Active Colloids: Nonequilibrium Dynamics and Fluctuation

Masaki Sano*
Hong-ren Jiang[1]
Ryo Suzuki*[2]
Natsuhiko Yoshinaga[3]

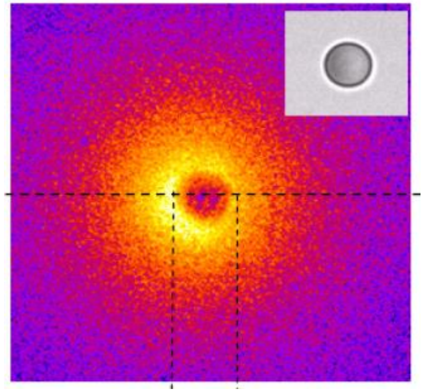
*Department of Physics, The University of Tokyo
[1]Institute of Applied Physics, National Taiwan University
[2]Department of Physics, Technical University of Munich
[3]WPI-AIMR, Tohoku University

What are the active colloids?

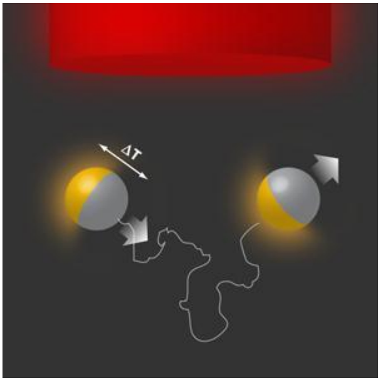
Self-propelled colloid:
Janus particles under uniform external fields

- By a local temperature gradient

  Self-Thermophoresis



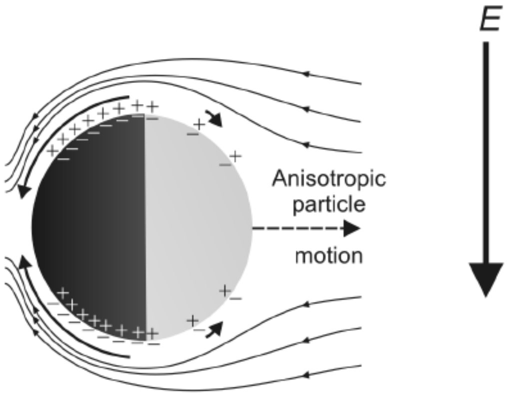
Jiang, Sano, PRL (2010)



APS Physics Viewpoint(2010)

- By an electric field:

  Induced Charge Electro-Osmosis (ICEO)



Gangwal et al. PRL (2008)

Why active colloids?

- Fundamental questions:

One can test fundamental physical laws using driven Brownian particles.

Out of equilibrium systems:
Driven system, Active systems, Feedback controlled systems
Enhanced Diffusion?

- Toward biological problems and applications:

What are the characteristics that distinguish life from non-life?

Effort to mimic self-propelling, self-replicating, … and other properties.

Taxis: self-propelling + feedback control of information

Thermodynamic Cross-Effect

	Thermodynamic Variable 1	Thermodynamic Variable 2	
Electrophoresis	Electric Potential	Concentration	
Thermophoresis	Temperature	Concentration	(Soret effect)
Diffusiophoresis	Concentration 1	Concentration 2	
Chemiosmosis	Concentration 1	Chemical Reaction/ Concentration 2	Molecular Motor Ion pump
Thermoelectricity	Temperature	Electric Potential	(Peltier-Seebeck effect)

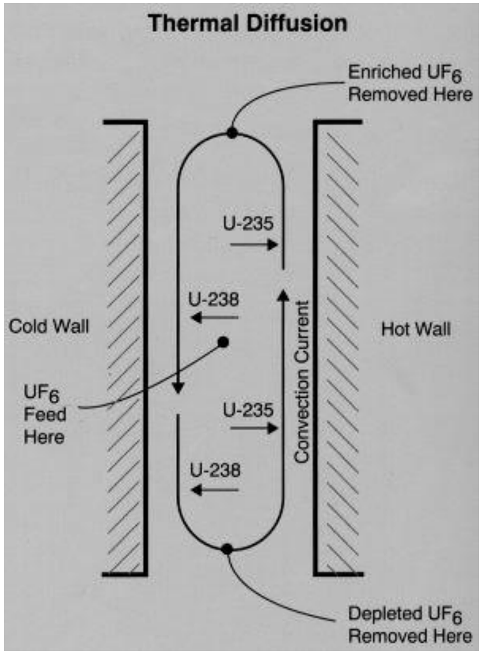
Hydrodynamics often plays important roles.

e.g. Charge + Hydrodynamics:
Electoro-osmosis
Nonlinear Electrokinetics, etc

Ludwig-Soret Effect

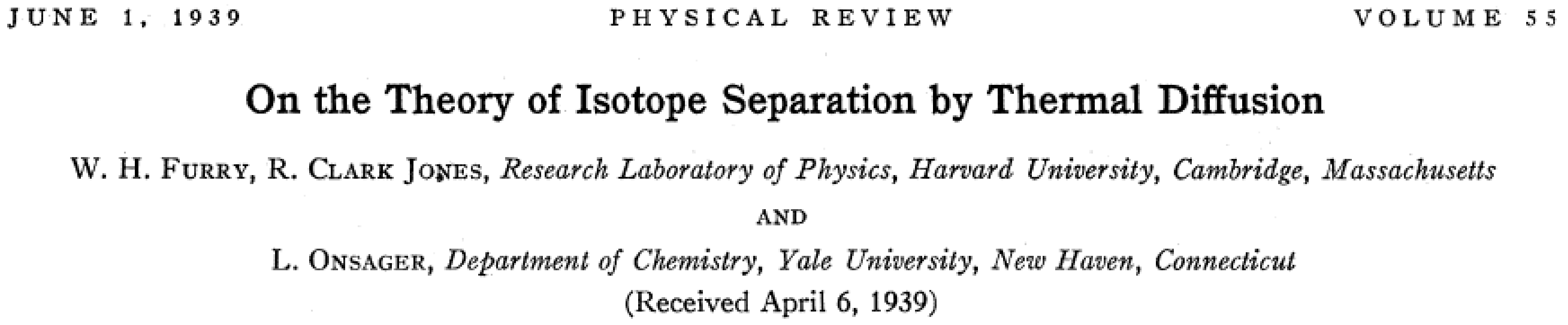
Carl Ludwig (1816-1895)

Charles Soret (1854-1904)



I. Onsager (1939)

同位元素の分離法に関する理論



JUNE 1, 1939 PHYSICAL REVIEW VOLUME 55

On the Theory of Isotope Separation by Thermal Diffusion

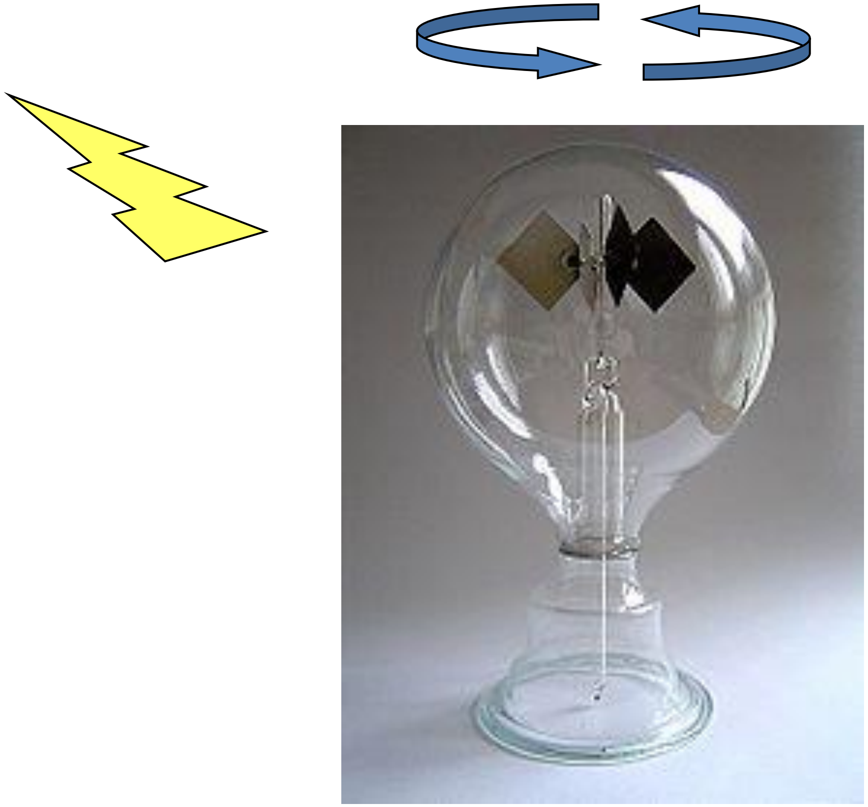
W. H. Furry, R. Clark Jones, *Research Laboratory of Physics, Harvard University, Cambridge, Massachusetts*

AND

L. Onsager, *Department of Chemistry, Yale University, New Haven, Connecticut*

(Received April 6, 1939)

Radiometer is a thermophoretic effect of gas



Crook's Radiometer

Williams Crooks (1873)

O. Reynolds: Thermal Transpiration

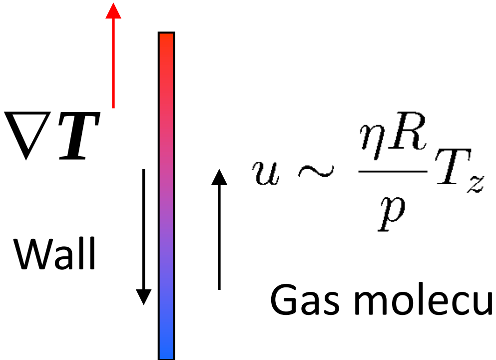
J.C. Maxwell (1879)

"The radiometer turns because of *tangential* stresses present at the *edges* of the vanes"

From the Boltzmann equation,

$$f(v) = [1 + C v_z (\frac{5}{2} - \frac{mv^2}{2k_B T})] f_0(v)$$

Maxwellian



∇T

Wall

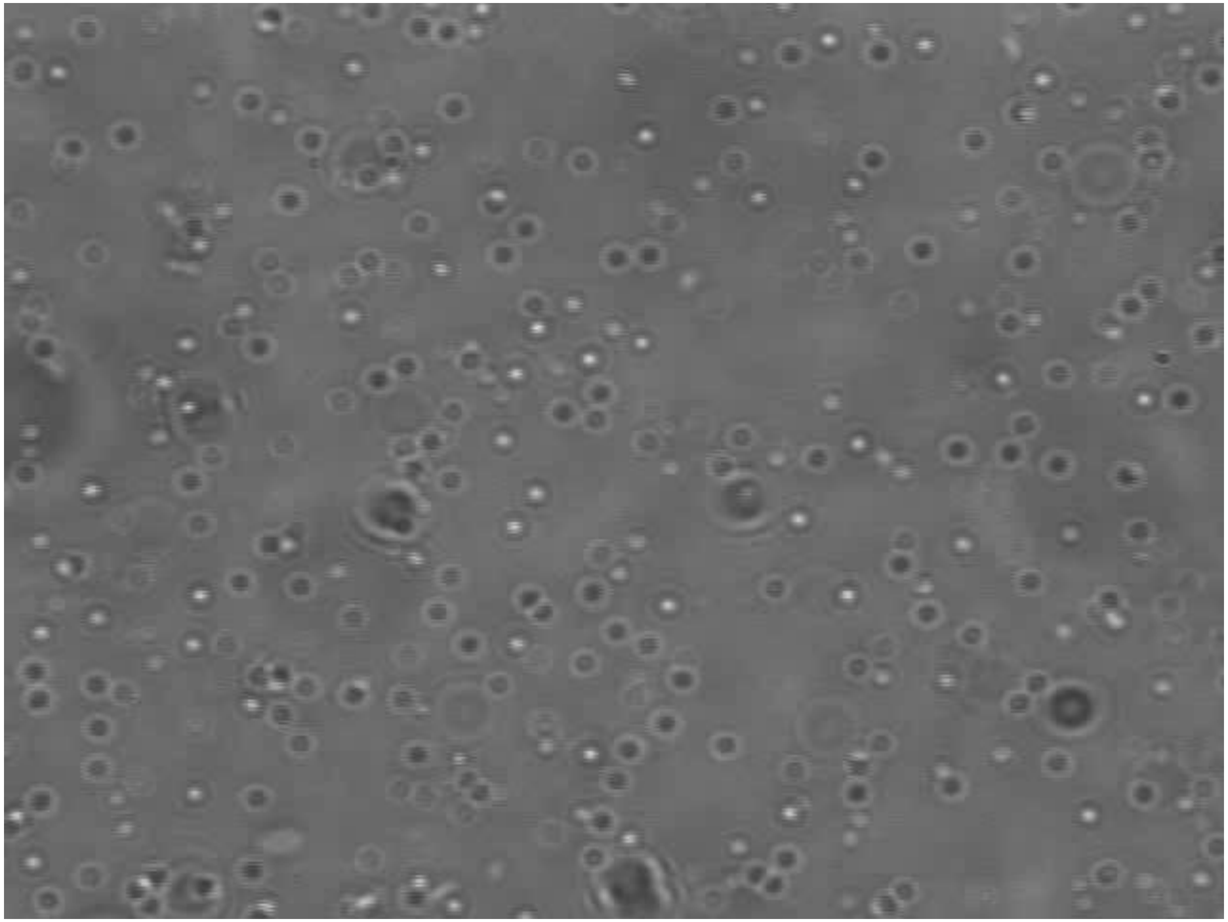
$$u \sim \frac{\eta R}{p} T_z$$

Gas molecules

Thermophoresis of silica beads in solution

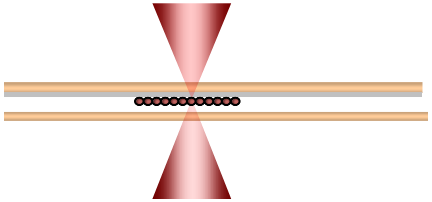
C: Density of Beads, ***T***: Temperature

