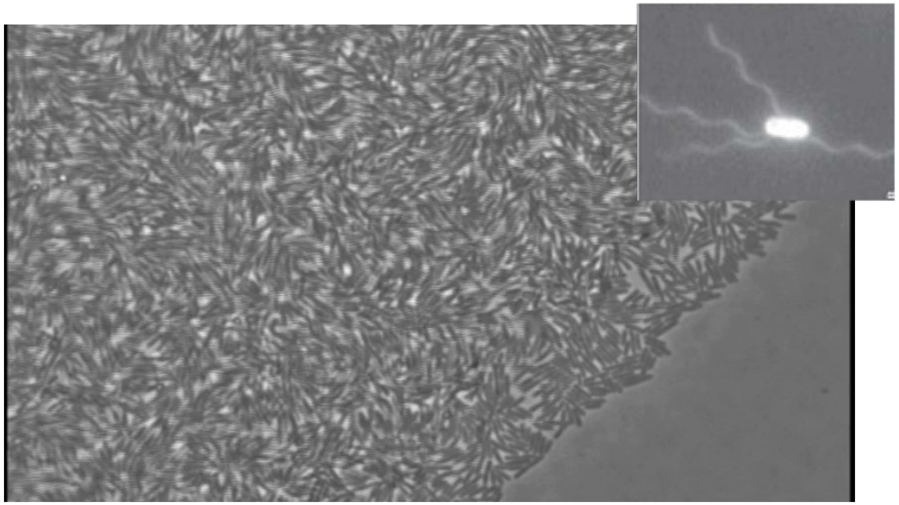
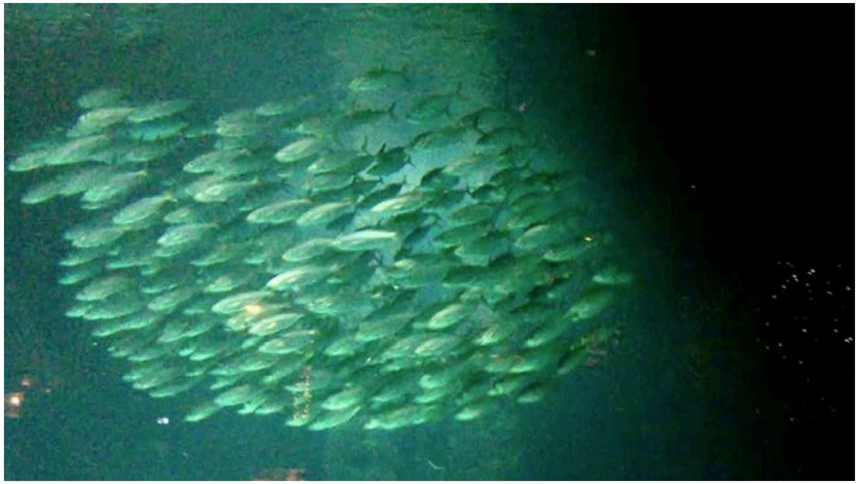
# Phoretic active matter and micromachines

Marisol Ripoll, Forschungszentrum Jülich, Germany

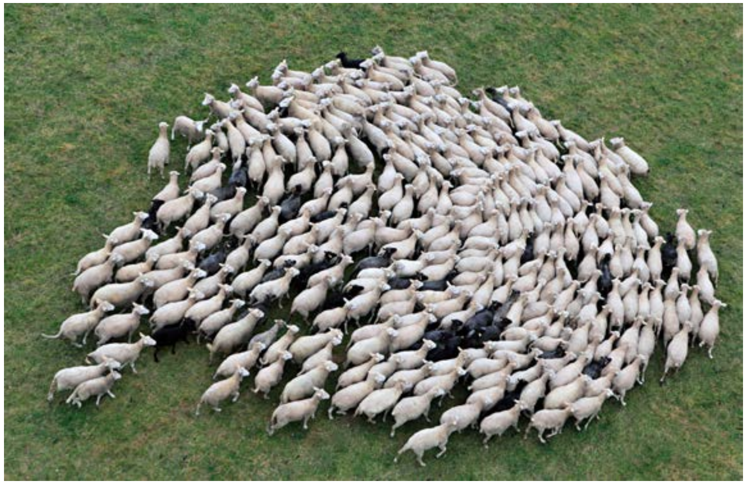
# Active matter : collective behavior



Bacteria colony



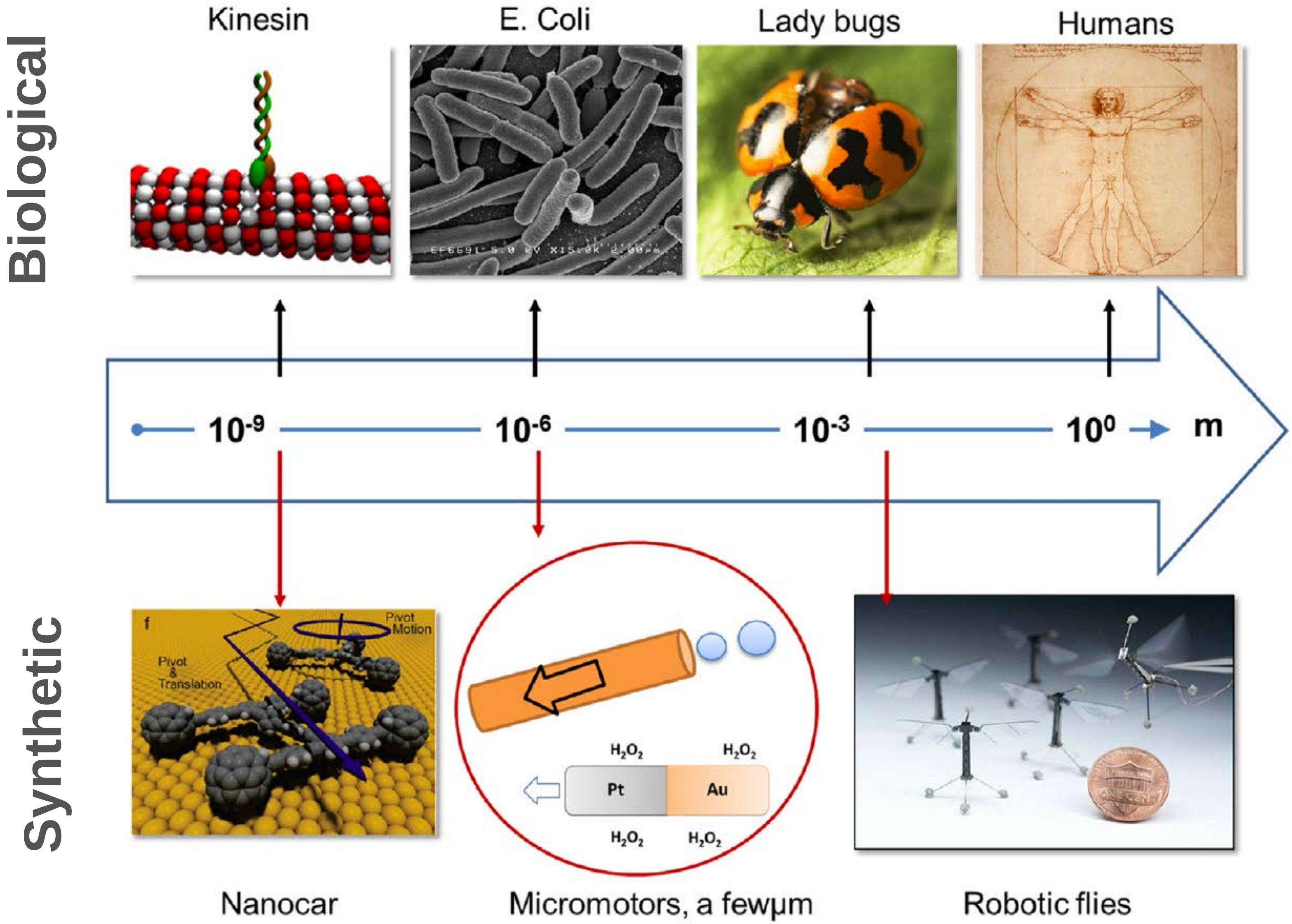
School of fish



Mammalian herd

Flock of birds

# Active matter : systems




Wang, Duan, Ahmed, Mallouk, Sen, *Nano Today* (2013) **8,** 531

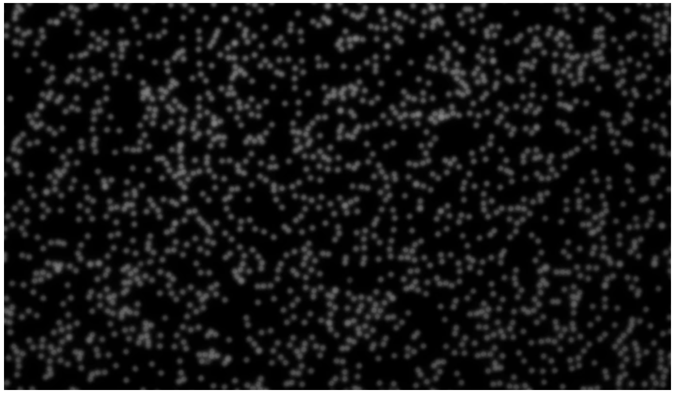
# Micromachines: Precise control at micro-nano scales

## Science fiction already thought about it



## True science is still working on it …

Di Leonardo *et al.*, *PNAS* (2010) **107,** 9541



Weinert and Braun, *PRL* (2008) **101,** 168301

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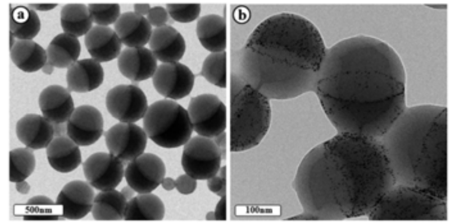
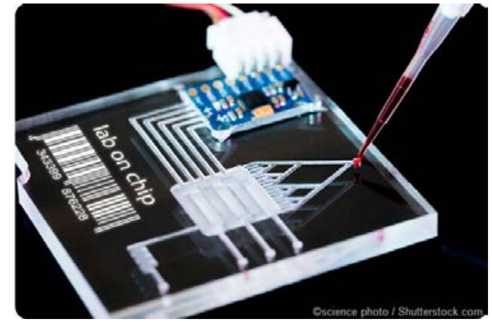
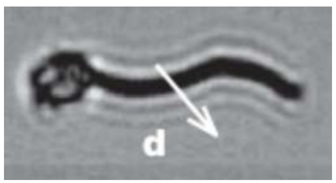
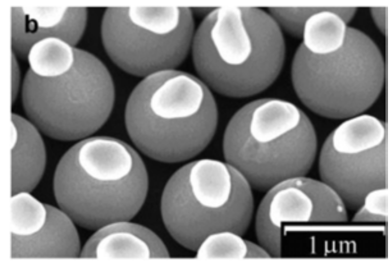
# Challenges:
# Active matter and micromachines







