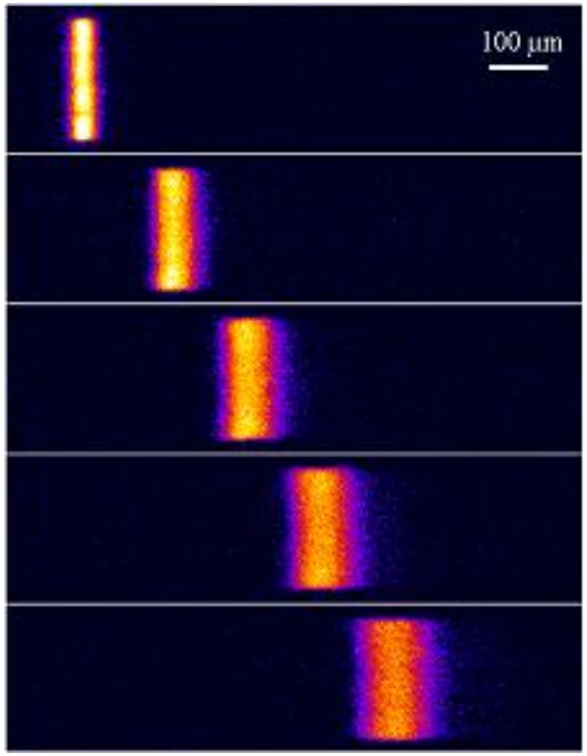
複雑流体の非平衡輸送現象:
分子から細胞集団へ

前多裕介[1,2,3] and Albert Libchaber[3]

[1] 京都大学白眉センター
[2] 科学技術振興機構さきがけ
[3] The Rockefeller University

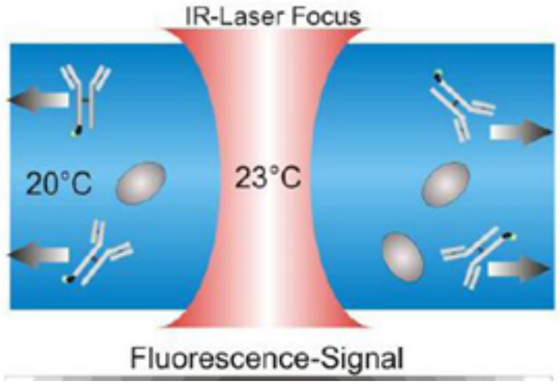
YITP, August 1, 2012

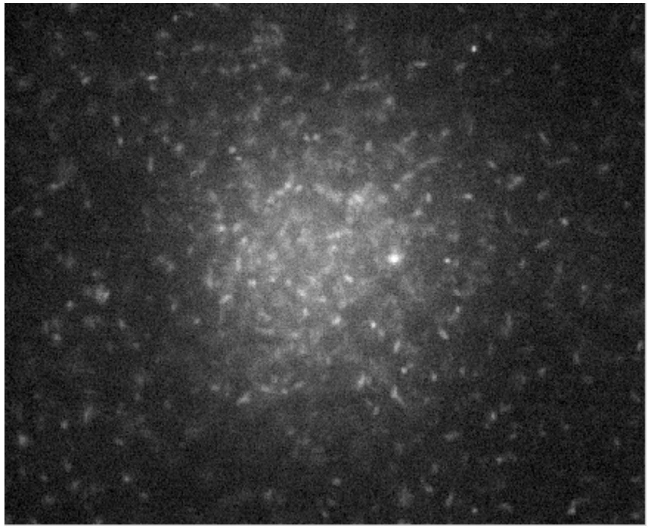
Transport and Directed motions in microenvironments



Electro-osmotic flow

Thermophoresis





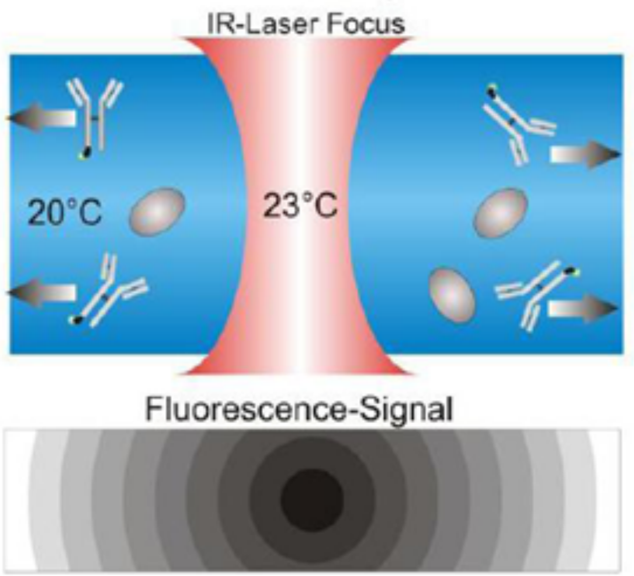
bacterial motility (Thermotaxis)

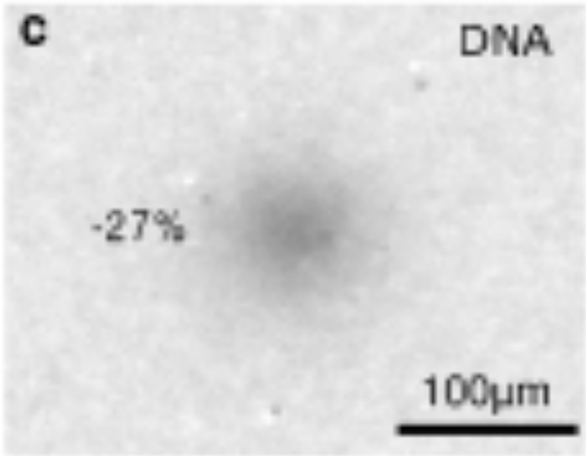
Directed motions in a gradient of thermodynamic variables

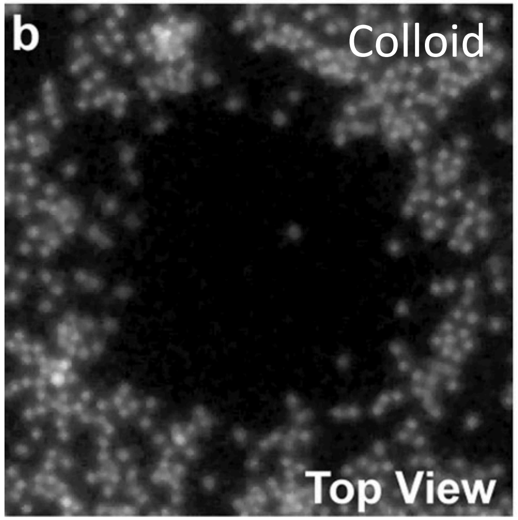
The Soret effect 1/3

The Ludwig-Soret effect: a solute move along a temperature gradient

C. Ludwig, S-B Akad. Wiss. Wien. *Nature* **20**, 539 (1856);
C. Soret. *Arch. Geneve*. **3**, 48 (1879)







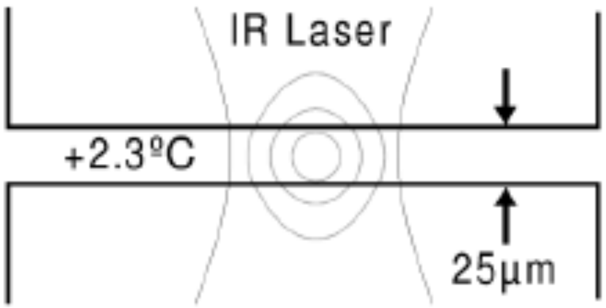
D Braun and A Libchaber. *Phys. Rev. Lett*. **89**, 188103 (2002)
S Duhr and D Braun. *Phys. Rev. Lett*. **101** 168301 (2008)

Charged molecules move along a temperature gradient

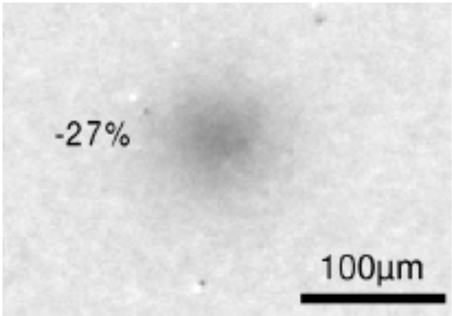
From HOT to COLD

The Soret effect 2/3

1.



2.



1. Local heating by infrared light focusing
2. Depletion of DNA from the hot region

$$J = -D\nabla c - cD_T \nabla T$$

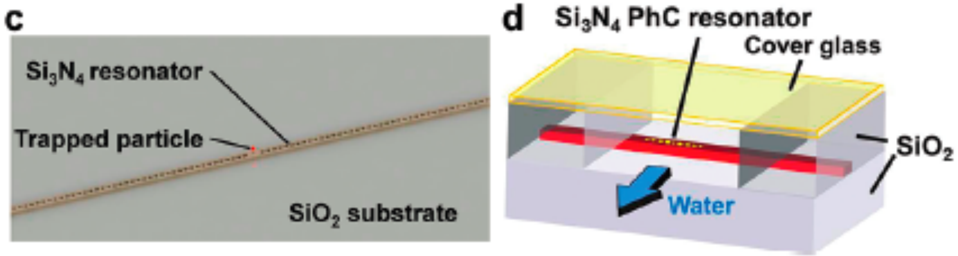
Diffusion — Thermal diffusion

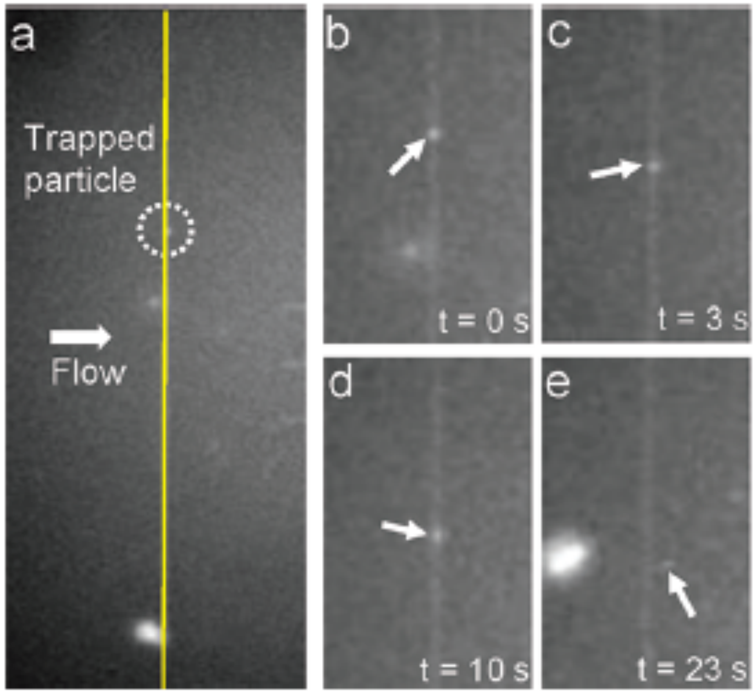
Distribution at the steady state

$$c(z) = c_0 \exp\left[-S_T\left(T(z) - T_0\right)\right]$$

The Soret coefficient $S_T = D_T / D$

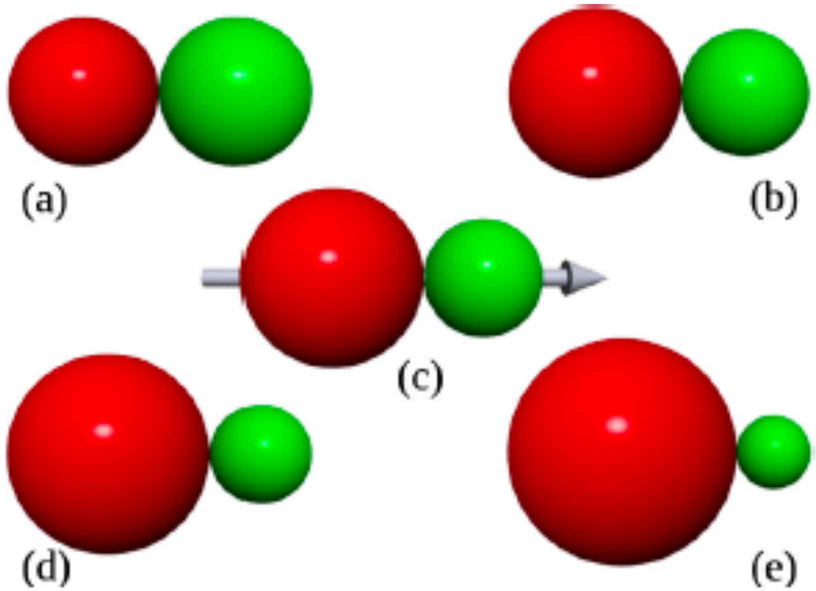
Dieter Braun, Albert Libchaber
Physical Review Letters **89:** 188103 (2002)





