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Thermophoresis of charged colloidal spheres and rods

12. März 2019

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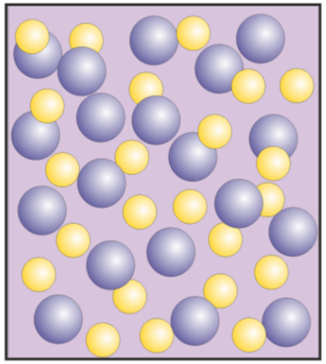
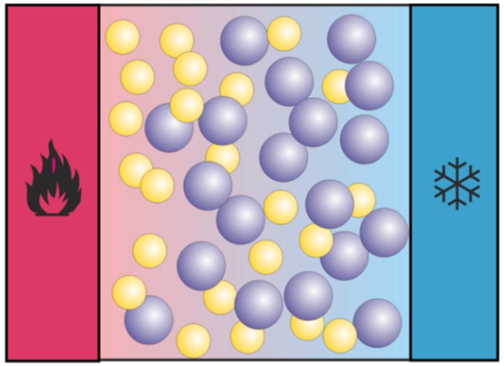
Doreen Niether, Zilin Wang, Hui Ning, Johan Buitenhuis, Jan K.G. Dhont

Phenomenological equation

(…, thermodiffusion, Soret effect) –

Movement of particles driven by a temperature gradient





$$\vec{j} = -D\vec{\nabla}c - c(1-c)D_T\vec{\nabla}T$$

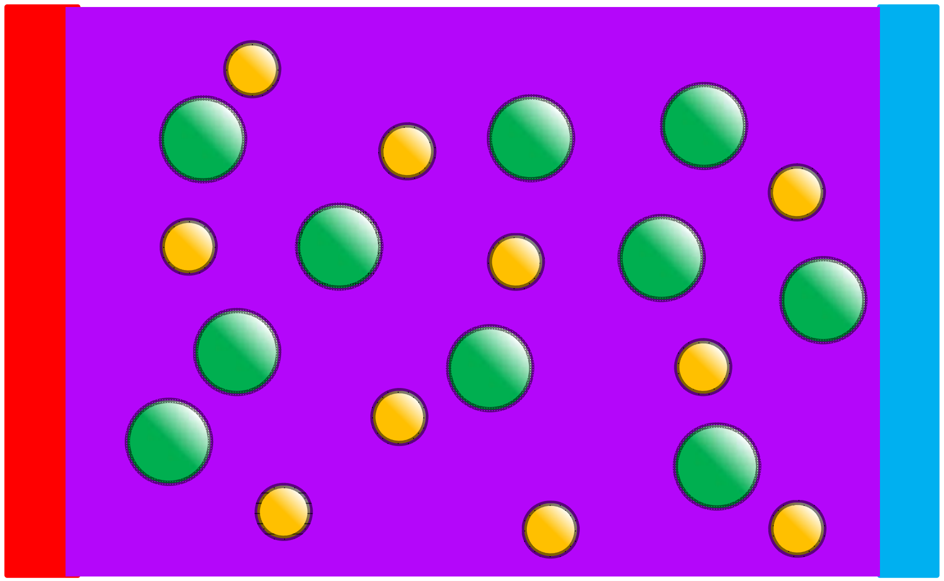
Steady state $\vec{j}=0$

$$S_T = \frac{D_T}{D} \propto \frac{\Delta c}{\Delta T}$$

D - diffusion coefficient,
c - concentration,
D_T - thermodiffusion coefficient,
$\vec{j}$ - flux, T – temperature
S_T – Soret coefficient

1. Fast process – *T*-equilibration

2. Slow process – *c*-equilibration



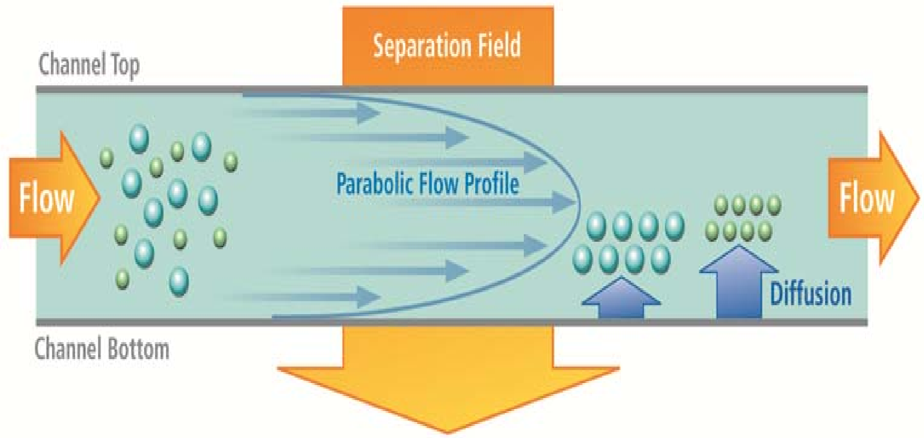
Thermophoresis: What ? Where is it used?

Application areas

- Characterization of crude oil fields
- **Characterization of macromolecules and colloids, e.g. ThFFF (thermal field flow fractionation)**
- Measuring equilibration constants of biochemical reactions
- ‘origin of life’ scenario combining convection & thermophoresis

Application examples

- Thermal field flow fractionation



Separation of mixtures (TFFF) //Wikipedia

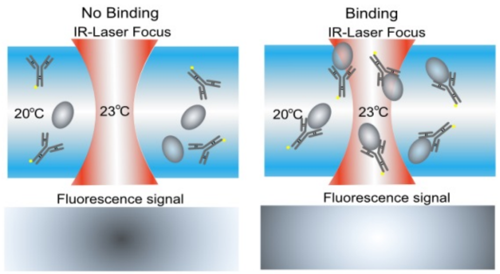
Thermophoresis: What ? Where is it used?

Application areas

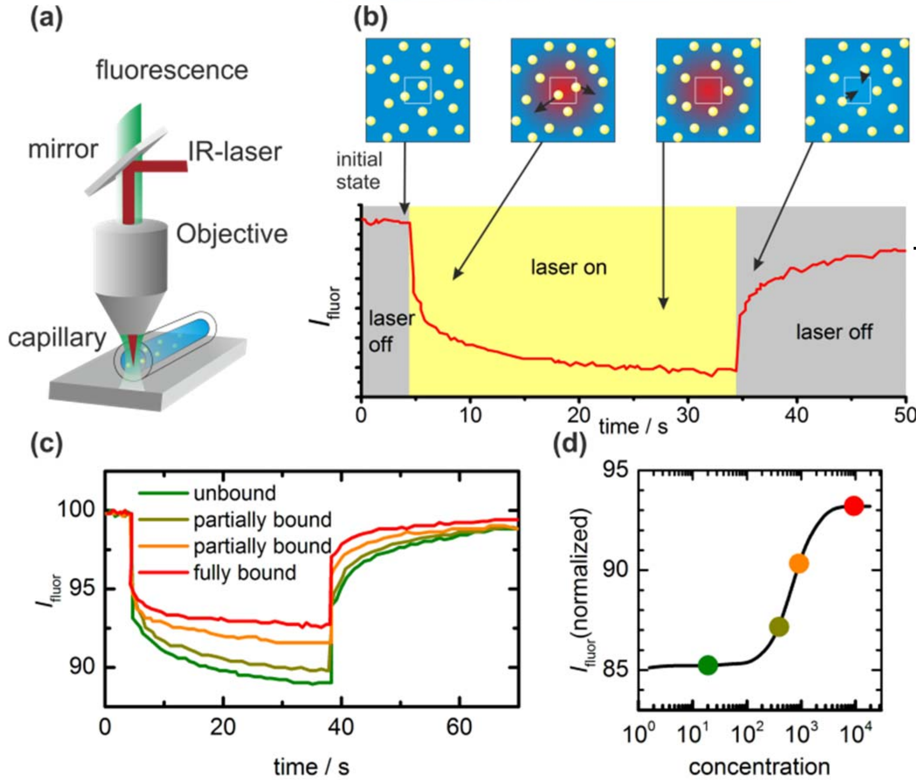
- Characterization of crude oil fields
- Characterization of macromolecules and colloids, e.g. TFFF (thermal field flow fractionation)
- **Measuring equilibration constants of biochemical reactions**
- ‘origin of life’ scenario combining convection & thermophoresis

Application examples

- Microscale thermophoresis



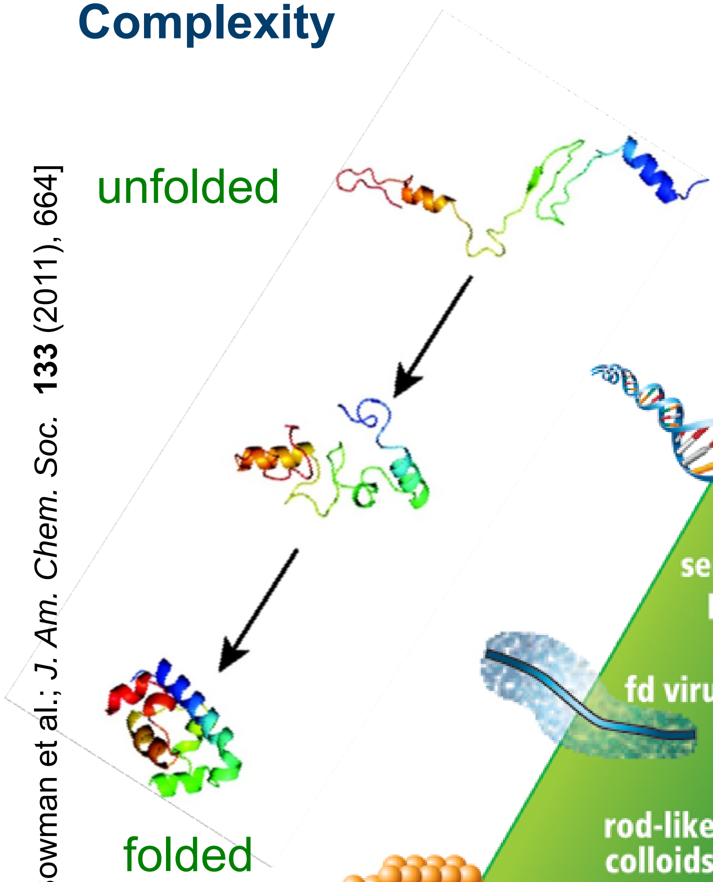
Microscale Thermophoresis: Technology and Applications //NanoTemper GMBH



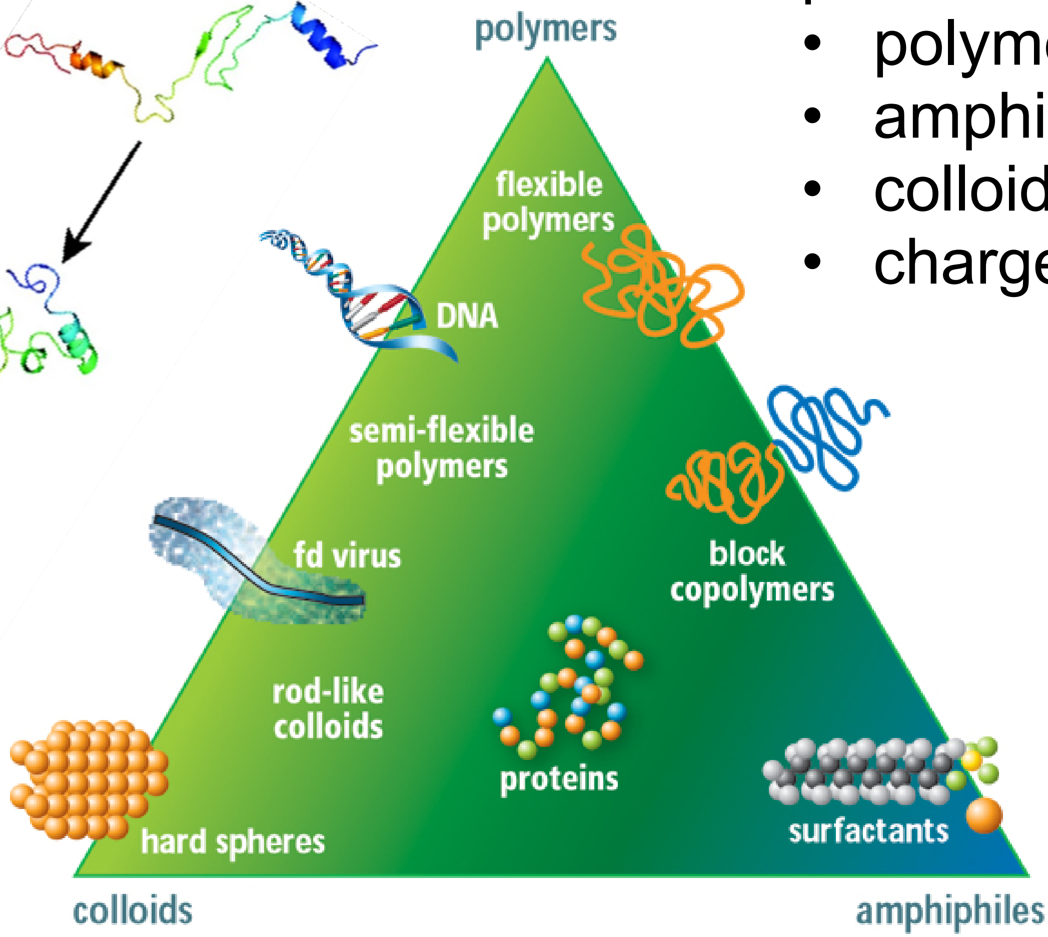
SW., *Introduction to thermal gradient related effects*, in *Functional Soft Matter*, J.K.G. Dhont, et al., Editors. 2015, Forschungszentrum Jülich: Jülich. p. F4.1-F4.24.