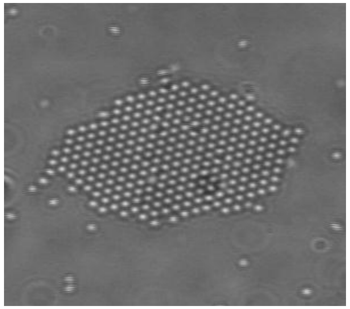
$$J = -D\nabla c - D_T c \nabla T$$



Transport of Micro-beads by Temperature Gradient

Sored Effect





Silica beads: 1 μm

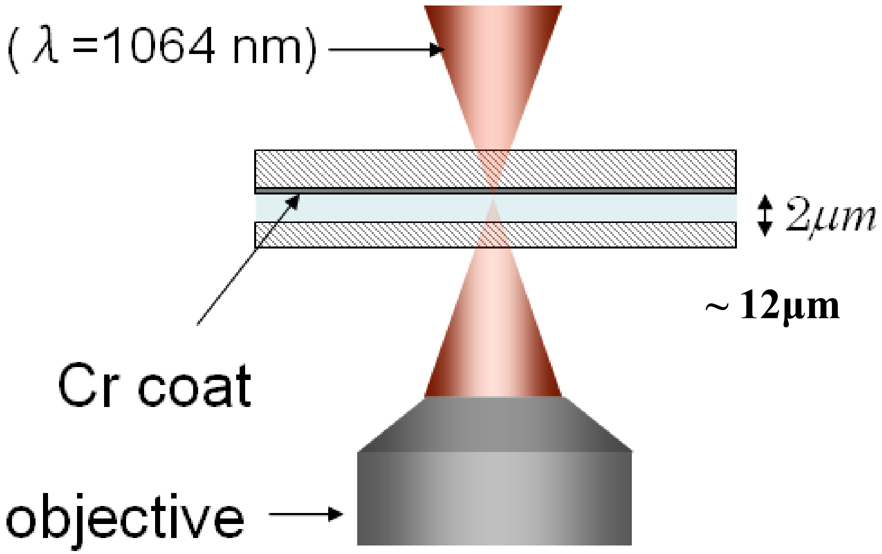
$$D_T < 0$$

Moves from cold to hot place

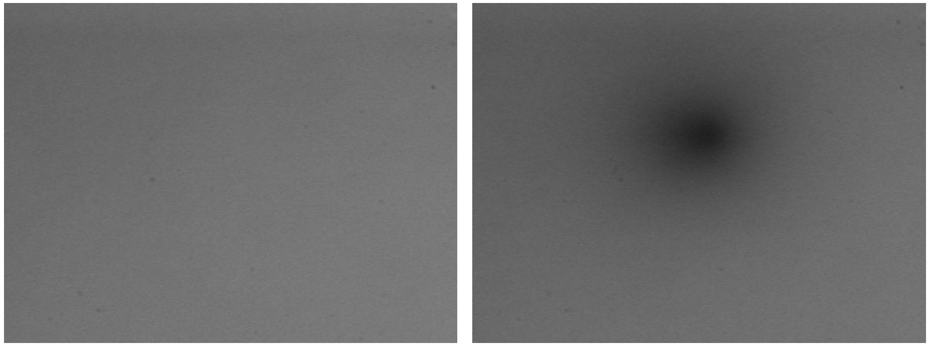
Experimental Setup

Laser: 1064nm, ~4mW

Thermal convection is negligible.

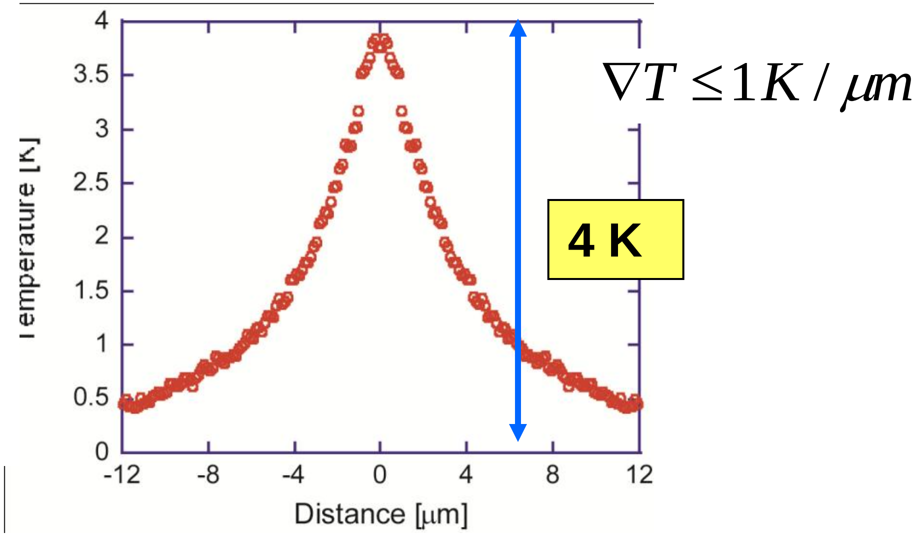


Temperature measured by fluorescent dye

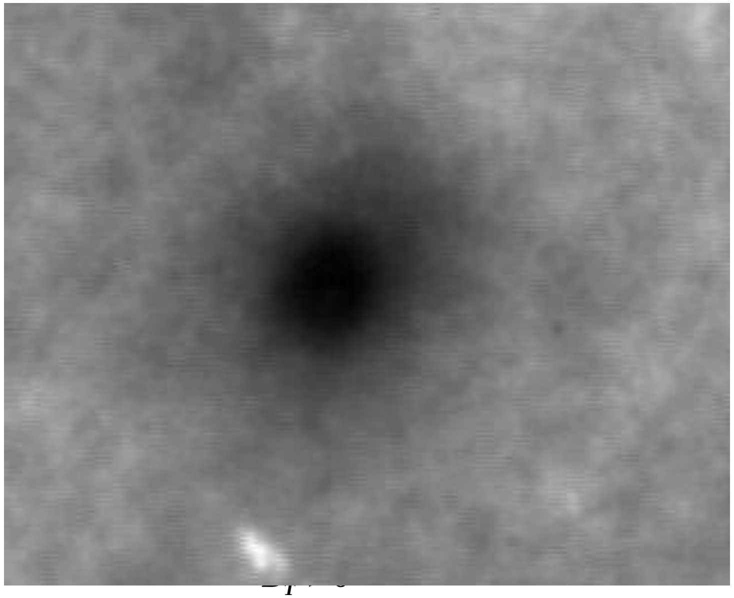


BCECF 50 uM
in 10mM Tris buffer

Temperature Distribution



Steady State Distributions of Polystyrene Beads



***D_T* is highly material dependent !**

100nm Fluorescent Polystyrene Beads

Move from hot to cold place

DNA also moves to cold place

$$D_T > 0$$

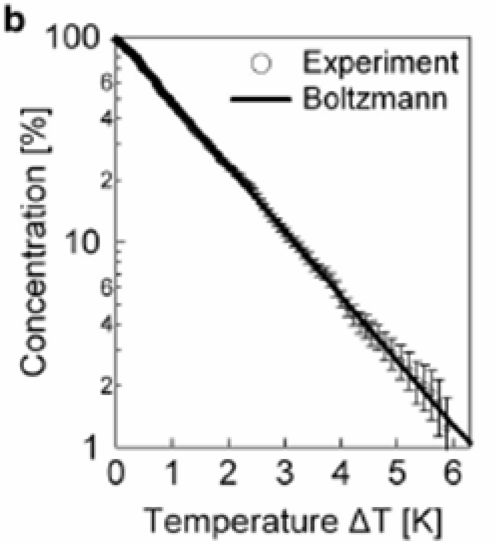
$$\boldsymbol{j}_m = -D\nabla c - D_T c \nabla T$$

$$S_T = \frac{D_T}{D} \text{ : Soret coefficient}$$

$$j_m = 0 \;\; \rightarrow \;\; \frac{dc}{c} = -\frac{D_T}{D} dT = -S_T dT$$

$$c(x) = c(x_0)\exp[-S_T(T(x) - T_0(x_0))]$$

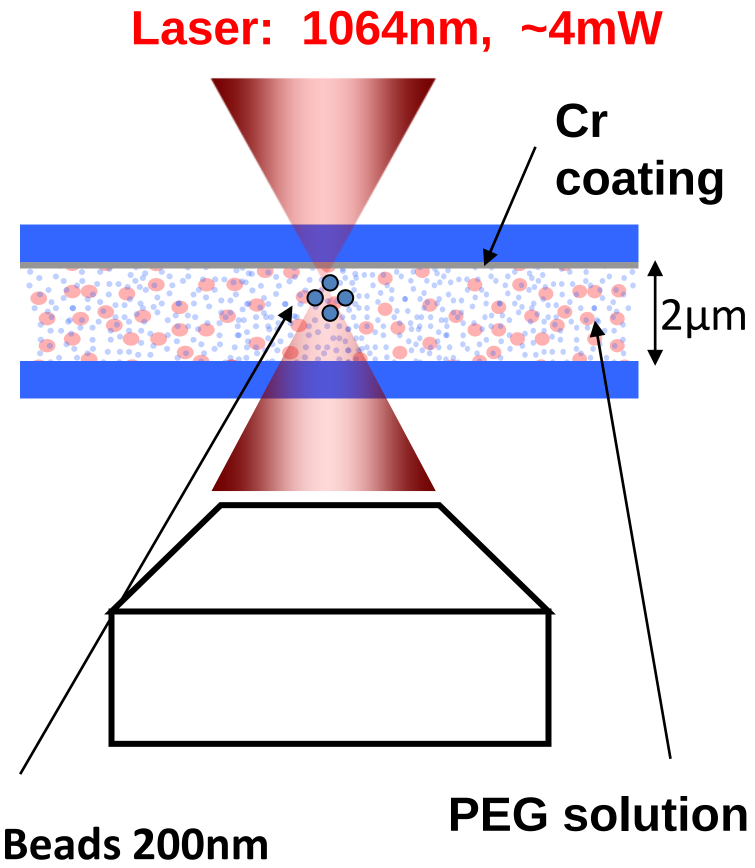
Soret coefficient can be measured from the slope of ***c*** vs ***T*** curve