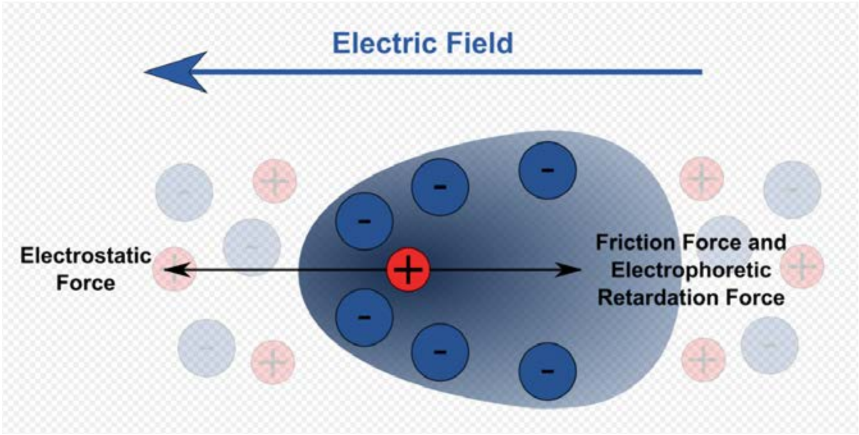

- Unravelling underlying mechanisms
- Precise control at micro-nanoscale:
  microfluidics, microsurgery, drug delivery
- Materials with novel properties
- Harvesting of waste energy / refrigeration

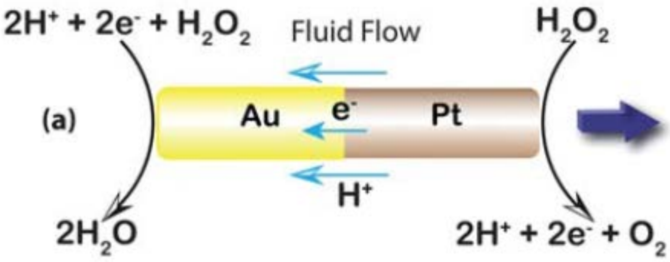
HELMHOLTZ
GEMEINSCHAFT

# Phoresis = 'migration'

## (Physics) particle drift due to a solvent gradient

- Electrophoresis
- Magnetophoresis
- Diffusiophoresis
- Thermophoresis



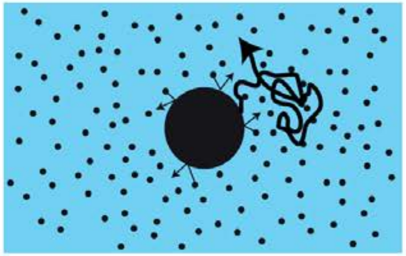



# What do we mean by thermophoresis ?

- Colloids are small particles (10 nm to 1 $\mu$m)

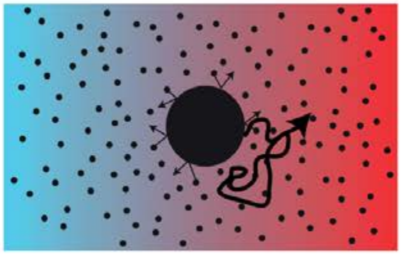
  that interact with even smaller solvent particles ($\sim 0.2$nm)

- Colloid-solvent interactions are random but balance on average → Brownian motion



No average displacemet: $\langle \Delta x = 0 \rangle$

- If the solvent temperature is not homogeneous



→ interactions do not necessarily balance

Net drift displacemet: $\langle \Delta x \neq 0 \rangle$

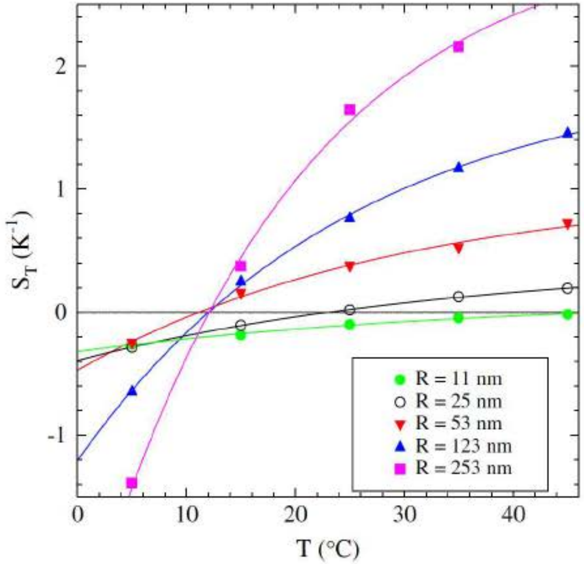
→ Thermophoresis (thermodiffusion)

- Typical gradients in the microsale are huge ($\nabla T \simeq 0.1 K/\mu m = 10^5 K/m$)

# Thermophoresis of colloids

Review: R. Piazza and A. Parola, *J. Phys.: Condens. Matter* **20** 153102 (2008)
A. Würger, *Rep. Prog. Phys.* **73** 126601 (2010)

Experiments: M. Braibanti, D. Vigolo, R. Piazza, *Phys. Rev. Lett.* **100** 108303 (2008)




- Thermophoretic behavior is very sentitive to various factors

$$\mathbf{f}_T = -\alpha_T k_B \nabla T \begin{cases} S_T = \alpha_T/T \text{.- Soret coefficient} \\ S_T > 0 \text{.- colloid to cold} \\ S_T < 0 \text{.- colloid to warm} \end{cases}$$

– Changing size or average temperature can change the direction of the drift

... and it is not always clear why

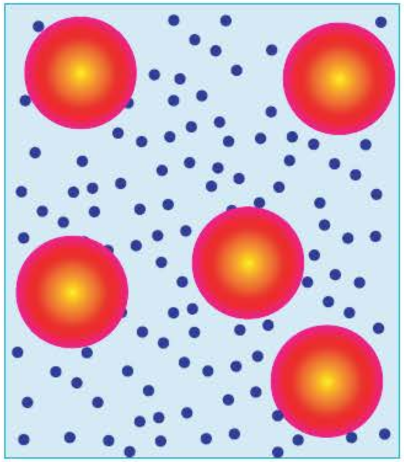
# Simulations of colloidal dispersions



Challenge:

- separation of relevant scales

  → coarse grained solvents



**LENGTH SCALES**

colloid: 10-1000 nm

solvent: 0.2 nm

**TIME SCALES**

characteristic time t*

$2Dt^* = a^2$

$t^* \sim \eta a^3/kT$

colloid: $t^* \sim 10^{-7} - 10^{-3}$ s

solvent: $t^* \sim 10^{-12}$ s

Requirements:

- Correct equilibrium description
- Hydrodynamic interactions
- Thermal noise
- Temperature gradient sustainability

Available methods:

- Brownian dynamics
- Lattice Boltzmann
- Dissipative particle dynamics
- Multi-particle collision dynamics

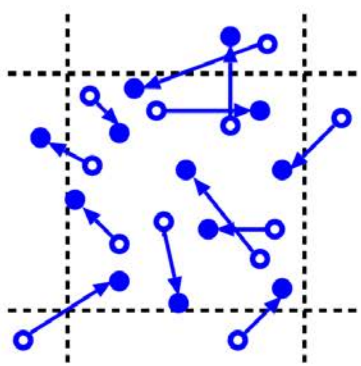
# Solvent: Multiparticle collision dynamics (MPC, SRD)

A. Malevanets, R. Kapral, *J. Chem. Phys.* **110** 8605 (1999)

$N$ point particles
- continuous positions $\mathbf{r}_i(t)$
- continuous velocities $\mathbf{v}_i(t)$
- discrete time increment $h$

Dynamics in two steps

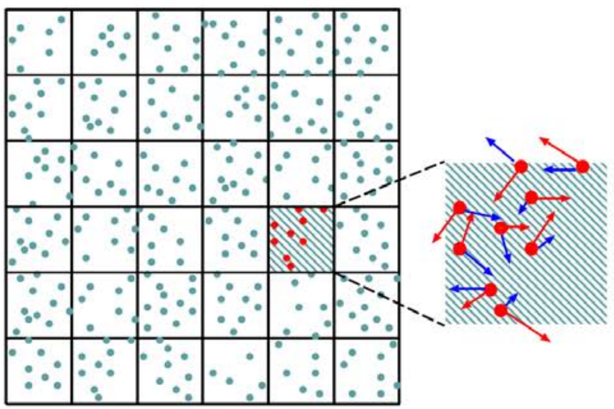
**Streaming**



- ballistic motion

$$\mathbf{r}_i(t+h) = \mathbf{r}_i(t) + h\mathbf{v}_i(t)$$

**Collision**



- particles are sorted into collision boxes
- stochastic rotation by angle $\alpha$

$$\mathbf{v}_i(t+h) = \mathbf{v}_{cm,i}(t) + \mathcal{R}(\alpha)\left[\mathbf{v}_i(t) - \mathbf{v}_{cm,i}(t)\right]$$

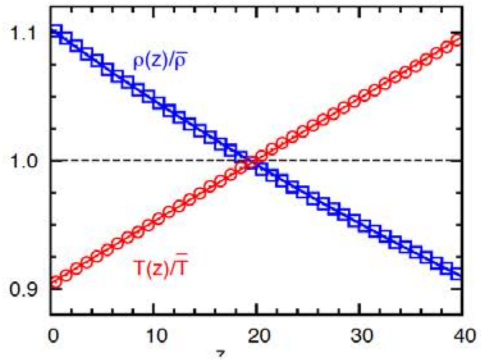
# MPC: Explicit mesoscopic solvent



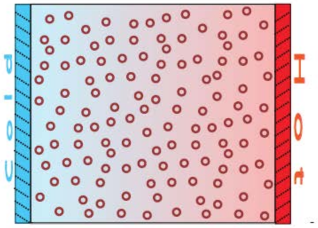
- ▶ Stochastic interactions
- ▶ Mass, momentum conservation
- ▶ Local energy conservation

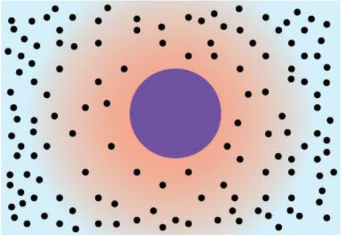
→

- Thermal noise
- Hydrodynamic interactions
- Temperature gradients




- MPC has the equation of state of an ideal gas
  → Density profiles varies with temperature
    - Compressibility effects ??