PROTEINS

Complexity



[G.R. Bowman et al.; *J. Am. Chem. Soc.* **133** (2011), 664]

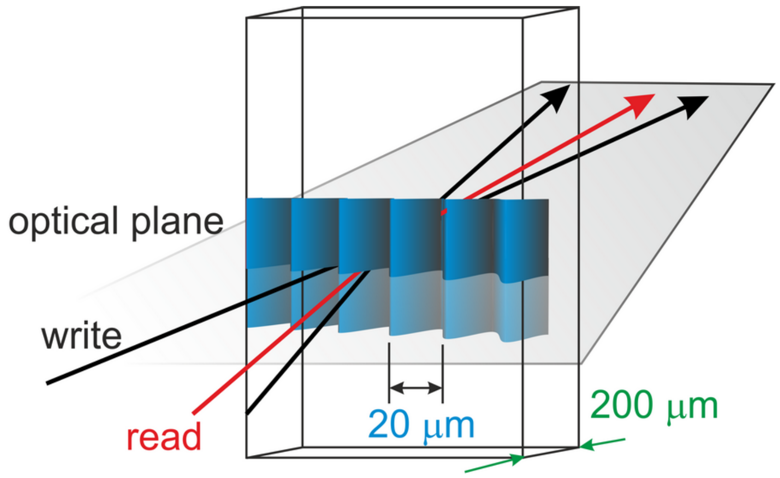


[G. Gompper et al., EPJ E, 26 (2008) 1]

protein:

- polymer
- amphiphilic character
- colloid
- charged

How do we measure?



IR-TDFRS – **I**nfra**R**ed -**T**hermal **D**iffusion **F**orced **R**ayleigh **S**cattering

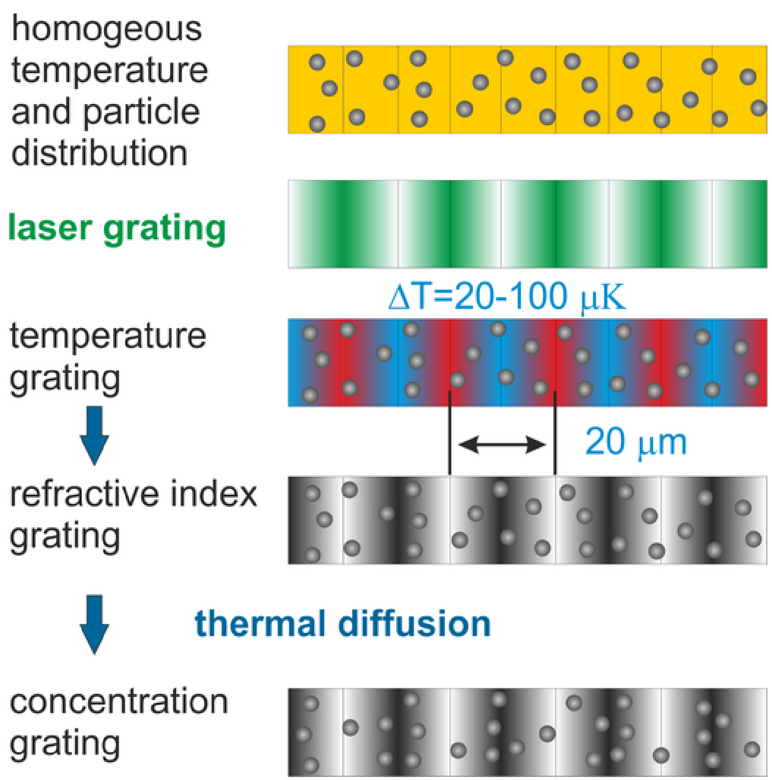
Advantages:

- small ΔT (no convection)
- no fluorescent labeling required
- wide molecular range

Disadvantages:

- buffer solutions: difficult
- colloids >100 nm: difficult.

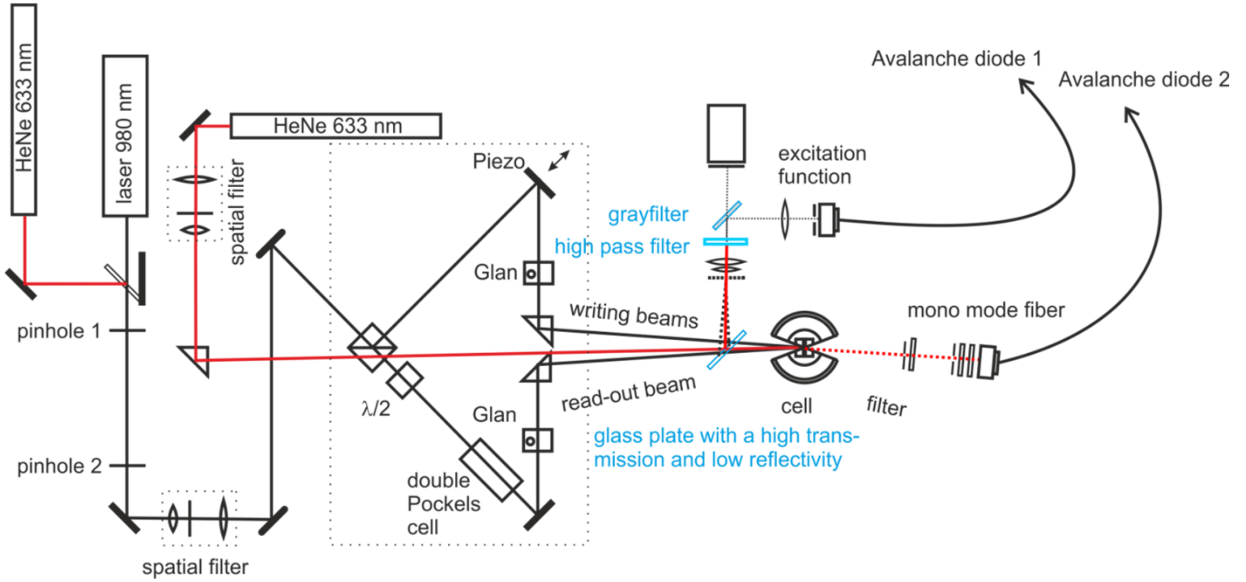
Measured quantity: Intensity of the diffracted beam

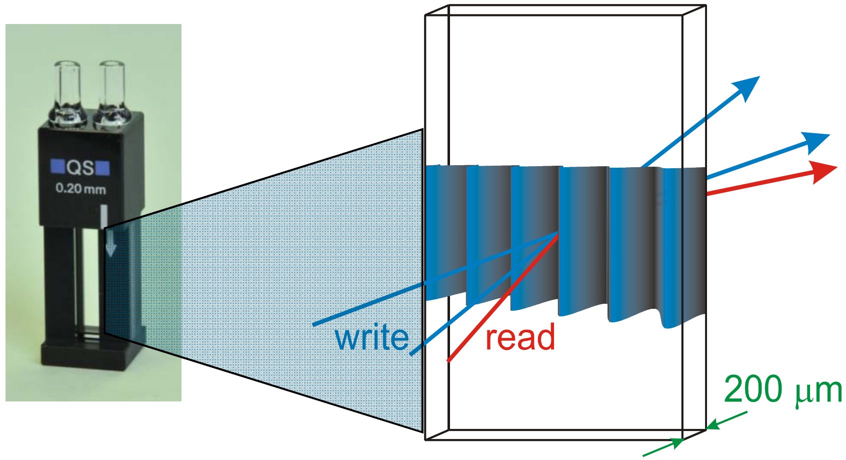


[S. Wiegand *et al.*, J. Phys. Chem. B, **111**(2007) 14169]

IR-TDFRS: set-up

- label-free method
- small T-gradient (1-10 K/m)
- Temperature and concentration grating → grating in refractive index of sample
- Measured quantity: intensity of diffracted reading beam



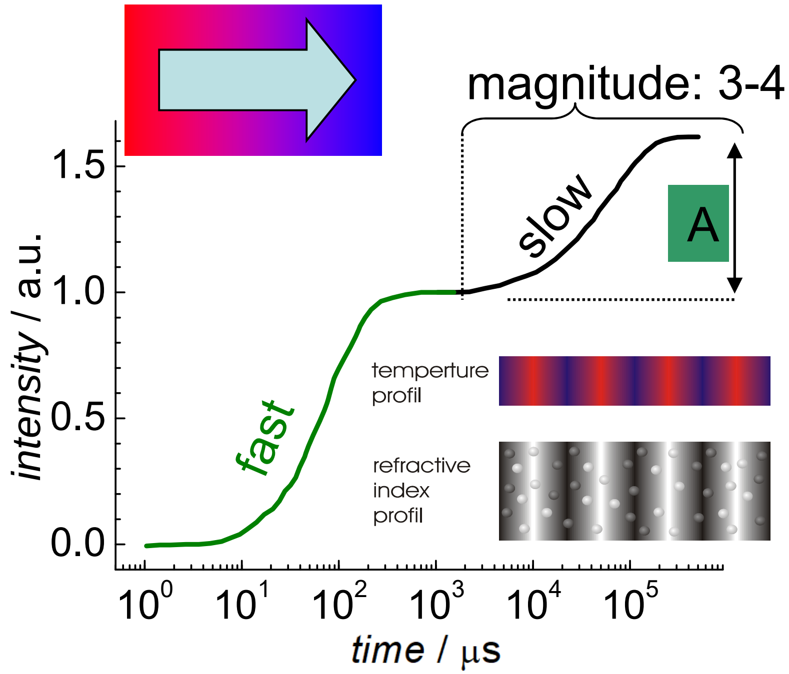


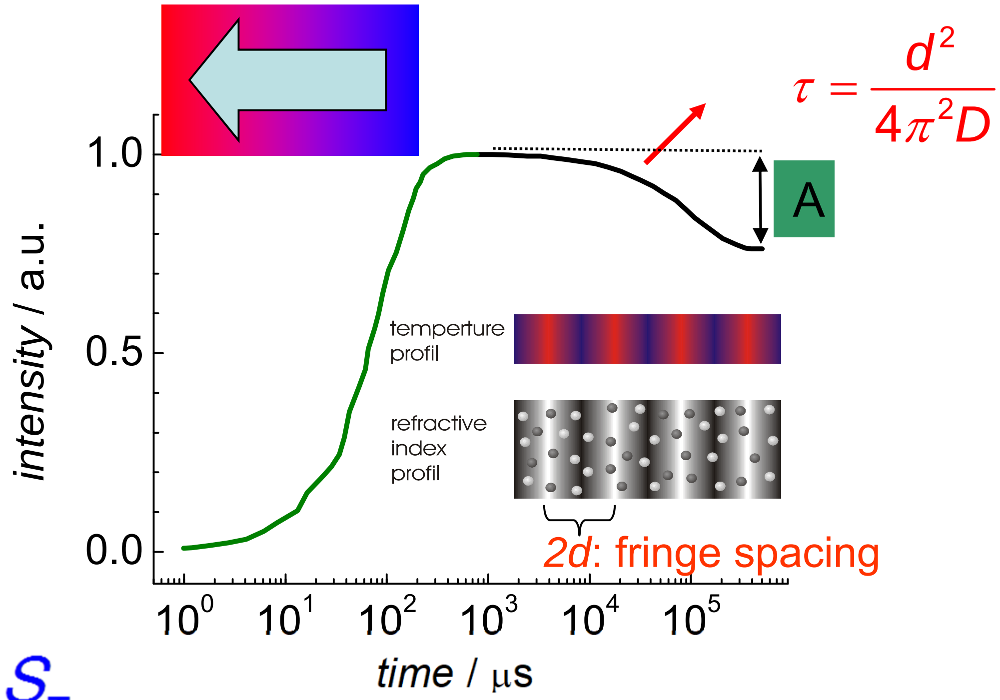
Wiegand et al., J. Phys. Chem. B 111 (2007), 14169

IR-TDFRS measurement signal

Molecules/colloides with higher refractive index moves to…

…cold side …warm side



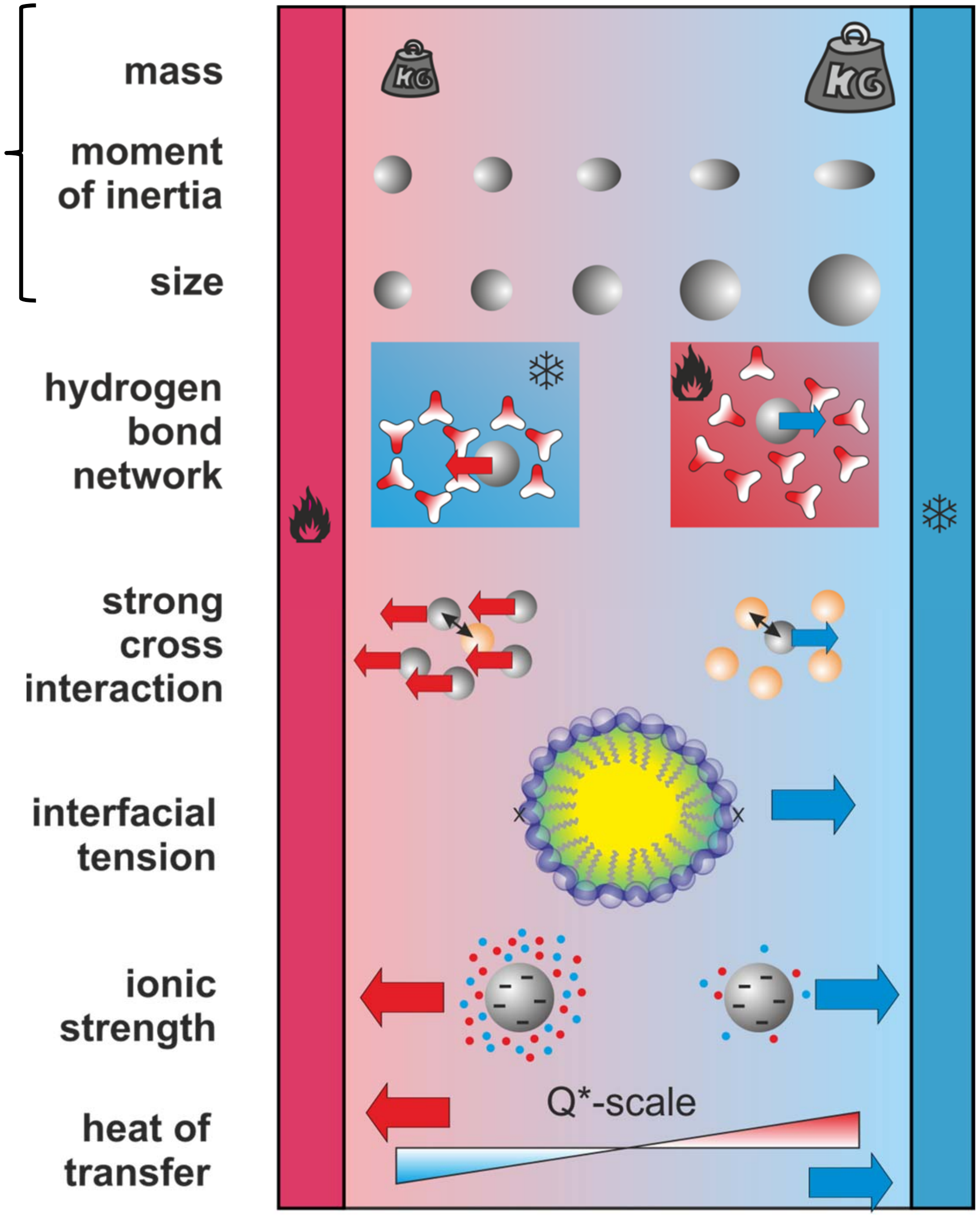


$$\varsigma_{het} = \underbrace{\left(1-e^{-t/\tau_{th}}\right)}_{\text{temperature}} - \underbrace{\frac{(\partial n/\partial c)_{p,T}}{(\partial n/\partial T)_{p,c}} \frac{D_T}{D} c(1-c)\frac{1}{\tau-\tau_{th}}}_{A} \left[\tau\left(1-e^{-t/\tau}\right) - \tau_{th}\left(1-e^{-t/\tau_{th}}\right)\right]$$

