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JÜLICH FORSCHUNGSZENTRUM

Thermophoresis of charged colloidal spheres and rods

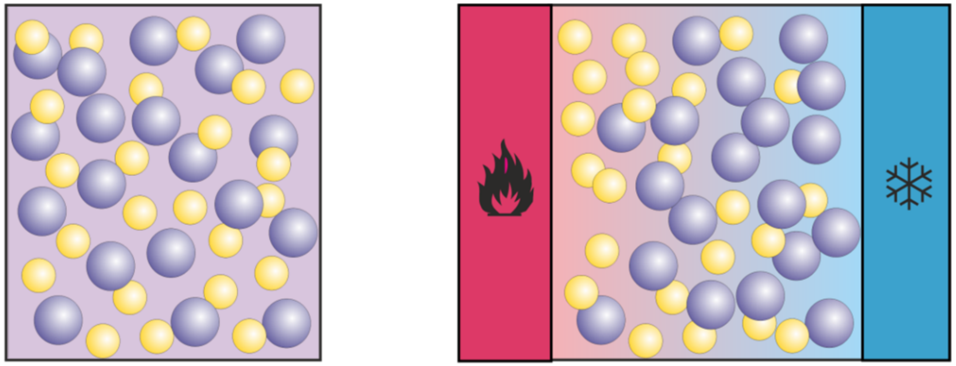
20. Mai 2015

| Simone Wiegand, Dzmitry Afanasenkau, Olga Syshchyk, Zilin Wang, Johan Buitenhuis and Jan K.G. Dhont

Phenomenological equation

(…, thermodiffusion, Soret effect) –

Movement of particles driven by a temperature gradient



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

D - diffusion coefficient,

c - concentration,

D_T - thermodiffusion coefficient,

$\vec{j}$ - flux, T – temperature

S_T – Soret coefficient

Steady state $\vec{j}=0$

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

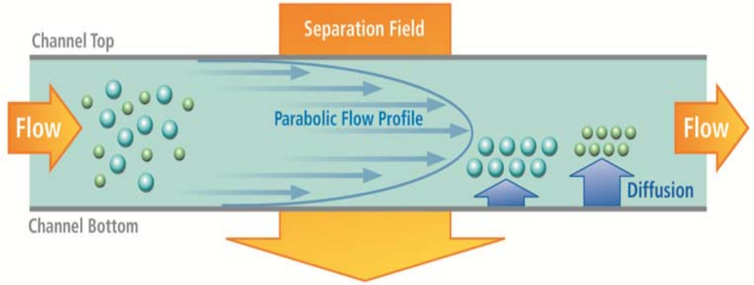
Thermophoresis: What ? Where is it used?

Application areas

- Characterization of macromolecules and colloids, e.g. TFFF (thermal field flow fractionation)
- Separation of mixtures, e.g. thermogravitational column
- **Measuring equilibration constants of biochemical reactions**
- **Studying interaction and folding of macromolecules**

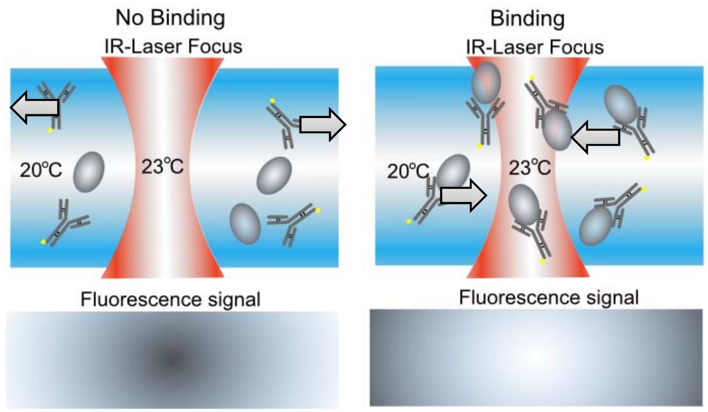
Application examples

- Thermal field flow fractionation



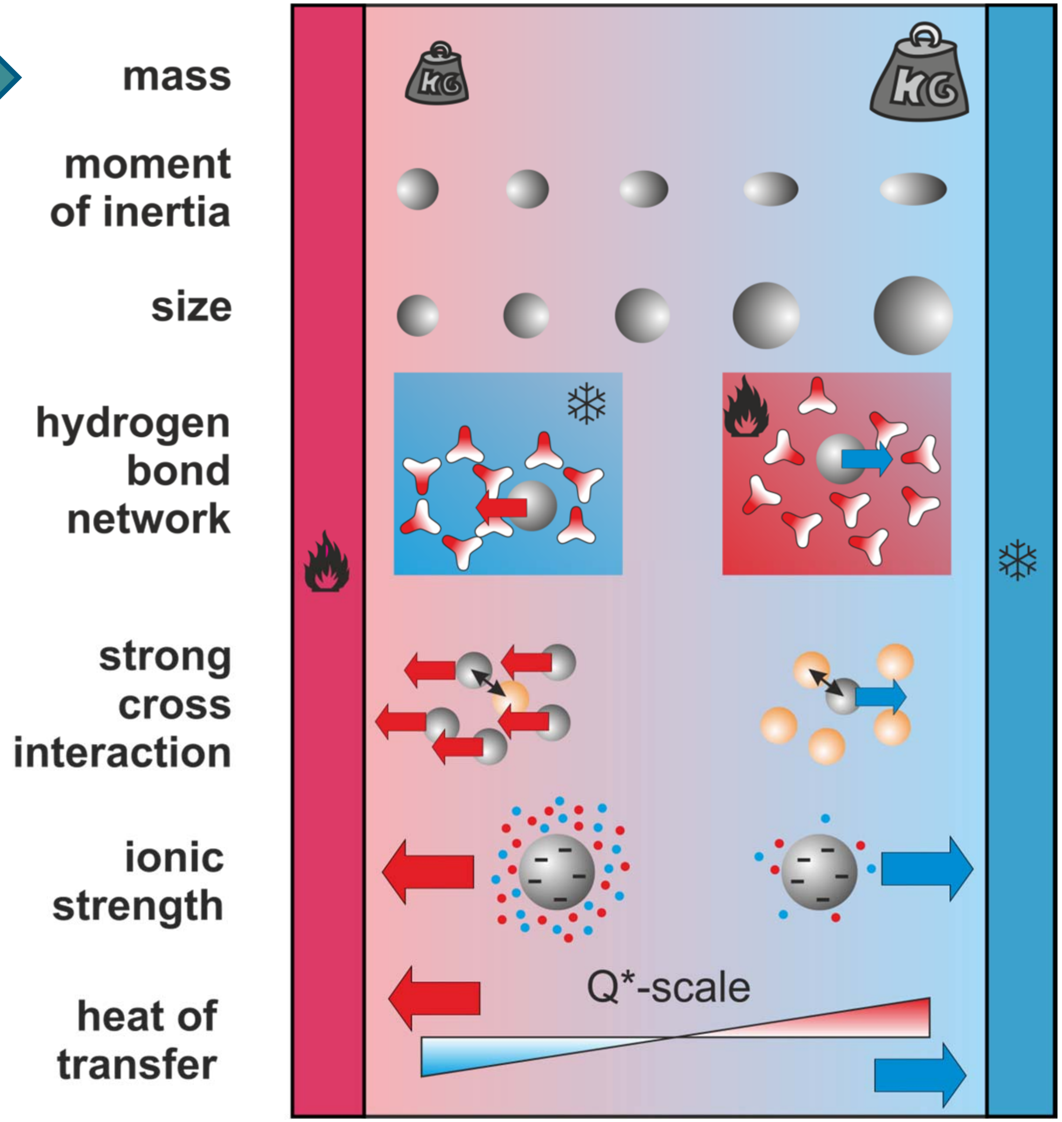
Separation of mixtures (TFFF) //Wikipedia

- Microscale thermophoresis



Microscale Thermophoresis: Technology and Applications //NanoTemper GMBH

To the warm or to the cold?

