Thermophoresis of charged colloidal spheres and rods

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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

  ![Diagram of Thermal field flow fractionation](./ThermalFieldFlowFractionation.png)

  Separation of mixtures (TFFF) // Wikipedia

- Microscale thermophoresis

  ![Diagram of Microscale Thermophoresis](./MicroscaleThermophoresis.png)

  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

Influence of charges

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

\begin{align*}
T & \quad \text{temperature} \\
I & \quad \text{ionic strength}
\end{align*}

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

\[ \delta \ W_{ev} \ = \ - \ \frac{F}{t} \]

internal force \( F_w \) due to change of the double layer structure on displacement of the sphere

electric force \( F_{el} \) due to non-spherical symmetry of the double layer structure.

solvent-friction force \( F_{sol} \) 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:

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

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

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

Effective diameter

- bare virus diameter, $d$
- $d + 2 \kappa^{-1}$

Measurement range

Single particle effects: charged colloidal rod

System: wt fd-virus

Theoretical description

Thin double layer

Thick double layer

Model | $\sigma$/enm$^{-2}$ | Offset
--- | --- | ---
Dhont | $0.050 \pm 0.003$ | -1.39
Capacitor | $0.016 \pm 0.002$ | -0.74
Calculated bare charge | 0.066

Charged colloidal rod with hairs

Ionic strength $>20$ mM

Ionic strength $<20$ mM

Steric vs. electric interaction

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

$B_2^{rod} = \frac{1}{4} \pi L^2 d_{eff}$

Debye length / nm

Ionic strength / mM

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

$T = f(\tau)$
Thermophoretic microfluidic cells

Temperature distribution

Temperature and concentration profiles

Intensity

\[ S_T = \frac{D}{D_T} = - \frac{1}{c} \frac{\nabla c}{\nabla T} = - \frac{1}{c} \frac{dc}{dx} \]
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.
Message to take home

Thermophoresis in aqueous systems is complex
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 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
\[ \Pi = \rho k_B T - \frac{2\pi}{3} \rho^2 \int_0^\infty dR R^3 \frac{dV^{DLVO}(R|T)}{dT} g(R|T) \]

\[ D = D_0 \left[ 1 + 2B_2 \phi \right] \]
\[ D_T = \frac{D_T^{\text{theo}}}{\rho} = \frac{D_0}{T} \left[ 1 + \frac{d(TB_2)}{dT} \phi \right] \]

- 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
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