YF Chen et al.
Nano Letters **12:** 1633 (2012)

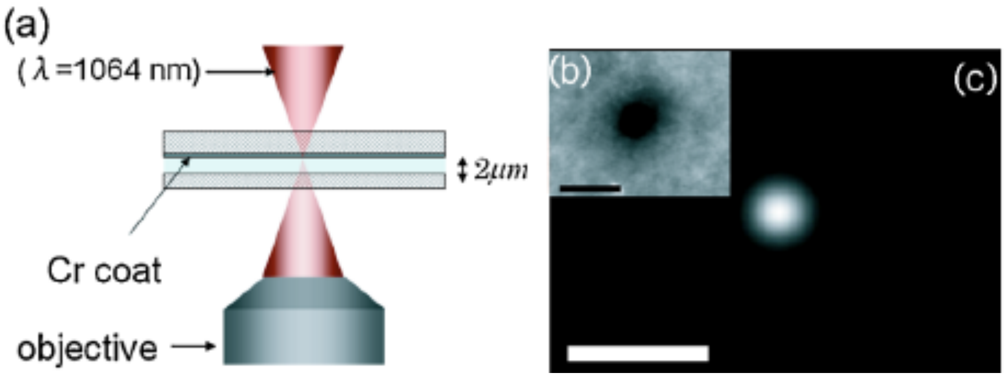
Alignment of anisotropic molecules

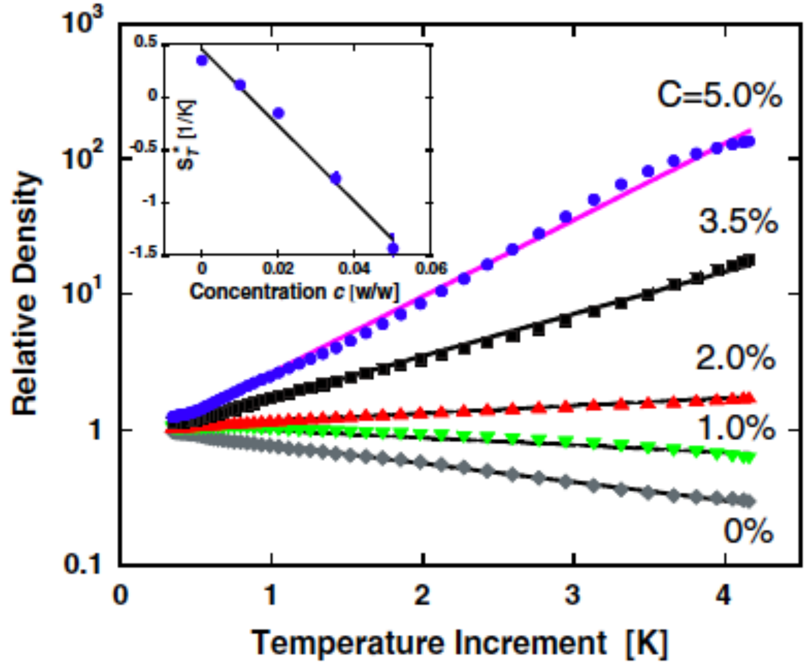


F Romer et al
Physical Review Letters **108:** 105901 (2012)

The Soret effect 3/3

- Thermophoresis of colloidal particles in a polymer solution
- Direction of colloidal transport is flipped.
  → Little material dependence

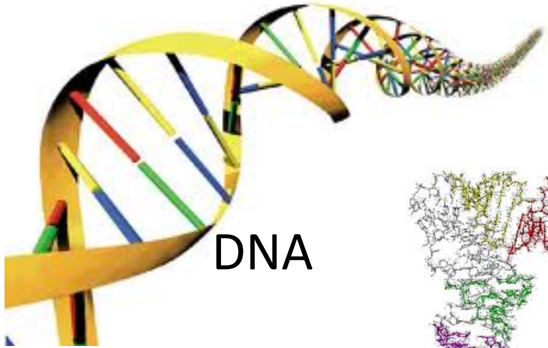




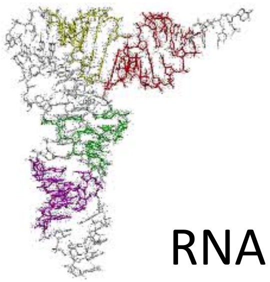
H.R.Jiang, H.Wada, N.Yoshinaga, M.Sano
Physical Review Letters **102**: 208301 (2009)

Focus in this study

Complex fluids in a temperature gradient



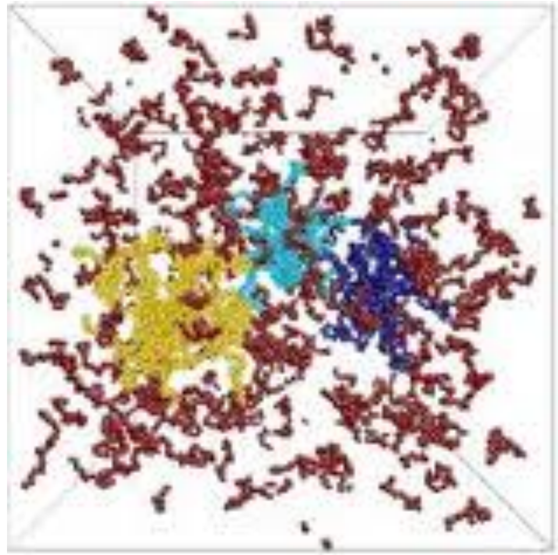
DNA



RNA

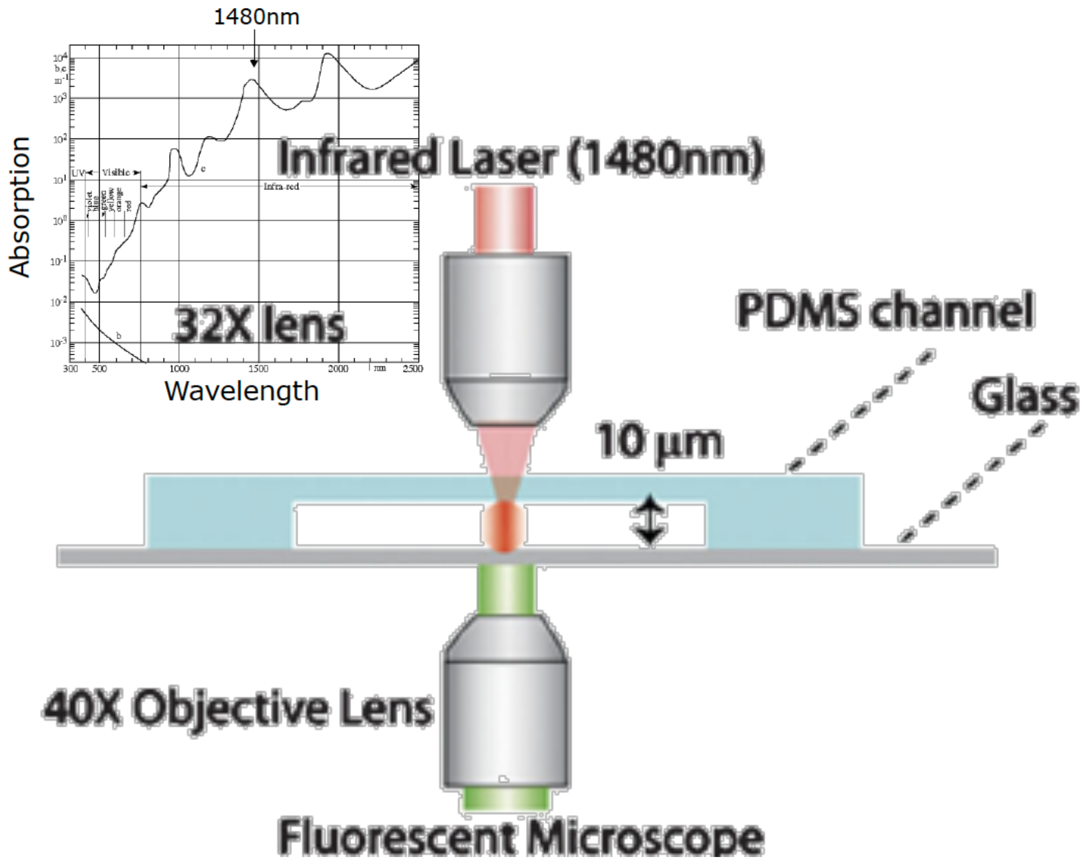
Another solute

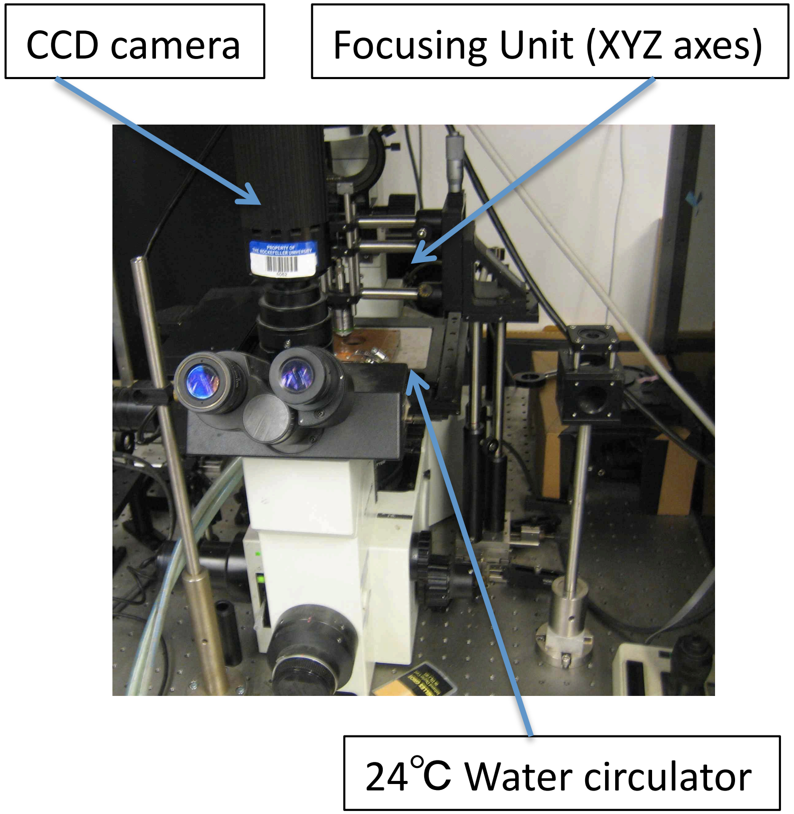
ΔT



1. Thermophoresis of complex fluids and molecular separation
2. The effects of molecular folding on thermophoresis
3. The origin of the entropic force

1. Thermophoresis of complex fluids and molecular separation

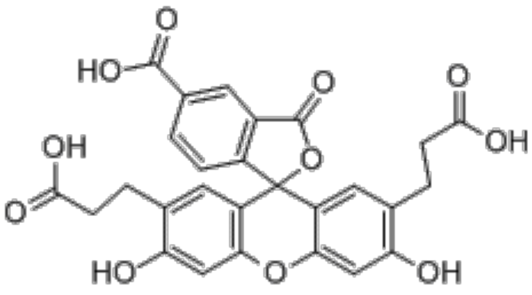




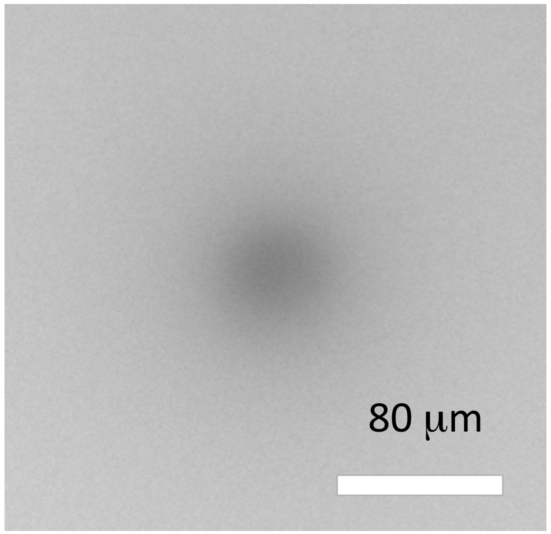
Polymer PEG10,000 (polyethylene glycol 10,000) solution of 0-5% volume fraction is enclosed in a thin chamber.