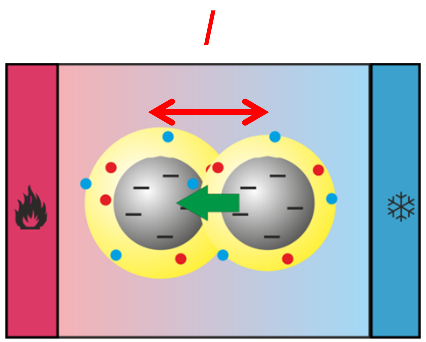


SW., *Introduction to thermal gradient related effects*, in *Functional Soft Matter*, J.K.G. Dhont, et al., Editors. 2015, Forschungszentrum Jülich: Jülich. p. F4.1-F4.24.

Influence of charges

$$\lambda_{DH} \propto \sqrt{\frac{T}{I}}$$

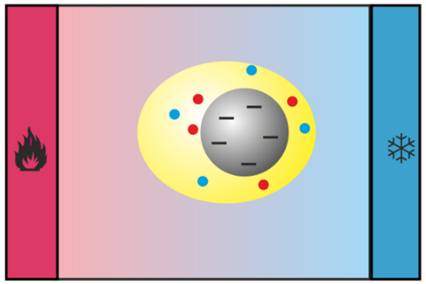
T .. temperature
I .. ionic strength



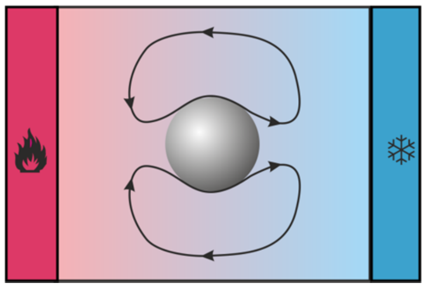
$$\delta W^{rev} = -I \cdot F_{tot}$$

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

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



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

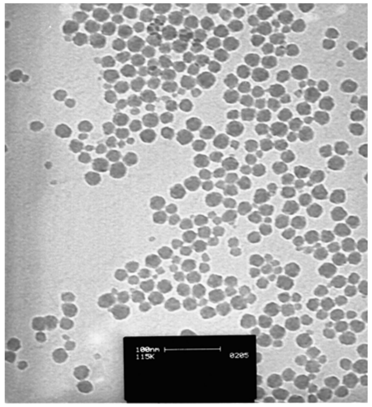


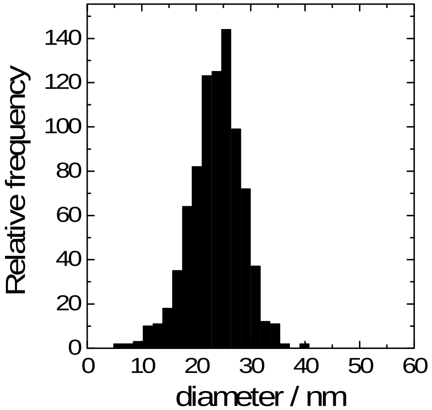
solvent-friction force $\boldsymbol{F}_{sol}$ due to solvent flow arising from the asymmetry of the double-layer structure.

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

Ionic strength effect

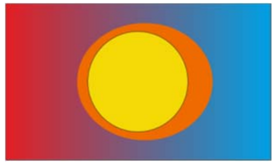
charged silica colloidal particles (Ludox)

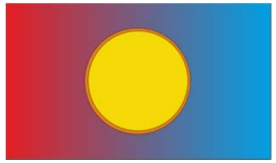




Hui Ning

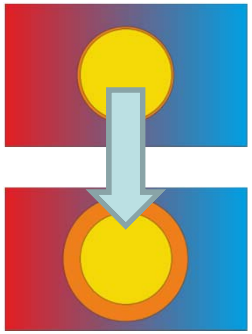
E. Rückenstein, J. Colloid Interface Sci. 83, 77 (1981)
S. Fayolle et al., Phys. Rev. Lett. 95, 208301 (2005)

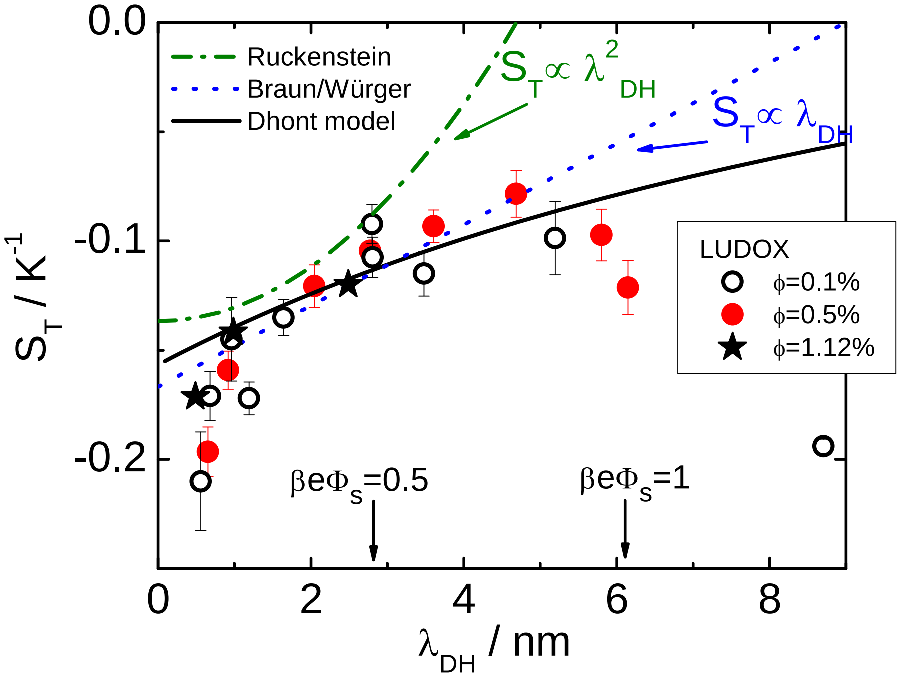




valid for thin and thick double layers:

- *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



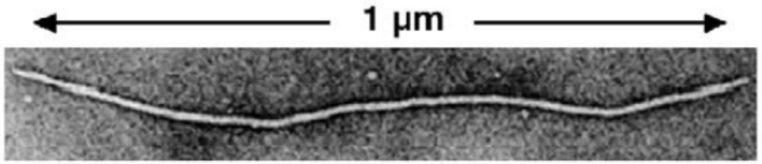


$$S_T=\frac{1}{T}\left\{1+\frac{1}{4}\left(\frac{4\pi l_B^2\sigma}{e}\right)^2\frac{1}{(1+\kappa a)^2}\frac{\kappa a^4}{l_B^3}\left\{1-\frac{d\ln\varepsilon}{d\ln T}\left(1+\frac{2}{\kappa a}\right)\right\}\right\}+A(T)$$

[H.Ning, J.K.G. Dhont, SW, Langmuir, 24 (2008), 2426]
[Dhont, J. K. G.; SW; Duhr, S.; Braun, D. Langmuir, 23 (2007), 1674]

