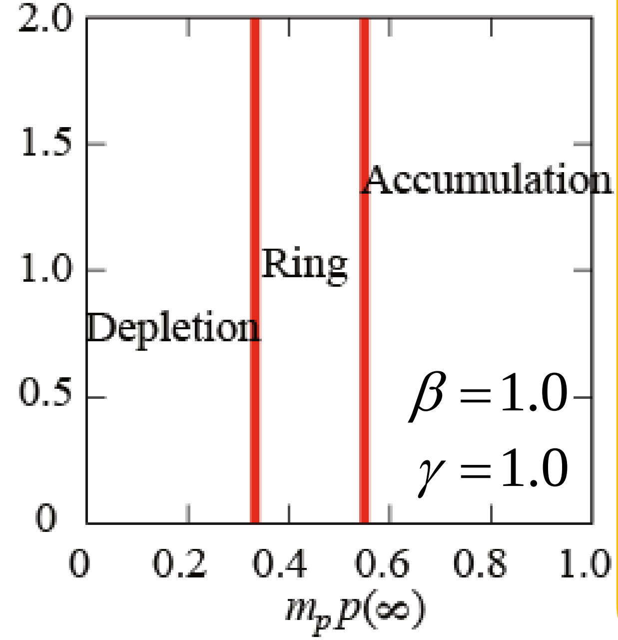
$$\frac{m_p p(\infty)}{1-m_p p(\infty)} < bR_g^{\beta-\gamma}$$

Phase diagram

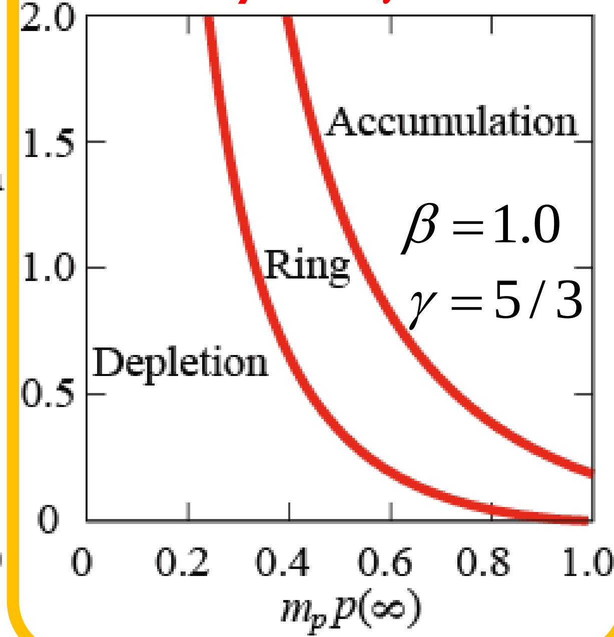
$\beta > \gamma$



$\beta = \gamma$



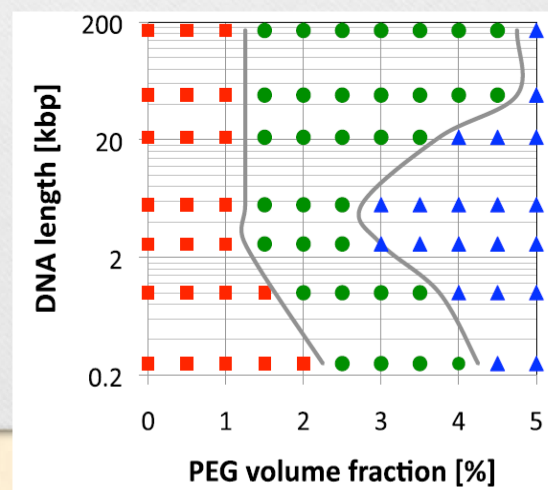
$\beta < \gamma$



$$S_T^c \sim R_g$$

$$m_c \sim R_g^{\frac{5}{3}}$$

3D excluded volume chain

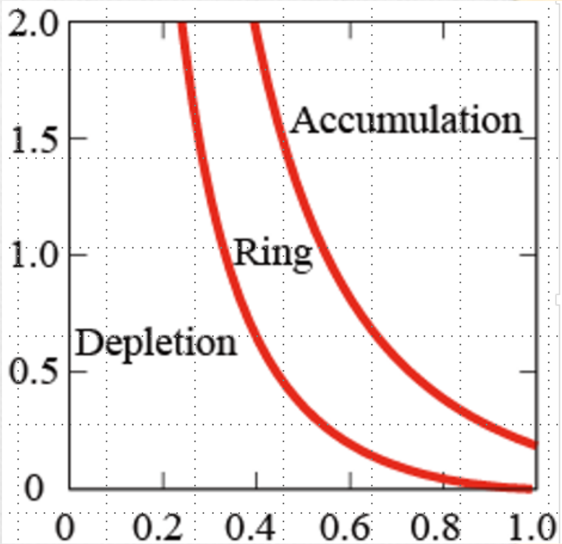


Experiment

Summary

Our model clarified that ring-like localization can be generated when the Soret effect is balanced against the entropic effect due to the excluded volume interaction.

We have also constructed the chain-like molecular model for colloidal pattern formation. The results of this model indicates that the size dependence of the Soret coefficient is important to set a behavior of phase diagram of colloidal pattern.



K. Odagiri, K. Seki, K. Kudo,
Soft Matter **8**, 2775-2781 (2012).