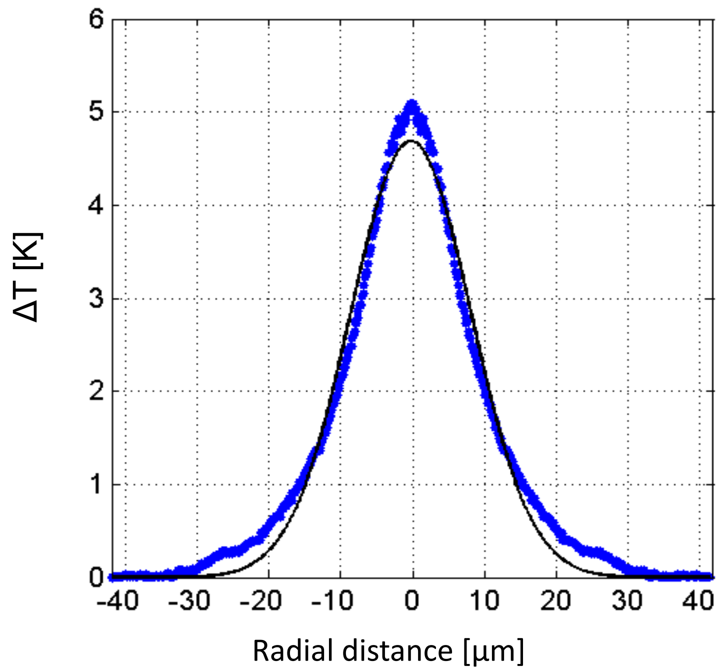
Temperature gradient in experiments

Temperature visualization using the intensity drop of fluorescent dye



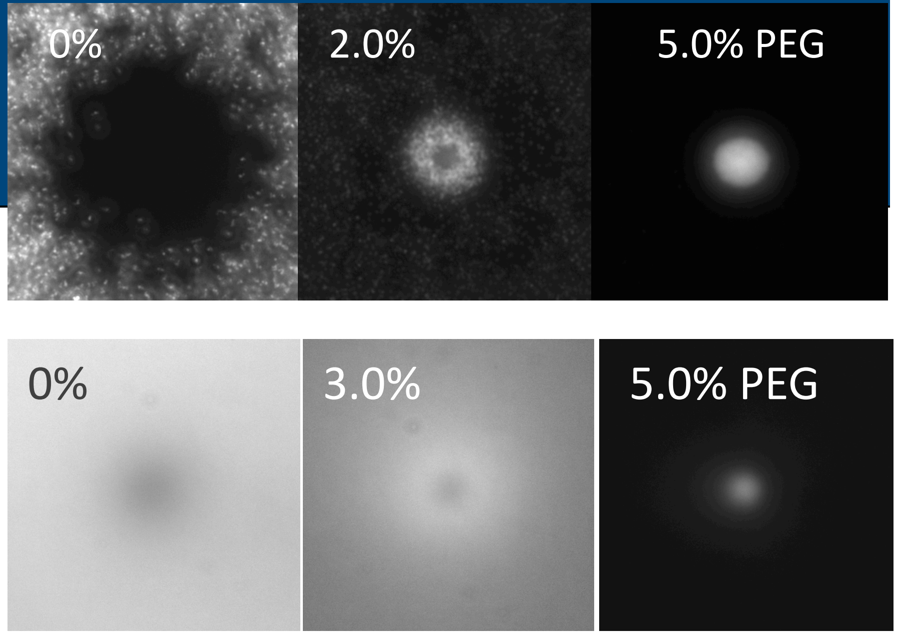
BCECF, fluorescein





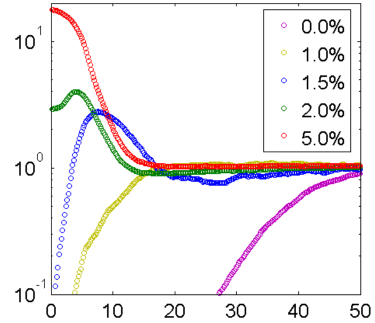
Beads
0.5 µm

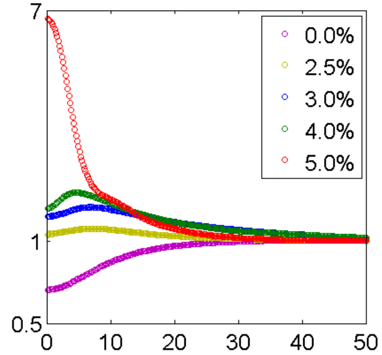
DNA
250bp



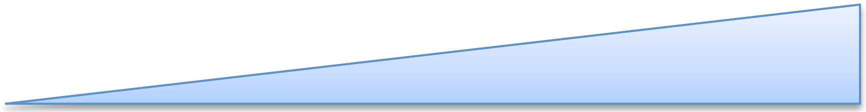
From HOT to COLD

From COLD to HOT



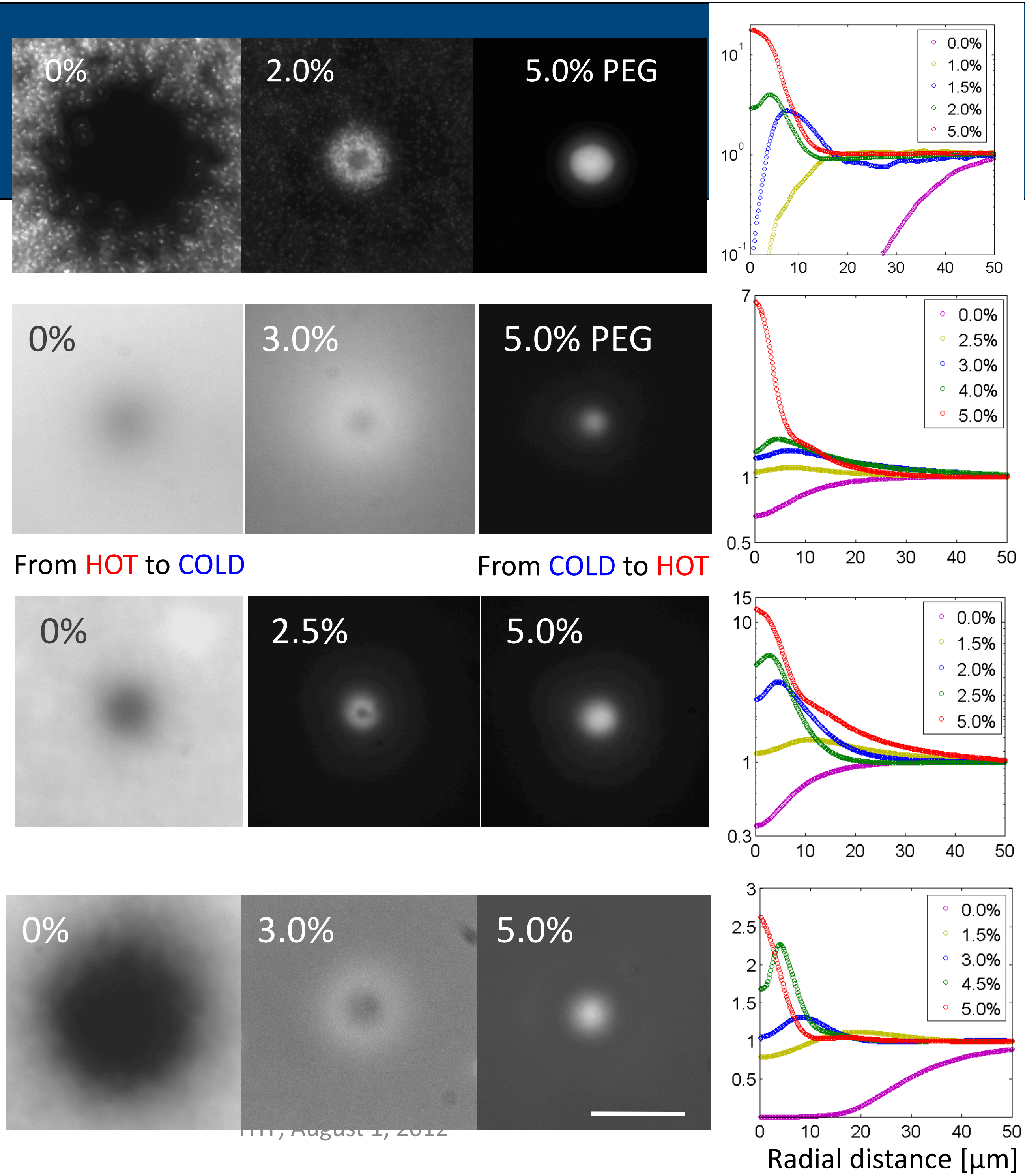


Radial distance [µm]



Polyethylene glycol (PEG)