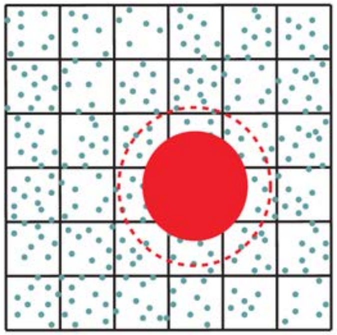




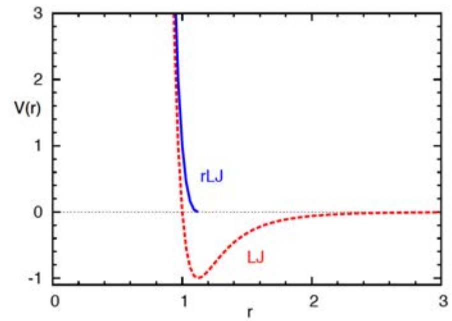
D. Lüsebrink, M. Ripoll, *J. Chem. Phys.* **136** 084106 (2012)

# Thermophoresis of colloids with MPC: MD

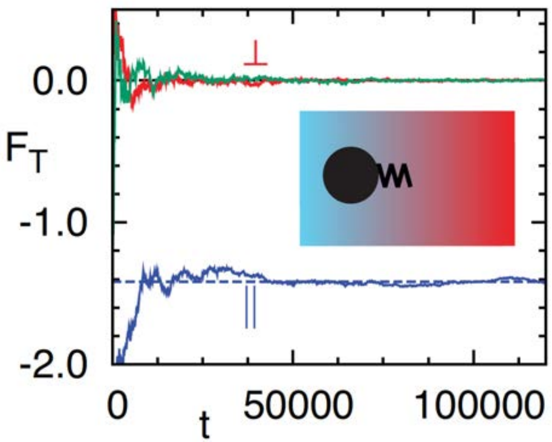
- Interactions occur in a boundary layer



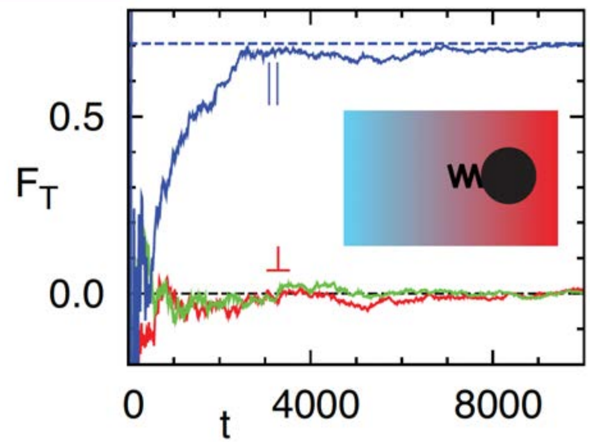
- MD: Lennard-Jones potential




Attractive → thermophobic




Repulsive → thermophilic




Thermophoretic force: $\mathbf{f}_T = -S_T k_B T \nabla T = -\alpha_T k_B \nabla T$

$\alpha_T$.- thermodiffusion factor (colloid property)

Lüsebrink, Yang, Ripoll, *J. Phys: Cond. Mat.* (2017) **24,** 284132

# Flow field by a drifting phoretic colloid

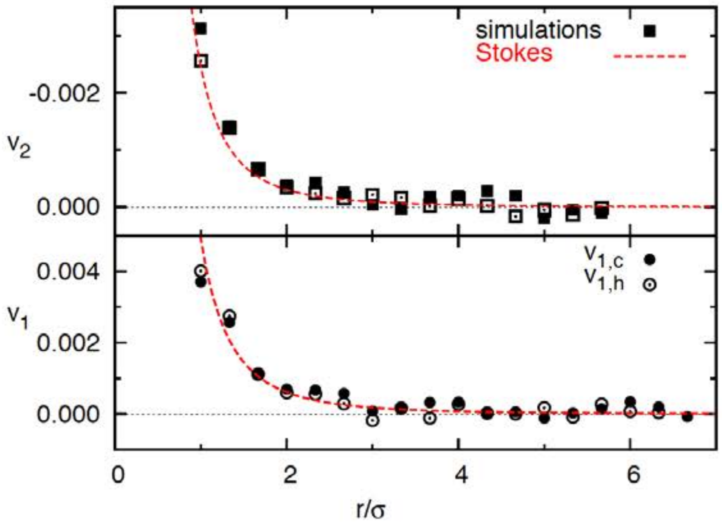
- Thermophoretic + Friction forces

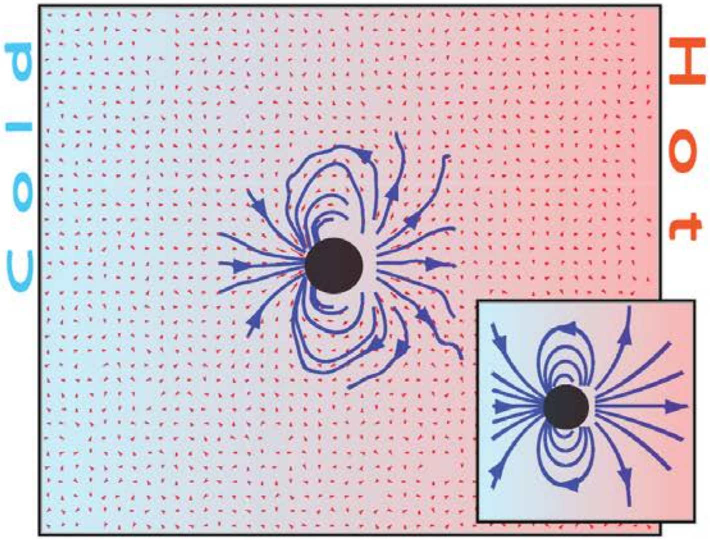
Velocity field from the Stokes equation:

$$\mathbf{v}(\mathbf{r}) = \frac{R^2}{2r^3}(3\hat{\mathbf{r}}\hat{\mathbf{r}} - \mathbf{I}) \cdot \mathbf{u}_T$$

