Thermophoresis of charged colloidal spheres and rods

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
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
- Microscale thermophoresis

Separation of mixtures (TFFF) //Wikipedia

Microscale Thermophoresis: Technology and Applications //NanoTemper GMBH
To the warm or to the cold?

mass
moment of inertia
size
hydrogen bond network
strong cross interaction
ionic strength
heat of transfer

Q*-scale
Influence of charges

\[ \lambda_{\text{DH}} \propto \sqrt{\frac{\Delta T}{I}} \]

- \( T \) .. temperature
- \( I \) .. ionic strength

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

\[ \delta W^{\text{rev}} = -I \cdot F_{\text{tot}} \]

- internal force \( F_w \) due to change of the double layer structure on displacement of the sphere
- electric force \( F_{\text{el}} \) due to non-spherical symmetry of the double layer structure
- solvent-friction force \( F_{\text{sol}} \) due to solvent flow arising from the asymmetry of the double-layer structure

Ionic strength effect

charged silica colloidal particles (Ludox)

valid for thin and thick double layers:

\( e \) ... elementary charge
\( l_B \) ... Bjerrum length
\( \sigma \) ... surface charge density
\( \kappa^{-1} = \lambda_{DH} \) ... Debye length
\( \varepsilon \) ... dielectric constant
\( a \) ... radius of the colloid

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


[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 = $1.64 \times 10^7$ g/mol

Effective diameter


<table>
<thead>
<tr>
<th>d eff / nm</th>
<th>ionic strength / mM</th>
</tr>
</thead>
<tbody>
<tr>
<td>70</td>
<td>1</td>
</tr>
<tr>
<td>60</td>
<td>10</td>
</tr>
<tr>
<td>50</td>
<td>100</td>
</tr>
<tr>
<td>40</td>
<td>1000</td>
</tr>
</tbody>
</table>

- bare virus diameter, $d$
- $d + 2 \kappa^{-1}$
Single particle effects: charged colloidal rod

System: wt fd-virus

Theoretical description

<table>
<thead>
<tr>
<th>Model</th>
<th>$\sigma$/enm$^{-2}$</th>
<th>Offset</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dhont</td>
<td>0.050±0.003</td>
<td>-1.39</td>
</tr>
<tr>
<td>Capacitor</td>
<td>0.016±0.002</td>
<td>-0.74</td>
</tr>
<tr>
<td>Calculated bare charge</td>
<td>0.066</td>
<td></td>
</tr>
</tbody>
</table>

[Zilin Wang
Folie 8]
Charged colloidal rod with hairs

Ionic strength $\geq 20\text{mM}$

- MPEG = 5000 g/mol

Ionic strength $< 20\text{mM}$

- Electric double layer

Steric vs. electric interaction

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

\[ B_2^{\text{rod}} = \frac{1}{4} \pi L^2 d_{\text{eff}} \]

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

TDFRS
Thermal diffusion forced Rayleigh scattering

Thermophoretic microfluidic cells
microwire chip

Objective: investigation of biomolecules in buffer solution

Thermophoretic microfluidic cells

FLIM – Fluorescence Life-time Imaging Microscopy

$T = f(\tau)$

Temperature distribution

Temperature and concentration profiles

Intensity

\[ S_T = \frac{D}{D_T} = - \frac{1}{c} \left| \nabla c \right| = - \frac{1}{c} \frac{dc}{dx} \]
Preliminary thermophoresis results

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

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

http://www.thermoscientific.com

The surface of particles is carboxylated. Suspension contains traces of detergent and preservative agent.
SW1

Needs work
Simone Wiegand; 18.05.2015
Thermophoresis in aqueous systems is complex

Message to take home

- mass
- moment of inertia
- size
- hydrogen bond network
- strong cross interaction
- ionic strength
- heat of transfer

Q*-scale

F_W

T

(a)

Chamber wall
Solution
Chamber wall
Glass
Objective
Thank you for your attention and thanks to...

Jan Dhont – support & theory

Hui Ning – Ludox particles

Zilin Wang – fd virus

Johan Buitenhuys – synthesis

Hartmut Kriegs - technical support

Dzmitry Afanasenkau - thermophoretic microfluidic cell

Bernhard Wolfrum – Magma Move chip

Deutsche Forschungsgemeinschaft
Charged colloidal rod with hairs

Without hydrodynamic interactions:

\[ D = \beta D_0 \frac{\partial \Pi}{\partial \rho} \]

\[ \rho D_T = D_T^{\text{theo}} = \beta D_0 \frac{\partial \Pi}{\partial T} \]

.. Osmotic pressure

\[ \Pi = \rho k_B T - \frac{2\pi}{3} \rho^2 \int_0^\infty dR R^3 \frac{dV_{\text{DLVO}}(R|T)}{dR} g(R|T) \]

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

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

- Both coefficients show an increasing trend
- Magnitude is comparable

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

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\( S_T \) – Soret coefficient