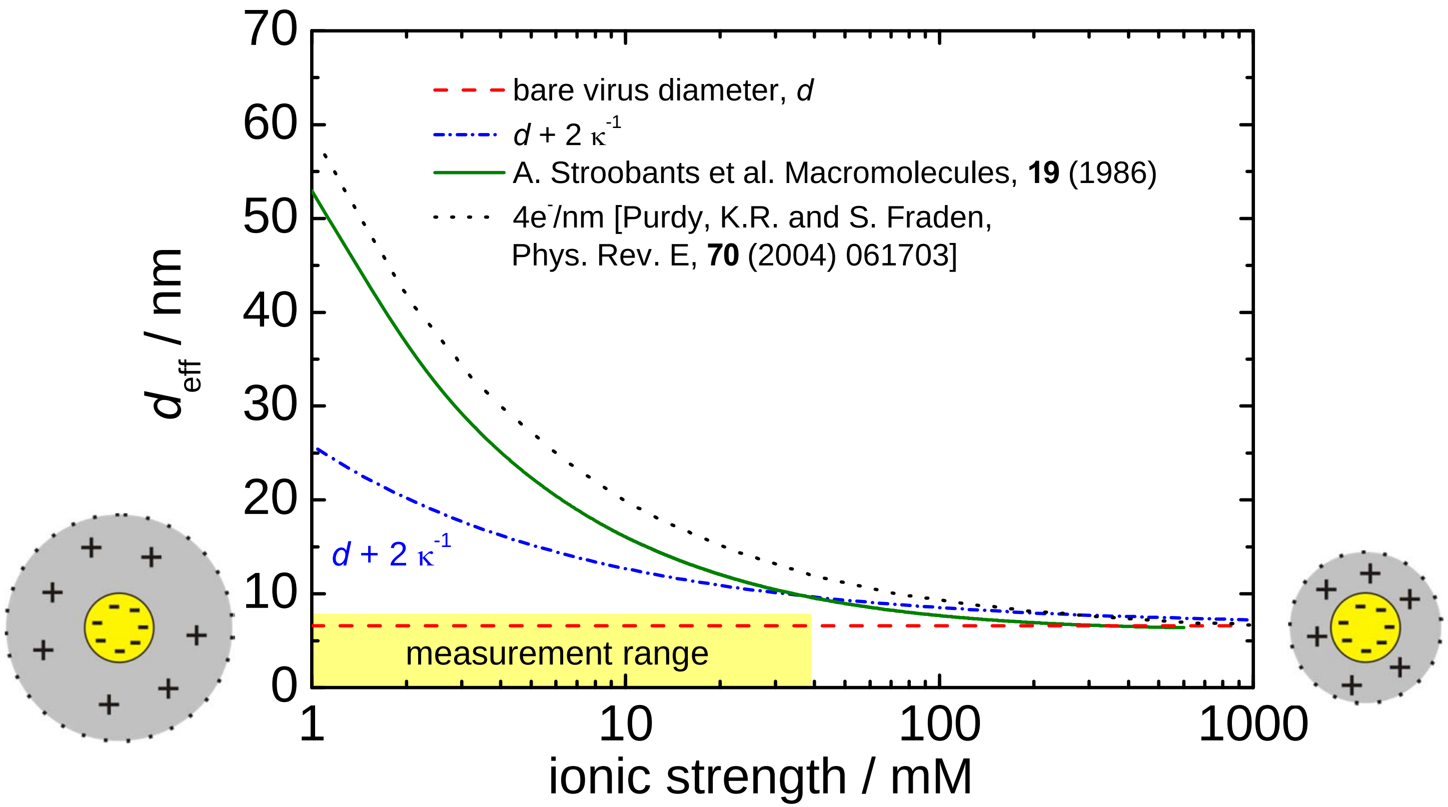
Model system for a charged rod: fd-virus

System: *wt* fd-virus



Diameter = 6.6 nm
Length = 880 nm
Molar mass =1.64x10^7 g/mol

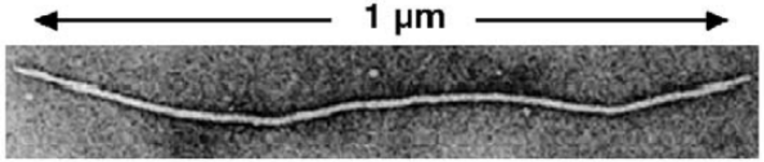
Effective diameter

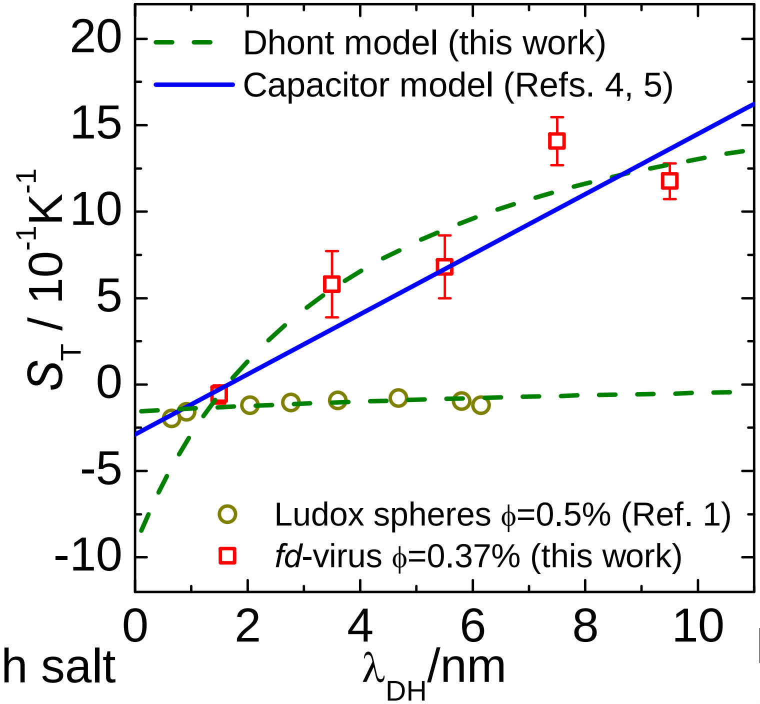


Onsager, L., Ann. N.Y. Acad. Sci, **51**(1949) 627-659.

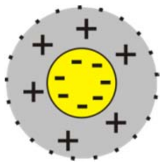
Single particle effects: charged colloidal rod

System: *wt* fd-virus

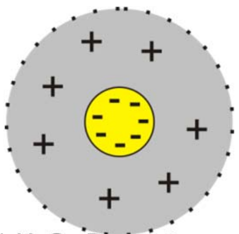




high salt

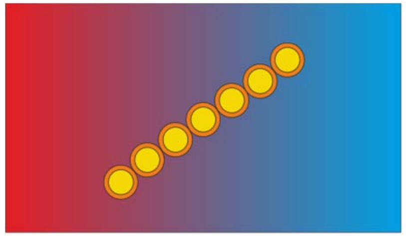


low salt

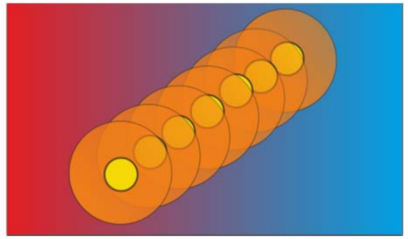


Theoretical description

Thin double layer



Thick double layer



Model	σ/enm^{-2}	Offset
Dhont	0.050±0.003	-1.39
Capacitor	0.016±0.002	-0.74
Calculated bare charge	0.066	

Zilin Wang

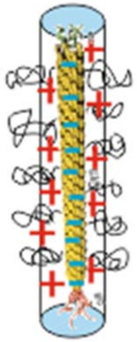
[Wang, Z., H. Kriegs, J. Buitenhuis, J.K.G. Dhont, and SW, Soft Matter, 9 (2013) p. 8697]