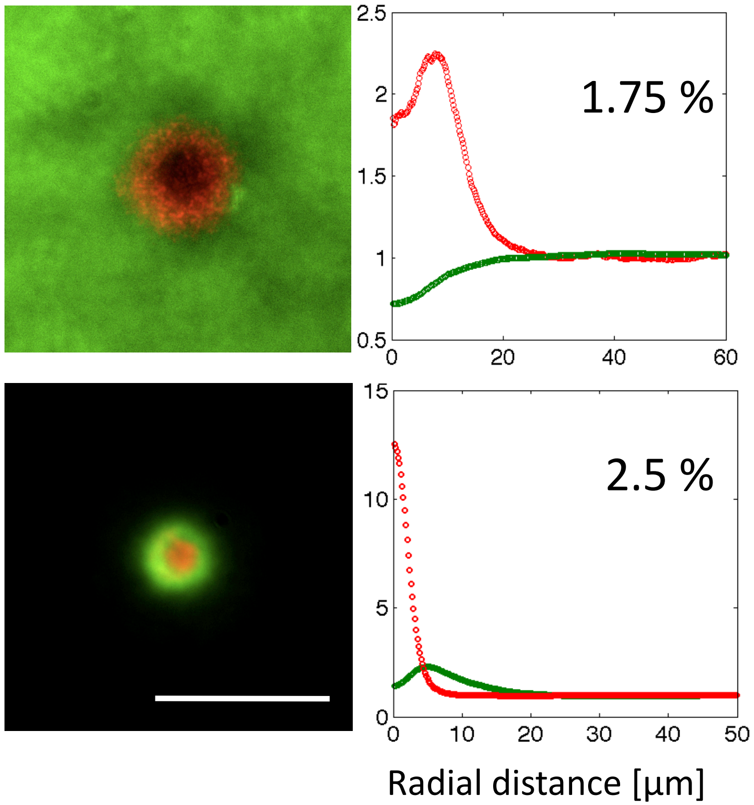
Scale bar 35µm



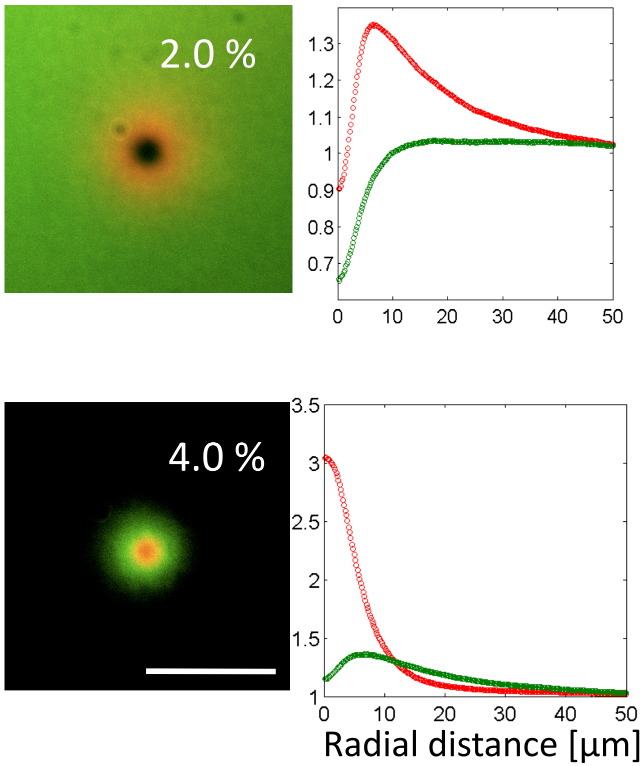
Scale bar 35μm

Size-dependent separation

Beads 0.5µm 0.1µm



RNA(1.5kb) DNA(250bp)

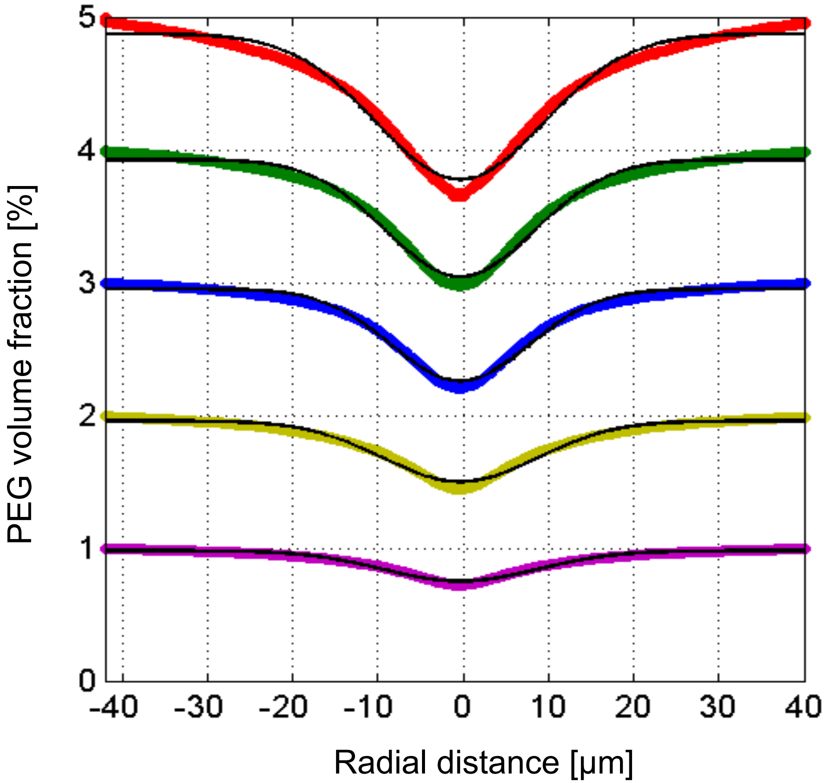


Yusuke T. Maeda, Axel Buguin, Albert Libchaber
Physical Review Letters **107**: 038301 (2011)

Scale bar 35µm

The mechanism of localization (1/4)

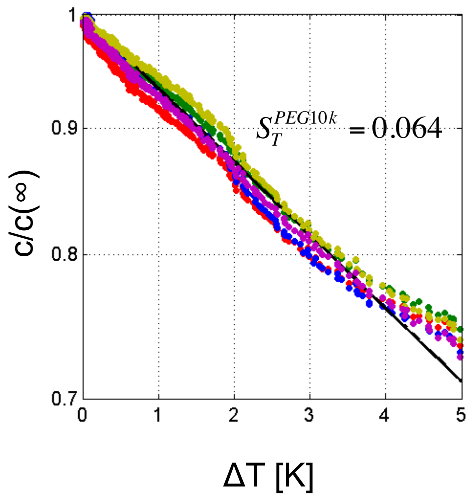
PEG molecules are also subject to thermophoresis



$$J = -D\nabla c - cD_T \nabla T$$

Diffusion　　Thermal diffusion

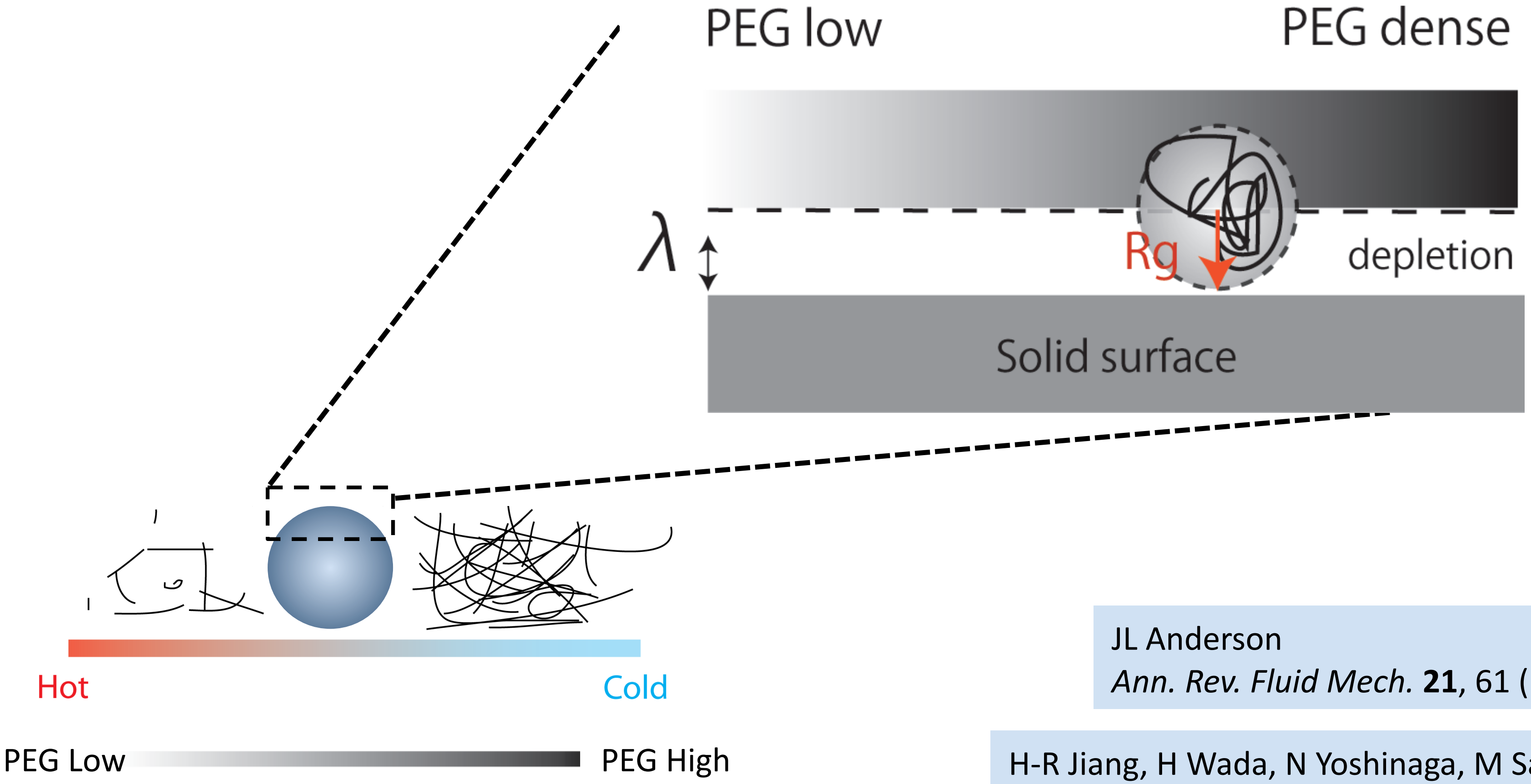
$$J = 0 \Rightarrow c(r) = c(\infty)\exp\left(-\frac{D_T}{D}\Delta T\right)$$



$S_T \equiv D_T / D$: Soret coefficient

The mechanism of localization (2/4)

$$c_{PEG}(r) = c_0 \exp\left[-S_T^{PEG}\left(T(r) - T_0\right)\right]$$



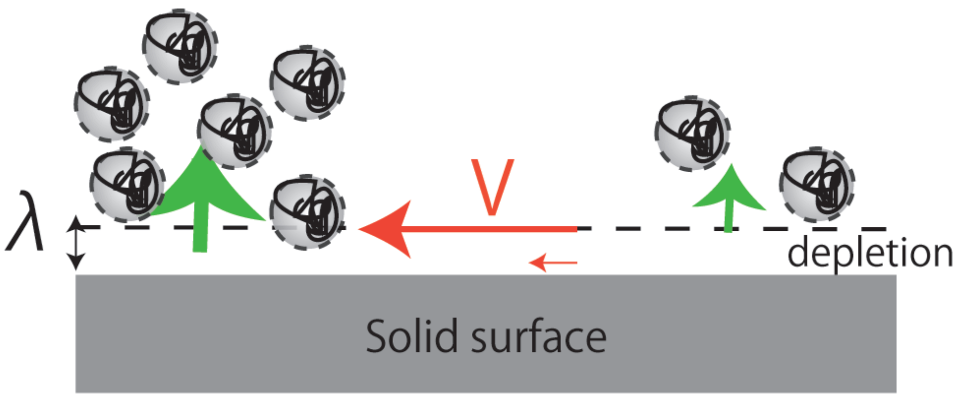
JL Anderson
Ann. Rev. Fluid Mech. **21**, 61 (1989)

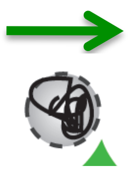
H-R Jiang, H Wada, N Yoshinaga, M Sano
Physical Review Letters **102**, 208301 (2009)

The mechanism of localization (3/4)

Depletion of PEG from the surface of a solute

$$c(x,z) \approx c_0(x)\exp\left[-\frac{U(z)}{k_B T}\right]$$





▪Balance of osmotic pressure and hydrostatic Pressure (No net force on a fluid in the bulk)

$$p(x,z) - k_B T c(x,z) = p_0 - k_B T c_0(x) = \text{constant}$$

$$\partial_x p(x,z) = k_B T \partial_x \left[c(x,z) - c_0(x)\right]$$

▪The diffuse-osmotic flow is balanced by viscous shear stress at equilibrium

$$\partial_x p(x,z) = \eta \partial_x^2 v_x$$

▪ The fluid velocity increase in the bulk is

$$V \approx \underbrace{\int_0^z dz'(e^{-U(z)/kT} - 1)}_{\text{Drop of solute}} \frac{dc_0}{dx} \approx -\frac{k_B T}{\eta} \lambda^2 \nabla c_0$$