S_T

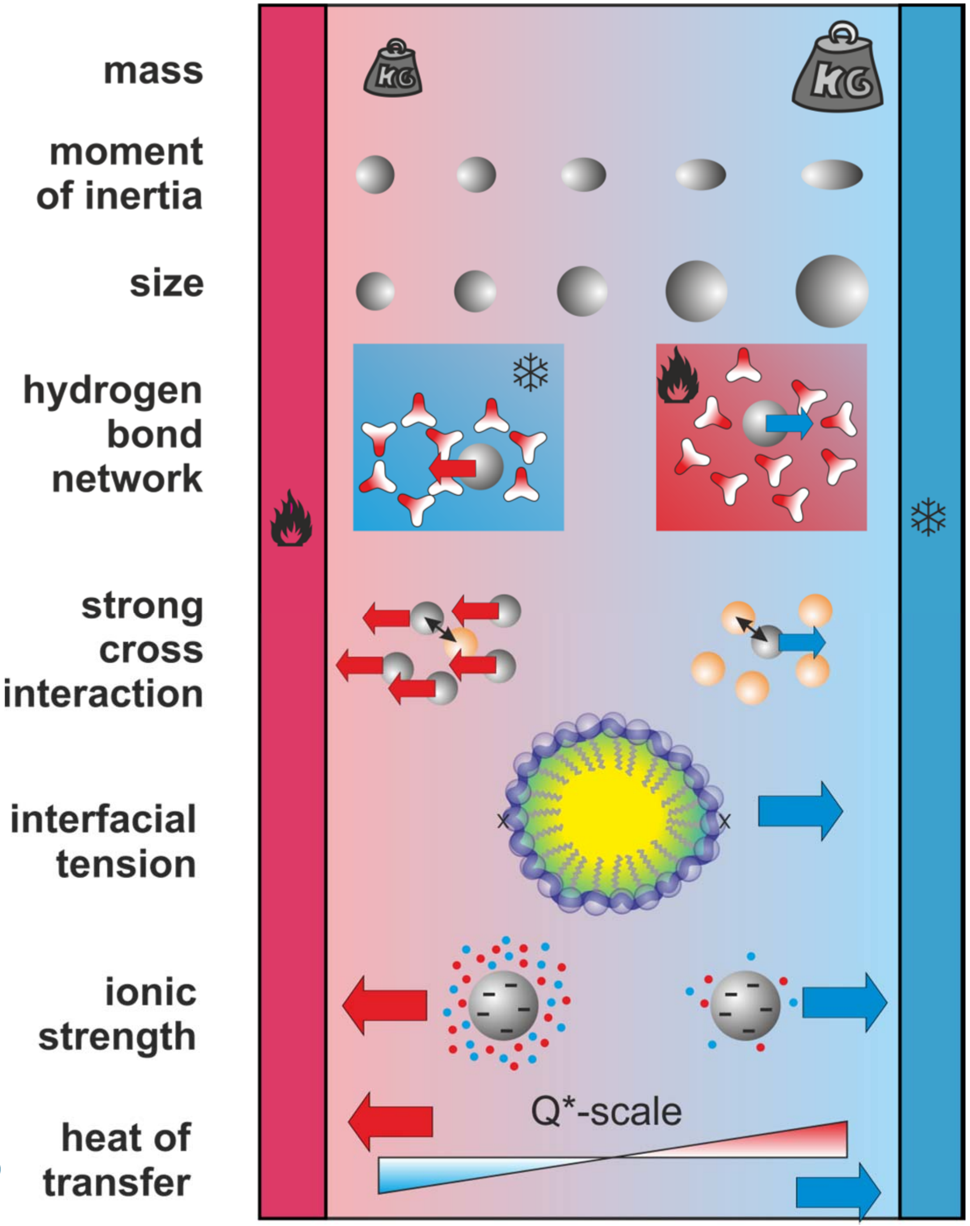
contrast factors

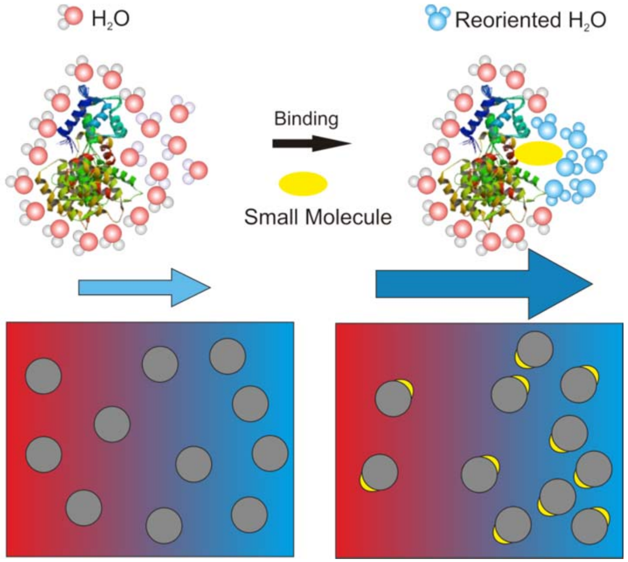
To the warm or to the cold?



SW., *Introduction to thermal gradient related effects*, in *Functional Soft Matter*, J.K.G. Dhont, et al., Editors. 2015, Forschungszentrum Jülich: Jülich. p. F4.1-F4.24.

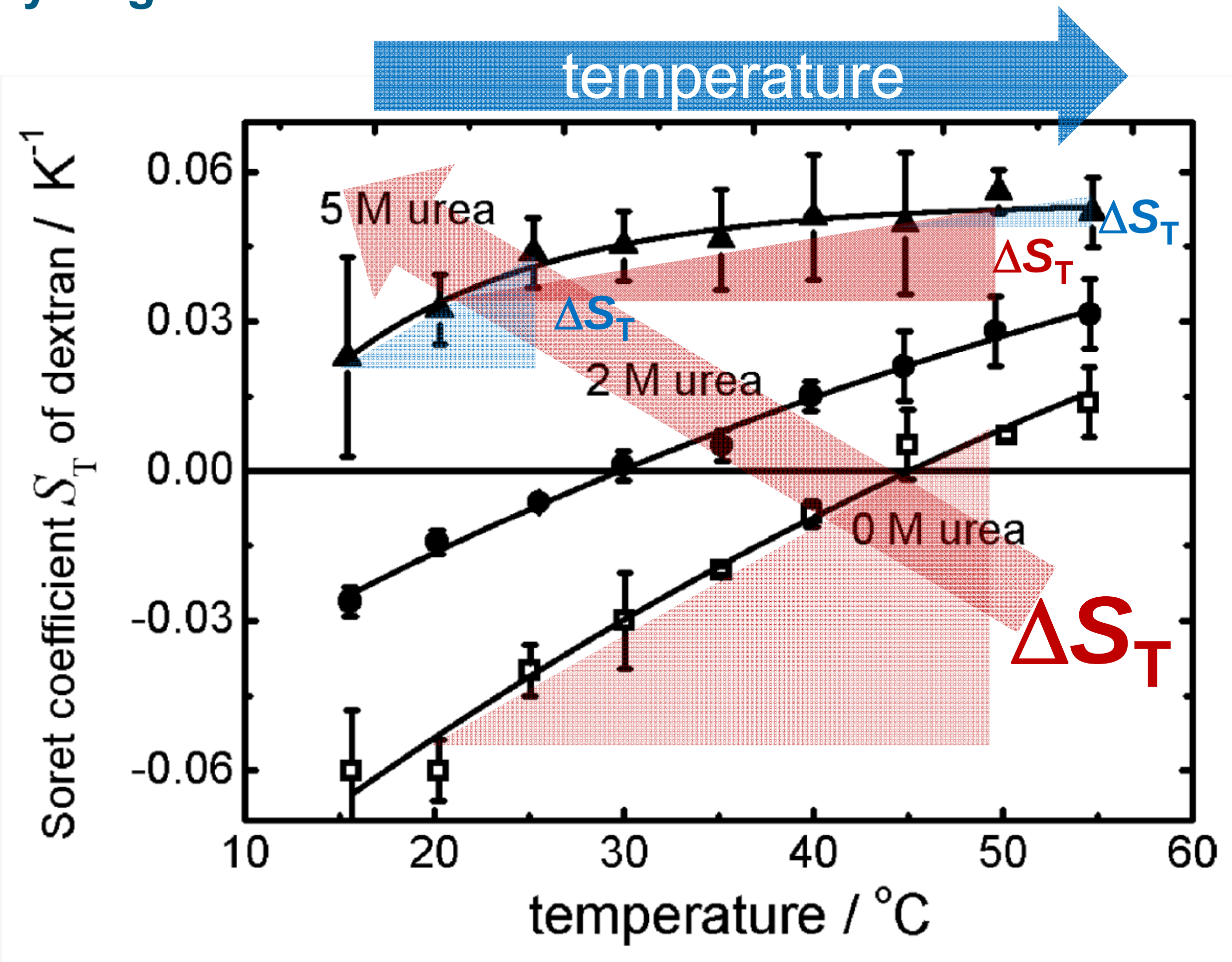
To the warm or to the cold?





T-dependence S_T

Hydrogen maker/breaker



System:
dextran/water + urea

less H-bonds with
temperature
- S_T increases
- **ΔS_T decreases**

less H-bonds with
dextran due to urea
- S_T increases
- **ΔS_T decreases**

[Sugaya, R., B.A. Wolf, and R. Kita. Biomacromolecules, **7** (2006) 435]

Thermophoresis: hydrophilicity

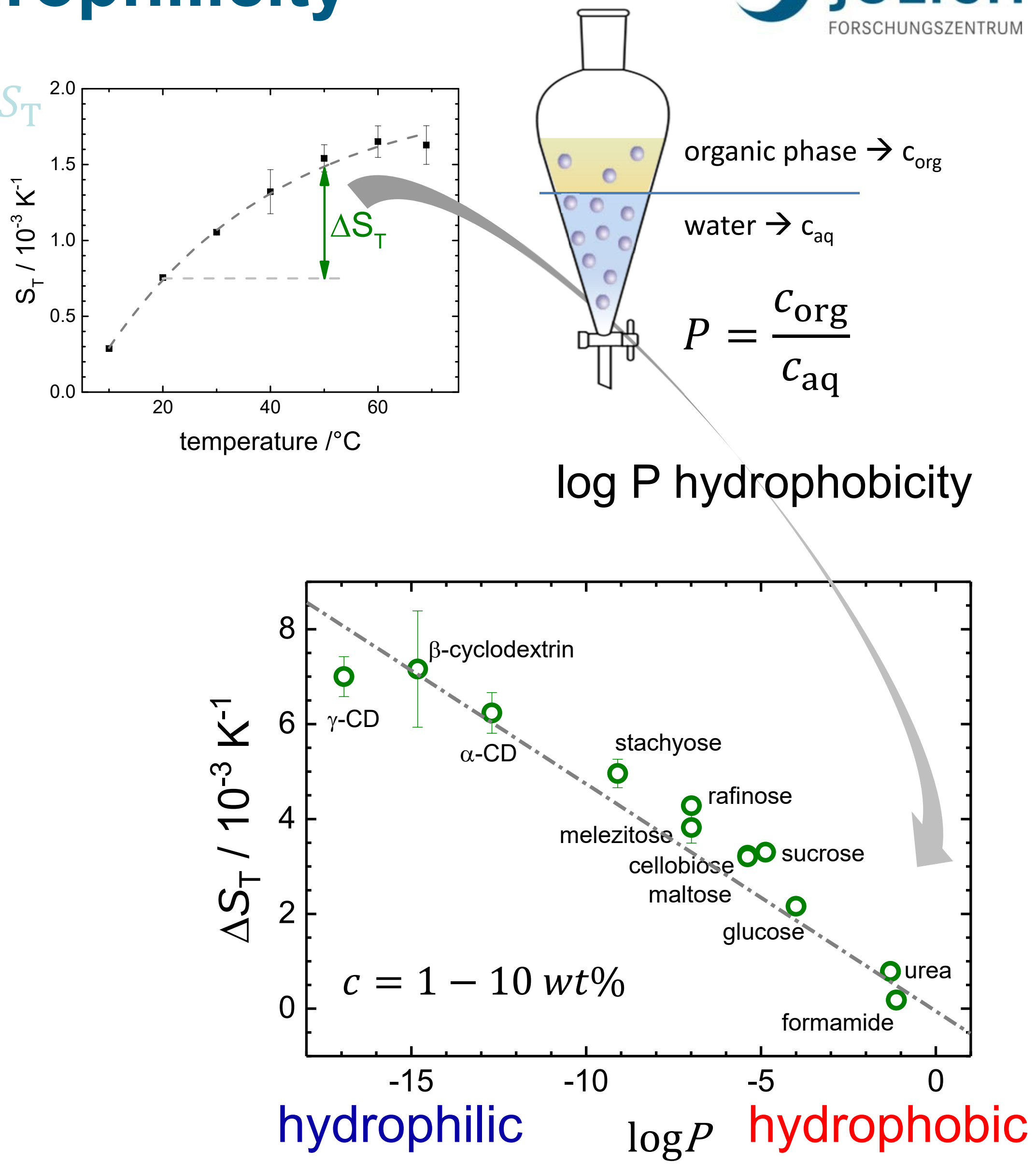
Correlation hydrophobicity and ΔS_T

$$\Delta S_T = S_T(50°C) - S_T(20°C)$$

- ΔS_T is a measure for temperature dependence

- → ΔS_T correlates with hydrophobicity ($\log P$)

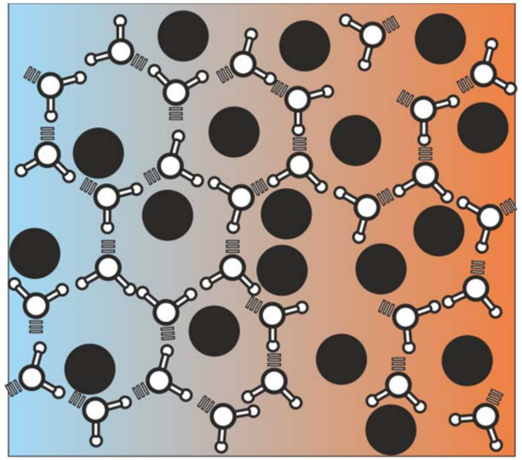
- connection between hydration and thermodiffusion



saccharides: P. Blanco et al., J. Phys. Chem. B 114, 2807 (2010)
urea: D. Niether et al., PCCP., 20, 1012 (2018).
formamide: D. Niether et al., PNAS, 113, 4272 (2016).