Charged colloidal rod with hairs

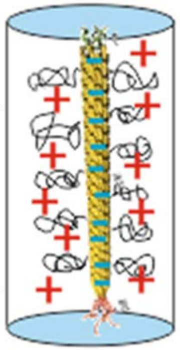
Johan Buitenhuis

Zilin Wang

Ionic strength>20mM



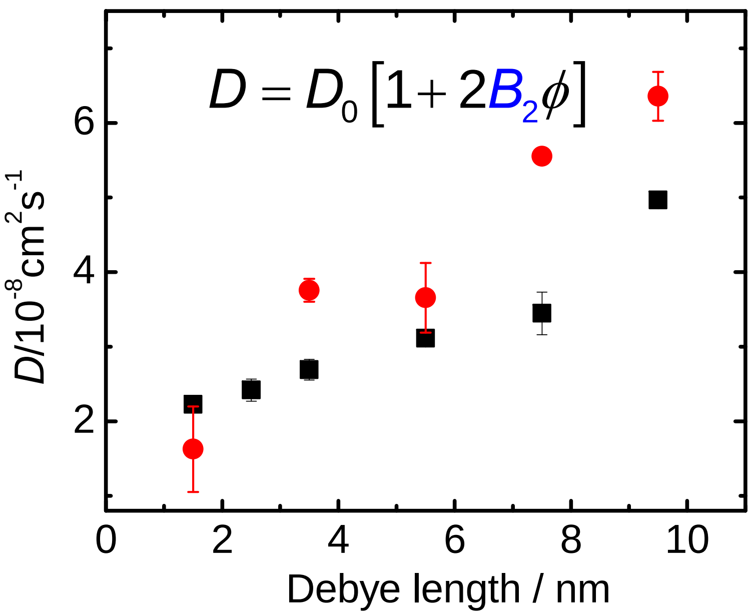
Ionic strength<20mM

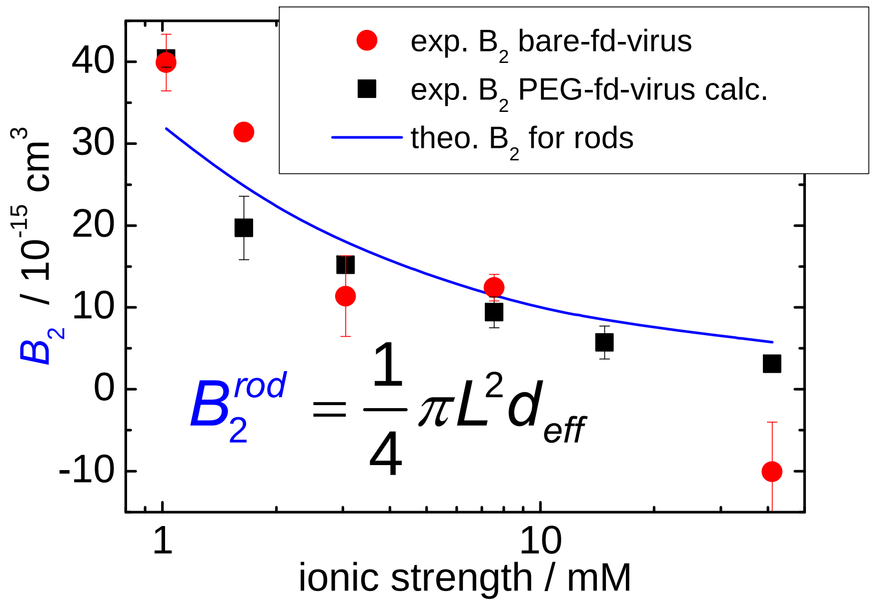


Electric double layer

MPEG=5000g/mol

Steric vs. electric interaction

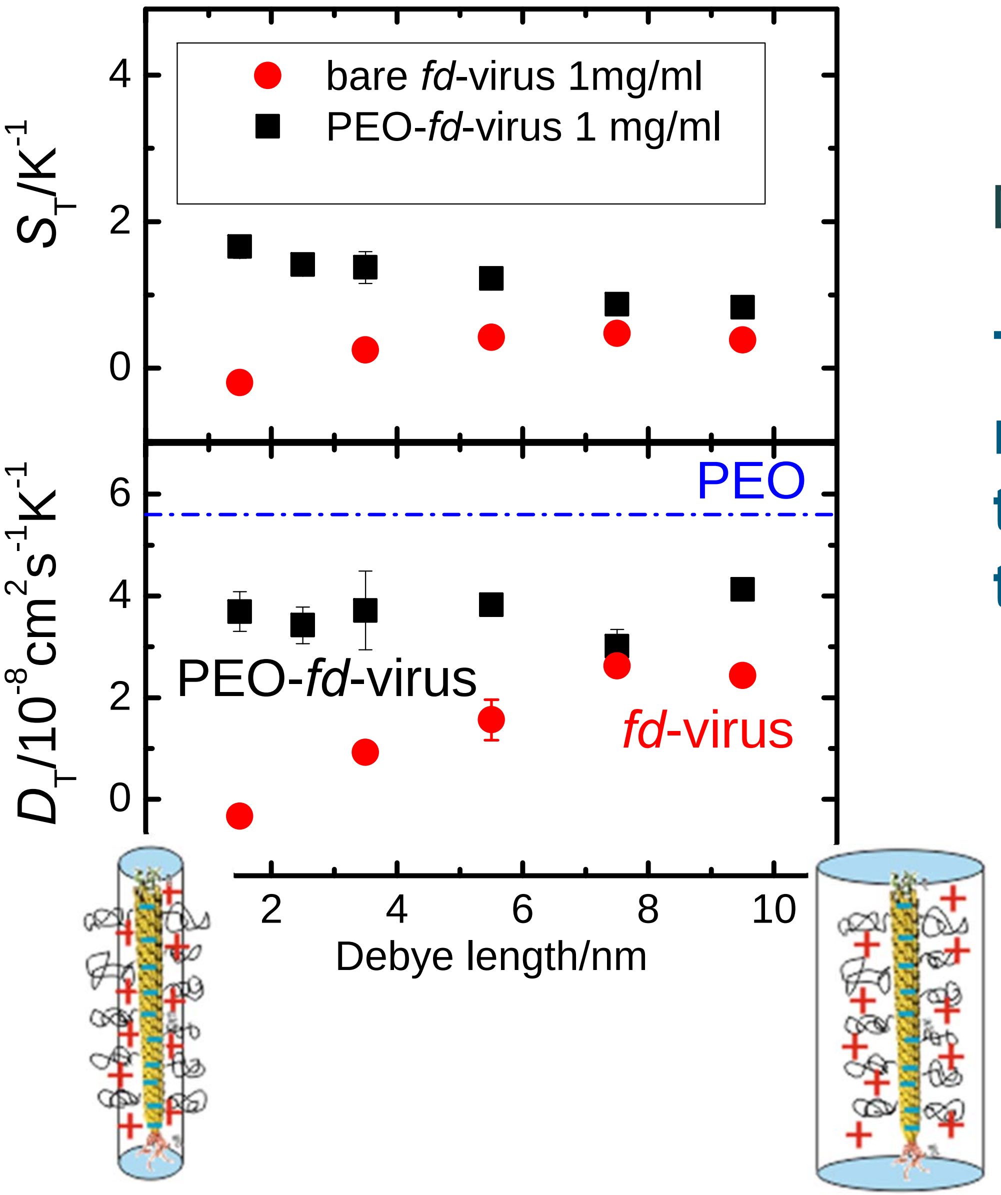




Onsager, L., Ann. N.Y. Acad. Sci, **51**(1949) 627-659.