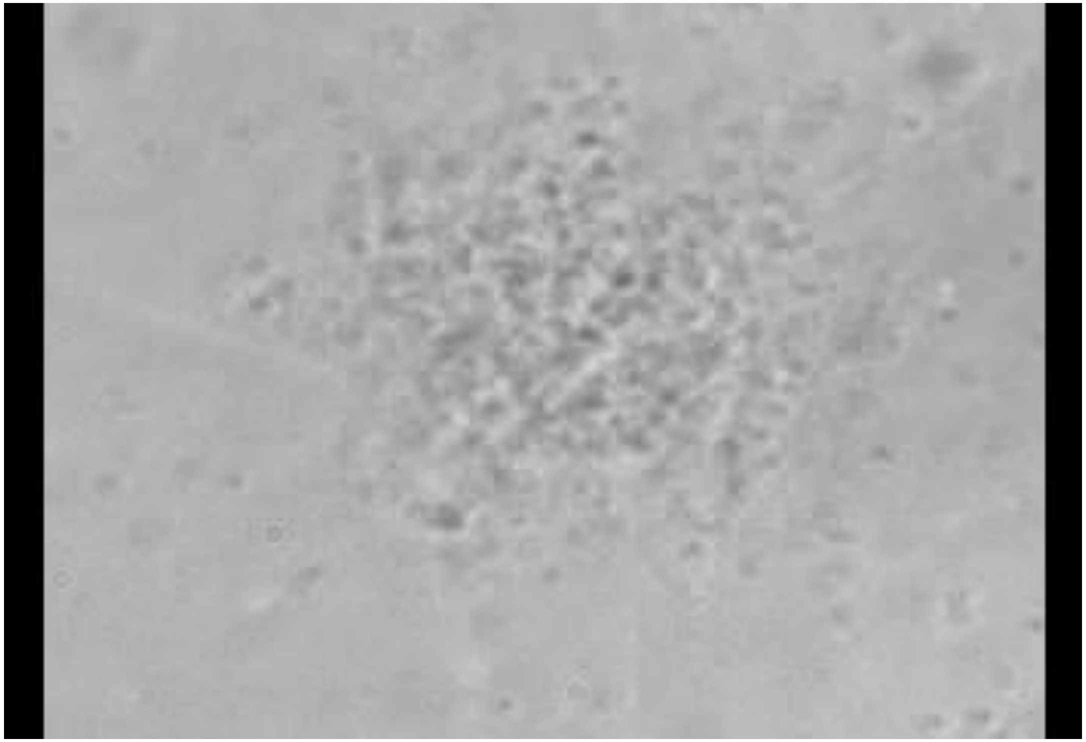


D. Braun, PRL(2006)

Thermal diffusion coefficient (D_T) is controllable in a polymer solution

Jiang, Wada, Yoshinaga, Sano, PRL (2009)





PEG (poly-ethylene-glycol)

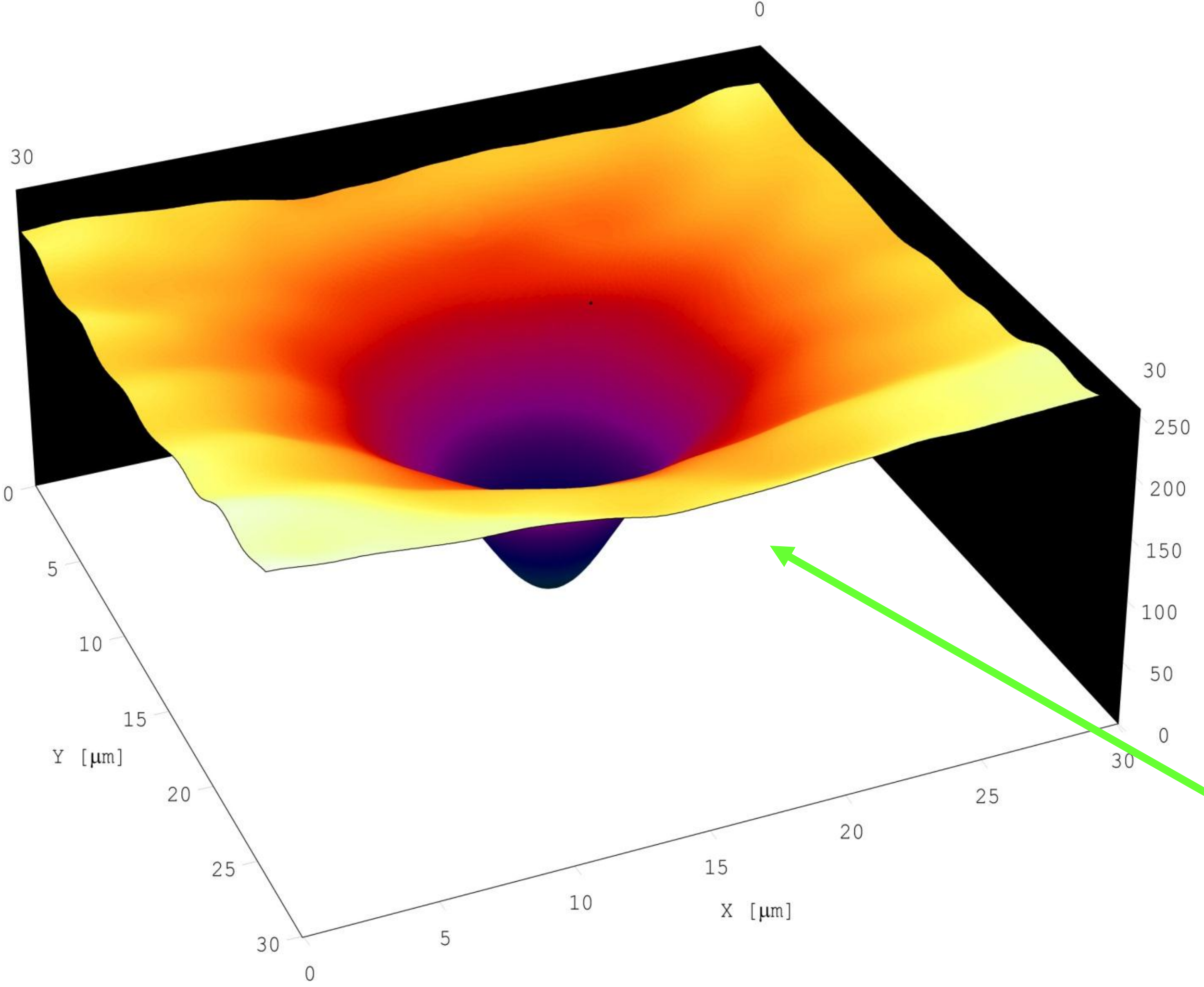
MW= 7500g

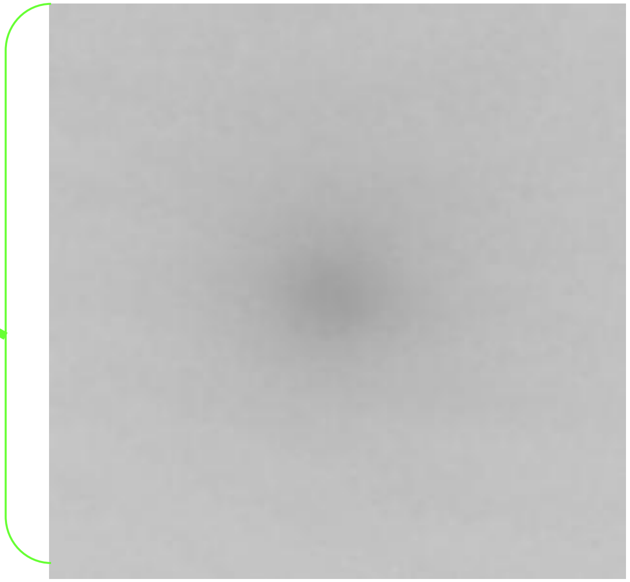
HO−(CH2−CH2−O)n−H

Possible Mechanism

Colloid Particle moves along the Gradient of Polymers

Thermo-Osmotic Trap

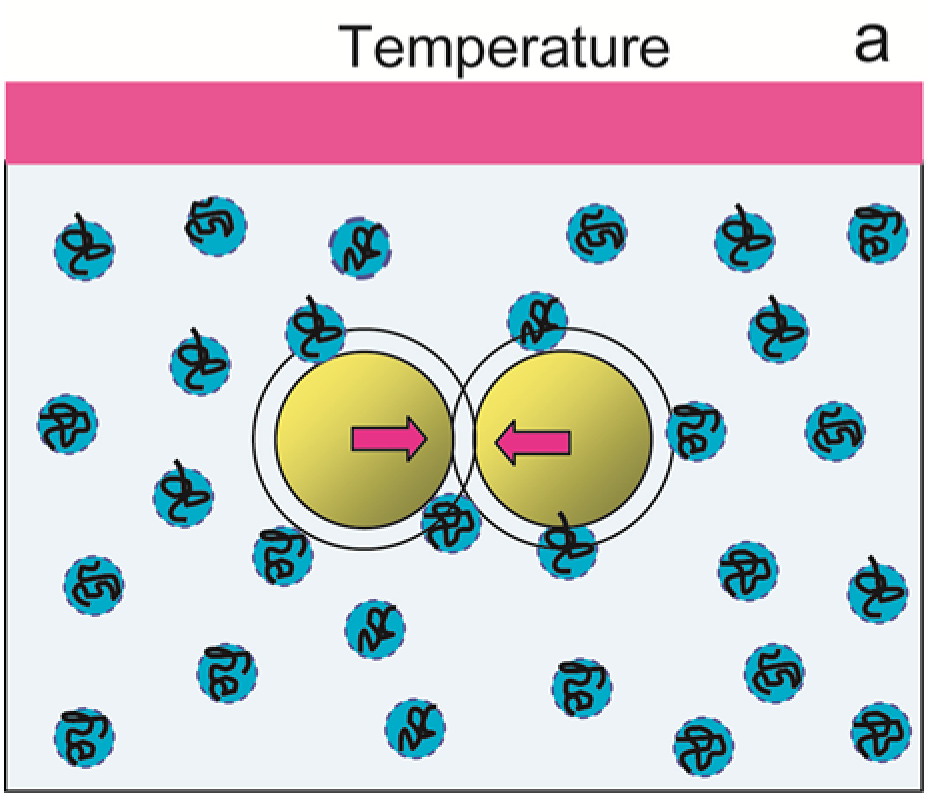




Distribution of Fluorescently Labeled PEG (PEG5000)

Possible Mechanism

Iso Thermal Condition



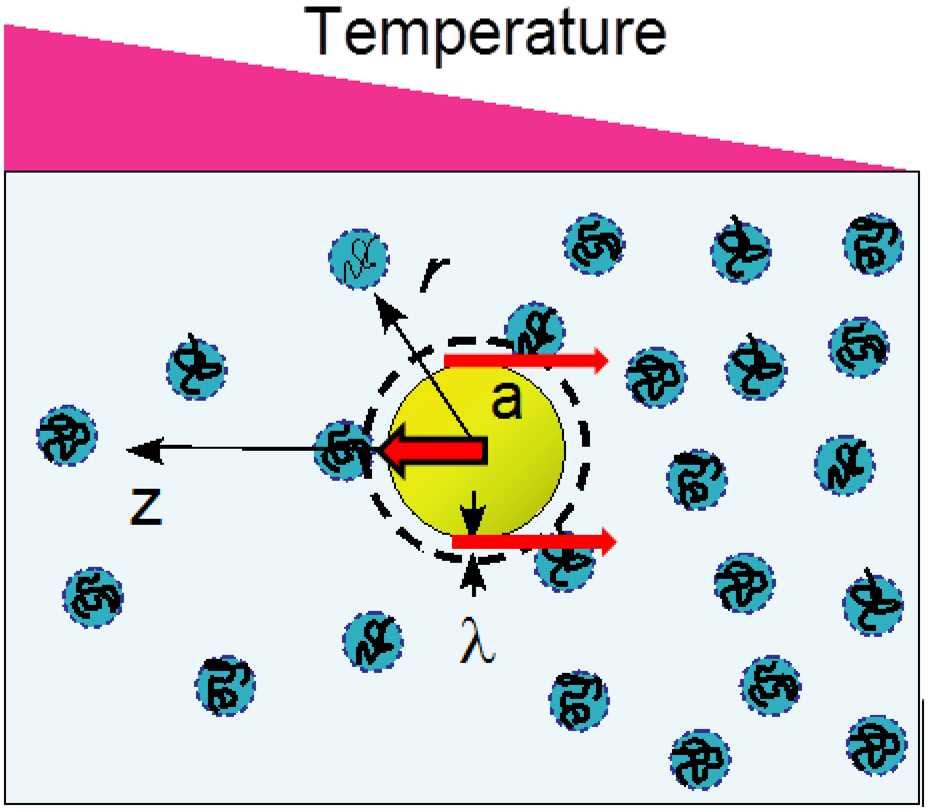
Depletion Force =

Osmotic Pressure

Oosawa, Asakura (1954)