Hydrogen bonds: temperature effect

Assuming local thermodynamic equilibrium



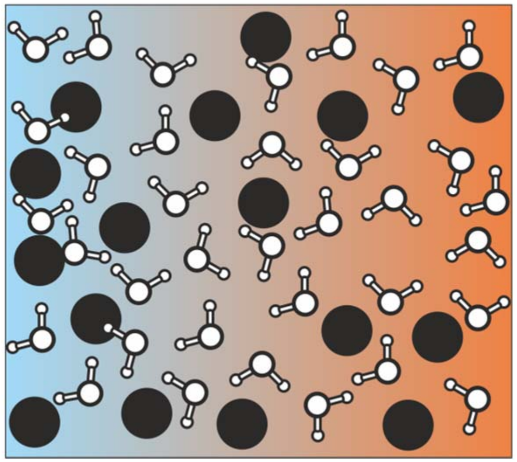
At low temperatures:

minimization of the free energy

$$F = U - TS$$

by forming hydrogen bonds ($\Delta U<0$).

→ water goes to the cold side



At high temperatures:

minimization of the free energy

$$F = U - TS$$

by entropy production ($\Delta S>0$).

→ water goes to the warm side

[Wang, Z., H. Kriegs, and S. Wiegand, J. Phys. Chem. B, 2012.]

To the warm or to the cold?

mass

moment of inertia

size

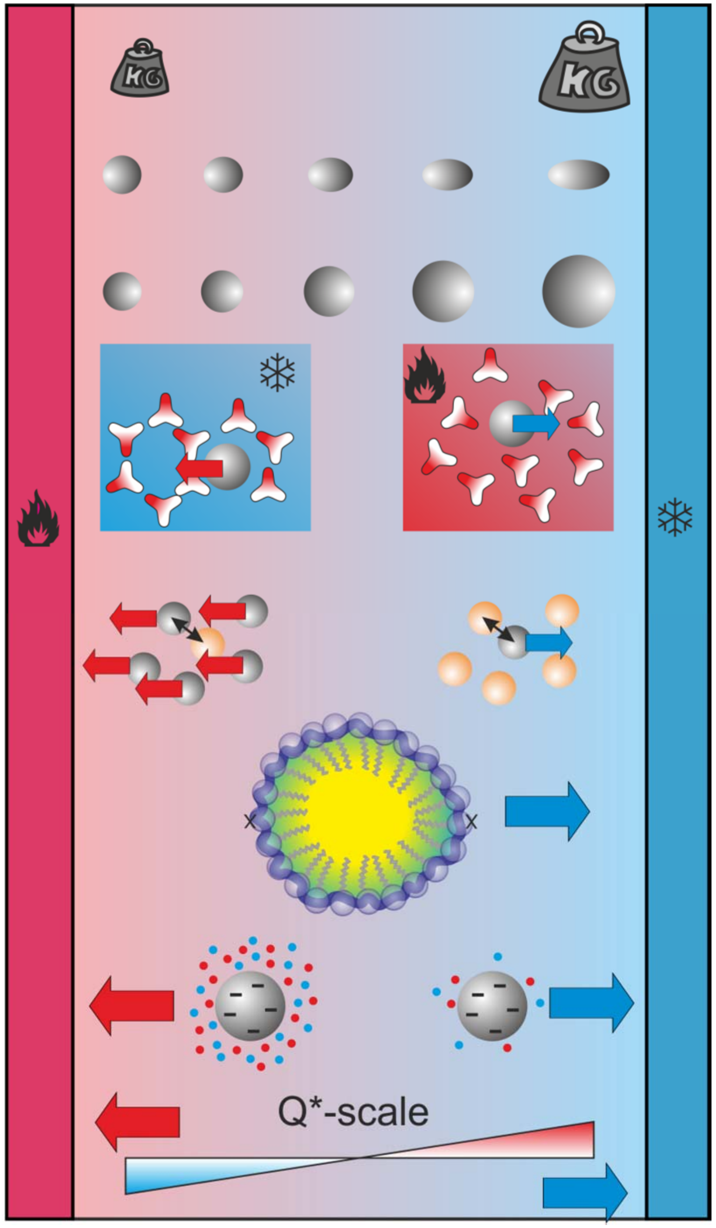
hydrogen bond network

strong cross interaction

interfacial tension

ionic strength

heat of transfer



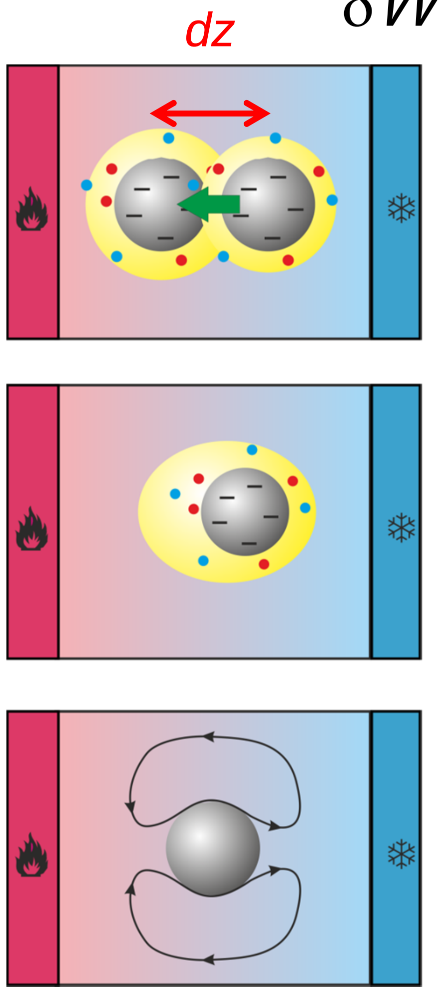
Three forces acting on a charged particle

$$\lambda_{DH} \propto \sqrt{\frac{\varepsilon(T)\cdot T}{I}}$$

T .. temperature
I .. ionic strength
ε ..dielectric constant

$$\delta W^{rev} = -dz \cdot F_{tot}$$

in water



F_W internal force $\boldsymbol{F}_w$ due to change of the double layer structure on displacement of the sphere

\+

F_{el} electric force $\boldsymbol{F}_{el}$ due to non-spherical symmetry of the double layer structure.

\+

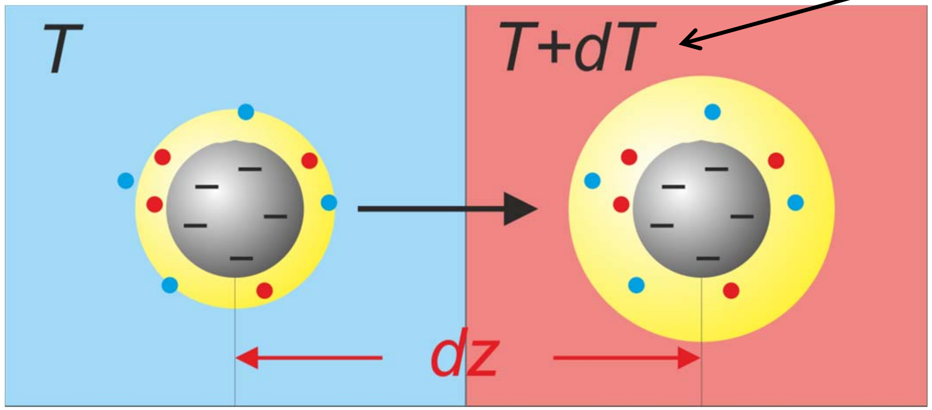
F_{sol} solvent-friction force $\boldsymbol{F}_{sol}$ due to solvent flow arising from the asymmetry of the double-layer structure.

F_{tot}

… of minor importance in water, but relevant in solvents with low dielectric constant

[J. K. G. Dhont and W. J. Briels, Eur. Phys. J. E **25** (2008) 61-76]

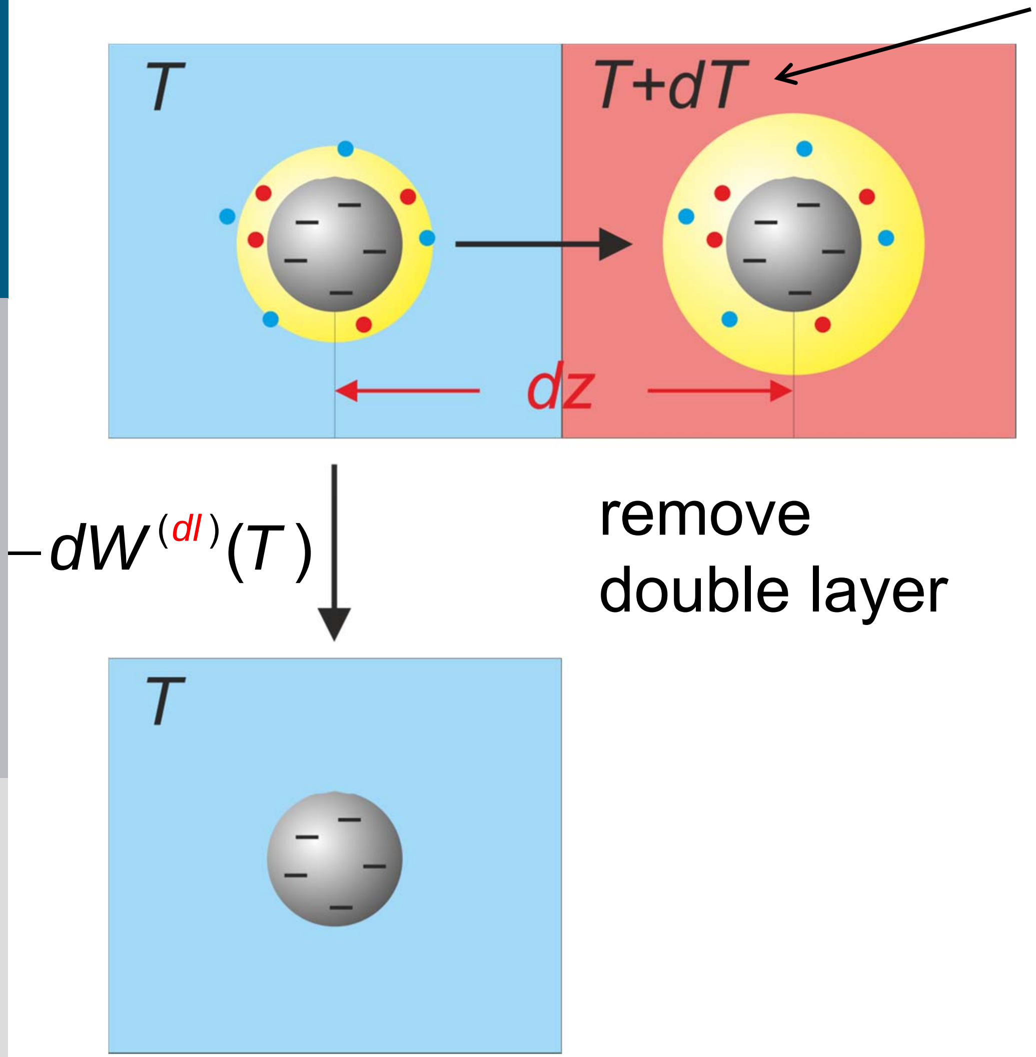
Heuristic consideration for the Force F_w