Diffusion remains almost the same

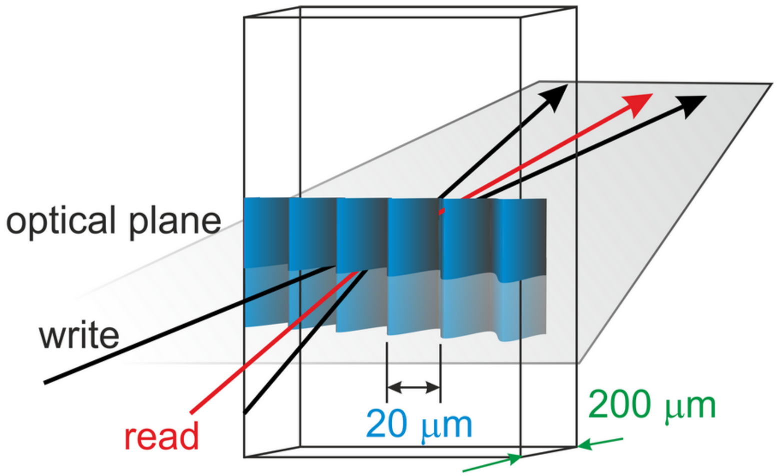
Charged colloidal rod with hairs

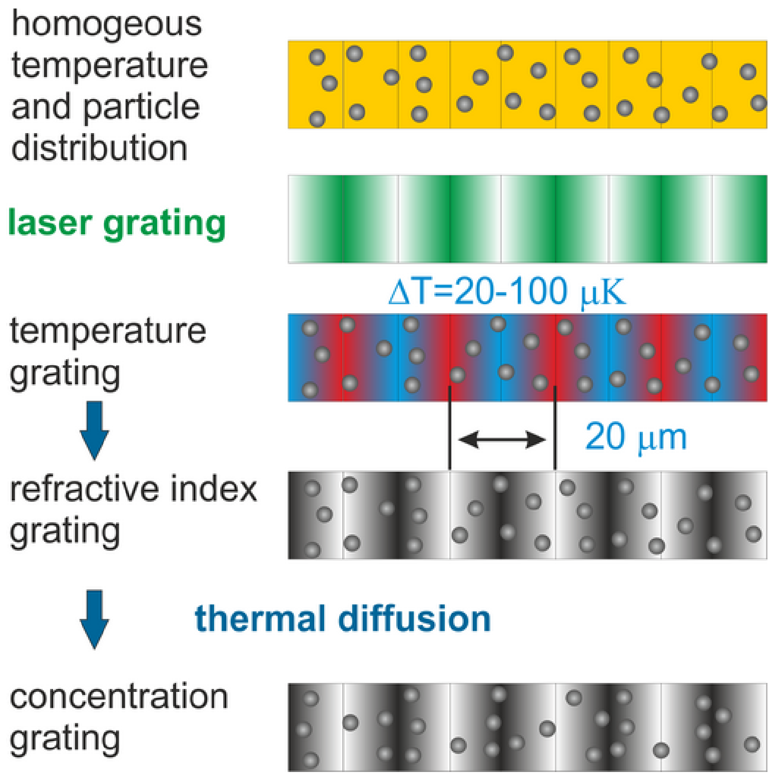


Thermal diffusion more sensitive to the grafting of the polymers

… (more) projects in progress, …..

Measured quantity:
Intensity of the diffracted beam





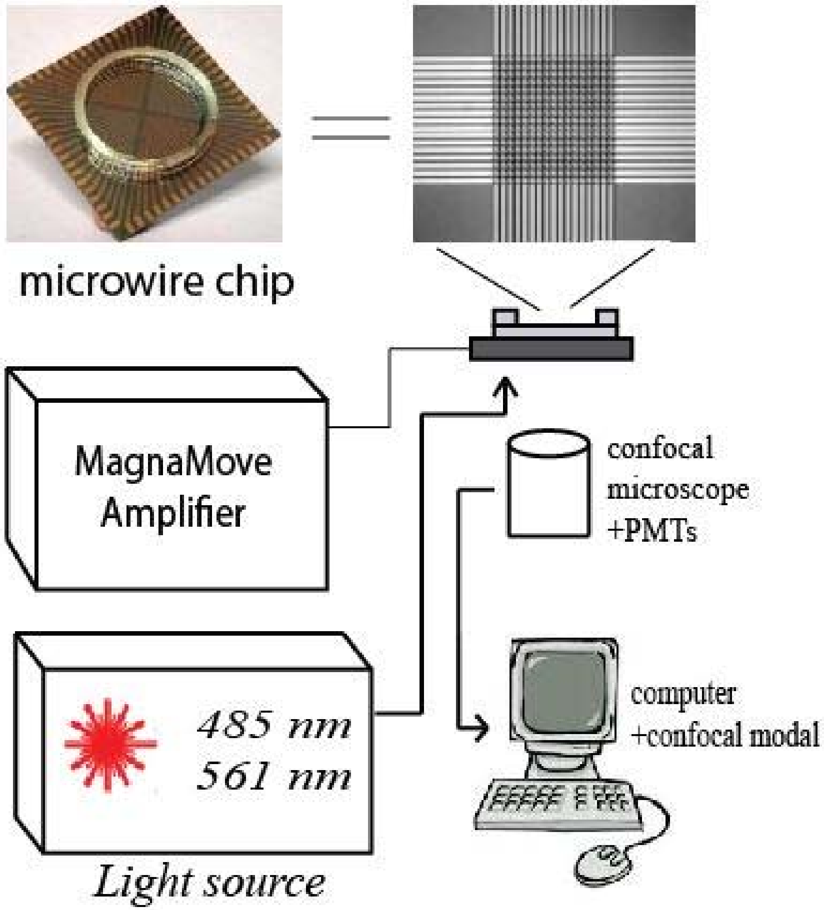
[S. Wiegand *et al.*, J. Phys. Chem. B, **111**(2007) 14169]

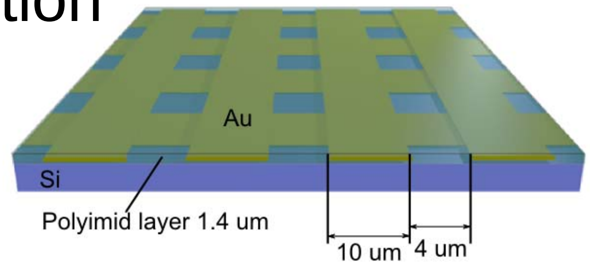
TDFRS

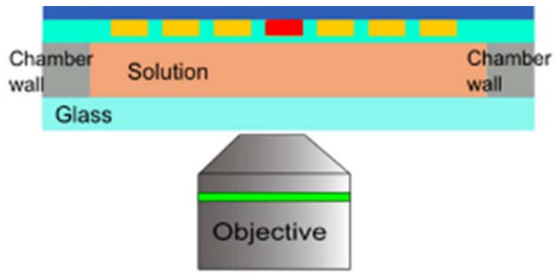
Thermal diffusion forced Rayleigh scattering

Thermophoretic microfluidic cells microwire chip

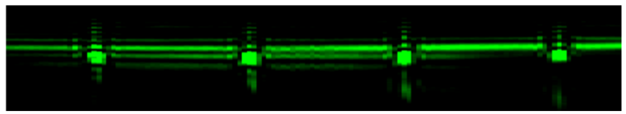
Objective: investigation of biomolecules in buffer solution

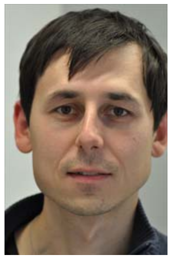






Confocal XZ slice (scattered light)