→ Fast decay of the flow velocity

→ Flow and force have the same direction



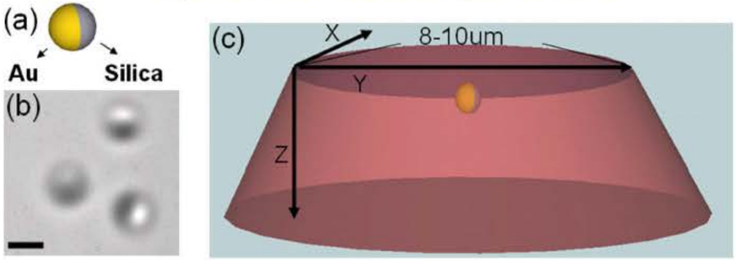

▶ Small left-right difference

→ no compressibility effects

M. Yang, M. Ripoll, *Soft Matter* **9** 4661 (2013)

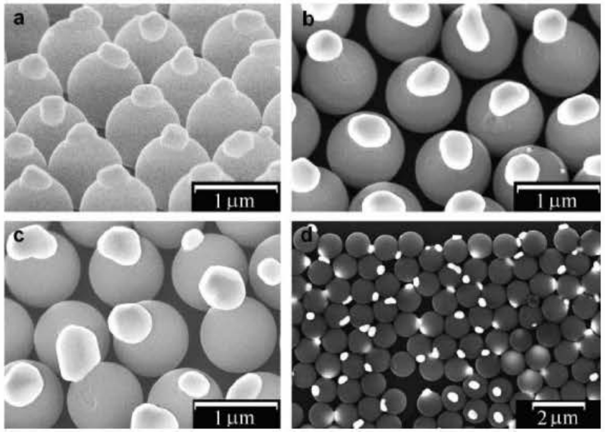
# Thermophoretically active particles

Spherical Janus particles



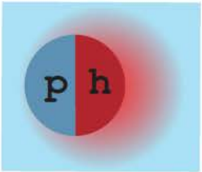

H. R. Jiang, N. Yoshinaga, M. Sano, *PRL* **105** 268302 (2010)

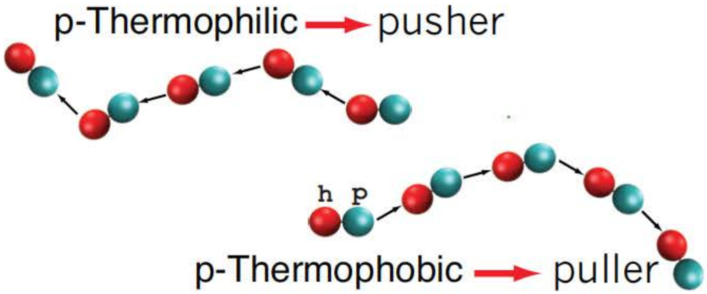
Dimeric colloids

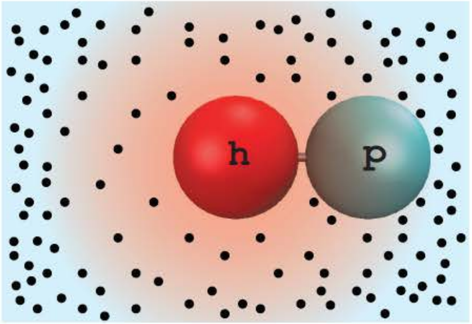



L. F. Valadares, Y.-G. Tao, N. S. Zacharia, V. Kitaev, F. Galembeck, R. Kapral, G. A. Ozin, *Small* **4** 565 (2010)

Simulations



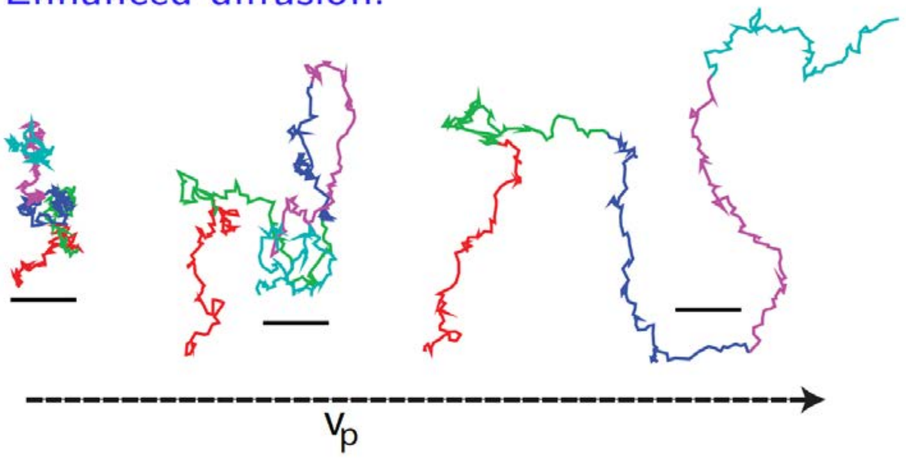




M. Yang, M. Ripoll, *Phys. Rev. E* **84** 061401 (2011)

M. Yang, A. Wysocki, M. Ripoll, *Soft Matter* **10** 6208 (2014)

# Phoretic active colloid: propelled velocity

Enhanced diffusion:

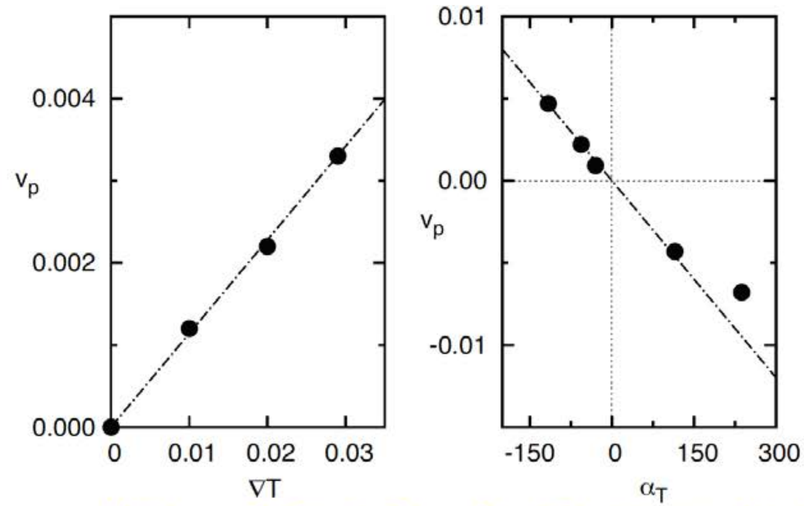



Propelled velocity: $\mathbf{v}_p = \langle \mathbf{v}_{cm} \cdot \mathbf{n} \rangle$

- Self-propelled velocity is determined by thermodiffusion properties

$$v_p = \mu_p f_T = -\mu_p \alpha_T \nabla k_B T$$

$\alpha_T$.- thermodiffusion factor (colloid property)



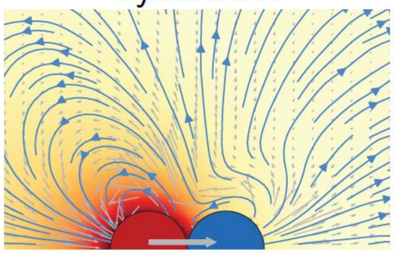

M. Yang, M. Ripoll, *Phys. Rev. E* 84 061401 (2011)

# Phoretic active colloid: hydrodynamics

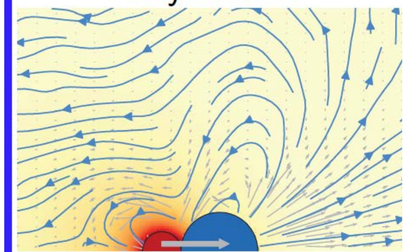
Thermophobic swimmers: From lateral repulsion to attraction (from puller to pusher)

Symmetric

Phoretic repulsion + Hydrodynamic repulsion



Asymmetric

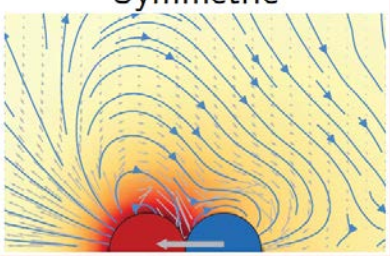


Phoretic repulsion + Hydrodynamic attraction

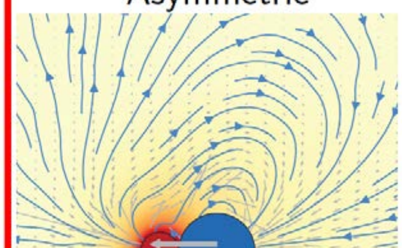
Thermophilic swimmers: From lateral attraction to repulsion (from pusher to puller)

Symmetric

Phoretic attraction + Hydrodynamic attraction



Asymmetric

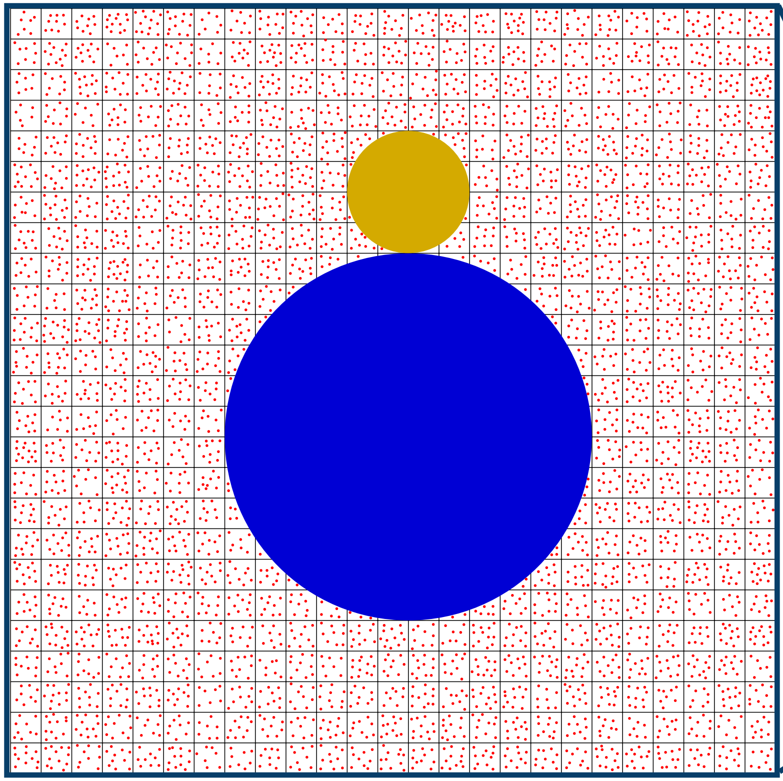


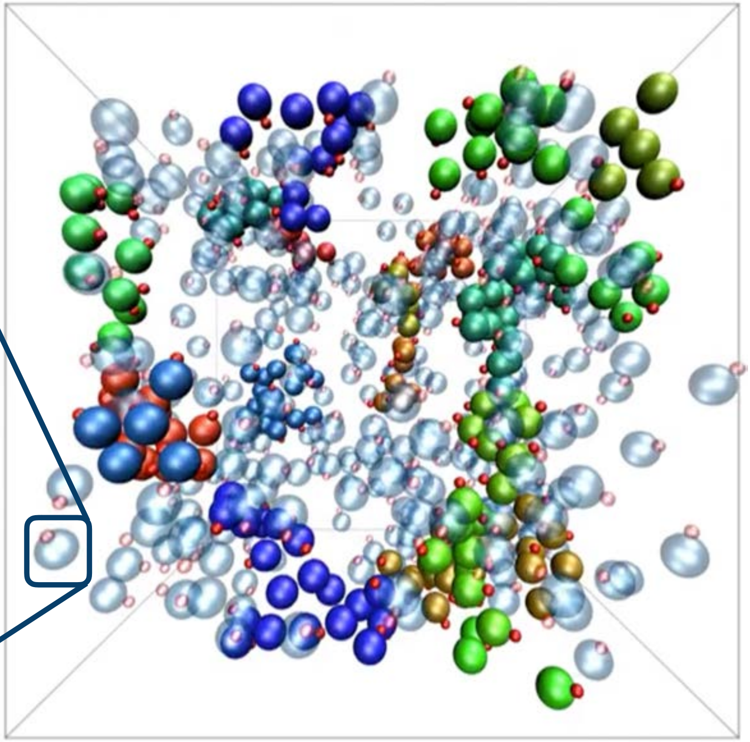
Phoretic attraction + Hydrodynamic repulsion