arbitrary
small T-gradients

$$F \bullet dz = -dW^{rev}$$

Heuristic consideration for the Force F_w

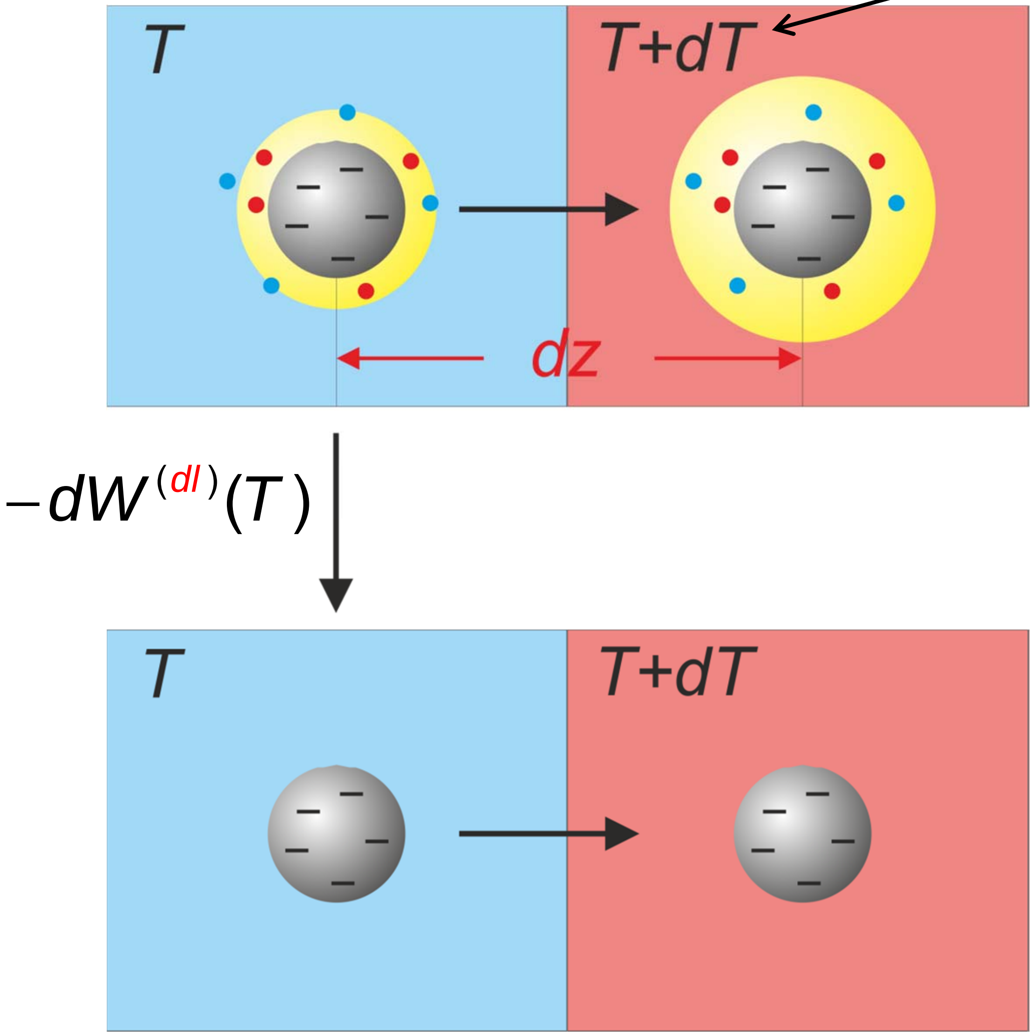


arbitrary
small T-gradients

$$F \bullet dz = -dW^{rev}$$

$$= -(-dW^{(dl)}(T) + \ldots$$

Heuristic consideration for the Force F_w



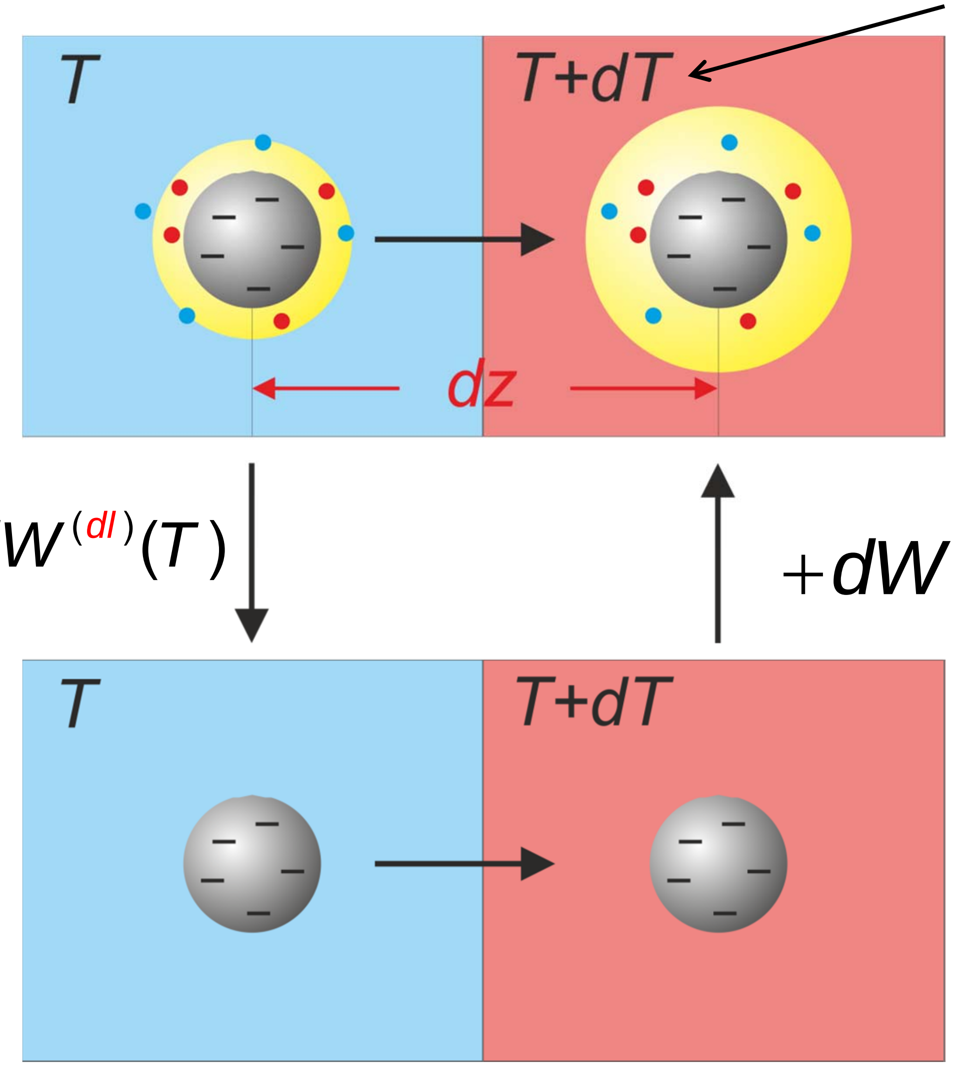
arbitrary
small T-gradients

$$F \bullet dz = -dW^{rev}$$

$$= -(-dW^{(dl)}(T) + \ldots$$

$$dW = 0$$

Heuristic consideration for the Force F_w



arbitrary
small T-gradients

$$F \bullet dz = -dW^{rev}$$

$$= -(-dW^{(dl)}(T) + dW^{(dl)}(T+dT))$$

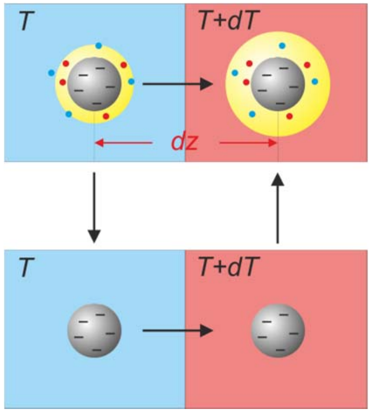
$$-dW^{(dl)}(T)$$

$$+dW^{(dl)}(T+dT)$$

rebuild
double layer

$$dW = 0$$

Heuristic consideration for the Force F_w



$$F \cdot dz = -(-dW^{(dl)}(T) + dW^{(dl)}(T + dT))$$
$$= -dT \, dW^{(dl)}(T) / dT$$

$$F = -(dT / dz) \, dW^{(dl)}(T) / dT$$

force-balance on the diffusive time scale

$$F + F_{friction} = F - 6\pi\eta_0 v_c = 0$$

colloid velocity

(neglect small contribution due to electrolyte friction)

$$v_c = -\frac{1}{6\pi\eta_0}(dT / dz) dW^{(dl)}(T) / dT$$

continuity equation

$$\frac{\partial \rho_c}{\partial t} = -\frac{\partial}{\partial z}(\rho_c v_c) = \frac{k_B T}{6\pi\eta_0} \beta \rho_c dW^{(dl)}(T) / dT \; (d^2T / dz^2) + \cdots (d^2\rho_c / dz^2)$$

to leading order in gradients *and* deviations from mean values

$= D_T$

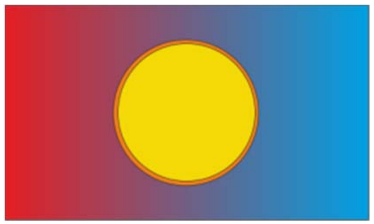
Fickian contribution

Soret coefficient of charged spheres

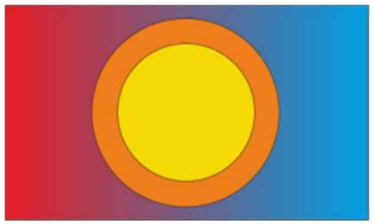
$$D_T = A\frac{d\ln\varepsilon}{d\ln T} + B \quad \begin{cases} A^{(\text{sphere})} = -\mathbb{F}\dfrac{\kappa a}{(1+\kappa a)^2}\left\{1+\dfrac{2}{\kappa a}\right\} \\ B^{(\text{sphere})} = \mathbb{F}\dfrac{\kappa a}{(1+\kappa a)^2} \end{cases} \quad \text{with } \mathbb{F} = \frac{1}{4}D_0\frac{\rho}{T}\left(\frac{4\pi l_B^2\sigma}{e}\right)^2\left(\frac{a}{l_B}\right)^3$$

e … elementary charge
l_B .. Bjerrum length
σ .. surface charge density

$\kappa^{-1}=\lambda_{DH}$ .. Debye length
ε .. dielectric constant
a .. radius of the colloid



thin &

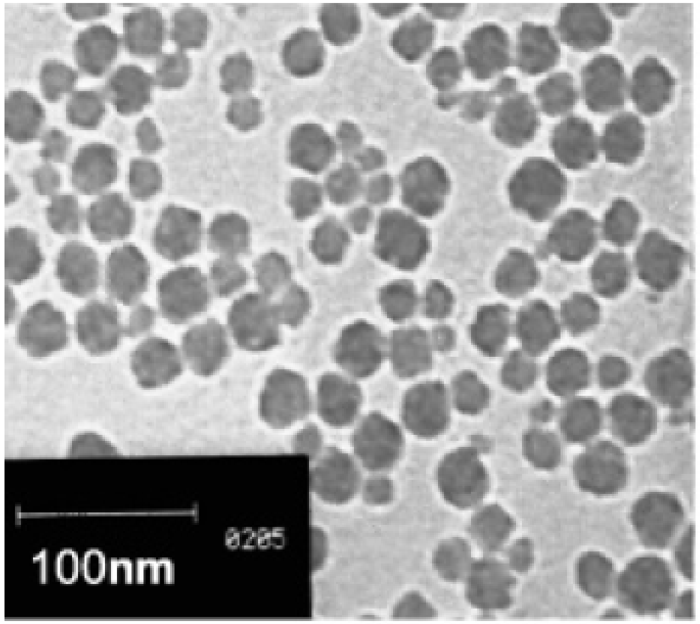


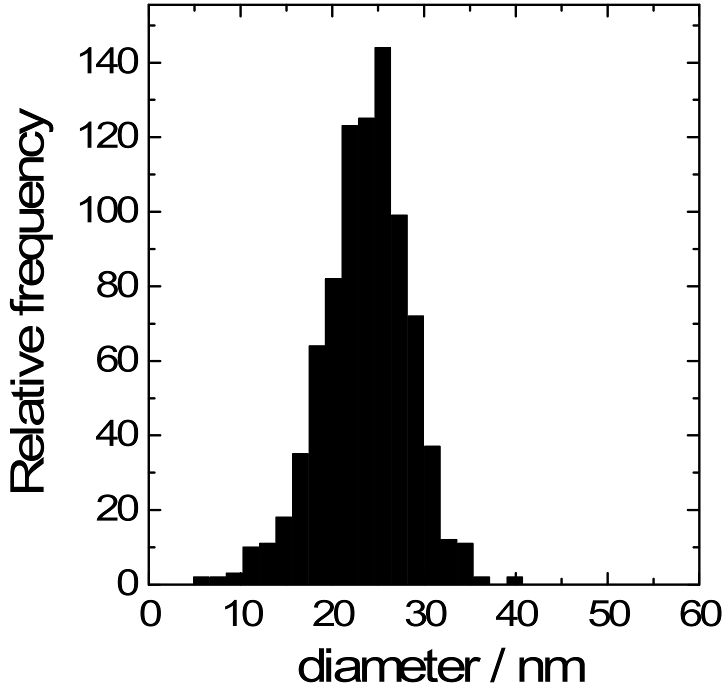
thick double layers

[J. K. G. Dhont and W. J. Briels, Eur. Phys. J. E **25** (2008) 61-76]
[Dhont, J. K. G.; SW; Duhr, S.; Braun, D. Langmuir, 23 (2007), 1674]

Charged spheres: system

charged silica colloidal particles (Ludox)





Hui Ning

Electrophoresis:

surface charge

$\sigma = 7 \times 10^{-18}$ C/particle

= 44 e/particle

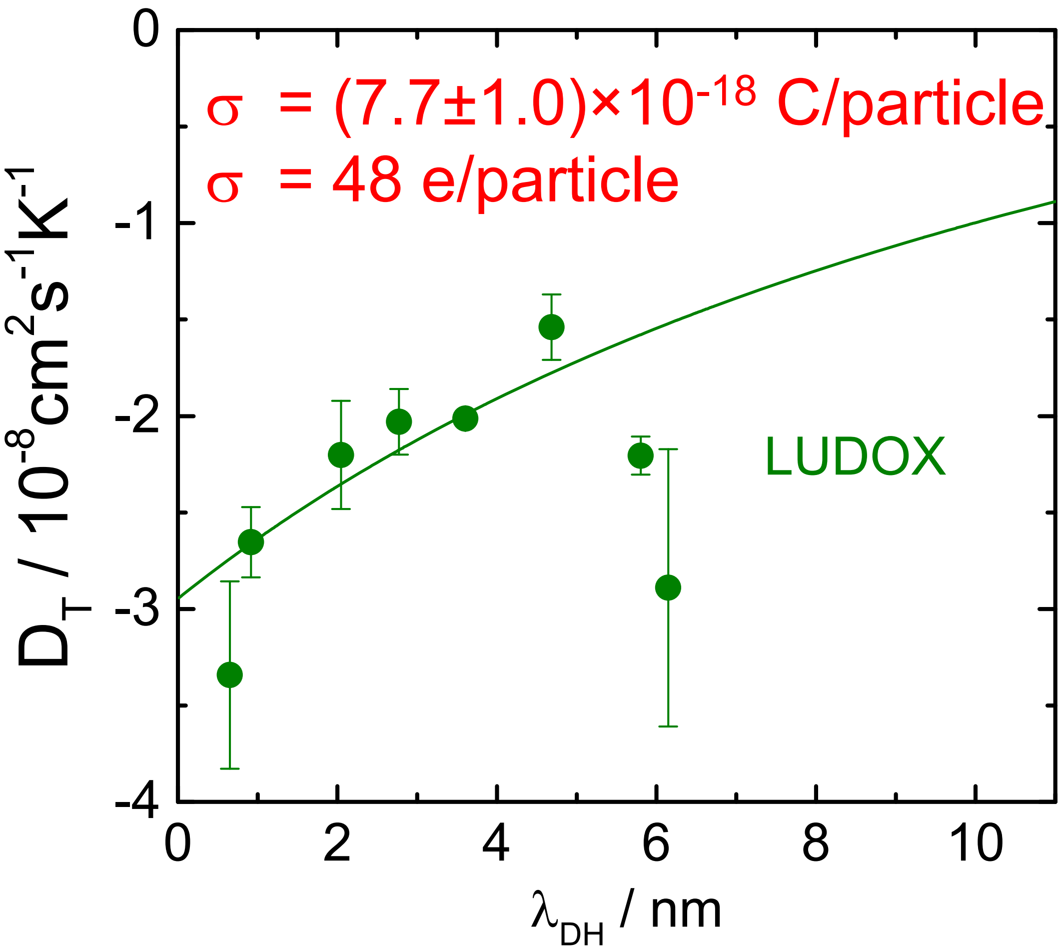
diameter$_{(TEM)}$ = 24.6 ± 4.8 nm

[H.Ning, J.K.G. Dhont, SW, Langmuir, 24 (2008), 2426]