The mechanism of localization (4/4)

No slip condition

$$J = -D\nabla c^b - c^b D_T \nabla T + c^b u,$$

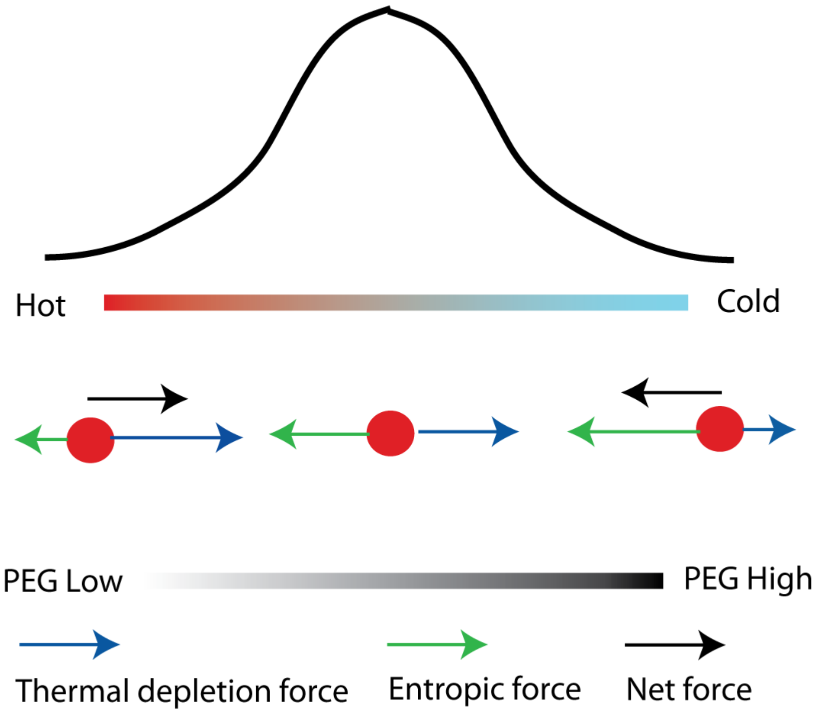
$$u = \frac{k_B T}{3\eta}\left(S_T^{PEG} - \frac{1}{T}\right)\lambda^2 c^{PEG}(r)\nabla T(r)$$

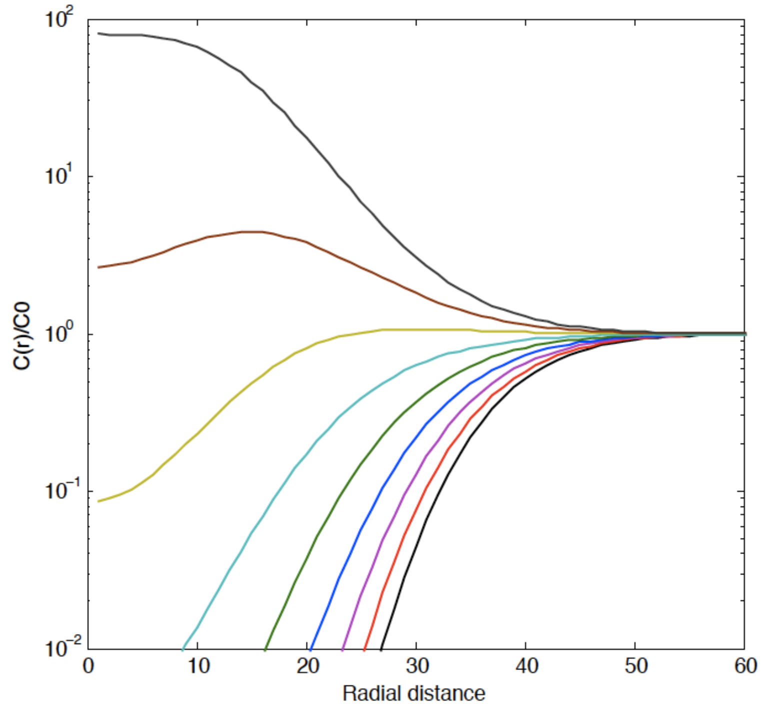
$$c^b(r) = c_0^b \exp\left[-S_T^b \Delta T(r) + \left(c_0^{PEG} - c^{PEG}(r)\right)V\right]$$

$$V = \pi\lambda^2 d$$

Soret effect

Entropic force

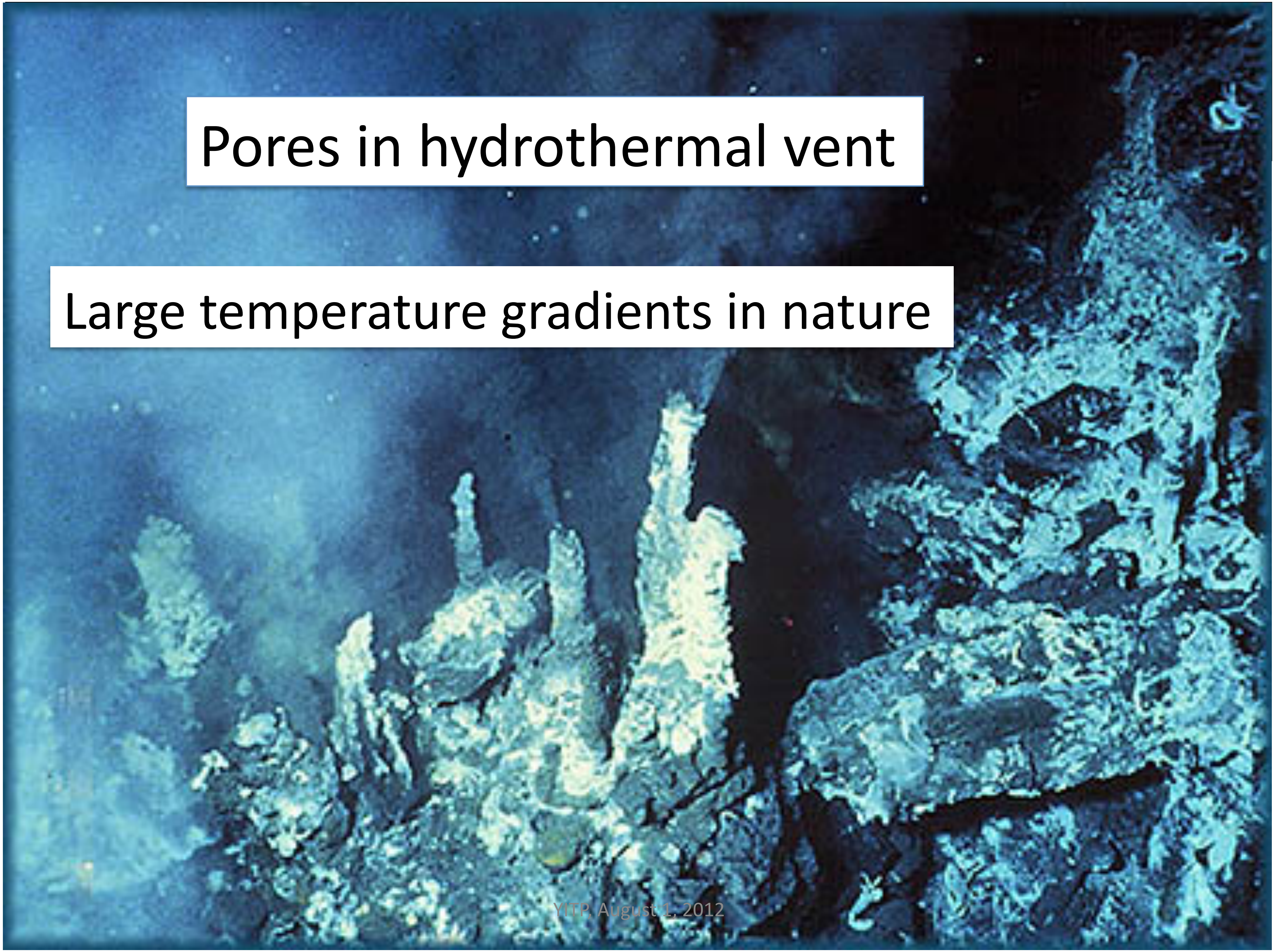




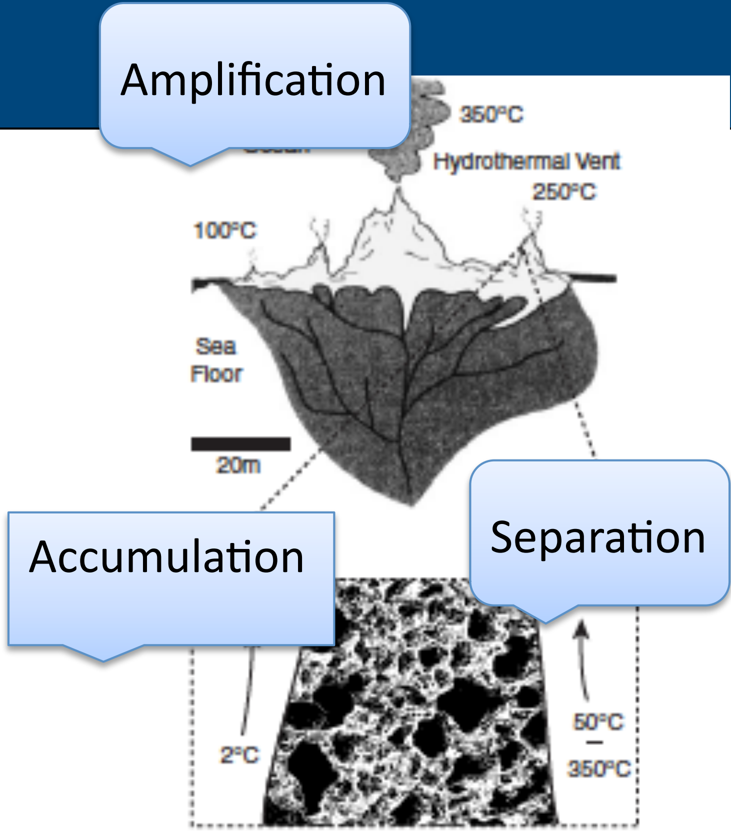
YT Maeda, A Buguin, A Libchaber
Physical Review Letters **107**, 038301 (2011)