→ Dimer shape changes single and collective behavior

# Large ensemble simulations : HPC

**Besides the swimmer, a huge amount of solvent particles is necessary**





**LAMMPS + own local code**

# Simulations of large ensembles of swimmers

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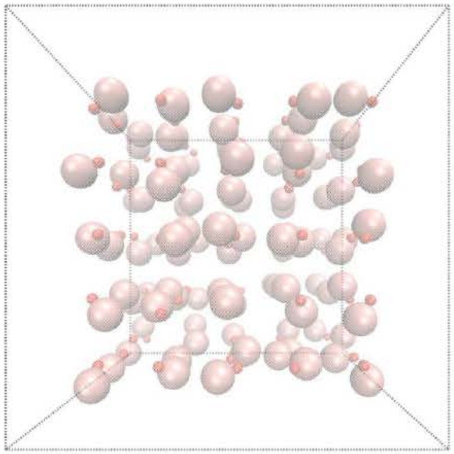
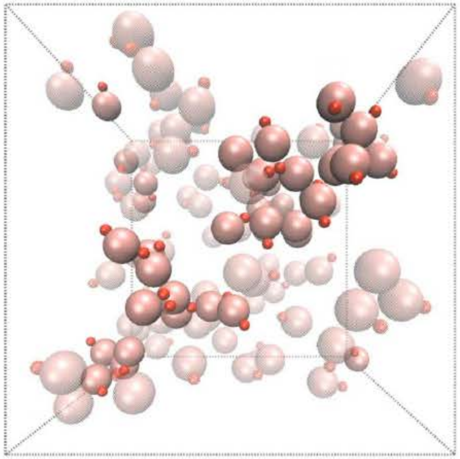
- For avoiding solvent induced depletion, while keeping strong phoretic effect we need LARGE swimmers
- 500 swimmers ( $10^7$ MPC solvent particles); Volume fraction, $\phi = 0.01 - 0.10$
- 3 dimensional bulk (periodic boundary conditions)
- Hot beads have fixed temperature → { no thermoplasmonic effect; no shadowing effects ≡ transparent beads; ... futher work in this direction is planned }



(initial configuration)

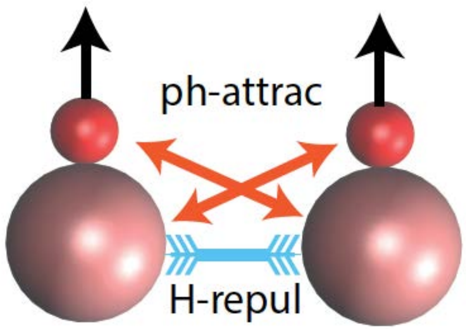


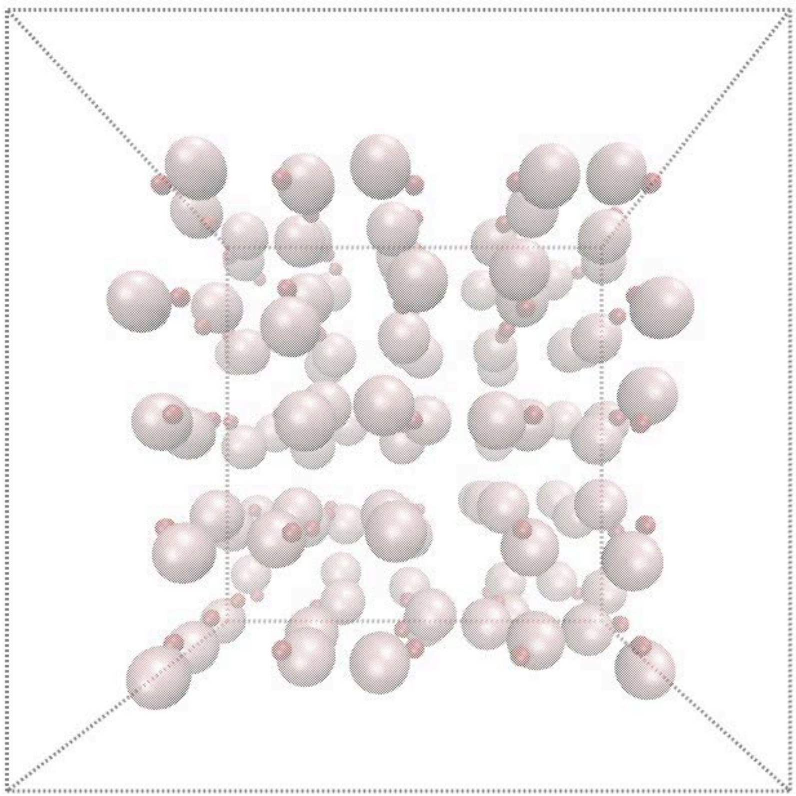
(color intensity related to clustering)

→ How do hydrodynamics and phoresis balance each other ?

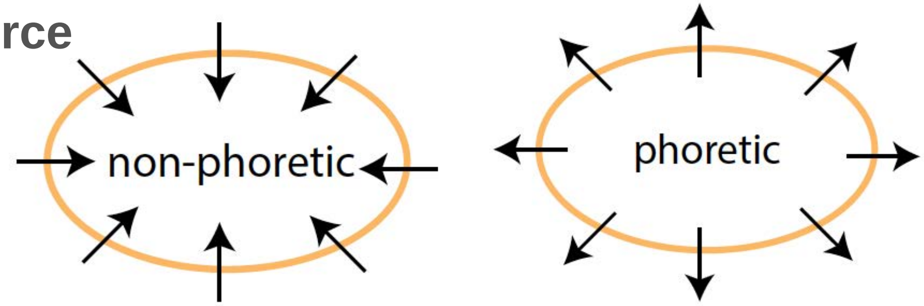
HELMHOLTZ GEMEINSCHAFT

# Collective asymmetric thermophilic

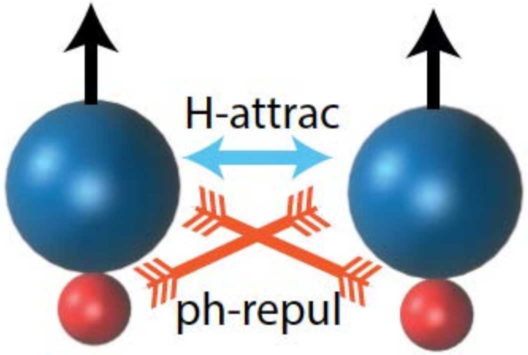


- **Phoresis diminishes hydrodynamics**
- **Reversible crystallization: dissolves with the heat source**
- **Aggregation process with opposite mechanism**