Charged sphere: results

$$D_T^{DL} = \frac{D_0}{T}\left\{\frac{1}{4}\mathcal{N}\left(\frac{4\pi\lambda_{Bj}^2\sigma}{e}\right)^2\left(\frac{a}{\lambda_{Bj}}\right)^3\frac{\kappa a}{(1+\kappa a)^2}\times\left[1-\frac{d\ln\varepsilon}{d\ln T}\left(1+\frac{2}{\kappa a}\right)\right]\right\}+A(T)$$

with $\mathcal{N}=1$



Electrophoresis:

surface charge

$\sigma = 7\times10^{-18}$ C/particle

$= 44$ e/particle

[H.Ning, J.K.G. Dhont, SW, Langmuir, 24 (2008), 2426]

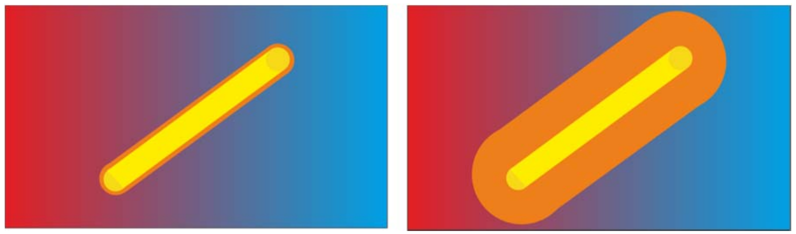
Extension of the model for colloidal rods

$$D_T = A\frac{d\ln\varepsilon}{d\ln T} + B$$

$$A^{(\mathrm{rod})} = -\mathbb{F}\frac{L}{\kappa a_c^2}\frac{K_0(\kappa a_c)}{K_1(\kappa a_c)}\left\{1+\frac{1}{2}\kappa a_c\left(\frac{K_0(\kappa a_c)}{K_1(\kappa a_c)}-\frac{K_1(\kappa a_c)}{K_0(\kappa a_c)}\right)\right\}$$

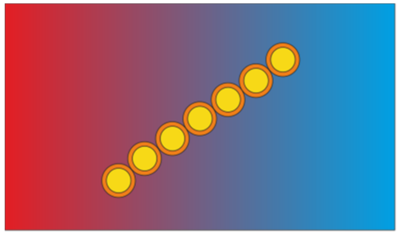
$$B^{(\mathrm{rod})} = \mathbb{F}\frac{L}{2a_c^2}\left(1-\frac{K_0^2(\kappa a_c)}{K_1^2(\kappa a_c)}\right)$$

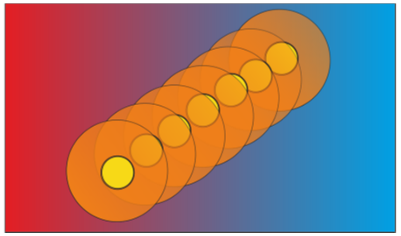
with $$\mathbb{F} = \frac{1}{4}D_0\frac{\rho}{T}\left(\frac{4\pi l_B^2\sigma}{e}\right)^2\left(\frac{a}{l_B}\right)^3$$



[Wang, Z., H. Kriegs, J. Buitenhuis, J.K.G. Dhont, and SW, Soft Matter, 9 (2013) p. 8697]

Extension of the model for colloidal rods





Solution for rods can be replaced by a chain of spheres

$$D_T^{DL} = \frac{D_0}{T}\left\{\frac{1}{4}\mathcal{N}\left(\frac{4\pi\lambda_{Bj}^2\sigma}{e}\right)^2\left(\frac{a}{\lambda_{Bj}}\right)^3\frac{\kappa a}{(1+\kappa a)^2}\times\left[1-\frac{d\ln\varepsilon}{d\ln T}\left(1+\frac{2}{\kappa a}\right)\right]\right\}+A(T)$$

with $\mathcal{N} = \frac{L}{2a}$ a .. radius

$\mathcal{N}$.. number of beads

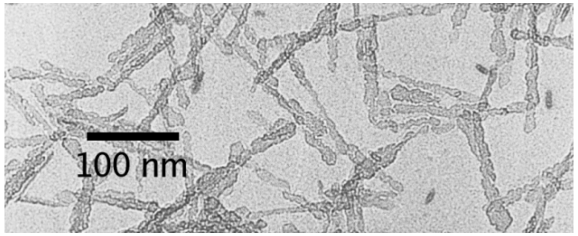
[Wang, Z., H. Kriegs, J. Buitenhuis, J.K.G. Dhont, and SW, Soft Matter, 9 (2013) p. 8697]

Colloidal rods

Inorganic rod-like particles

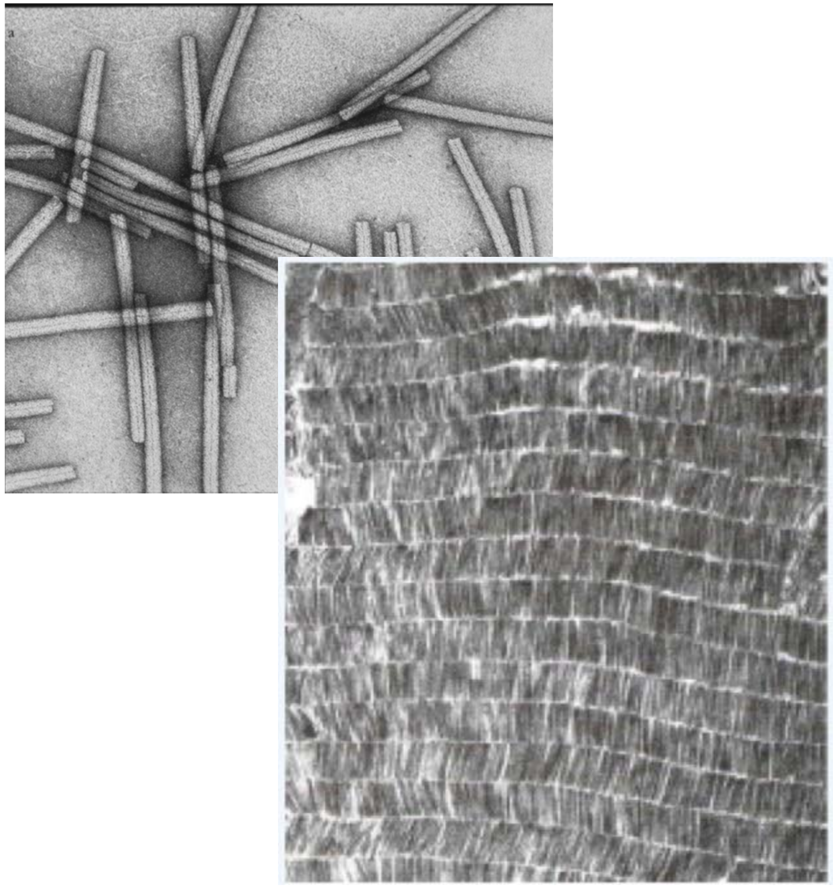
*V_2O_5, **Zocher** (1925)*

Polydisperse!
Need help from biology.



Biological rod-like particles

*TMV, **Bawdwn et al**, (1935)*

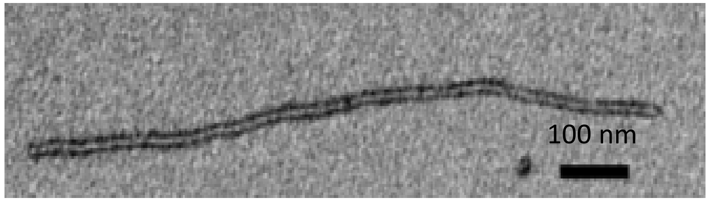


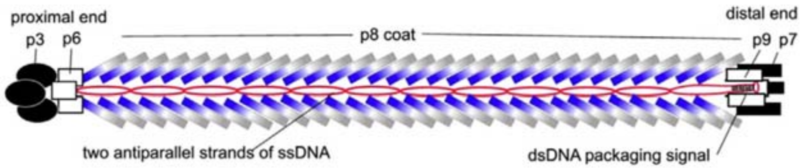
H.Zocher, Anorg Allg.Chem, 147, 91 (1925)

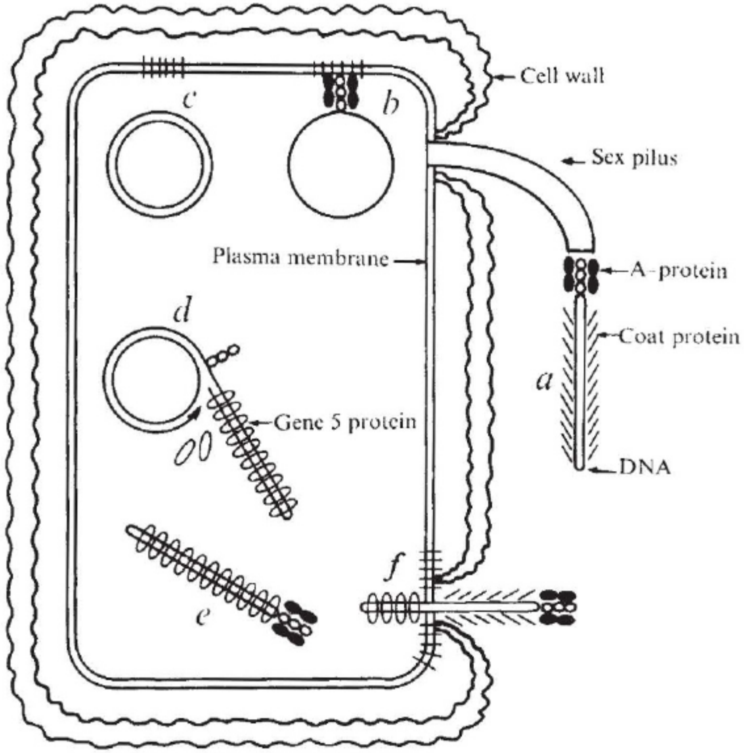
Wetter, Biologie in unserer Zeit, 17, 81 (1985)

Colloidal rods:
fd virus as model system

produced by E.coli bacteria







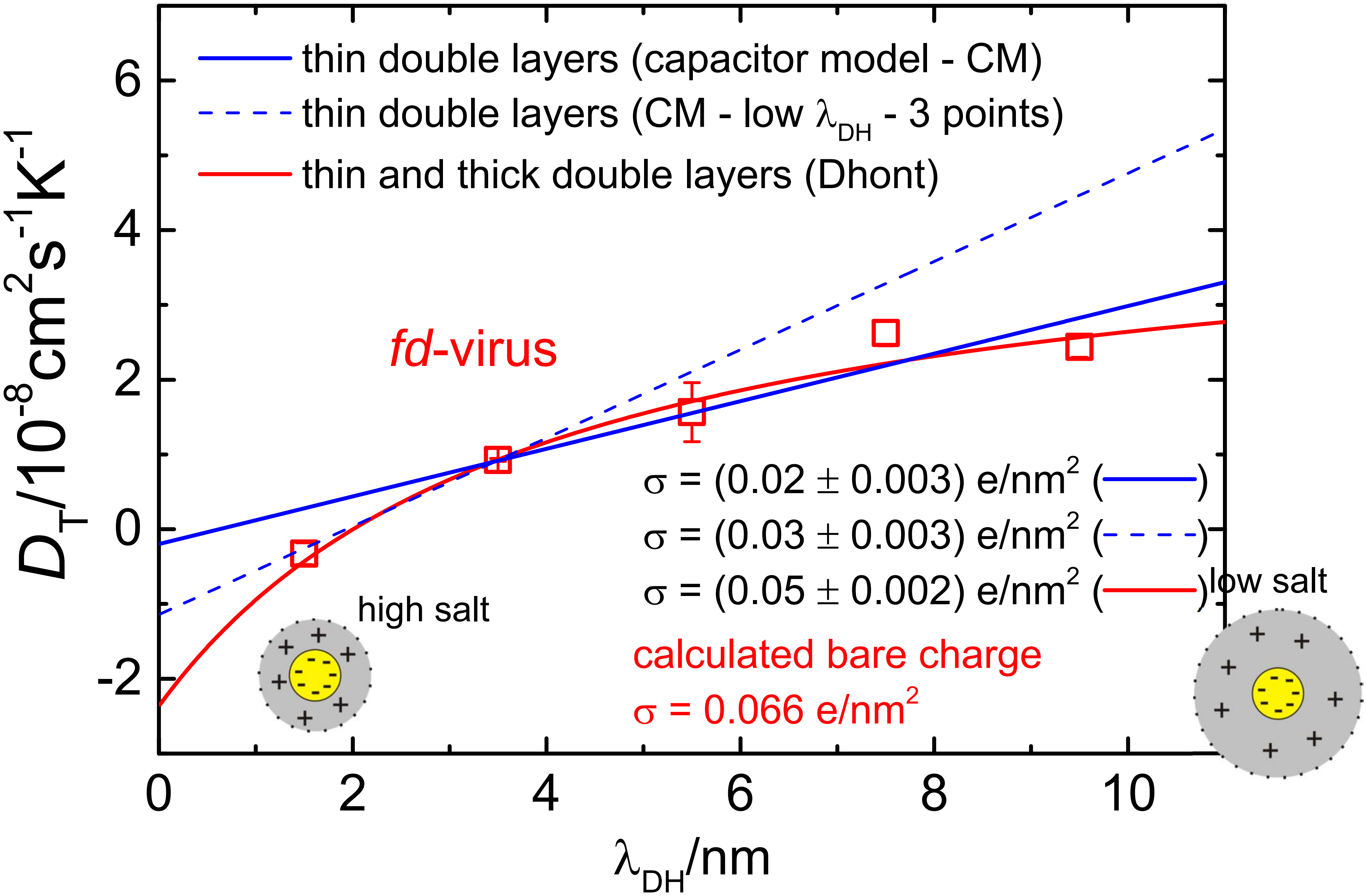
D. A. Marvin and E. J. Wachtel, Nature 253, 19 (1975).