Pores in hydrothermal vent

Large temperature gradients in nature

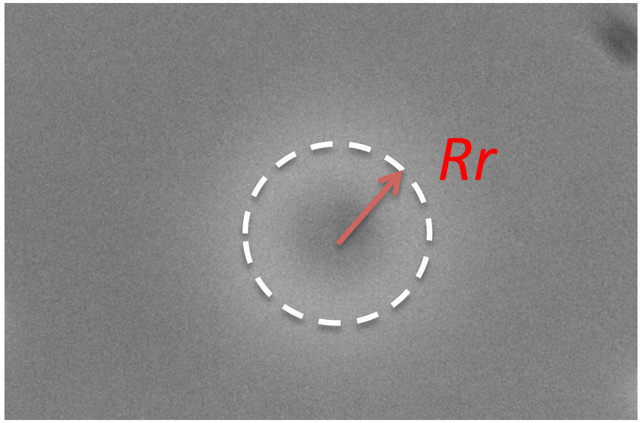


4000,000,000 BC



2,000 AD

2. The effect of molecular folding on thermophoresis



非公開

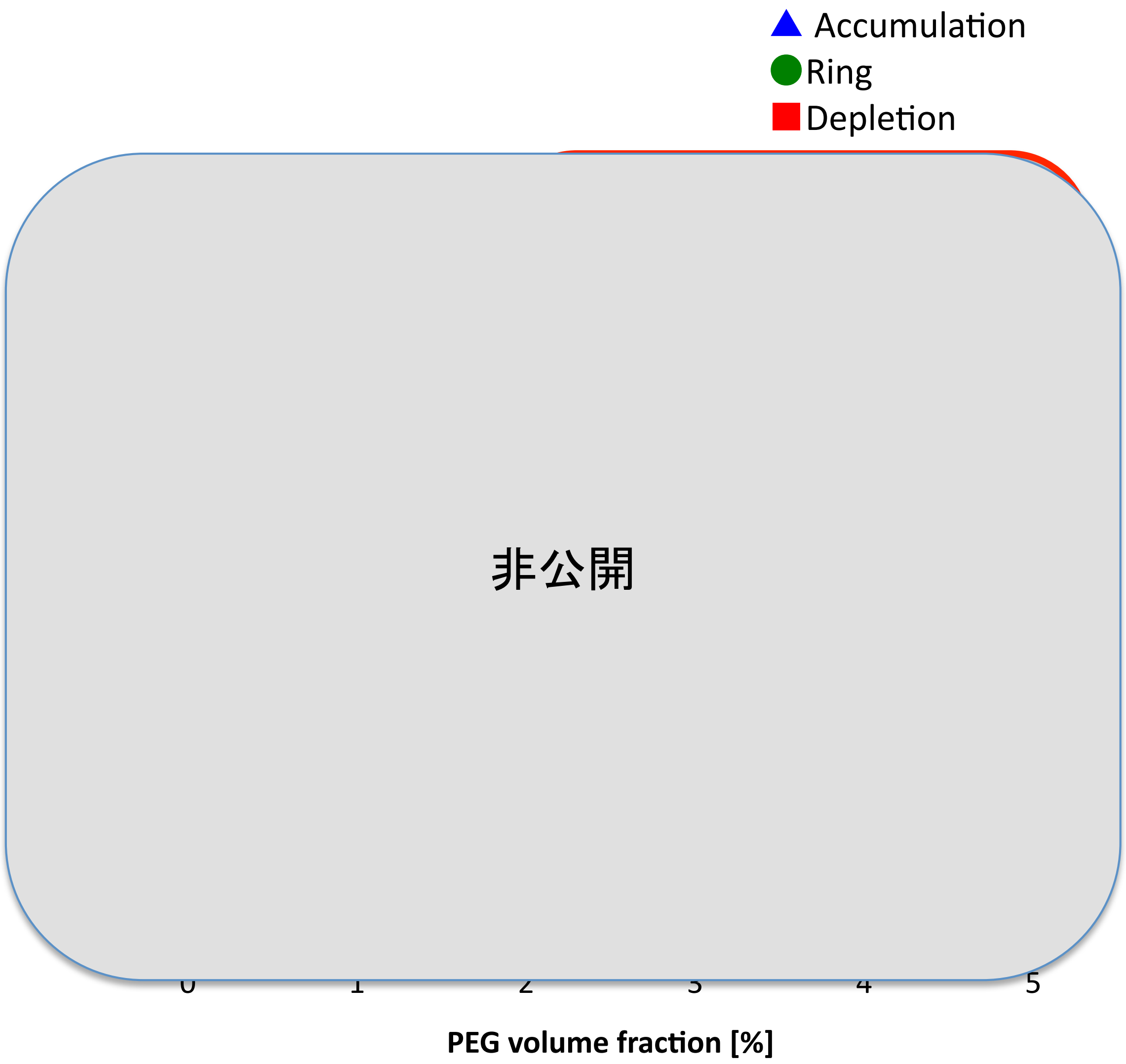
DNA size [kbp]

Below 5.6kbp
Ring shrinks as DNA becomes longer

Above 5.6kbp
Ring expands as DNA becomes longer

Behavior is reversed at around 5.6 kbp

Reversed size-dependence above 5.6kbp



150 bp = 1 persistence length
5 kbp > 20 persistence lengths

Is DNA molecule expanded coil?

Coil-globule transition occurs in a PEG

非公開

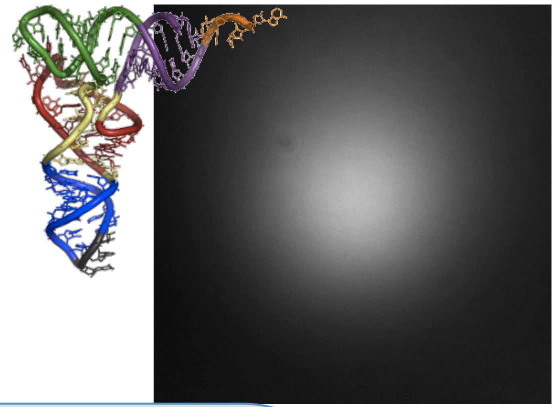
Single molecule observation

非公開

The effect of stem-loop on RNA transport

Next question: Why the force from a PEG gradient can act on small RNA?

tRNA (〜5 nm) can be accumulated in a PEG (〜3 nm) solution.



非公開

Folding dependent accumulation

非公開

・The accumulation of small RNA and DNA is folding-dependent.

Rigid part is essential

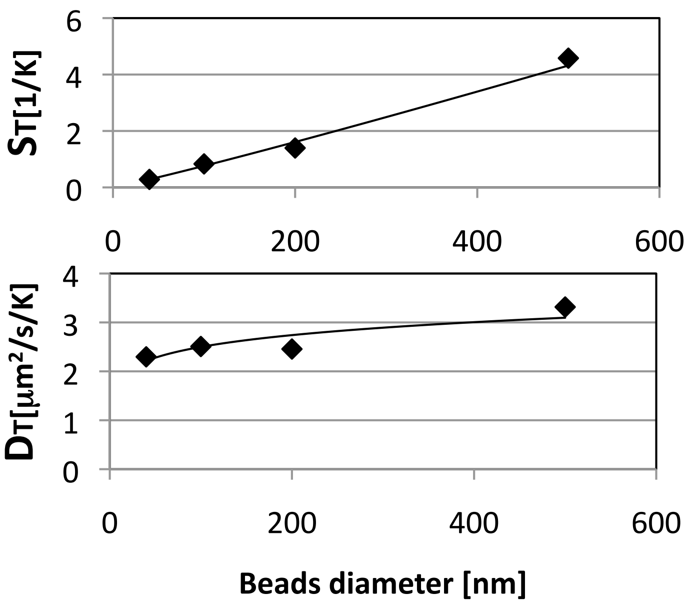
非公開

・The stem (double-stranded, rigid) of RNA and DNA strongly enhances accumulation while the loop (single-stranded, flexible) has few effect.

3. The origin of entropic force: diffusiophoresis

Thermophoresis

$$V_T = -D_T \nabla T(r)$$



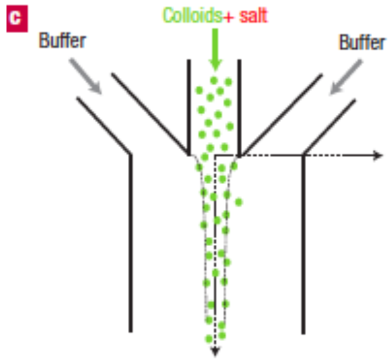
$$S_T \sim a^{1.1} \quad D_T \sim a^{0.1}$$

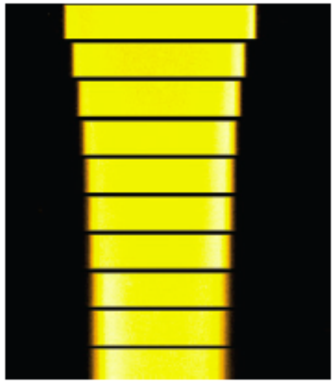
Entropic force (Diffusiophoresis)

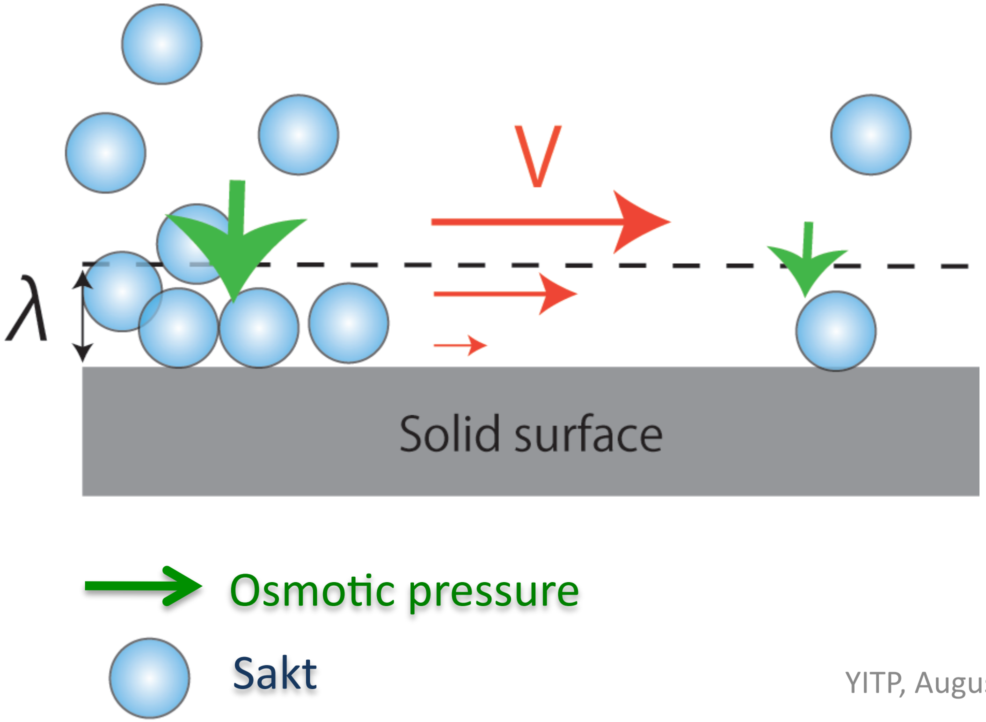
$$V = ??$$

- D_T has little size-dependence and it cannot account for observed separation.
- Size-dependence should present in entropic force.

Salt and migrate: Diffusiophoresis







- The fluid velocity increase in the bulk is

$$V = -\frac{k_B T}{\eta}\Gamma L \nabla_x c_0$$

Excess of solute $$\Gamma = \int_0^\infty \left(e^{-\frac{U(z)}{k_B T}} - 1 \right) dz$$

The range of attraction $$L = \Gamma^{-1} \int_0^\infty z \left(e^{-\frac{U(z)}{k_B T}} - 1 \right) dz$$

$$V \approx -\frac{k_B T}{\eta}\lambda^2 \nabla_x c_0 \approx -D_{DP} \nabla_x \log c_0$$

$$\lambda^2 = \varepsilon k T / 2q^2 c_0 \qquad D_{DP} = \varepsilon k^2 T^2 / 2q^2 \eta$$

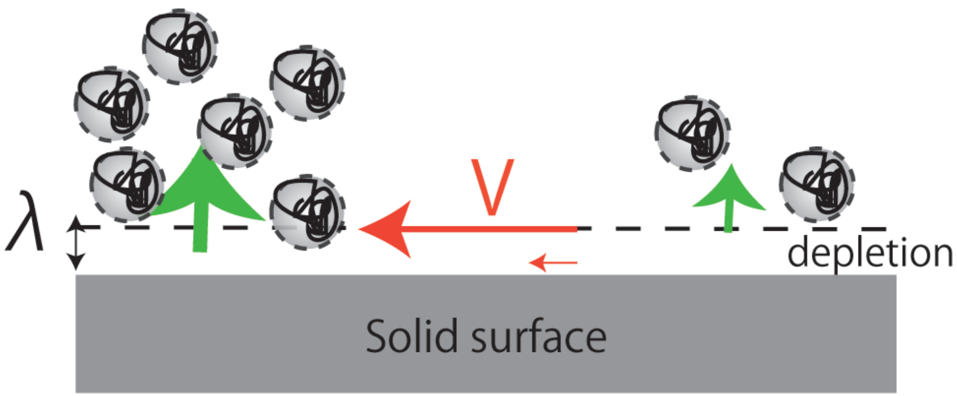
B Abecassis, et al
Nature Materials **7**, 785 (2008)