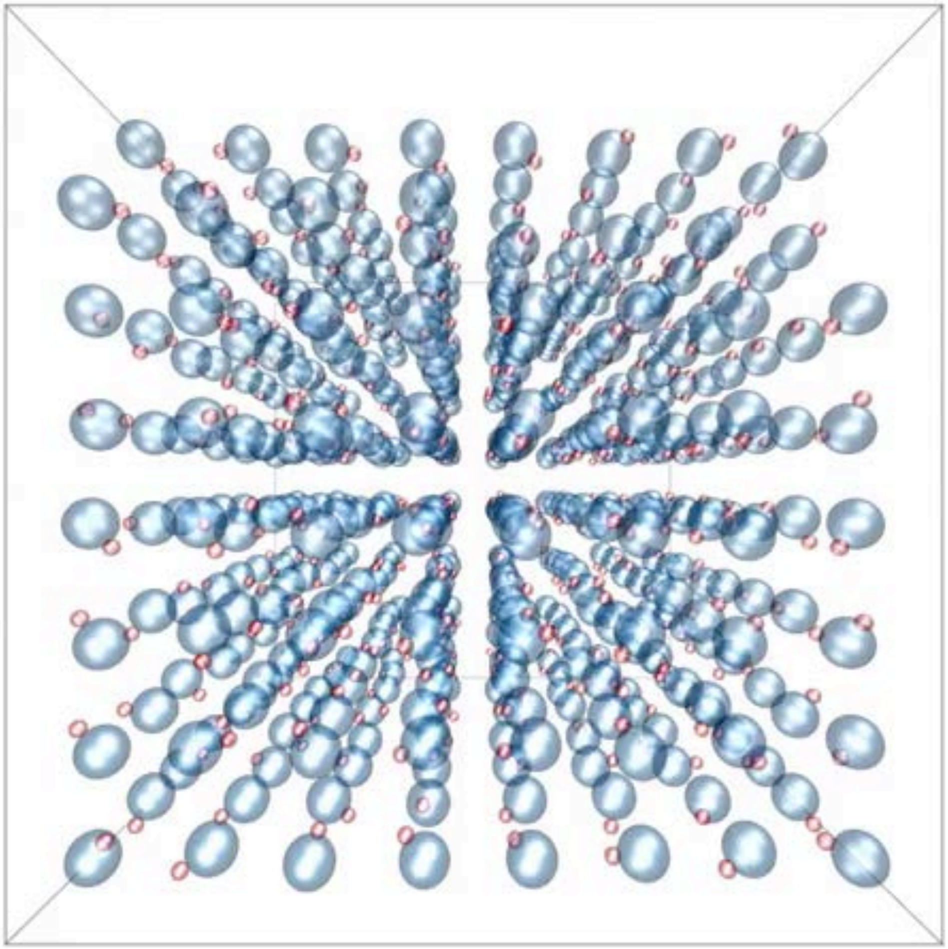


# Collective asymmetric thermophobic




- **Hydrodynamic swarming**: Planar assembly in oriented moving structures

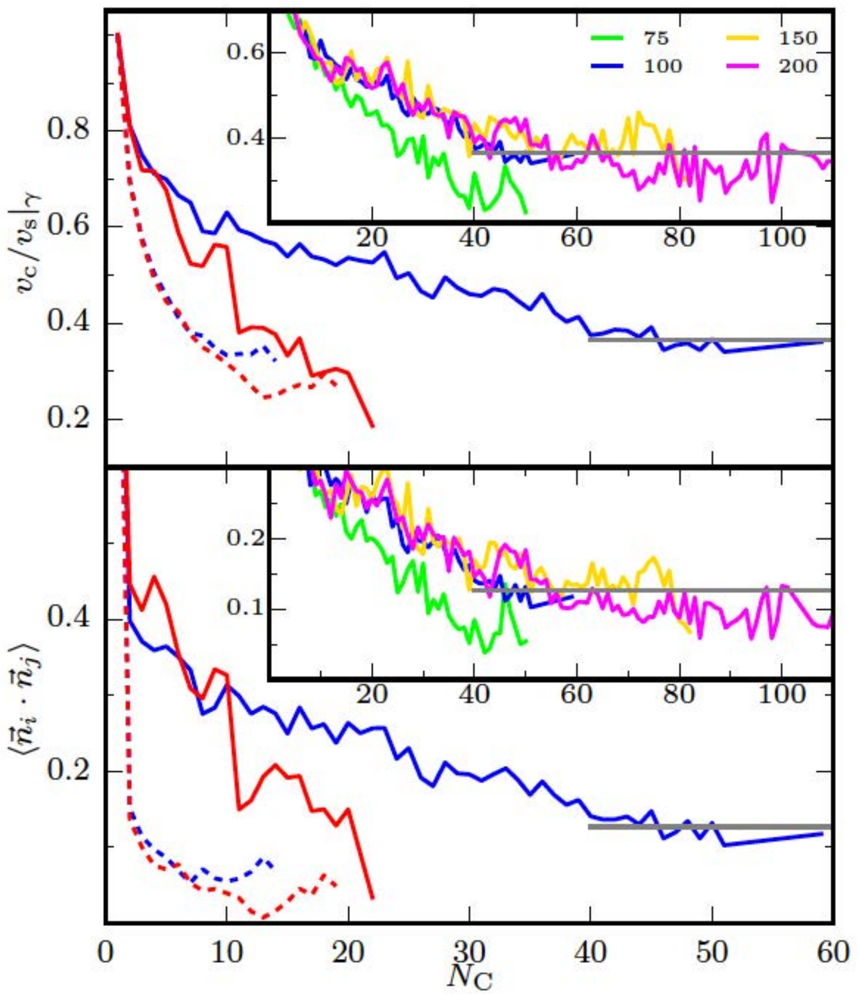
- **After some persistent motion the clusters collide and reassemble**

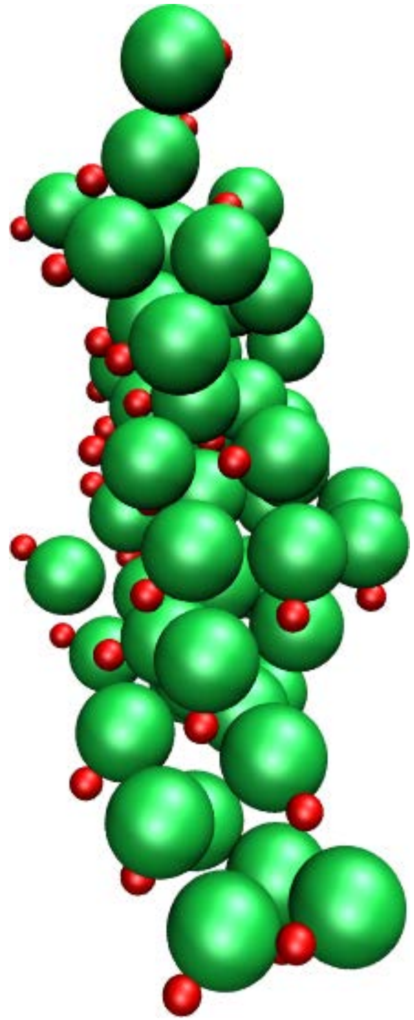


Wagner, Ripoll, *EPL* (2017) **119,** 66007

# Collective asymmetric thermophilic

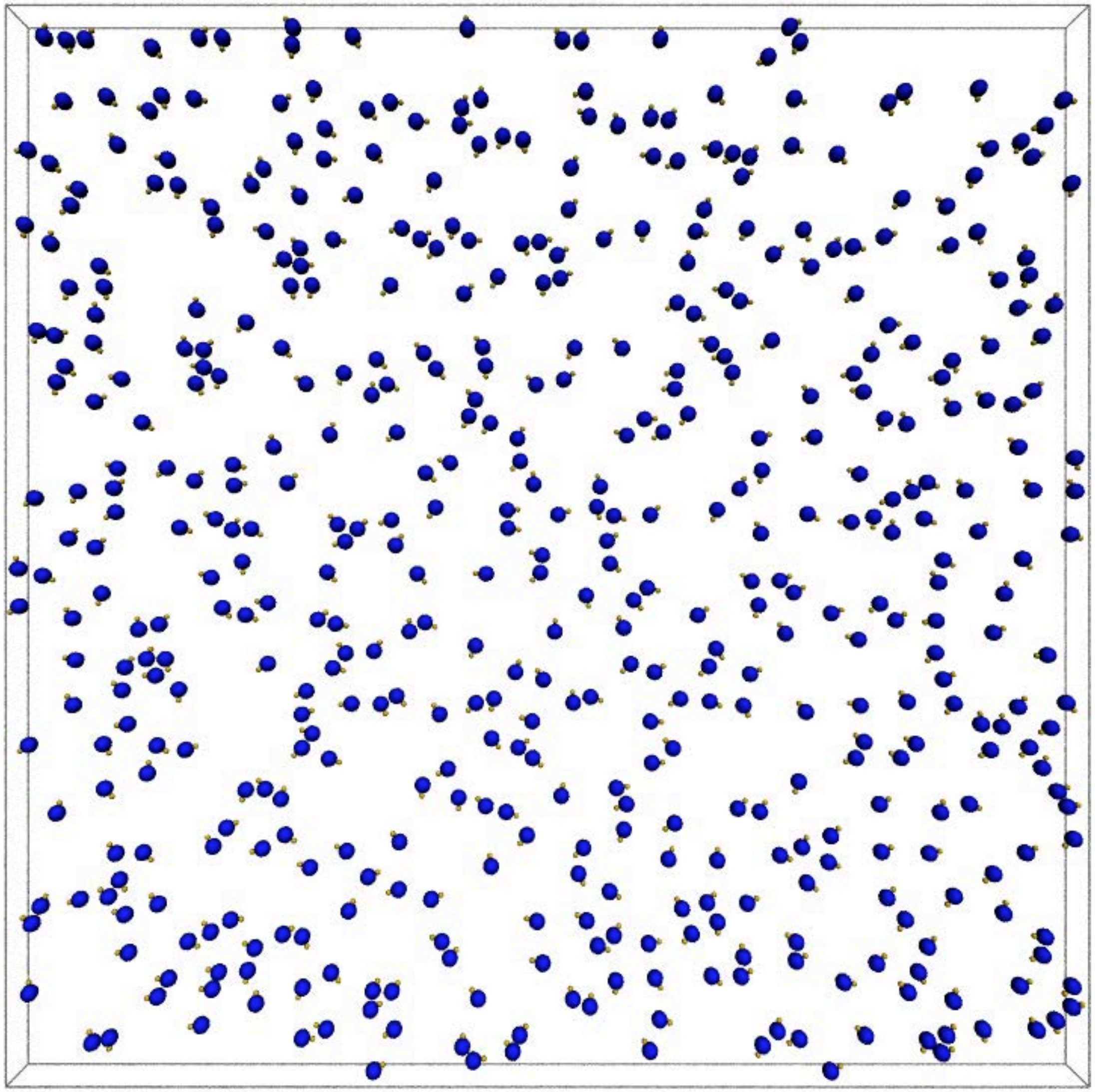
- **Hydrodynamic swarming**:
  **Planar assembly in oriented moving structures**



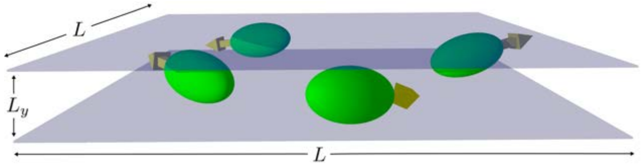



Wagner, Ripoll, *EPL* (2017) **119,** 66007

# Thermophobic active colloids in a slit : quasi 2D



Planar swarming should convert into ***lateral chain formation***

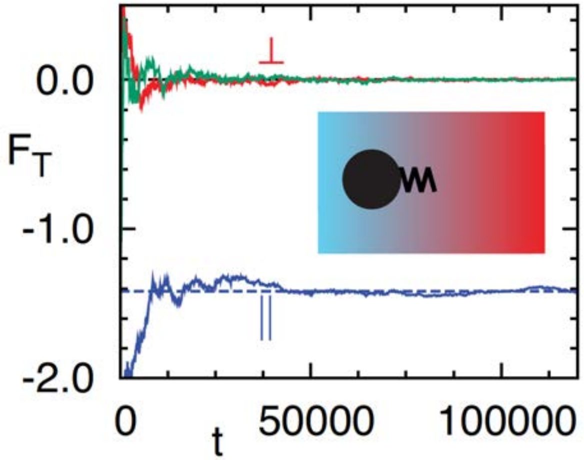



… preliminary results indicate that this is the case

simulations still ongoing

# Anisotropic thermophoresis

For spherical particles phoresis is well-defined

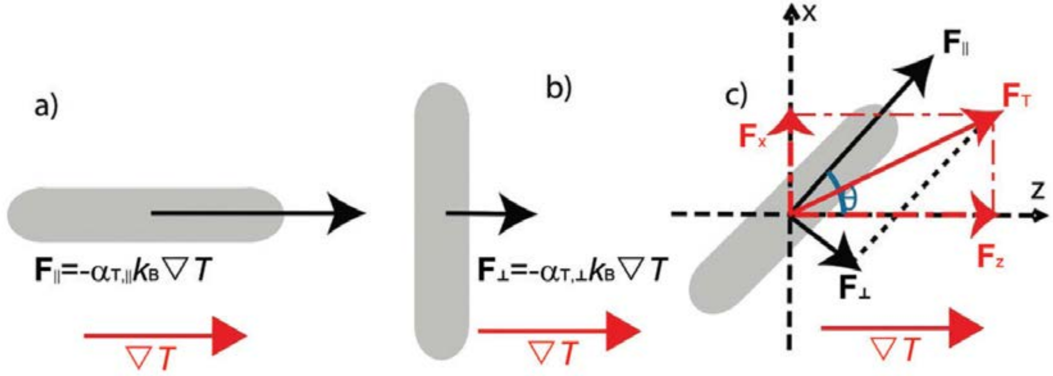



Thermophoretic force: $\mathbf{f}_T = -S_T k_B T \nabla T = -\alpha_T k_B \nabla T$

$\alpha_T$.- thermodiffusion factor (colloid property)

But how is it for elongated particles ?