Genetic Modification

system	L [µm]	L_p [µm]
fd wild type	0.88	2.8
fd Y21M	0.91	9.9
Pf1	1.96	2.8
M13k07	1.2	2.8

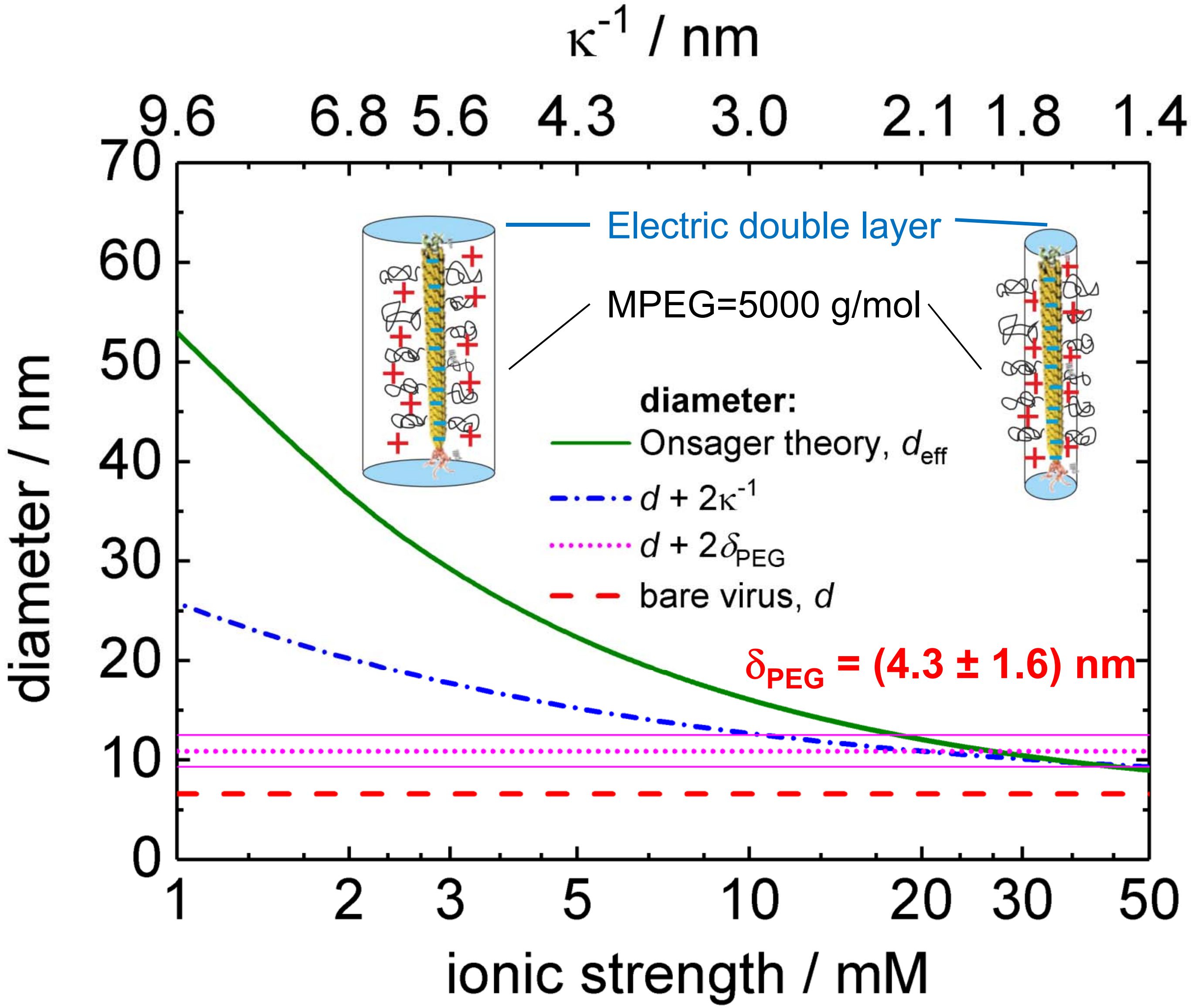
Diameter = 6.8 nm
Molar mass =1.64×10^7 g/mol

Charged colloidal rod: results



[Wang, Z., H. Kriegs, J. Buitenhuis, J.K.G. Dhont, and SW, Soft Matter, 9 (2013) p. 8697]

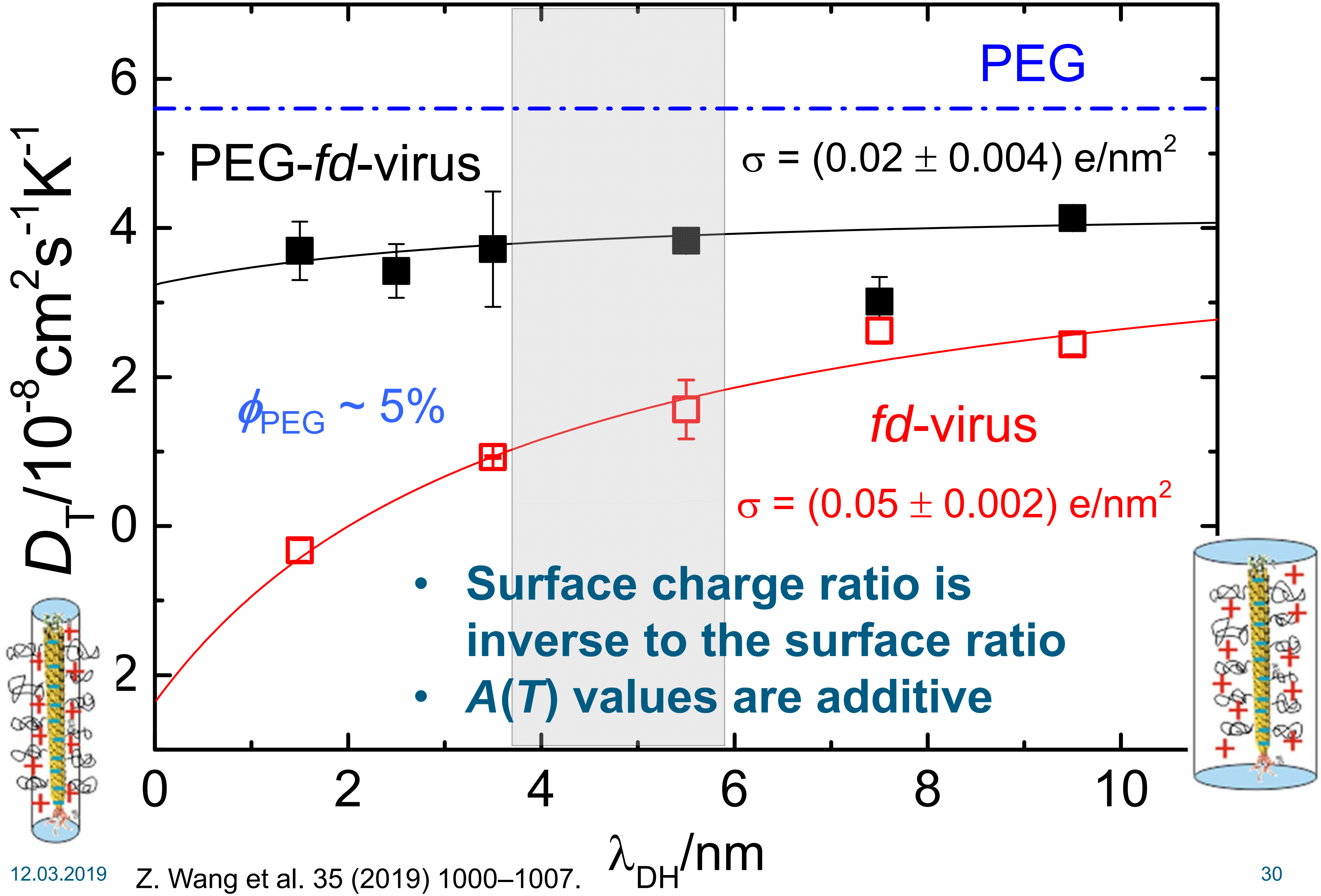
Charged colloidal rod with ‚hairs‘: system



Onsager, L., Ann. N.Y. Acad. Sci, **51** (1949) 627-659.

Z. Wang et al. 35 (2019) 1000–1007.

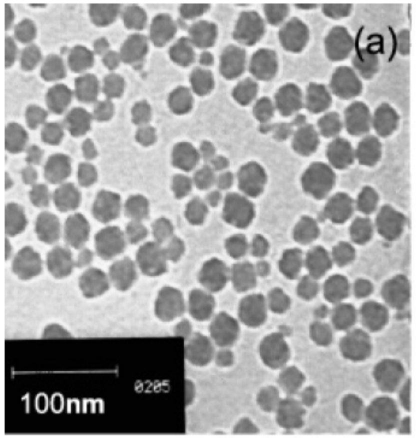
Charged colloidal rod with hairs

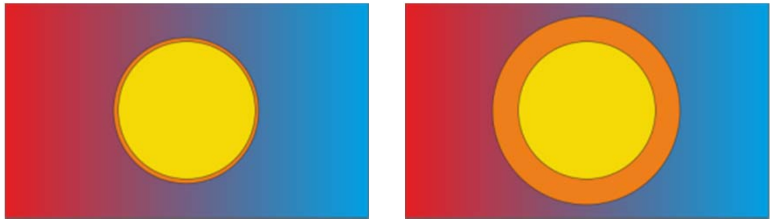


- **Surface charge ratio is inverse to the surface ratio**
- ***A*(*T*) values are additive**

Z. Wang et al. 35 (2019) 1000–1007.

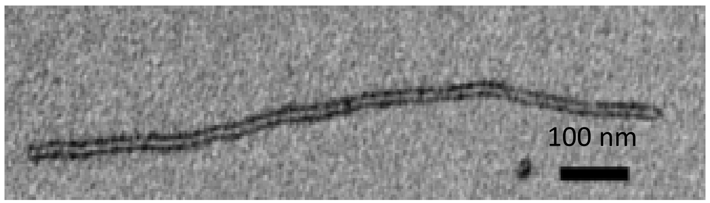
Take home message

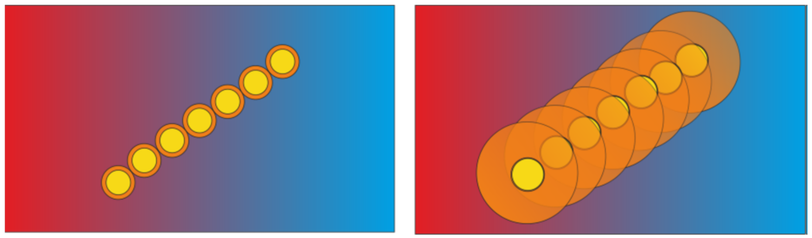




Charged colloidal model systems can be fully described by the double layer contribution

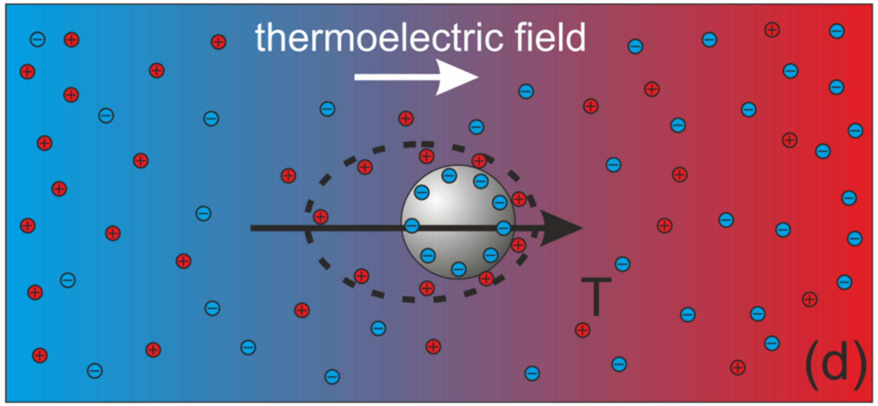
Microscopic understanding of the charge distribution of colloids with grafted polymers needs more work.



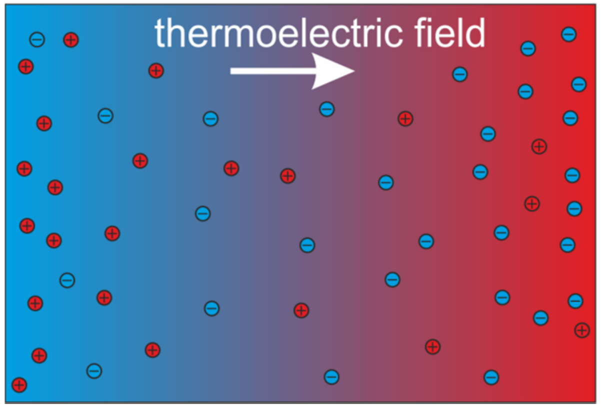


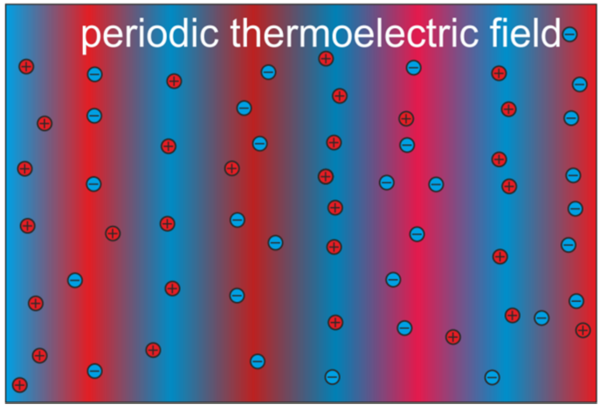
Some final remarks

Well defined monodisperse systems are required to separate different contributions