Force is balanced for isolated particle

In Temperature Gradient

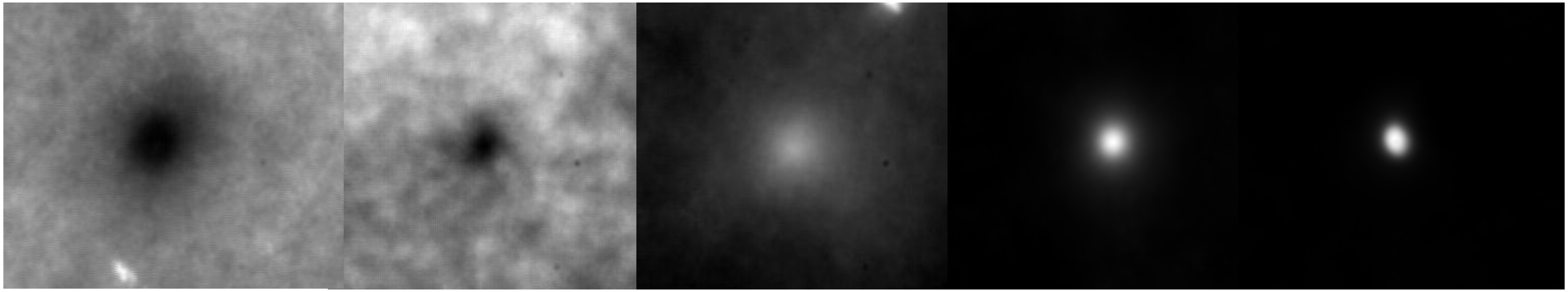


Asymmetry of polymer distribution exerts force to the isolated particle

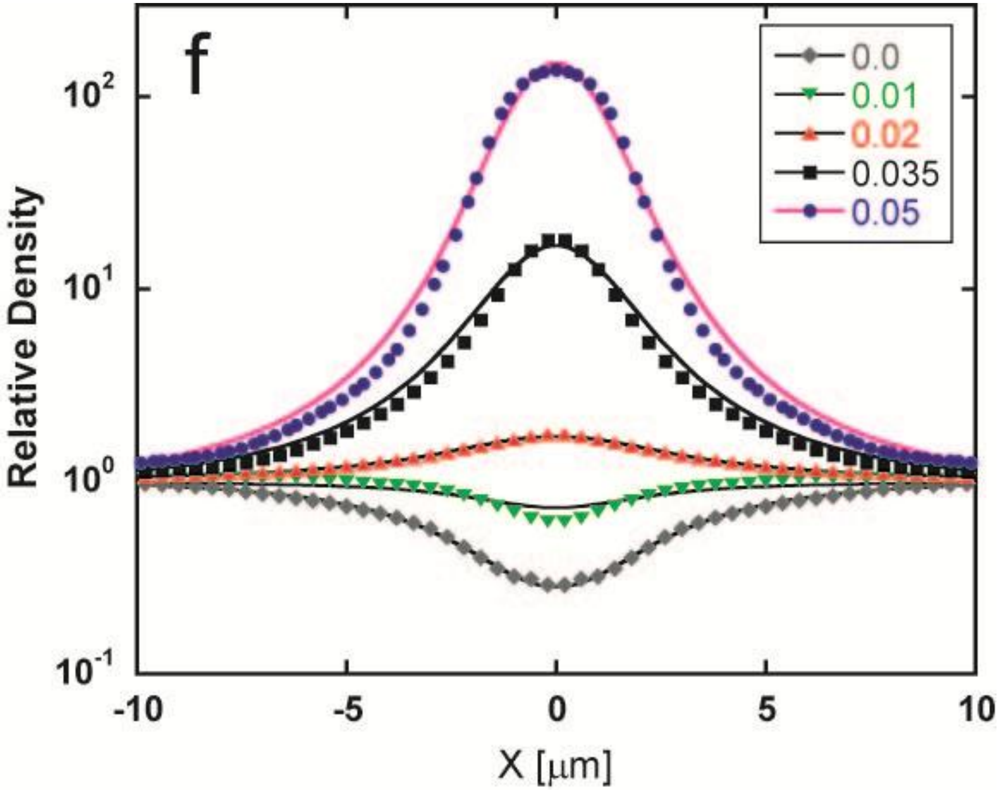
Thermophoresis driven Diffusiophoresis

$$u \propto \frac{k_B T}{\eta}\lambda^2 \nabla\rho \Rightarrow S_T = \frac{D_T}{D} \propto a\lambda^2 \nabla T$$

Accumulation of Beads depending on PEG concentration



PEG: 0% **1%** **2%** **3.5%** **5%**



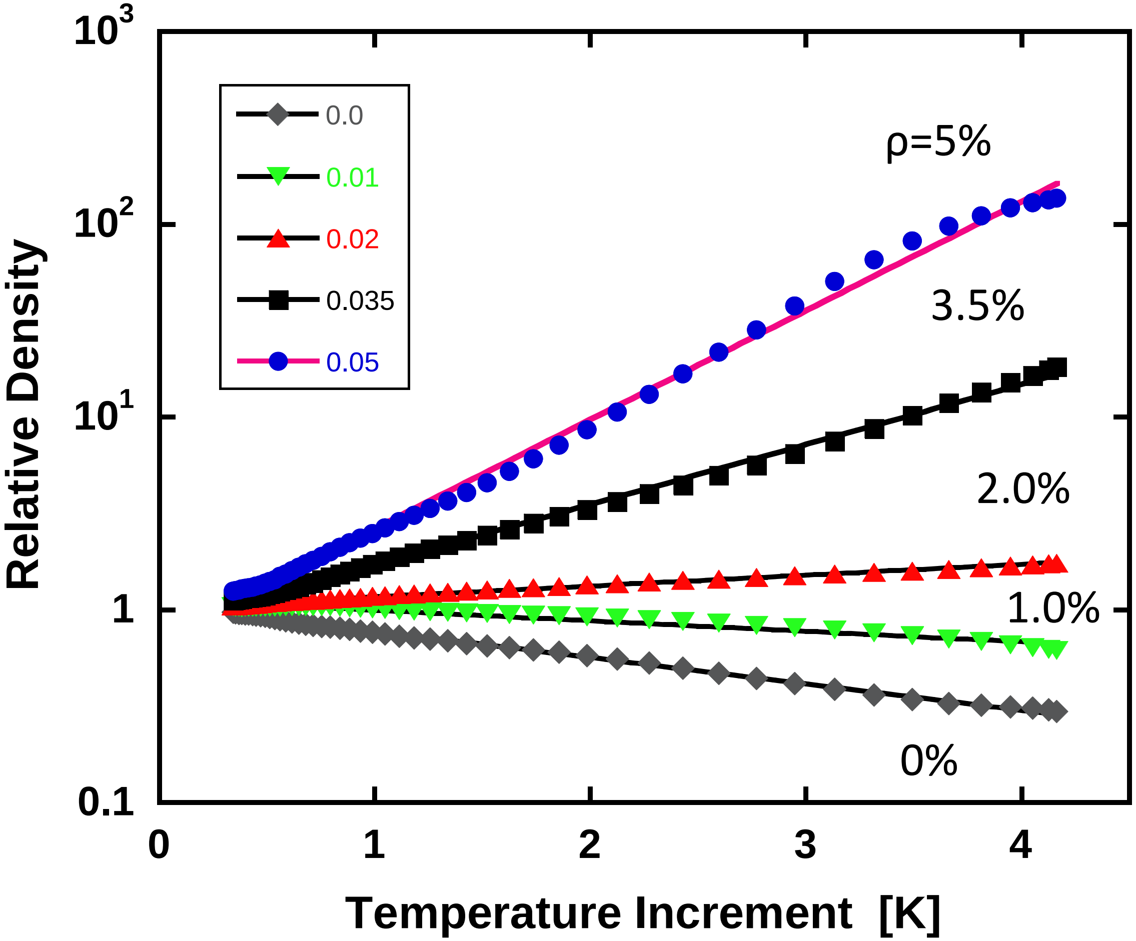
Jiang, Wada,

Yoshinaga, Sano

PRL, (2009)

Change of effective Soret Coefficient

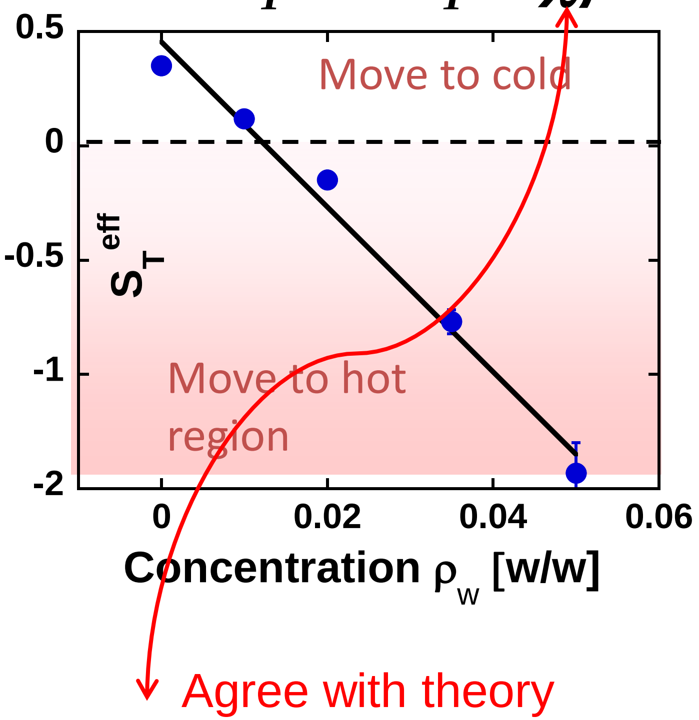
Effective Soret Coefficient vs. PEG concentration



Prediction:

$$\boxed{\chi = 2\pi(S_T^p - 1/T)a\lambda^2}$$

$$S_T^{eff} = S_T - \chi\rho$$



Agree with theory

Rg= 3nm ← λ=5nm

$$c(x) = c(x_0)\exp[-S_T^{eff}(T(x) - T_0)]$$

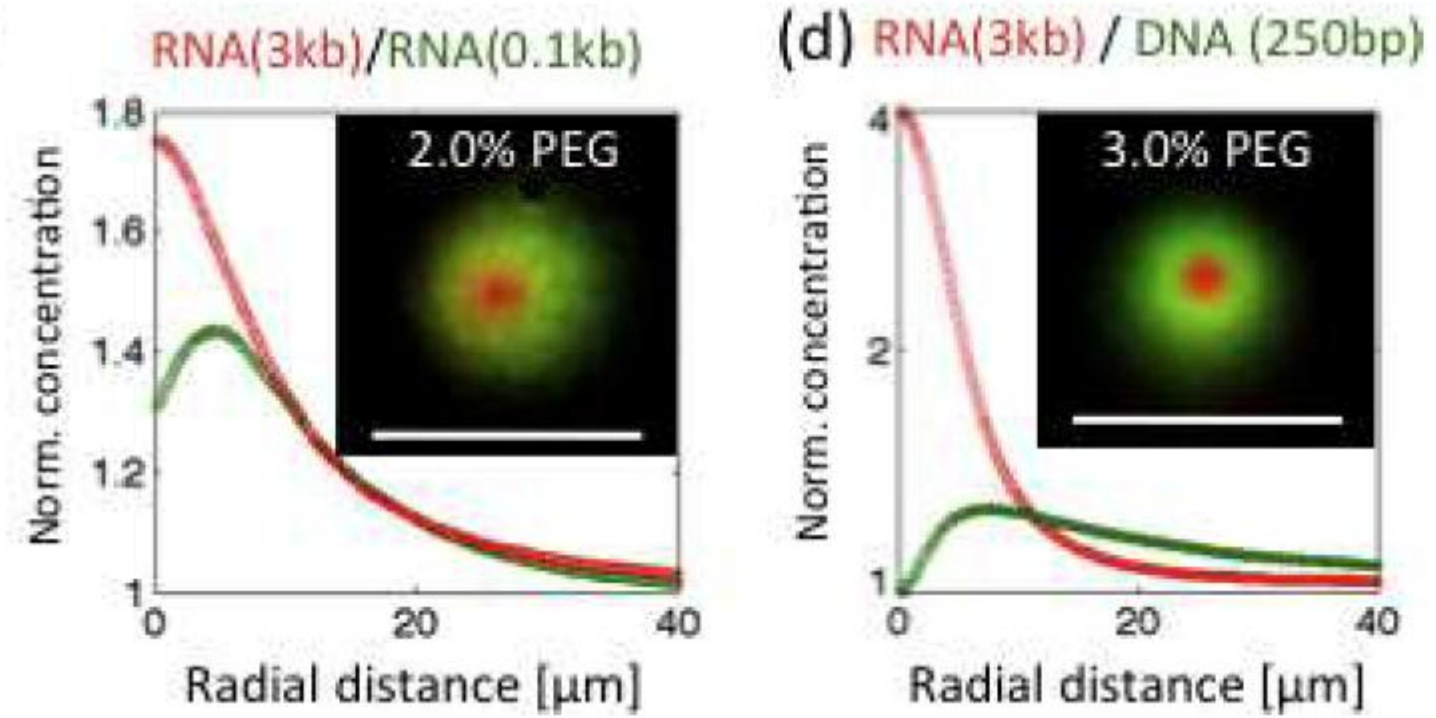
$$S_T^{eff} = S_T^{bead} - \rho_0 V_{dep} S_T^{poly} = S_T^{bead} - \chi\rho_0$$

Separation and Accumulation of RNA/DNA

New discovery (private comm.):

Even small RNA (10bases)
can be accumulated !!