PEG and Diffusiophoresis

Repulsion of PEG in the surface of a solute

$$c(x,z) \approx c_0(x) \exp\left[-\frac{U(z)}{k_B T} \right]$$

$$U(z) > 0$$



- The fluid velocity increase in the bulk is

$$V \approx -\frac{k_B T}{3\eta} \lambda^2 \nabla c_{PEG}$$

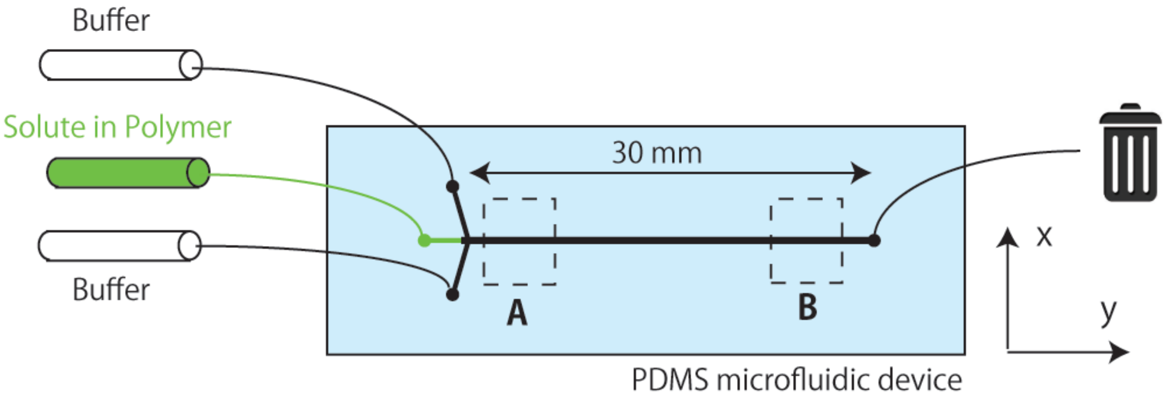
Diffusiophoresis velocity in no-slip condition is independent of the particle size.

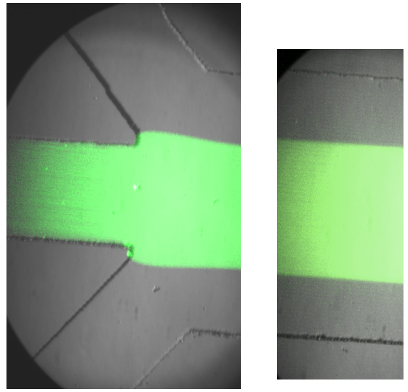
We check if this relation holds or not, in the absence of temperature gradient.

Osmotic pressure

PEG molecule

Experimental setup: microfluidics





- Laminar flows in PDMS microfluidics
- Microchannel: Width 2 mm, Height 50 μm
- Polymer in a solution is PEG1000

$$c_{PEG}(x,y) = \frac{c^0_{PEG}}{2} erf\left(\frac{x - h/4}{\tau}\right) - \frac{c^0_{PEG}}{2} erf\left(\frac{x - 3h/4}{\tau}\right)$$

$$erf(x) = \frac{2}{\sqrt{\pi}} \int_0^x dx e^{-x^2}$$

$$\tau = \sqrt{y/U}$$

$$D_{PEG} = 1.35 \times 10^2 \ \mu m^2/s$$

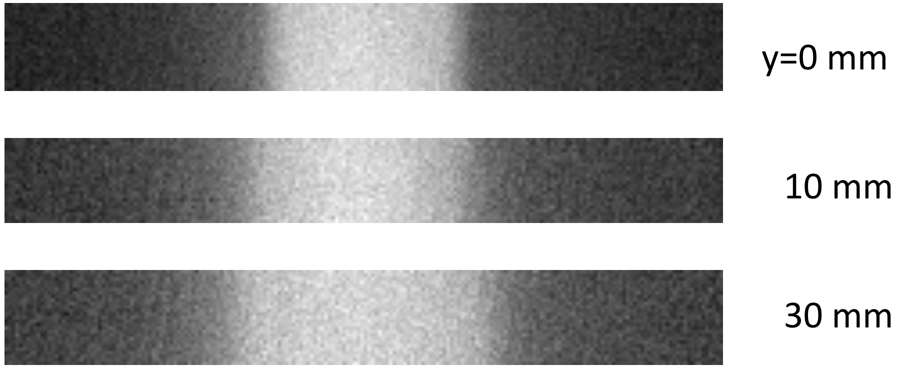
$$U = 1.16 \ mm/s$$

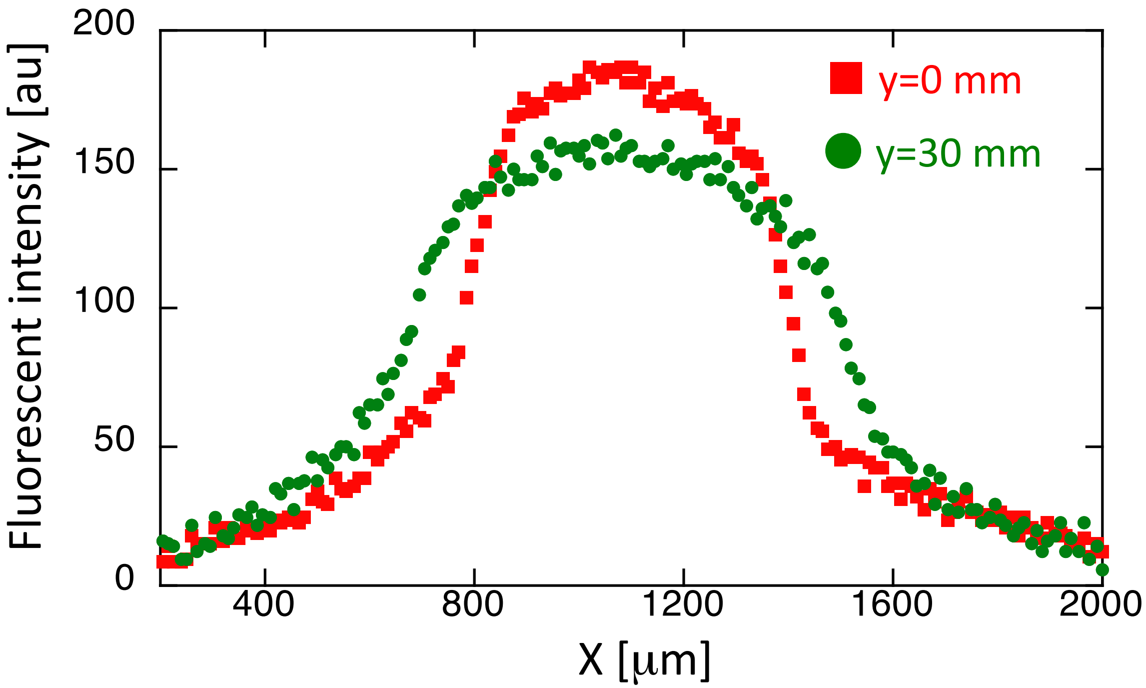
$$\nabla c_{PEG} \approx c^0_{PEG} / \sqrt{D_{PEG} y / U} \approx 0.5 \ \%/\mu m$$

PEG1,000 gradient-driven transport

Colloid (fluorescent)
0.1 μm, $2.0*10^{-3}$ %

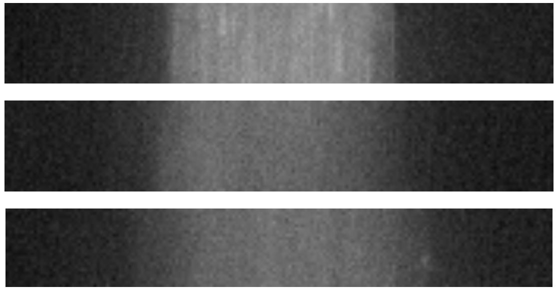
PEG1,000, 20%
(Not PEG10,000 !)