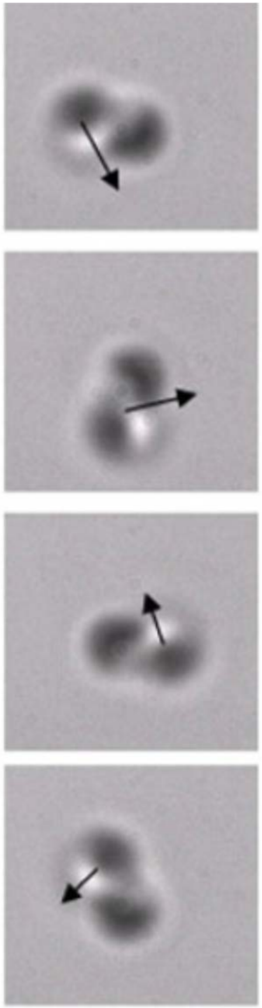


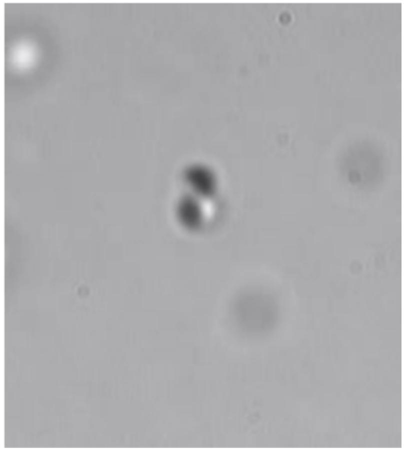
Conceptually different solid wall / sinusoidal grating





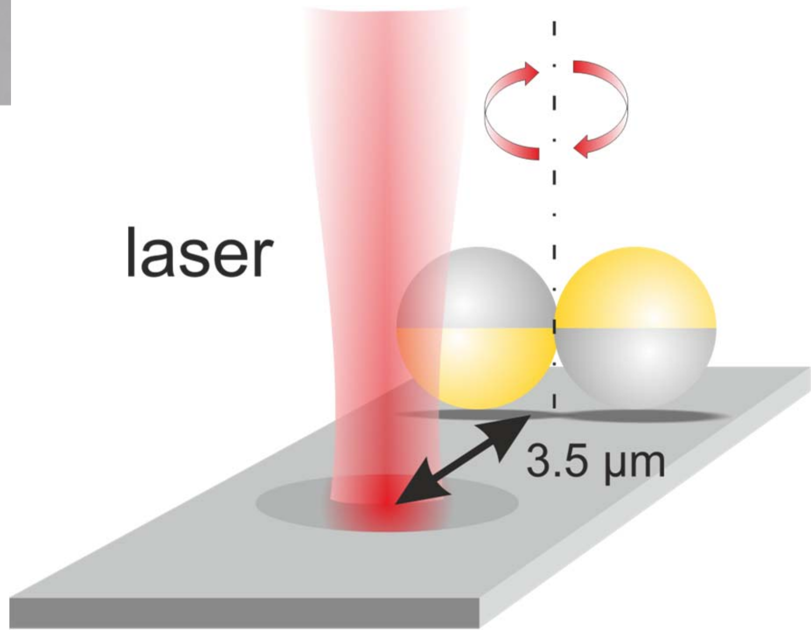
„Janus“ microrotor





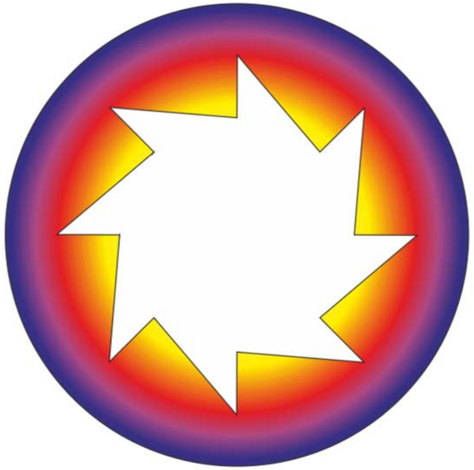
twin gold-silica Janus particle

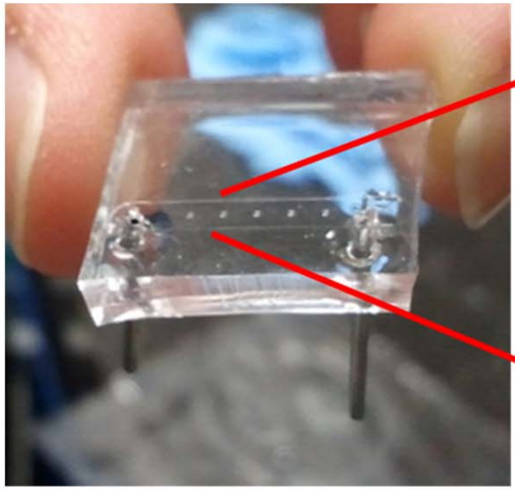
a temperature gradient leads to a rotation of the twin particle

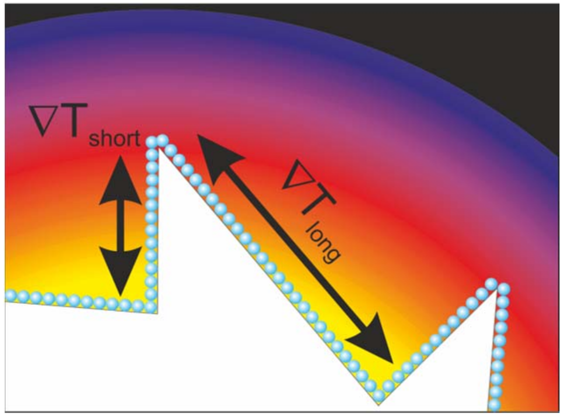


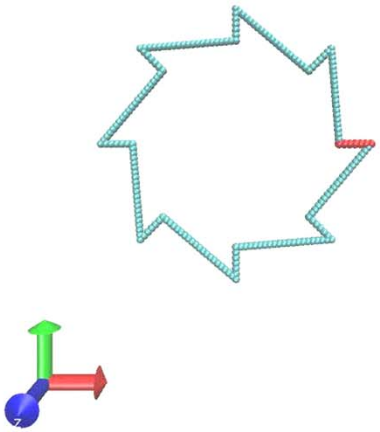
[H.-R. Jiang, N. Yoshinaga and M. Sano, Phys. Rev. Lett., **105** (2010) 268302]

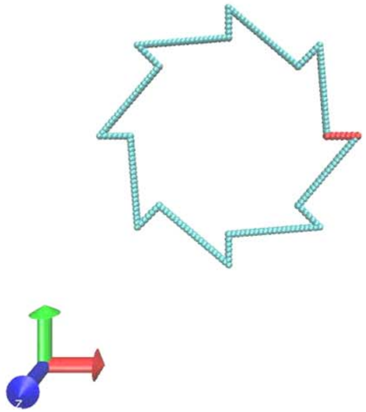
Thermophoretic machines: micro gear





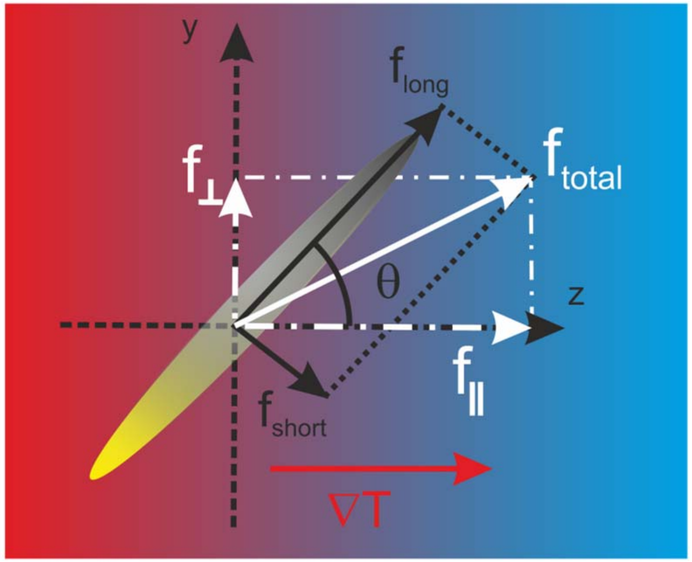


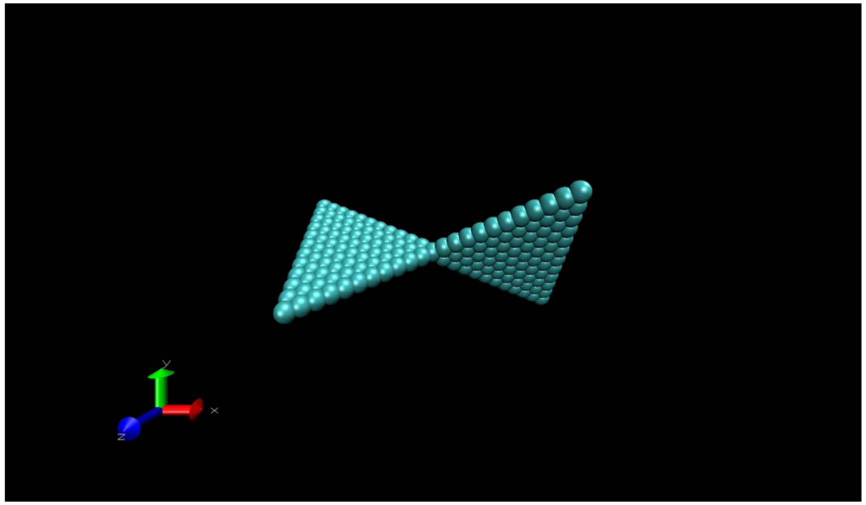


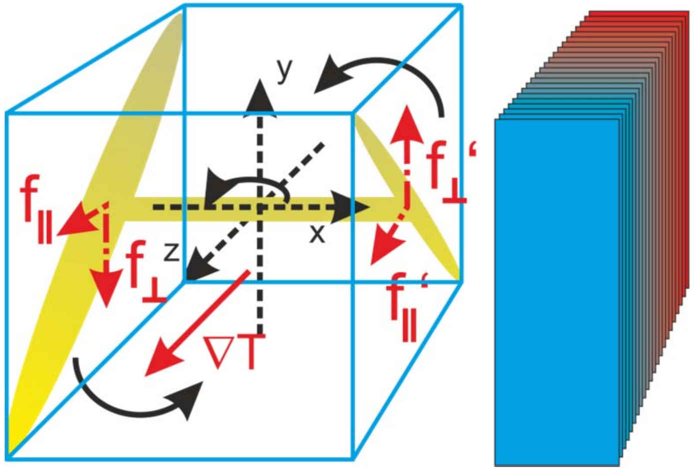


[M. C. Yang and M. Ripoll, Soft Matter, 10 (2014) 1006-1011.
D. Afanasenkau experiments in progress]

Thermophoretic machines: turbine



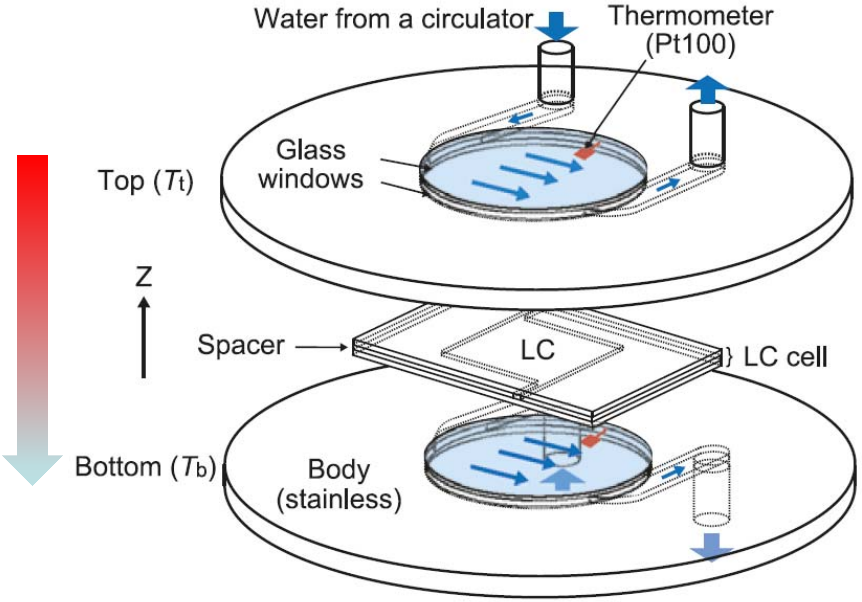


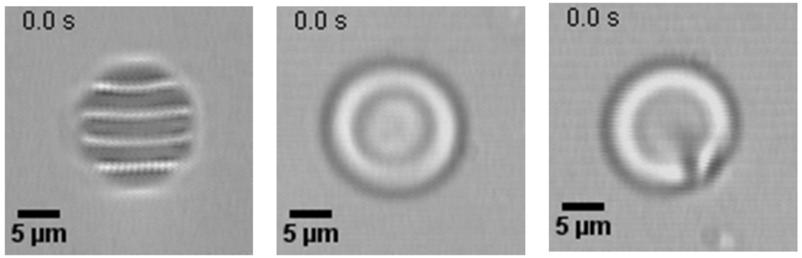


If two ellipsoidal blades with opposite orientation angles connected by a rigid bond, which is perpendicular to an external thermal gradient they can rotate.

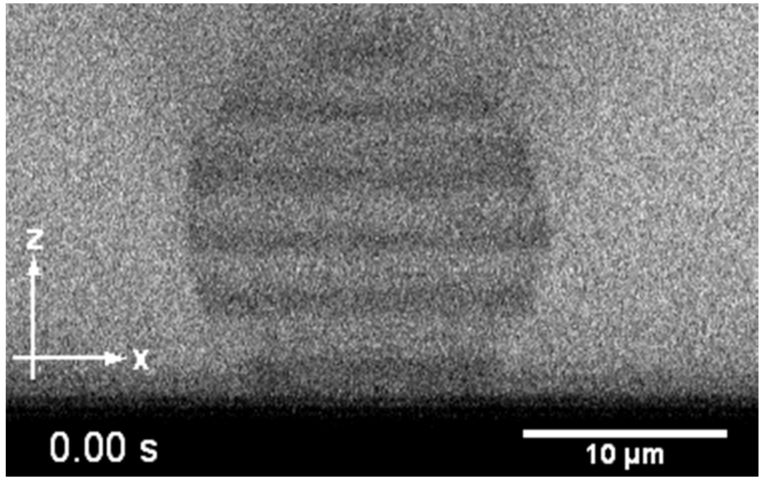
[M. Yang, R. Liu, M. Ripoll and K. Chen, Nanoscale, 6 (2014) 13550-13554.]

Rotating cholesteric liquid crystal droplet





cholestric liquid crystal droplets under a temperature gradient (the Lehmann effect)



[Lehmann, O., Annalen Der Physik, 2(1900) 649-705.;
T. Yamamoto, M. Kuroda and M. Sano, EPL (Europhysics Letters), 109 (2015) 46001]

Thank you for your attention and thanks to…

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Zilin Wang – fd virus

Johan Buitenhuis – synthesis

Hartmut Kriegs - technical support

Doreen Niether – PEG-fd virus