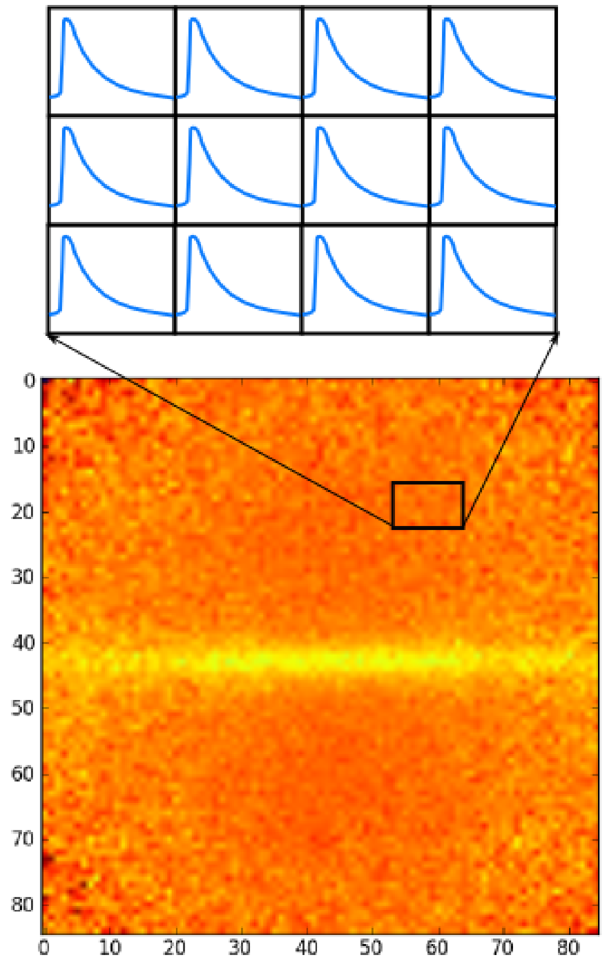




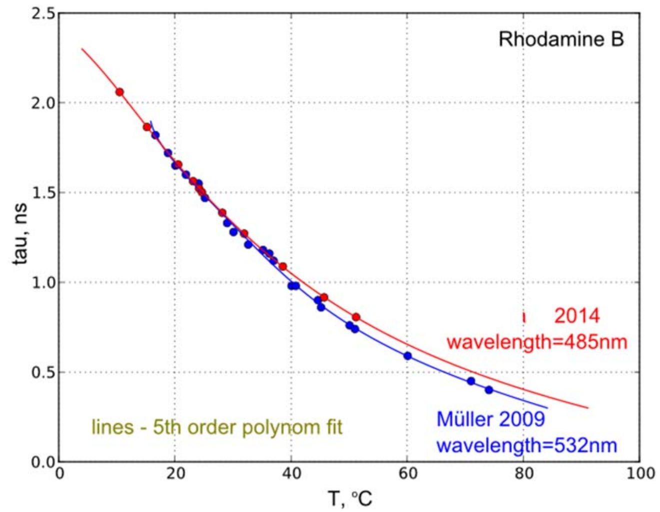
[Rinklin, P., D. Afanasenkau, SW, A. Offenhäusser, and B. Wolfrum, Lab on a Chip, 15 (2015) 237-243]

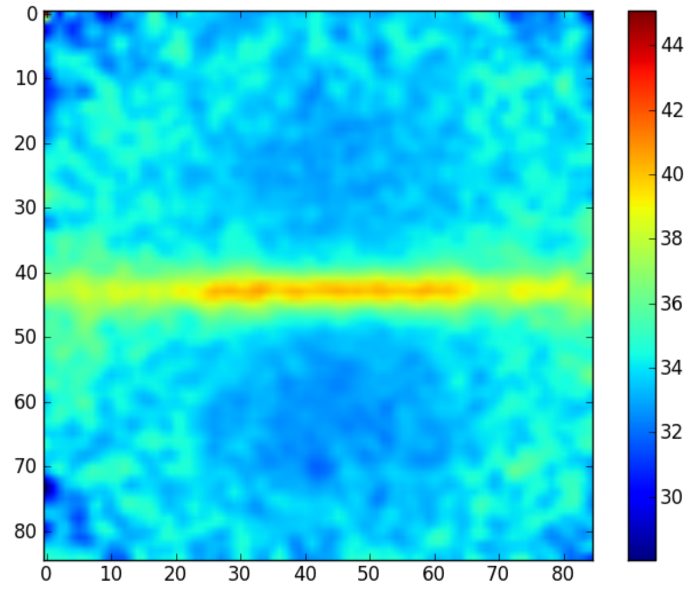
Thermophoretic microfluidic cells

FLIM –
Fluorescence Life-time Imaging Microscopy



T=f(τ)

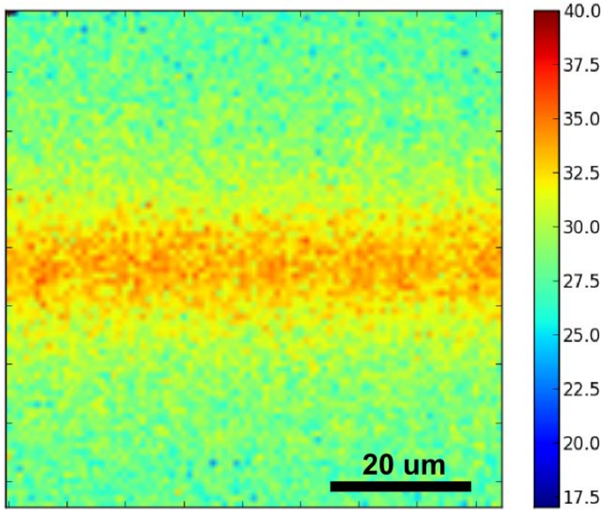




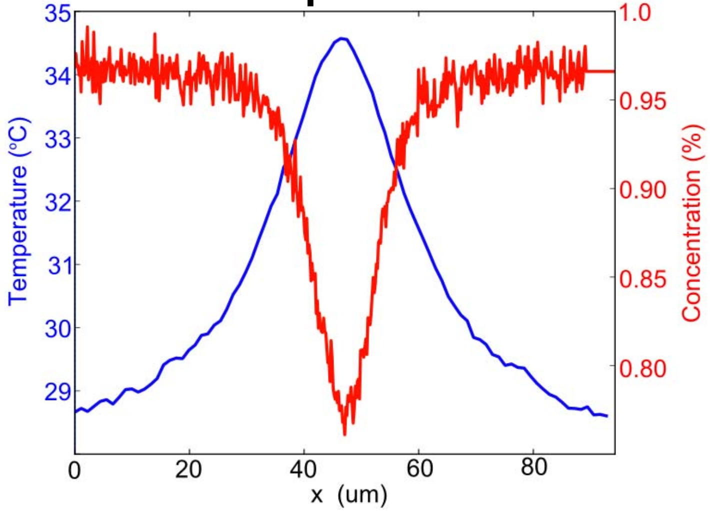
[Rinklin, P., D. Afanasenkau, SW, A. Offenhäusser, and B. Wolfrum, Lab on a Chip, 15 (2015) 237-243]