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

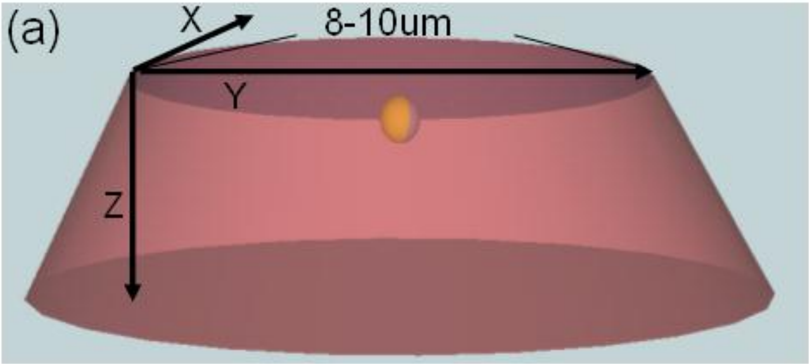


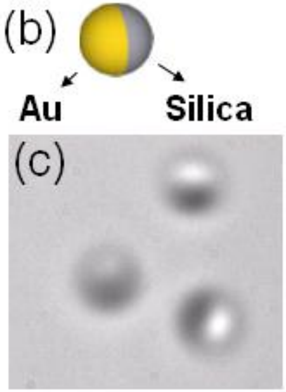
$$c(r) = c_\infty \exp\left[-S_T^b \Delta T(r) + V\left(\rho_\infty - \rho(r)\right)\right]$$

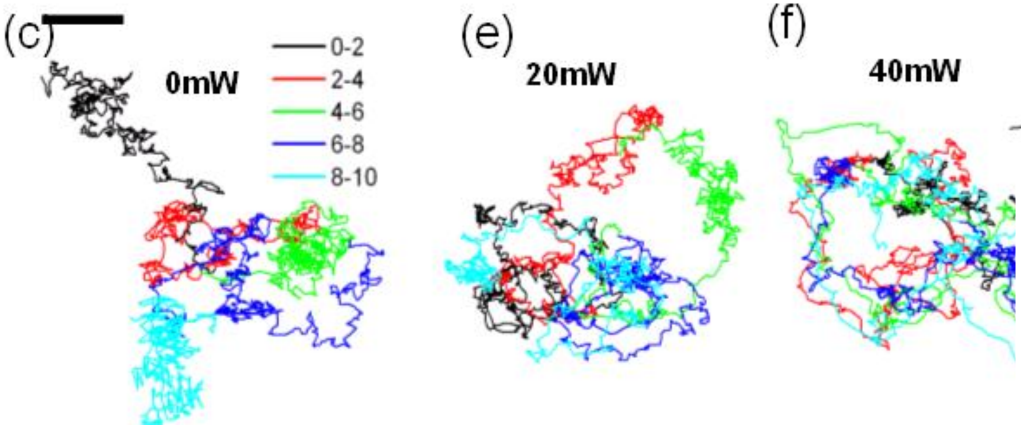
Ring formation! $\left|\frac{d\ln c(r)}{dr}\right|_{T_m} = 0$

$$\xrightarrow[S_T^P \Delta T \ll 1]{} \qquad c(r) = c_\infty \exp\left[-(S_T^b - \rho_\infty V S_T^p)\Delta T(r)\right]$$

Self-propulsion of Janus particle I : Self-thermophoresis



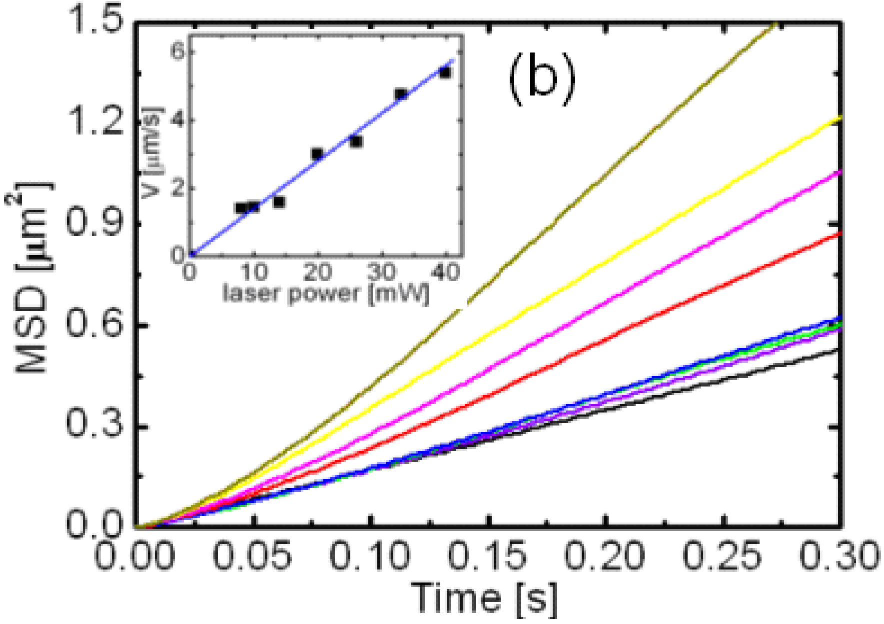




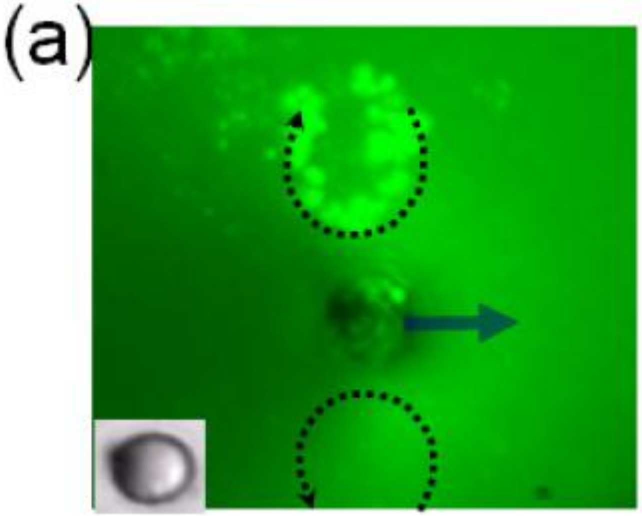
$$\left\langle \Delta r^2(t) \right\rangle = 2\tau V^2[t - \tau(1 - e^{-t/\tau})]$$

$$\left\langle \Delta r^2(t) \right\rangle \sim V^2 t^2, \qquad t << \tau$$

$$\left\langle \Delta r^2(t) \right\rangle \sim \tau V^2 t, \qquad t >> \tau$$

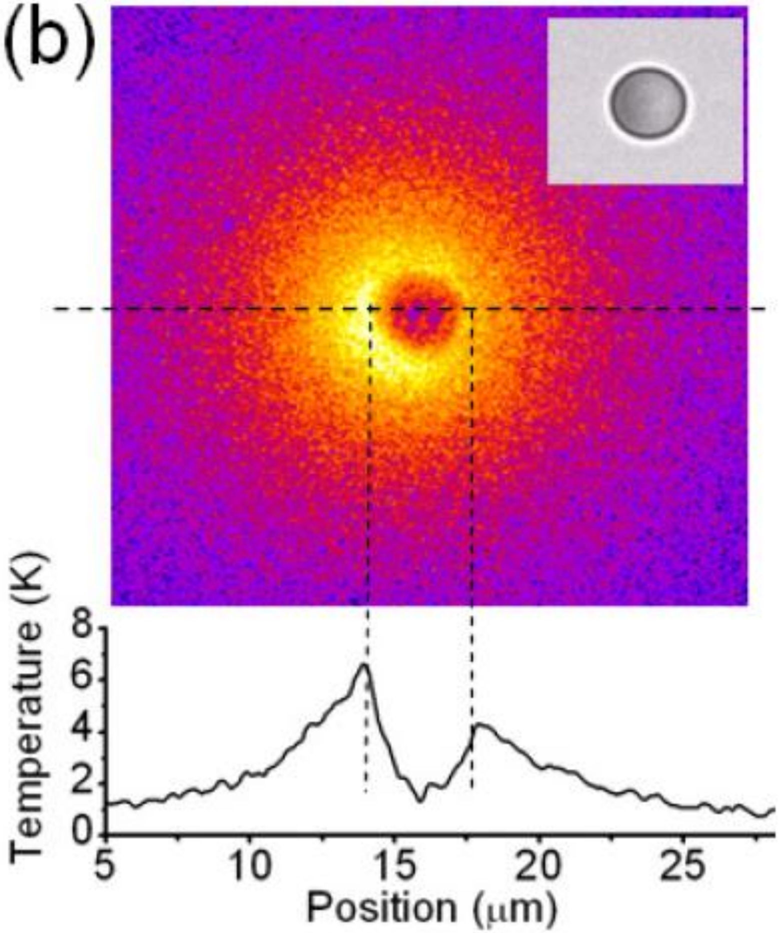


HR Jiang, Yoshinaga, Sano, PRL, 105, 268302 (2010)



Induced flow visualized by tracer particles around the fixed Janus particle

Temperature distribution around a Janus Particle



Temperature distribution :

$$T(R) = T_\infty + \sum_{n=1}^{\infty} \frac{q_n R}{(n+1)\kappa_o + n\kappa_i} P_n(\cos\theta).$$

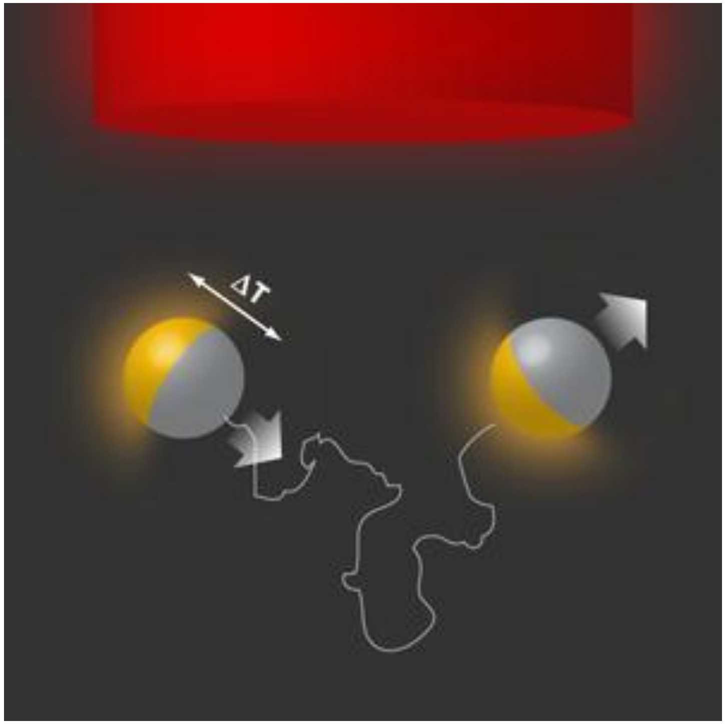
$$q(\theta) \;=\; \kappa \mathbf{e}_n \cdot \nabla T$$

$$\Delta T = 3\epsilon I R / 2(2\kappa_o + \kappa_i)$$

Seed of self-thermophoresis of Janus particle is related to the response to the external gradient

$$V = -\frac{1}{4} D (S_T^0 + S_T^G) \frac{\epsilon I}{2\kappa_o + \kappa_i}.$$

Theoretical calculation



Viewpoint in Physics, PRL (2010)

Light is absorbed on the metal side:

$$-\kappa_o \mathbf{n}\cdot\nabla T_o + \kappa_i \mathbf{n}\cdot\nabla T_i = q(\theta).$$

$$T(R) = T_0 + \sum_{n=0}^{\infty} \frac{q_n R}{(n+1)\kappa_o + n\kappa_i} P_n(\cos\theta)$$