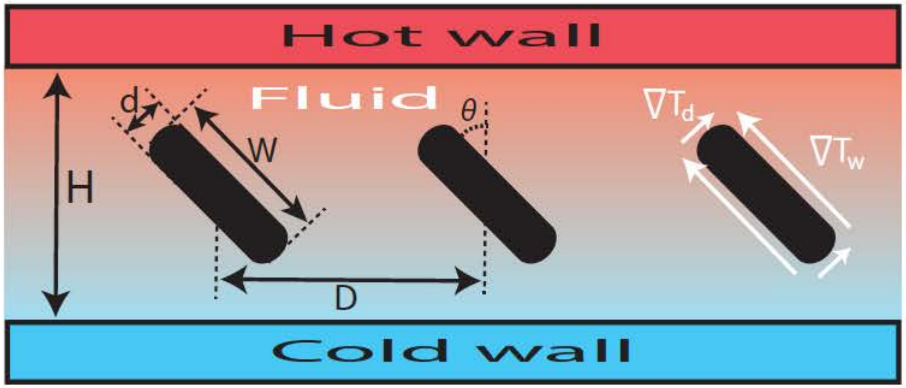
It might vary with orientation



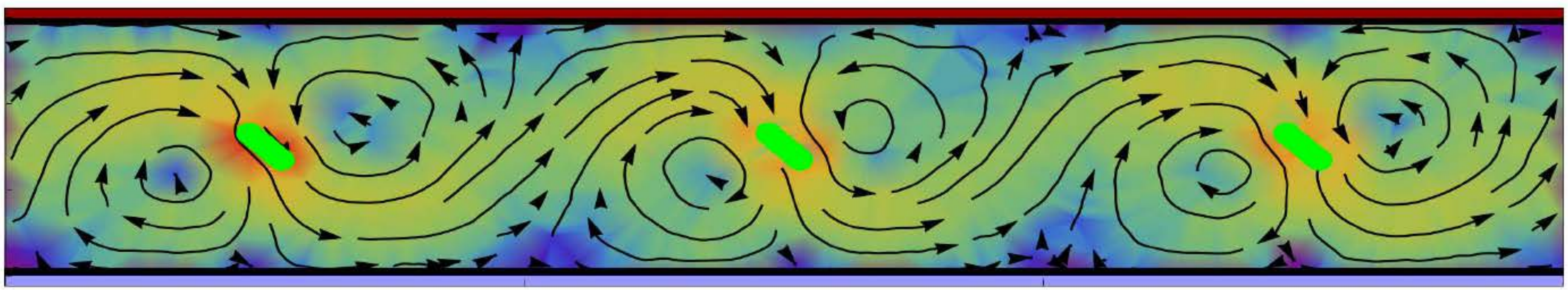

There could be a force perpendicular to the gradient !!!

Tan, Yang, Ripoll, Soft Matter (2017) **13,** 7283

# Microfluidic pump based in anisotropic thermophoresis



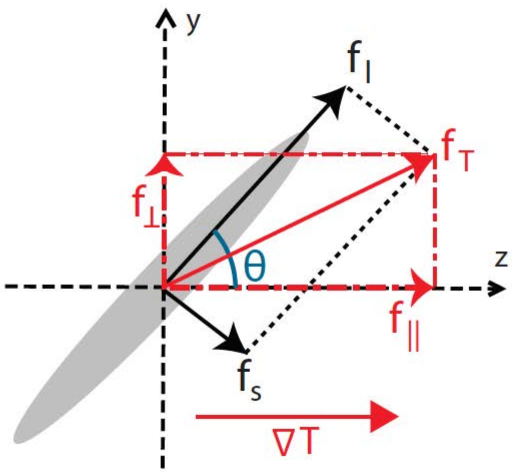

- Fluid flux can be induced perpendicular to the temperature gradient

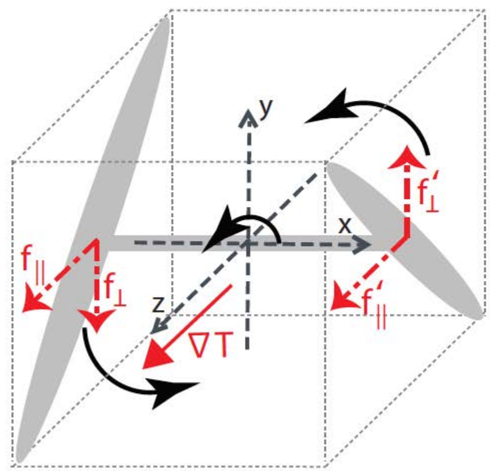


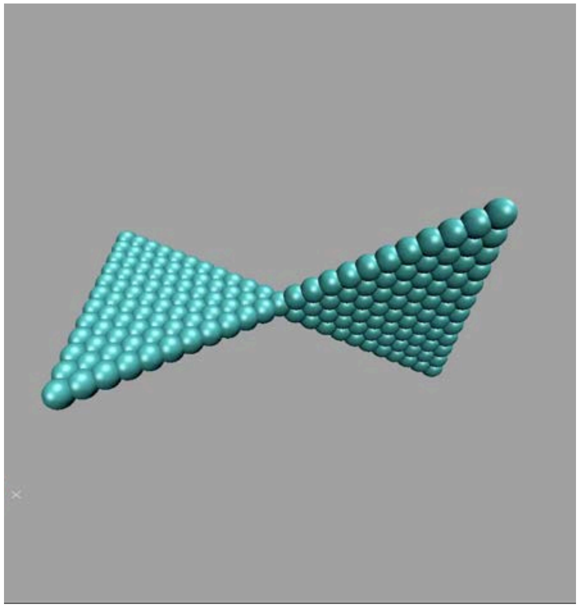
Tan, Yang, Ripoll, Preprint (2018)
Patent application (2017)

# Thermophoretic microturbine

**Anisotropic thermophoresis in a chiral structure**



**This structure works in an external temperature gradient**

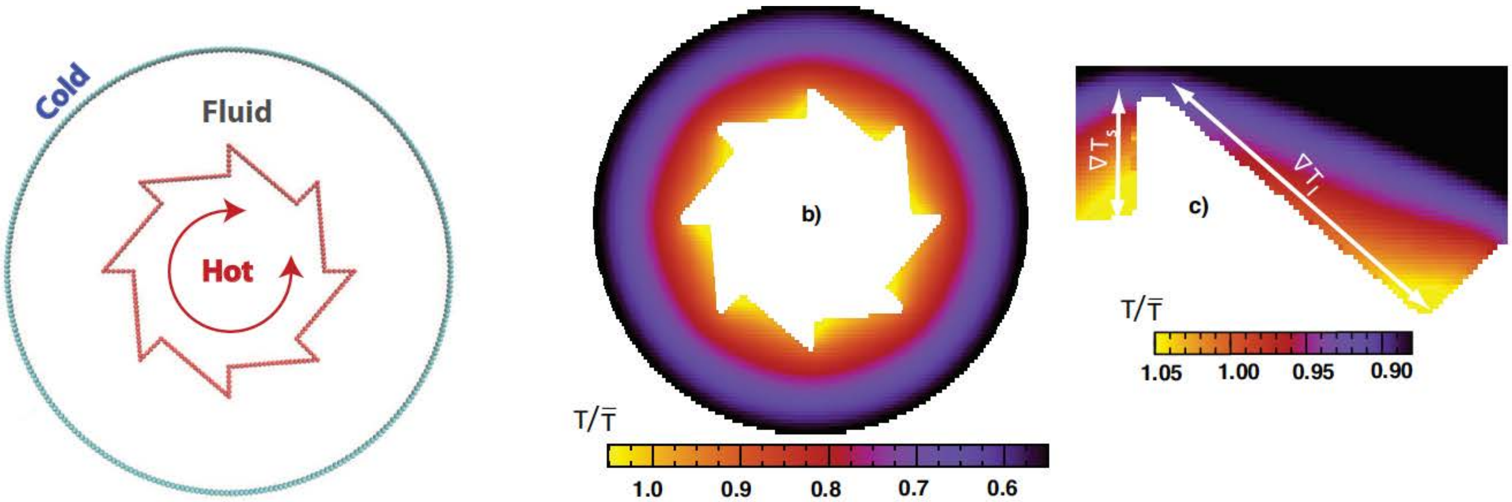
**harvesting of waste energy**

M. Yang, R. Liu, M. Ripoll, K. Chen, *Nanoscale* **6** 13550 (2014)

M. Yang, Rui Liu, M. Ripoll, K. Chen, *Lab Chip* **15** 3912 (2015)

**It also works with diffusiophoresis (chemical gradients)**

# Phoretic micromotors




- Temperature difference along each edge → exerted thermophoretic force

long edge: $\nabla T_l \rightarrow \mathbf{f}_{T,l} = -\alpha_T k_B \nabla T_l$

short edge: $\nabla T_s \rightarrow \mathbf{f}_{T,s} = -\alpha_T k_B \nabla T_s$

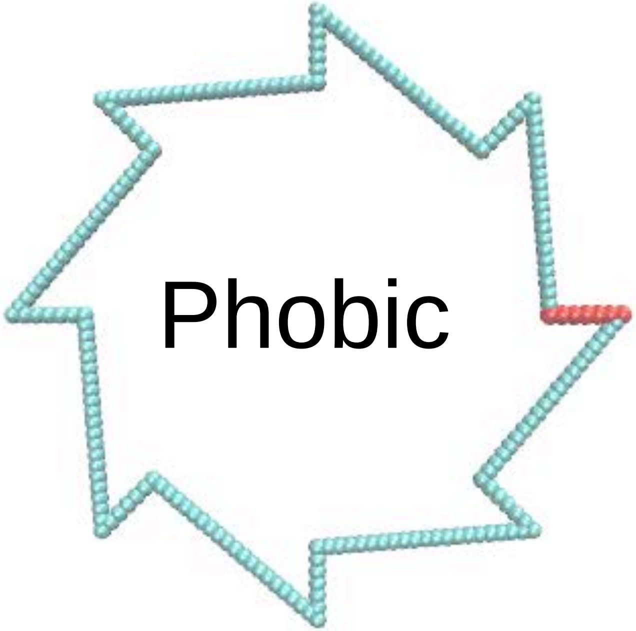
Total torque: $\mathcal{T} = \Sigma(\mathbf{R}_l \times \mathbf{f}_{T,l} + \mathbf{R}_s \times \mathbf{f}_{T,s})$