Thermophoretic microfluidic cells

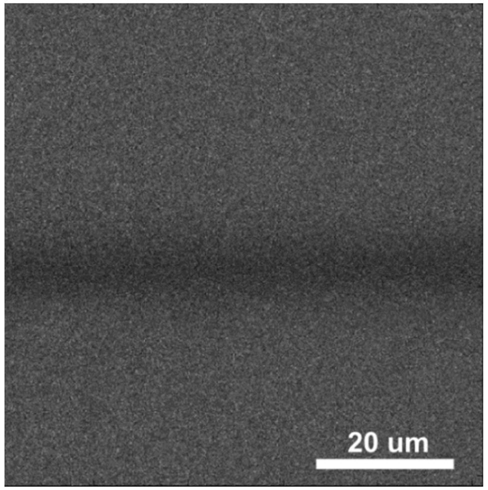
Temperature distribution



Temperature and concentration profiles

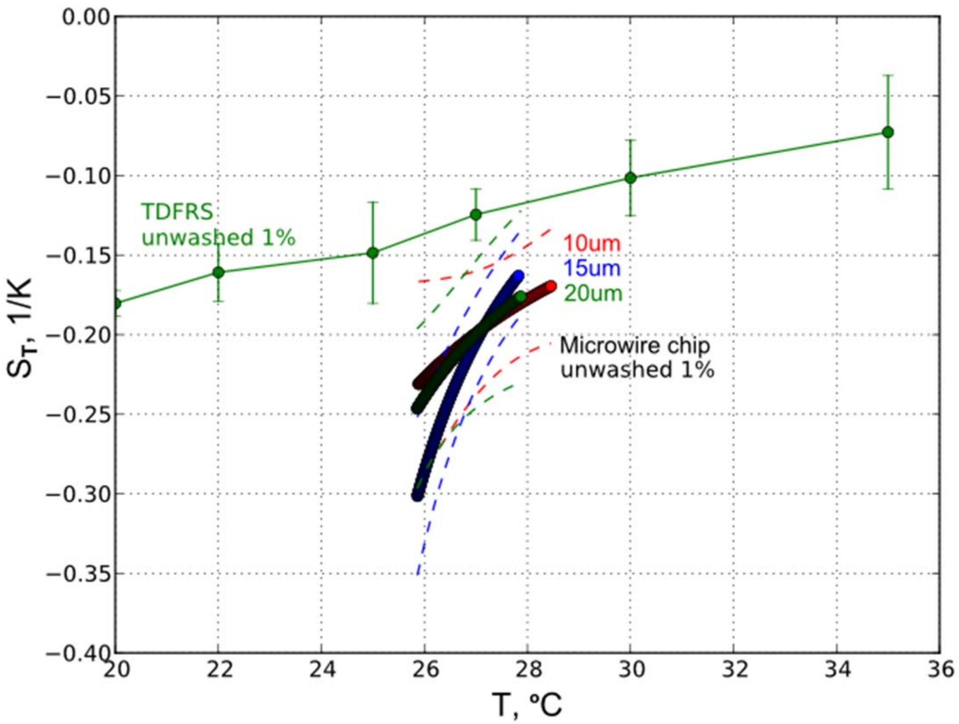


Intensity

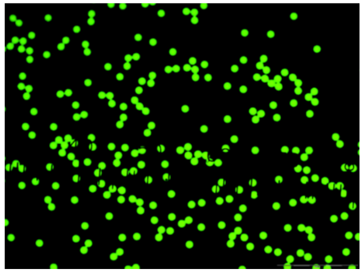


$$S_T = \frac{D}{D_T} = -\frac{1}{c}\frac{|\nabla c|}{|\nabla T|} = -\frac{1}{c}\frac{\left(\frac{dc}{dx}\right)}{\left(\frac{dT}{dx}\right)}$$

Preliminary thermophoresis results



System:
Fluoro-Max Dyed Green Aqueous Fluorescent Particles (G25) from Thermo Scientific



http://www.thermoscientific.com

The surface of particles is carboxylated. Suspension containes traces of detergent and preservative agent.

SW1

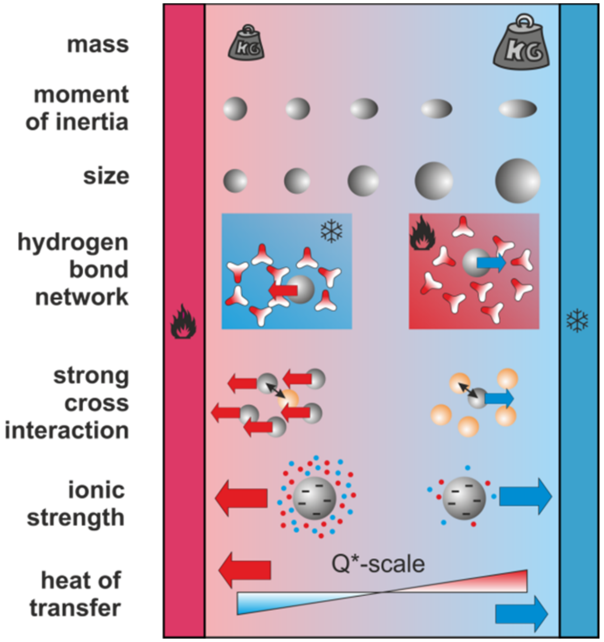
<u>Technical problems</u>

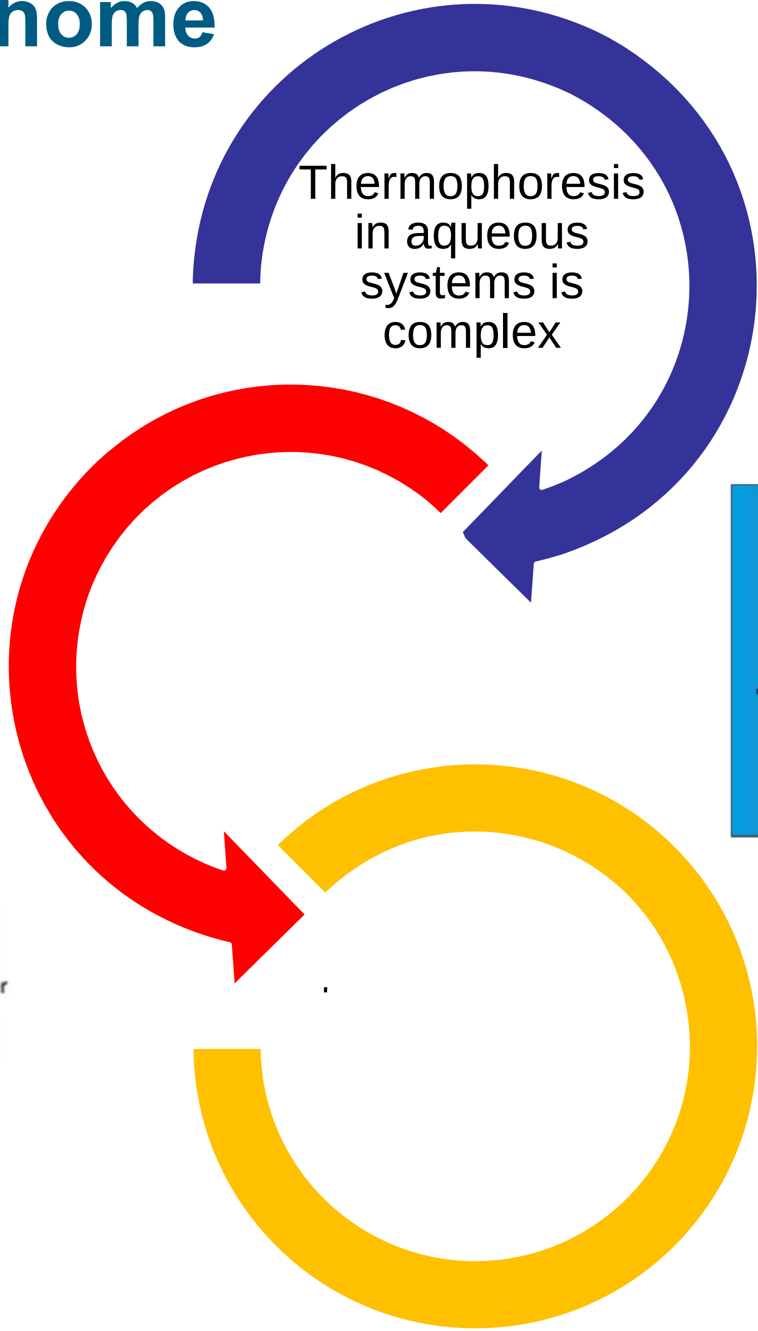
- Concentration changes
- Zero level
- Convection
- T measurements error (~20%)