Theoretical calculation by N. Yoshinaga

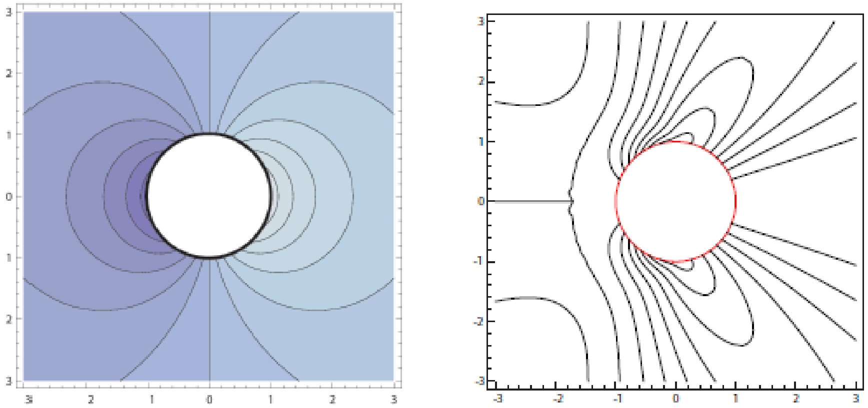
Effective slip velocity: $\boldsymbol{v}_s = v_s \boldsymbol{e}_\theta = \mu |\nabla T|_s \boldsymbol{e}_\theta$

$$\mu = -(k_B/\eta)\Gamma\lambda$$

Characteristic length: $\lambda = \Gamma^{-1}\int c_0 y(e^{-\beta U_0} - 1)dy$

U_0 : Interaction potential between the surface and fluid

$$\Gamma = \int c_0(e^{-\beta U_0} - 1)dy \qquad V = -\frac{1}{2}\int_0^{\pi} v_s \sin^2\theta d\theta.$$



Migration in an uniform external temperature gradient

$$V = -\mu T_1 = -DS_T T_1$$

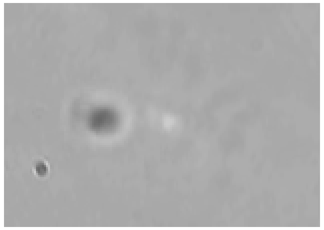
T_1 : Temperature diff. across the particle

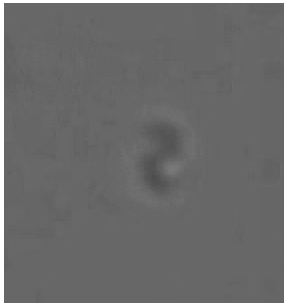
$$\mu = DS_T$$

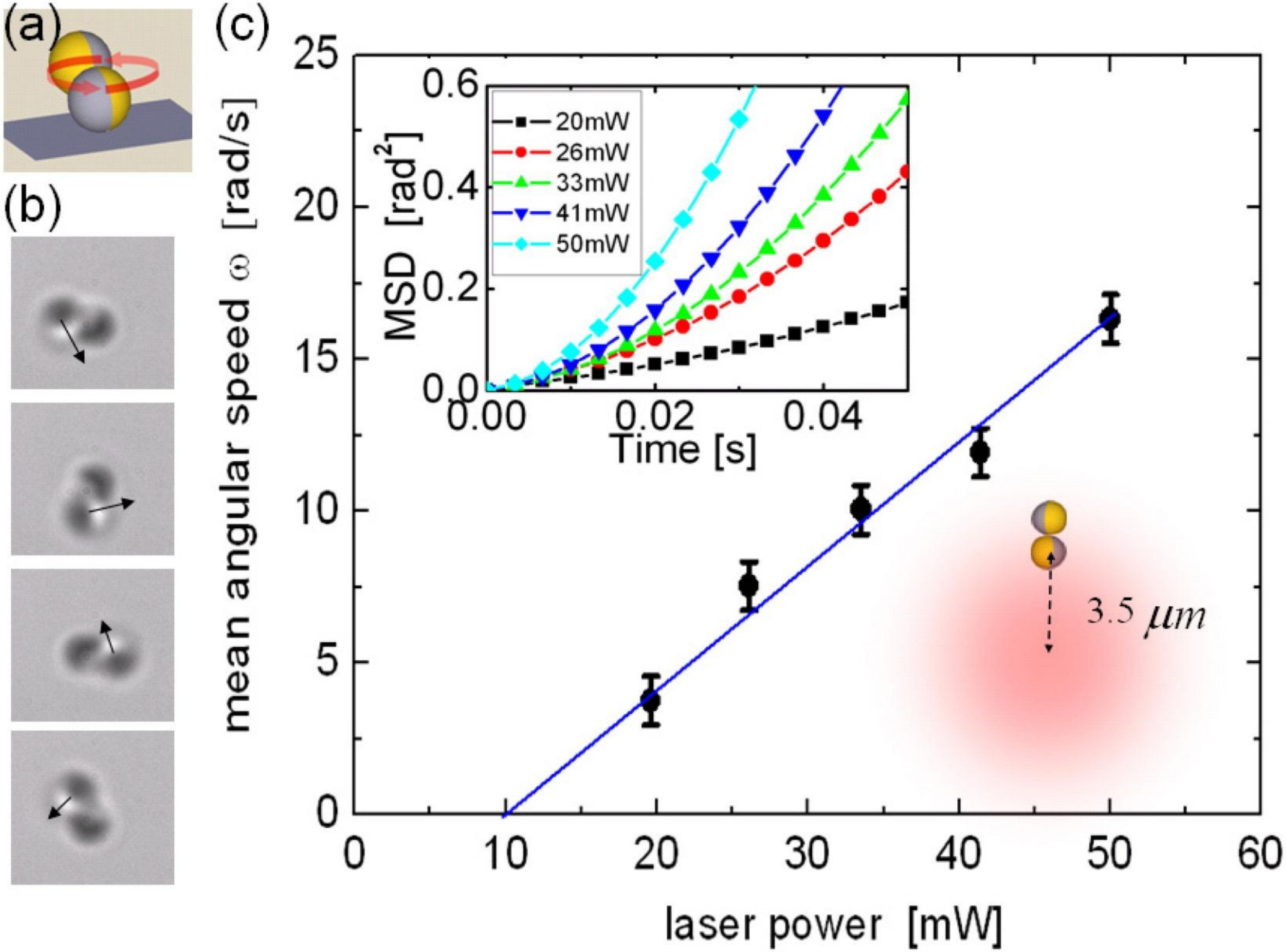
$$V = -\frac{1}{4}D(S_T^0 + S_T^G)\frac{\epsilon I}{2\kappa_o + \kappa_i}.$$

Migration speed is determined by the average of Soret coeff.

Rotation of Chiral Doublet: Thermophoresis



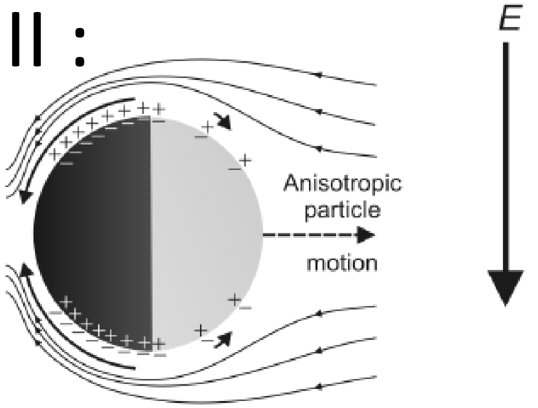




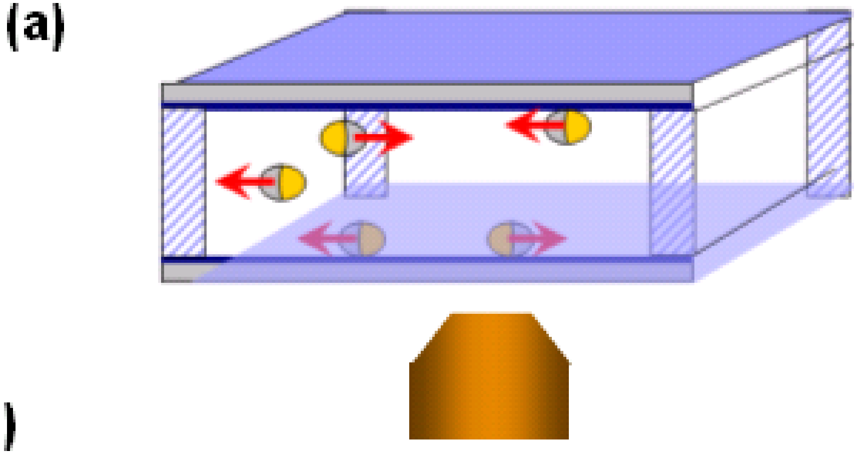
HR Jiang, Yoshinaga, Sano, PRL (2010)

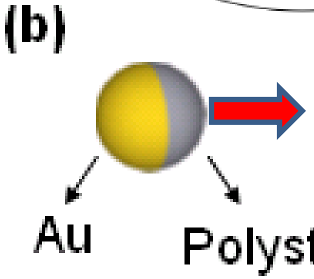
Self-propulsion of Janus particle II : Electric field

ICEO (Induced Charge Electro Osmosis)



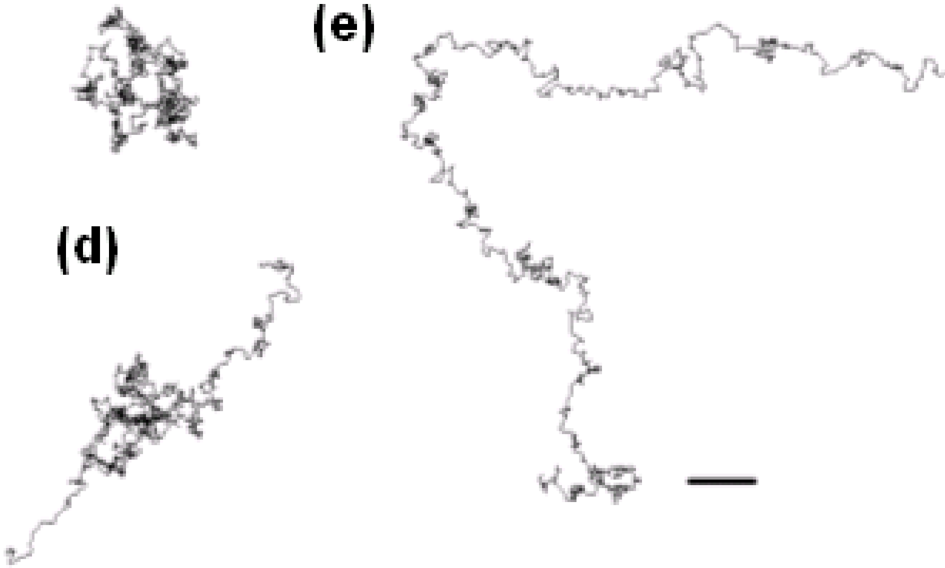
Gangwal et al. PRL (2008)