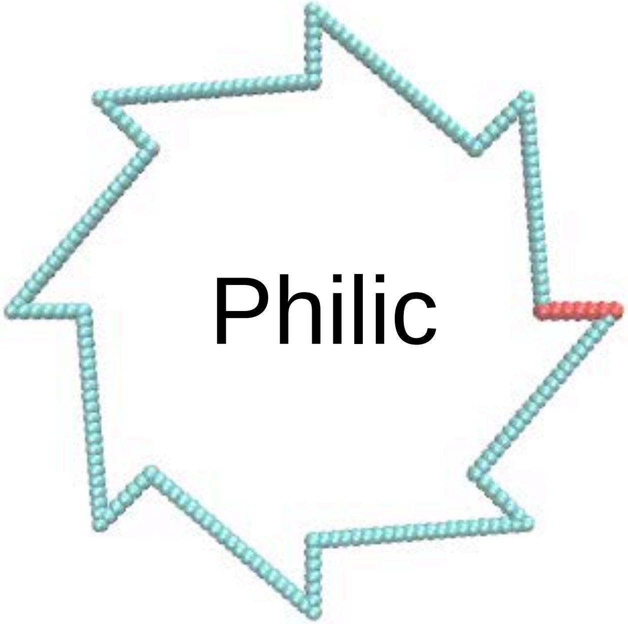
- If the gear is asymmetric → net torque

M. Yang, M. Ripoll, *Soft Matter* **10** 1006 (2014)

Pending patent application (2013)

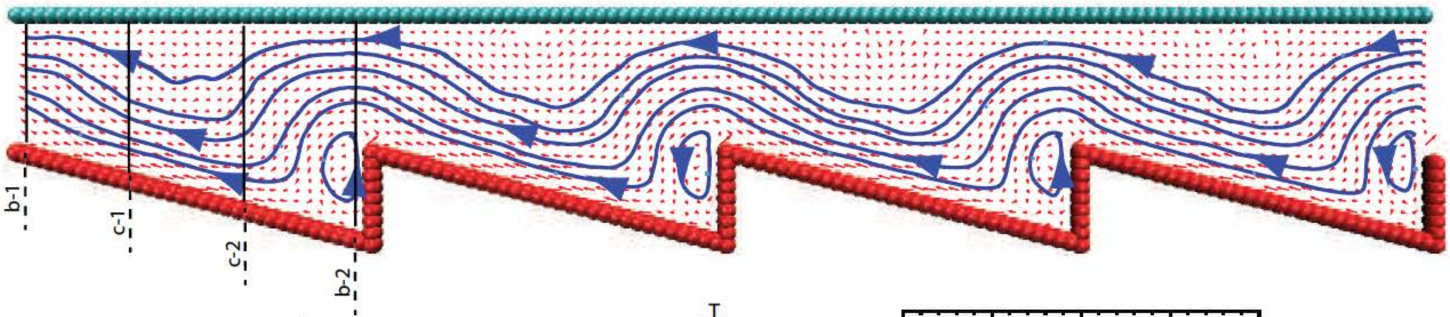
# Phoretic microrotors

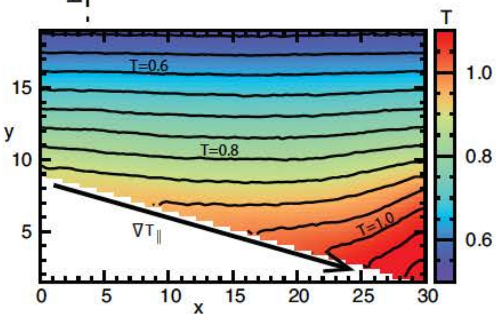


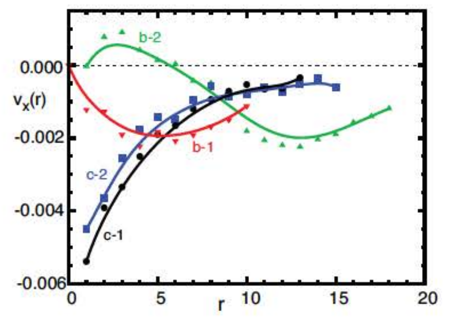



# Phoretic microfluidics: ratcheted structures

JÜLICH FORSCHUNGSZENTRUM

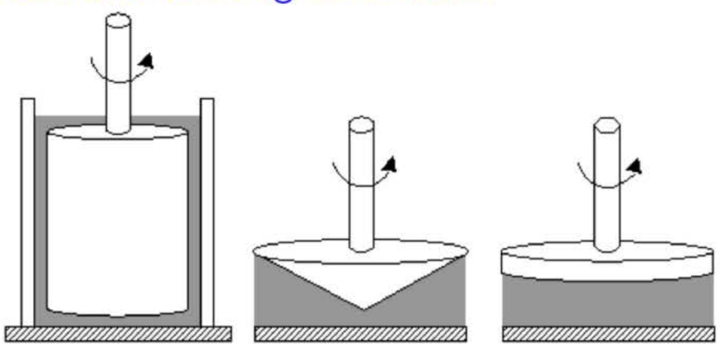



– This is a shear-like flow

Basics of existing rheometers

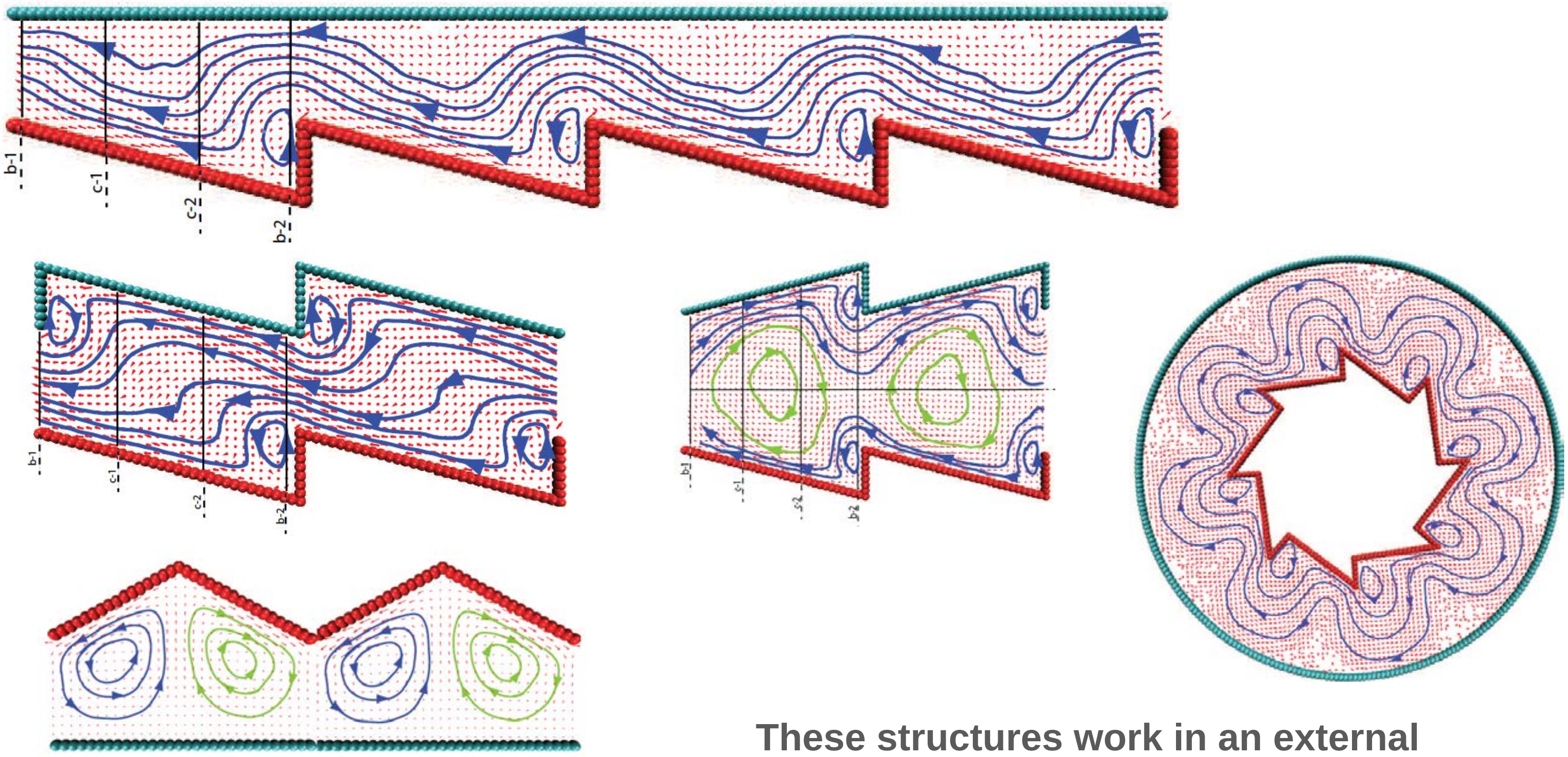


→ .. and it allows us to build a rheometer without movable parts !

Yang, Ripoll, *Soft Matter* (2016) **12**, 8564

HELMHOLTZ GEMEINSCHAFT

# Phoretic microfluidics: ratcheted structures



These structures work in an external temperature gradient

**harvesting of waste energy**

Yang, Ripoll, *Soft Matter* (2016) **12**, 8564
Shen,Ye, Liu, Chen, Yang, Ripoll, *J. Chem. Phys. (2016)* ***145****, 124119*

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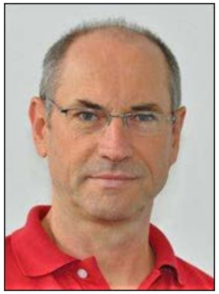
R. Winkler


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# Funding & computing


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Directed Structure at the meso-scale

cost
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MICRO-
SWIMMERS

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# Thanks for your attention !

# Questions ?