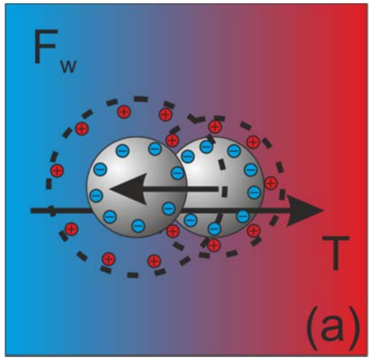
Folie 15

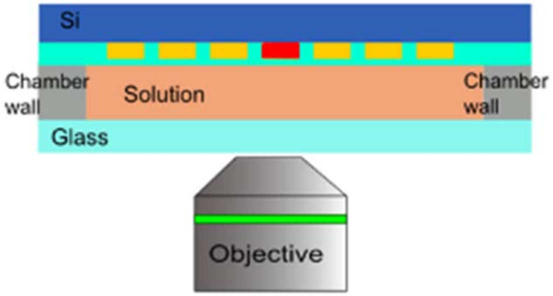
SW1 Needs work
Simone Wiegand; 18.05.2015

Message to take home









Thank you for your attention and thanks to…

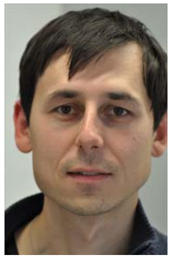
Jan Dhont – support & theory

Hui Ning – Ludox particles

Zilin Wang – fd virus

Johan Buitenhuis – synthesis

Hartmut Kriegs - technical support

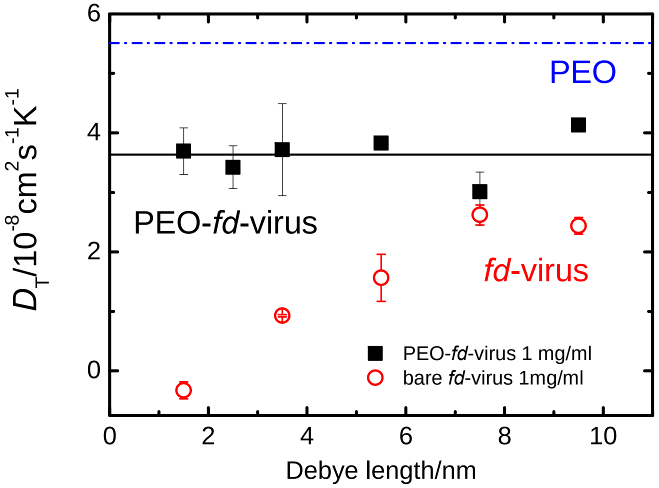


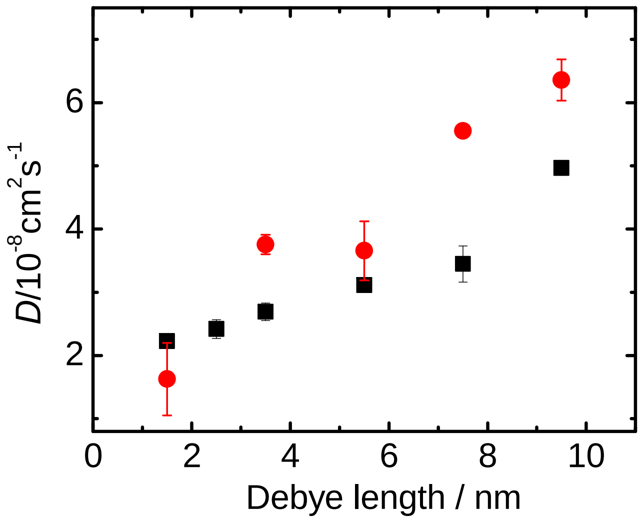
Dzmitry Afanasenkau - thermophoretic microfluidic cell

Bernhard Wolfrum – Magma Move chip

Deutsche Forschungsgemeinschaft

Charged colloidal rod with hairs





Without hdyrodynamic interactions:

$$D = \beta D_0 \frac{\partial \Pi}{\partial \rho}$$

$$\rho D_T = D_T^{theo} = \beta D_0 \frac{\partial \Pi}{\partial T}$$

.. Osmotic pressure

$$\Pi = \rho k_B T - \frac{2\pi}{3}\rho^2 \int_0^\infty dR\, R^3 \frac{dV^{DLVO}(R|T)}{dR} g(R|T)$$

$$D = D_0\left[1 + 2B_2\phi\right]$$

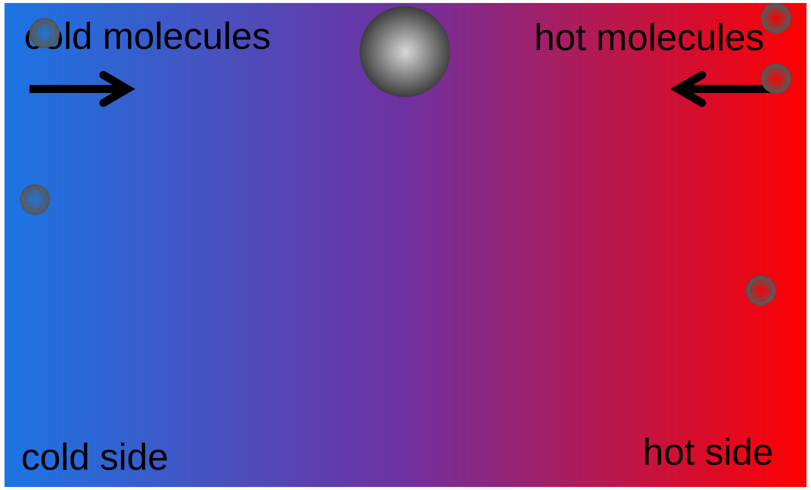
$$D_T = \frac{D_T^{theo}}{\rho} = \frac{D_0}{T}\left[1 + \frac{d(TB_2)}{dT}\phi\right]$$

- Both coefficients show an increasing trend
- Magnitude is comparable

[Dhont, J.K.G., J. Chem. Phys., **120**(2004) 1632-1641]

More theoretical work is required

Mass effect: animation

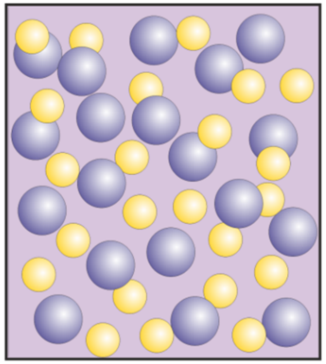


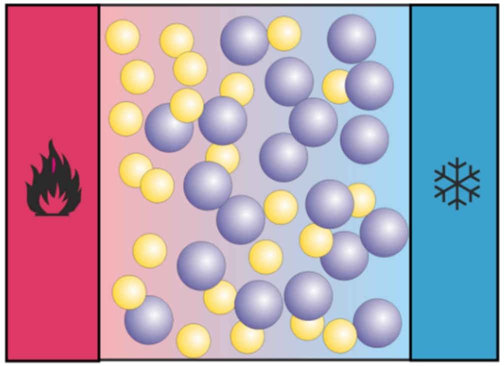
higher momentum transfer
from the warm side

Enrichment of the heavy particles on the cold side

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