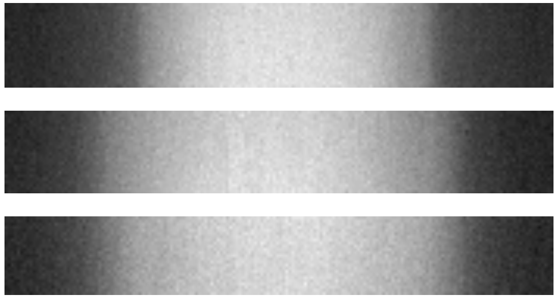


Different sized-colloids in a gradient of small PEG1,000

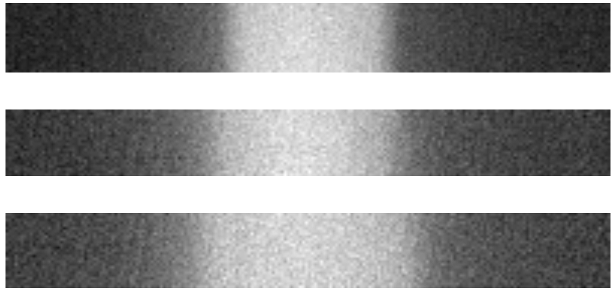
Colloid 0.5 μm

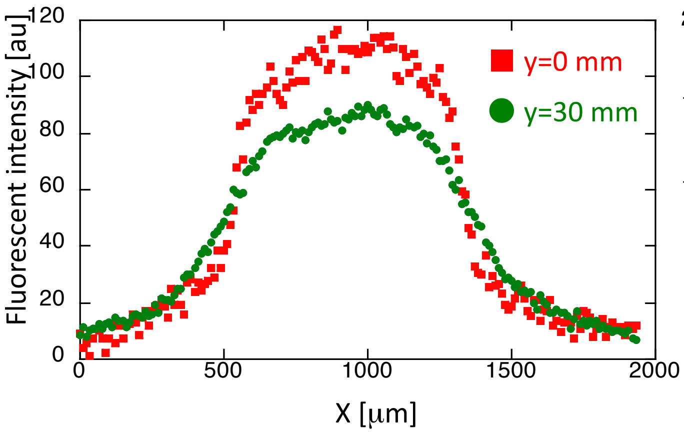


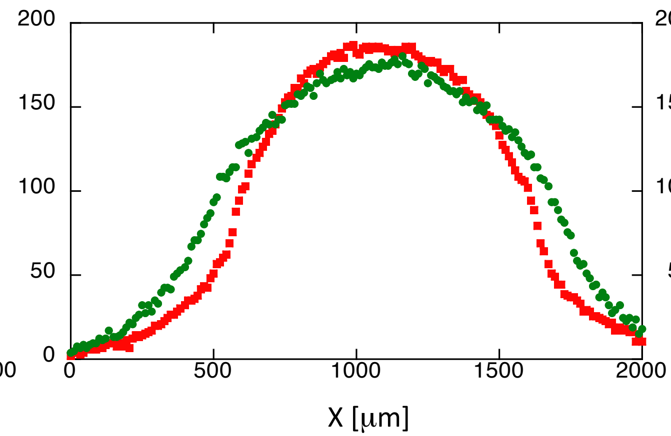
Colloid 0.2 μm

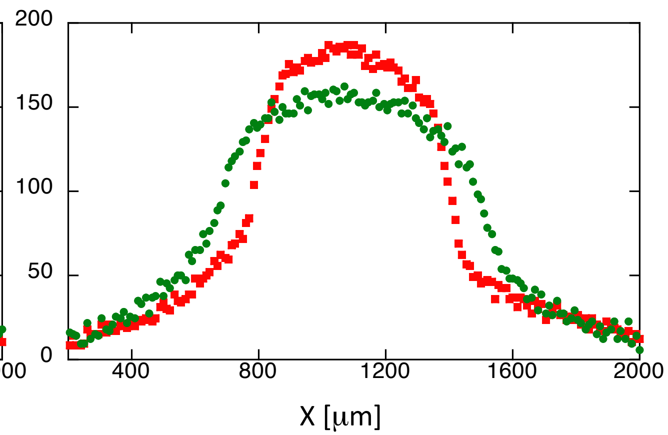


Colloid 0.1 μm

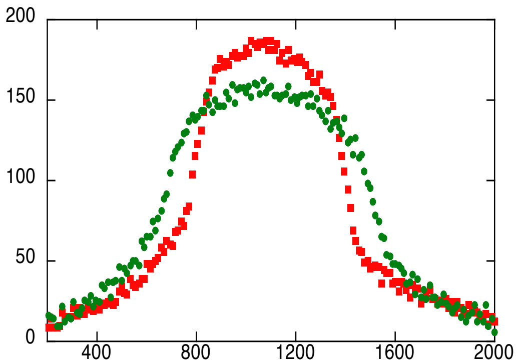


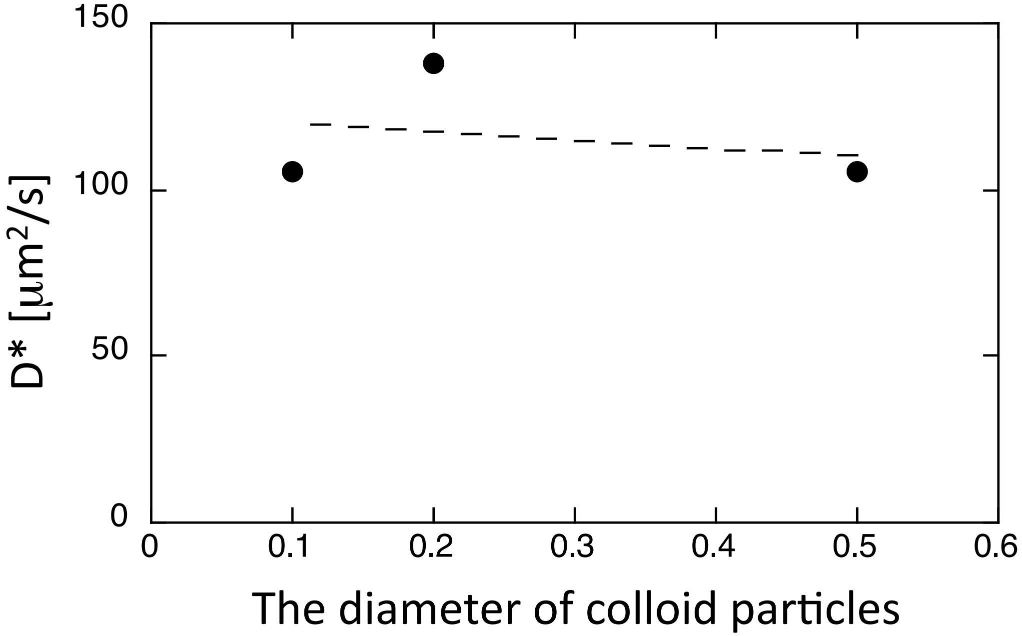






$$w(y) - w_0 \approx \sqrt{D^* \cdot U / 2y}$$



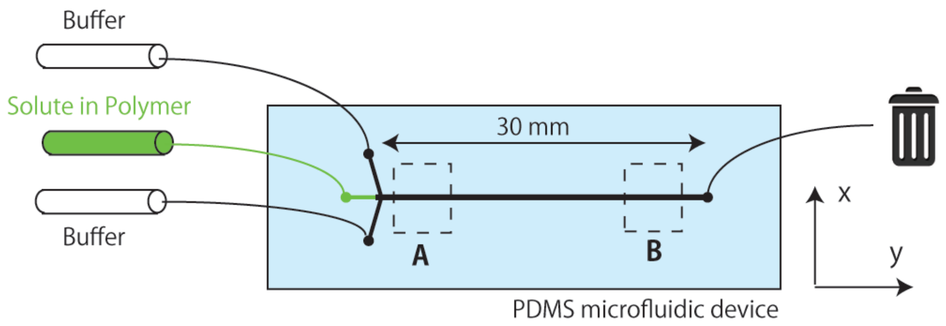


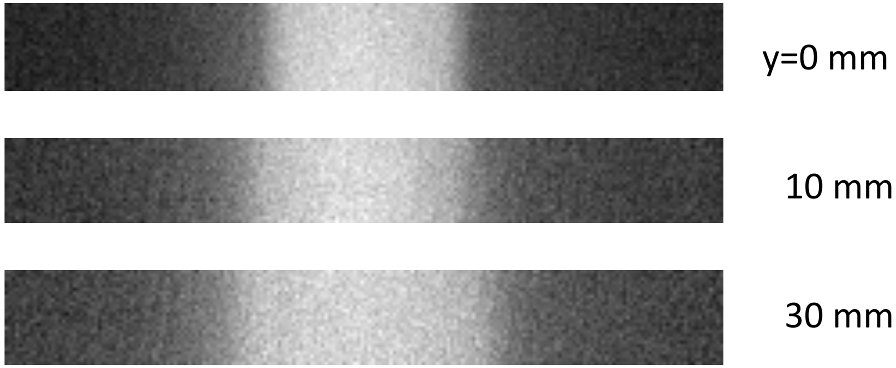
・In small PEG such as PEG1,000, the velocity of diffusiophoresis is not strongly dependent on particle size.

・It is because 10% PEG1,000 is still in a dilute regime, which is included in a model.

Future works

- The mechanism of size-dependent separation





Diffusiophoresis through the repulsive interactions
of the solute (colloid, DNA) and another polymer (PEG)

Viscosity?

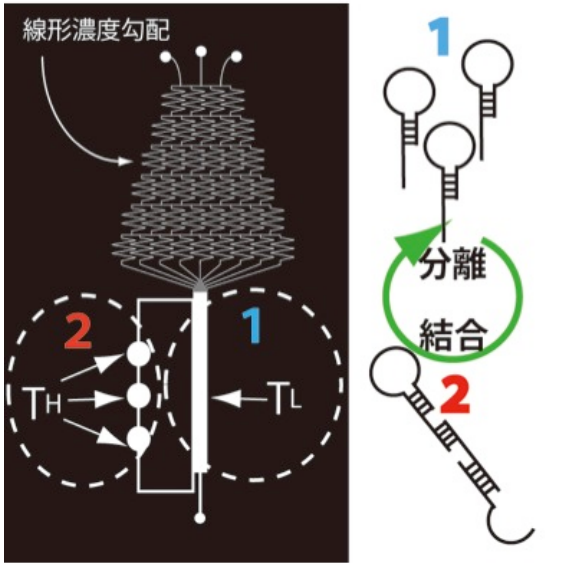
Many-body interactions?

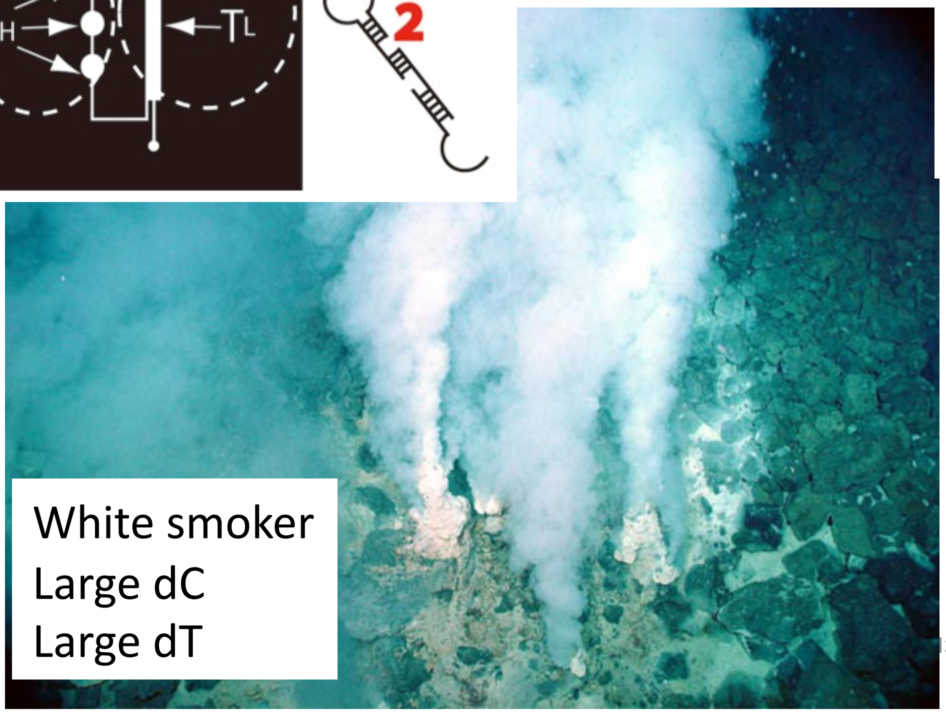
K Odagiri, K Seki, K Kudo
Soft Matter **8**, 2775 (2012)

- The mechanism of trapping small RNA by comparable PEG

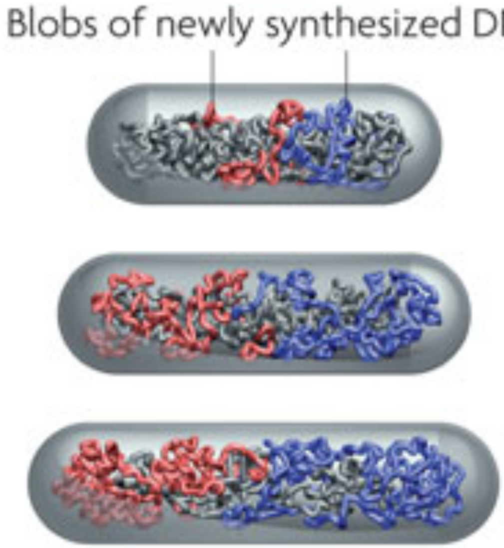
(Putative) Relevance of biological systems

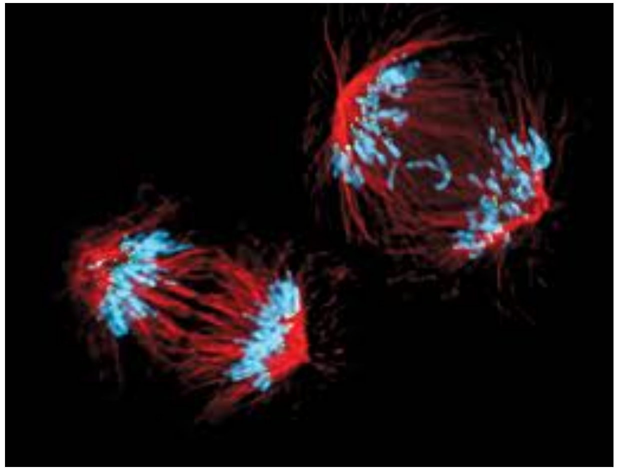
1. Selection and evolution of small RNA





2. Transport and segregation of genome





Conclusions

☐ DNA and RNA of various sizes show ring-like localization or accumulation under a temperature gradient in PEG.

☐ The entropic force gradient generated by the PEG gradient on the surface of solute, called diffusiophoresis, can push solute to the hot region.

☐ Simple microfluidic device allows us to study the transport by repulsive PEG. In a dilute regime, the clear size-dependence is not observed.

☐ Size-dependence of DNA localization is reversed for a long DNA >5.6kbp. PEG osmotic pressure induces coil-globule transition and decreases its effective size.

☐ The attraction by PEG concentration gradient is folding-dependent: Small RNA having stem-loop can be accumulated while poly-U of random chain cannot.

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