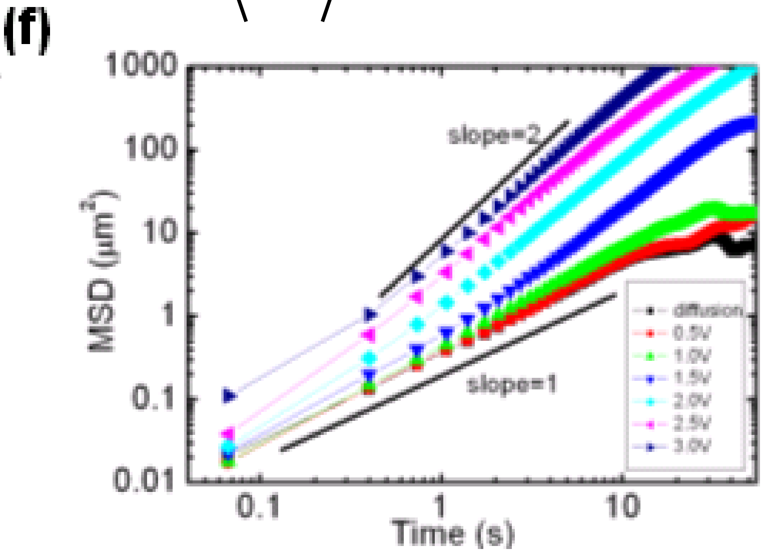




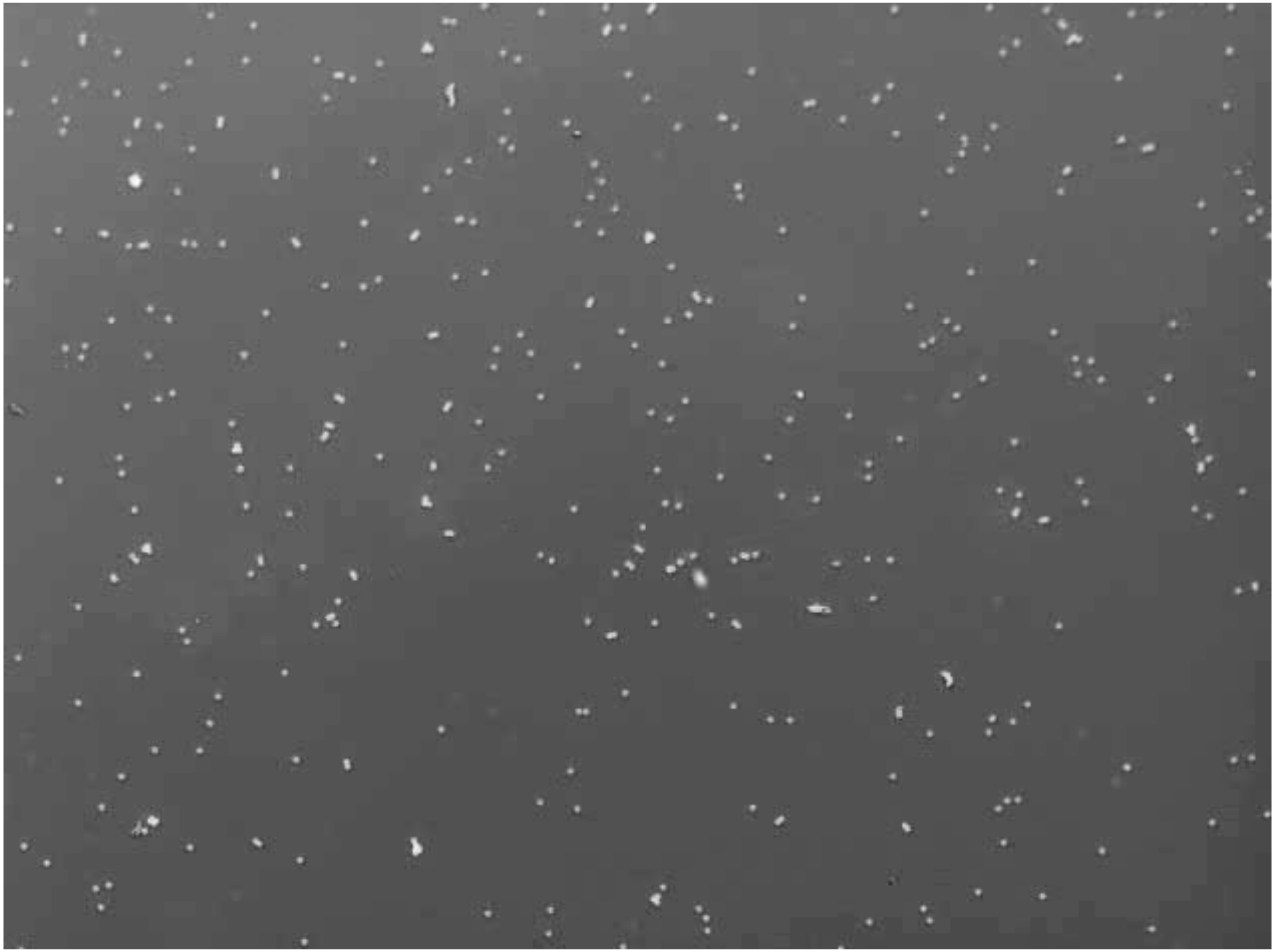
$$V_{ICEO} \sim \frac{\epsilon \varepsilon R E^2}{\gamma}$$

$$\langle r^2 \rangle = 4Dt + V^2 t^2$$

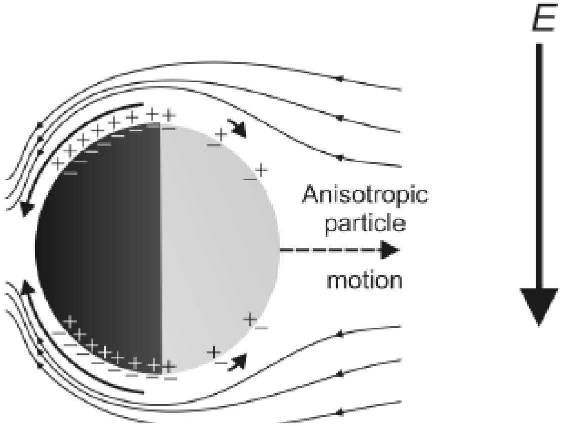




Motion of Janus Particle: Top View



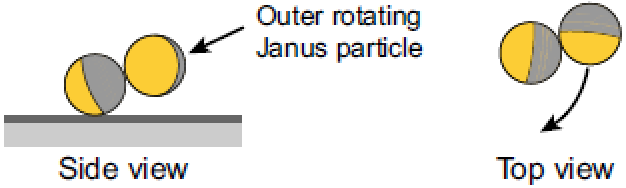
Surface slip flow drives particle

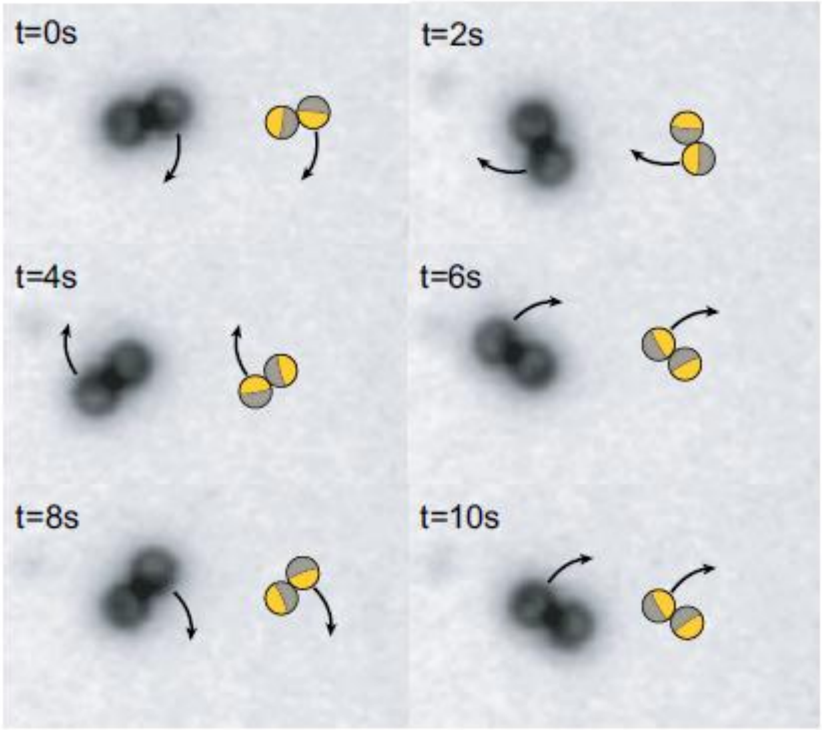


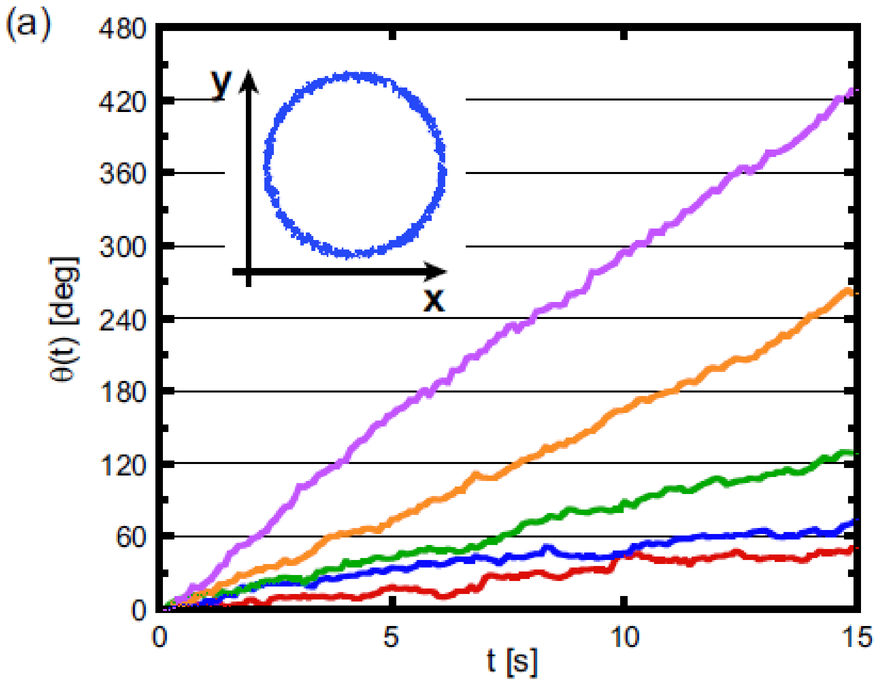
Visualization: Tracer particle 200nm fluorescent beads

Janus Particle: 6 µm

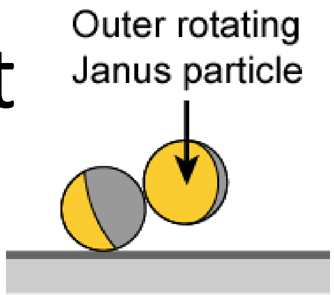
Rotation of Janus doublets by chiraliry







Fluctuation in Janus Chiral Doublet



Use of Fluctuation Theorem

$$\ln\left[P(\Delta\theta)/P(-\Delta\theta)\right] = \tau\,\Delta\theta/k_B T \quad \Leftarrow \quad \frac{p(\sigma)}{p(-\sigma)} = e^{\sigma}$$

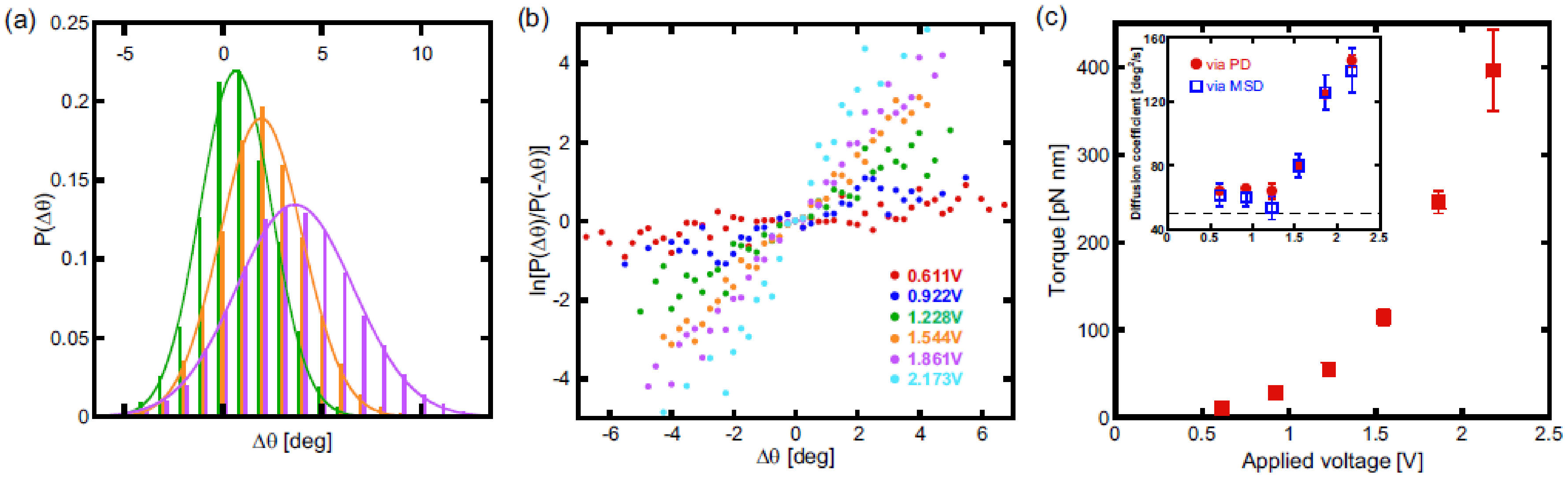
Precise determination of torque without using Stokes drag force.

However, fluctuations seem to be enhanced in nonequilibrium states.

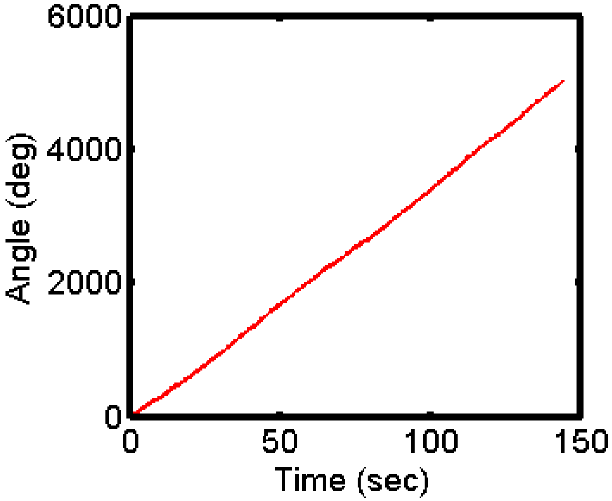
$$p(\Delta\theta, \Delta t) = \frac{1}{\sqrt{4\pi D\Delta t}} \exp\{-\frac{(\Delta\theta-\omega\Delta t)^2}{4D\Delta t}\}$$

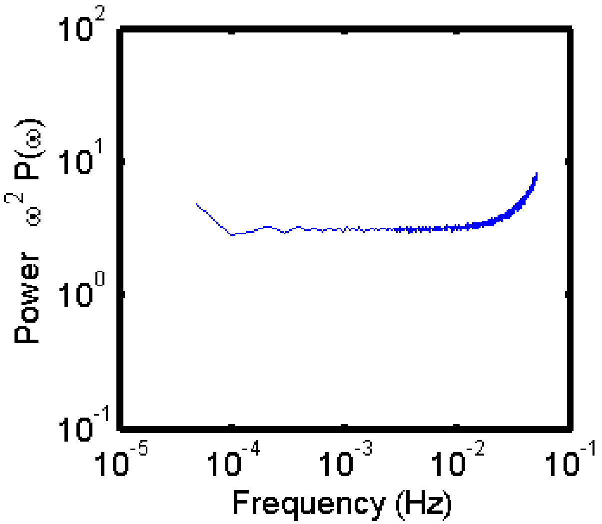
D: Increases with voltage

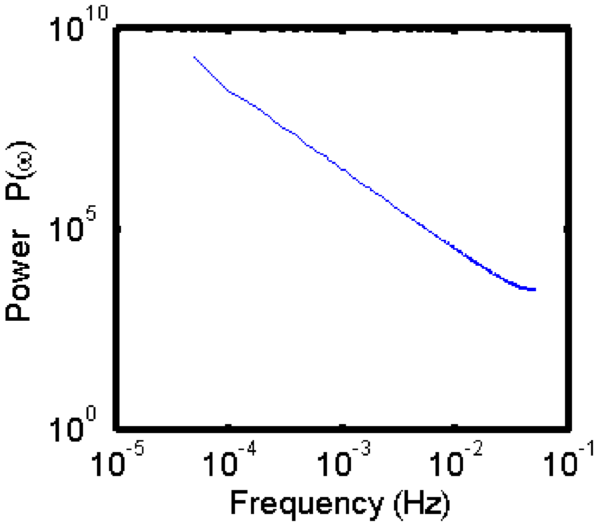
R. Suzuki, HR Jiang, M. Sano, in preparation

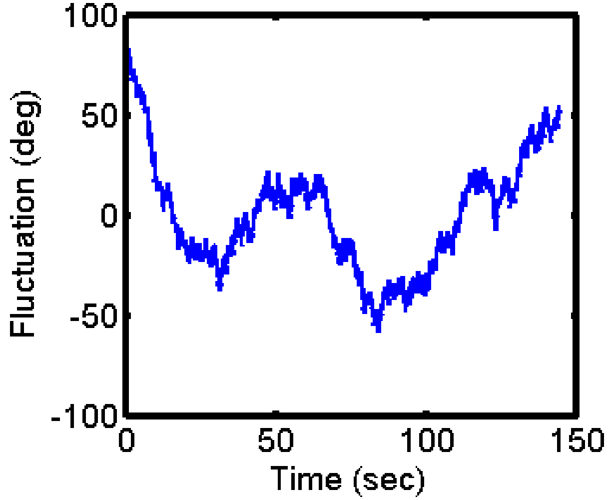


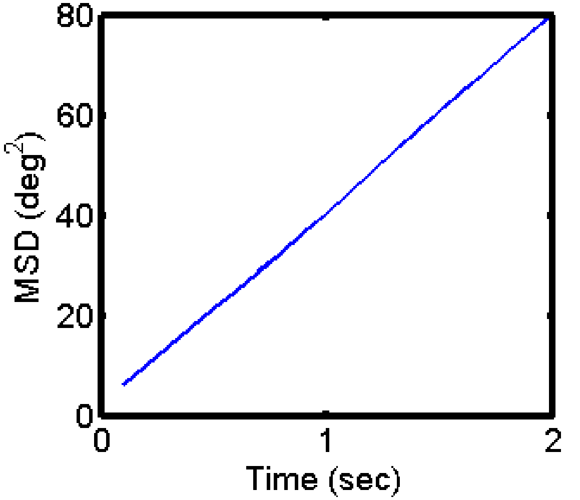
Diffusion is enhanced at far from equilibrium











Controlling Interaction between Janus Particle

- Existence of Crossover frequency: fc

- f< fc: Repulsive Interaction
- f> fc: Reversal of velocity,
  Attractive Interaction
  ⇨ Emergence of collective behavior

- Possible mechanism
  Dipole-Quadrupole Transition

Information and Feedback in Different Systems

	Fluctuation	**Information**	**Feedback**	**Outcome**
Maxwell's demon	Thermal	Speed, position	Biased Choice of fluctuations	Gain Free Energy
Active Particle	Thermal	-------	--------	Enhanced Diffusion
Bacteria (*Escherichia coli*)	tumbling	Chemotactic Signal	Change tumbling freq.	Chemotaxis
Amoeboid cell (*Dictyostelium Discoideum*)	Instability of cell shape	Chemotactic Signal	Biased Choice of random protrusion	Chemotaxis

Summary

- Different kinds of phoresis can be used to create self-propelled particles and control interaction of particles.

- In ICEO, direction of motion of Janus particles change sign, and interaction changes from repulsive to attractive at high frequency.

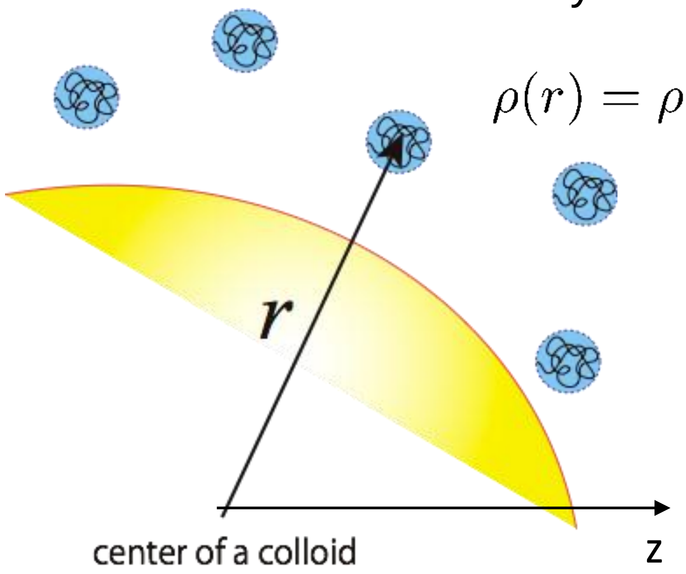
  (Diplole-Quadrupole transition?)

- Fluctuation increases at far from equilibrium.

Force acting from polymer to the fluid

We consider two component systems, water and polymer, and calculate the effect on a single colloidal particle. Polymer-colloid surface interactions drive the fluid

Polymer density obeys Boltzmann distribution



$$\rho(r) = \rho_0(z)e^{-U(r)/k_BT}, \qquad \delta\rho(r) = \rho_0(e^{-\beta U(r)} - 1)$$

force density on the fluid

$$\boldsymbol{f} = -\rho(r)\nabla U(r)$$

Force density acting on the fluid

$$\boldsymbol{f} = \nabla[k_BT\delta\rho(r)] + k_BT(S_T - \frac{1}{T})\delta\rho\nabla T$$

$$\frac{\rho}{\rho_0} = -S_T^p\nabla T$$

thermophresis of polymer at infinity

Solve the Stokes equation

$$\eta\nabla^2\boldsymbol{v} = \nabla p + \boldsymbol{f}, \quad \nabla\boldsymbol{v} = 0$$

Axial force due to temperature gradient

$$\begin{aligned}\eta\nabla^2\boldsymbol{v} &= \nabla(p + k_BT\delta\rho(r)) + f_0(r)\boldsymbol{e}_z \\ f_0(r) &\equiv k_BT\rho_0(S_T - \frac{1}{T})(1 - e^{-\beta U})T_z \equiv A(1 - e^{-\beta U(r)})T_z\end{aligned}$$

Force acting back to the particle

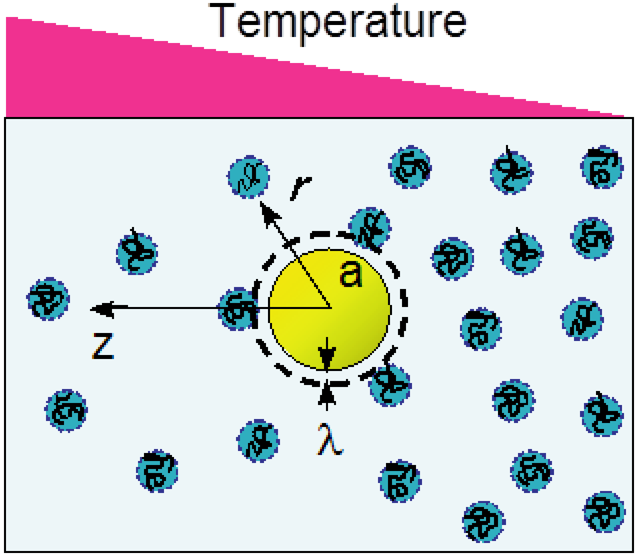
No external force is acting on the particle

$$\mathbf{F}_{tot} = \int_0^\pi 2\pi a^2 \sin\theta d\theta \left(\sigma^0_{rr}\cos\theta - \sigma^0_{r\theta}\sin\theta\right)_{r=a} - \underline{\int_a^\infty 4\pi r^2 dr f_0(r)\hat{\mathbf{e}}_z} = 0$$

viscous stress

non-equilibrium stress → $f_z\hat{\boldsymbol{e}}_z$

$$\begin{aligned} f_z &= -4\pi \int_a^\infty r(r-a) f_0(r) dr \\ &= -4\pi A T_z \int_a^\infty r(r-a)(1-e^{-\beta U}) dr \\ &= -2\pi k_B T \rho_0 (S_T^p - \frac{1}{T}) a \lambda^2 T_z \end{aligned}$$



$$U(r) = \begin{cases} \infty & (a < r < a+\lambda) \\ 0 & (a+\lambda < r) \end{cases}$$

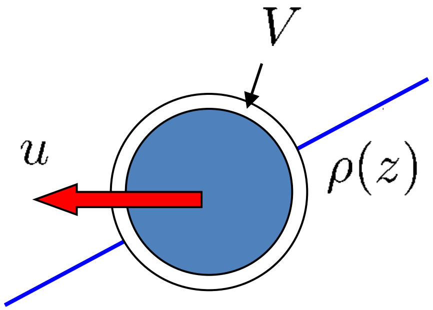
for stick boundary condition

$$S_T = -\beta f_z / (\frac{dT}{dz}) = S_T^0 - 2\pi (S_T^p - \frac{1}{T}) a \lambda^2 \rho_0 \propto a\lambda^2 \rho_0$$

λ : Size of polymer

Interpretation by energy dissipation

Free energy (Entropy) change due to migration:



$$\delta G \sim k_B T \delta\rho$$

$$\frac{\partial G}{\partial t} \sim k_B T V \frac{\partial \rho}{\partial t} \sim k_B T a^2 \lambda u \nabla \rho$$

$$\text{Depletion Volume} : \boldsymbol{V} \sim \boldsymbol{a}^2 \lambda$$

Dissipation by shear: $$J \sim \eta \dot{\gamma}^2 V \sim \eta(\frac{u}{\lambda})^2 a^2 \lambda \sim \eta \frac{u^2}{\lambda} a^2$$

Energy balance: $$\frac{\partial G}{\partial t} \sim J$$

$$u \sim \frac{k_B T}{\eta} \lambda^2 |\nabla \rho| \sim \frac{k_B T}{\eta} \rho_0 S_T^p \lambda^2 |\nabla T| \sim -D_T |\nabla T|$$

$$S_T = -\frac{D_T}{D} = -\frac{6\pi\eta a D_T}{k_B T} \propto \rho_0 S_T^p a \lambda^2$$

Same as the result of hydrodynamic calculation !