Thermodiffusion of charged nanoparticles dispersed in Ionic Liquids and in mixtures of molecular solvents

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Conference on Modern Concepts and New Materials for Thermoelectricity

International Centre for Theoretical Physics - Trieste - Italy - March 11-15 2019

Outlook

- Background on Magnetic Fluids / Ferrofluids (FF)
- Synthesis methods for dispersing charged NPs
- SAS determination of interparticle interaction
- Forced Rayleigh Scattering (FRS) technics
- Thermophoretic properties of FF in Molecular Solvents

  FRS at T=295 K

    Hydroxyl-coated NPs in water and DMSO

    Citrate-coated NPs in water

  FRS at T>295K

    Hydroxyl-coated NPs in water and DMSO

    Citrate-coated NPs in water
- Thermophoretic properties of FF in Ionic Liquids at T>295 K

    Citrate-coated NPs in EAN

    TFSI-SMIM-coated NPs in EMIM-TFSI
- Summary – Perspectives

Target : **Study of thermophoretic effects in ionic colloidal dispersions**

Systems with big ionic species, and a lot of small ones

$\vec{\nabla} T$ induces $\vec{E}_e = S_e \vec{\nabla} T$ thanks to Seebeck effect

and also $\vec{\nabla} n = - n S_T \vec{\nabla} T$ thanks to Soret effect

n : number of NPs per volume unit

Thermophoretic and thermoelectric properties are interconnected

They both depend on $\hat{S}_i$ of all the ionic species (i) in solution

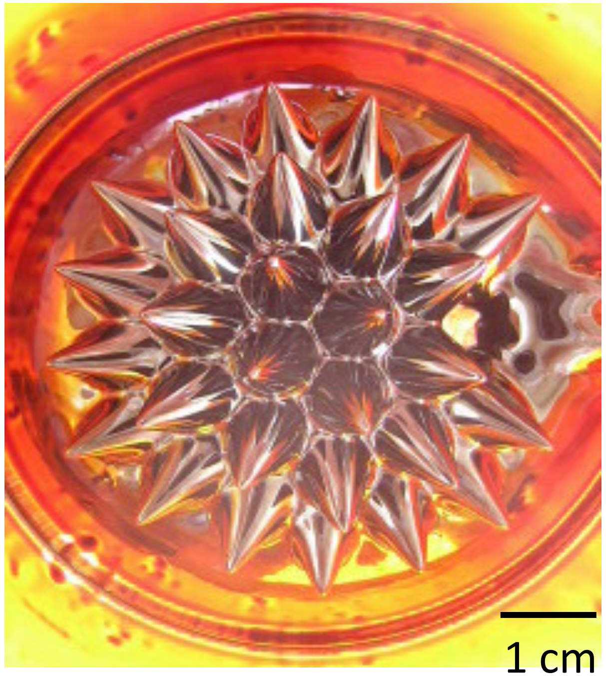
$\hat{S}_i$: Eastman entropy of transfer of species (i) in the medium
characteristic of their interaction with the external medium
(Heat transport/T)

Thus necessary :

- to limit the number of different species, identify them and their n_i
- to choose media suitable for thermoelectric voltage measurements.

Background on
Magnetic Fluids / Ferrofluids (FF)

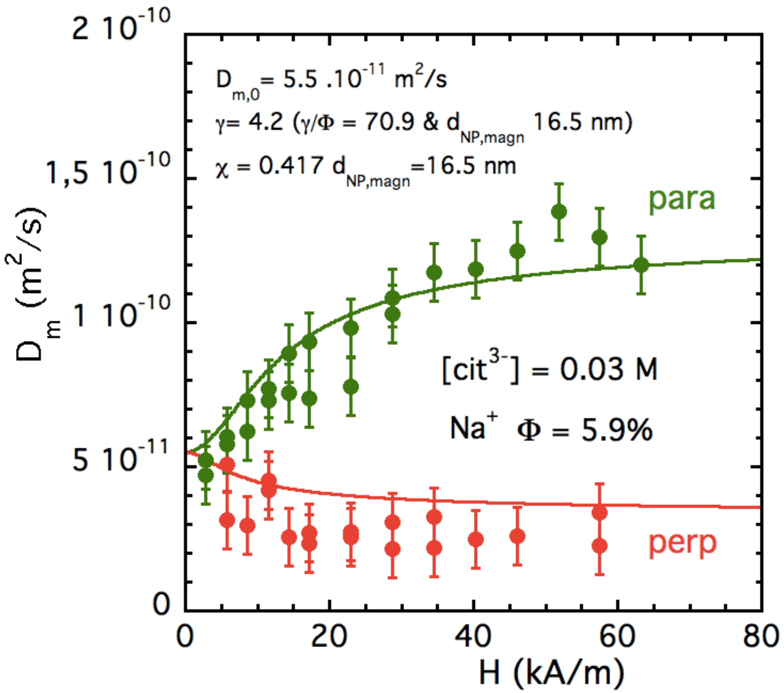
Colloidal suspensions of magnetic nanoparticles

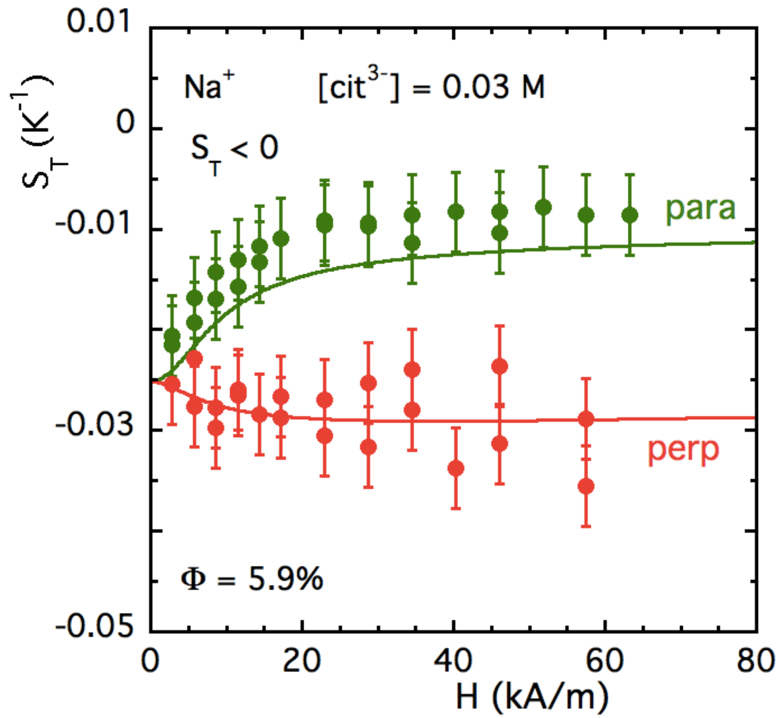


A material which is fluid and magnetic with spectacular instabilities and numerous applications

Automotive : Shock-absorbers (Magneride®)
Electronic devices : liquid seals for Hard Disks, loudspeakers
Optics : obturators, modulators
Heat transfer : coolant (Smart-fluids®)
Medecine : MRI contrast agent, antibody titration, cell labelling, magneto-thermocytolysis, drug delivery

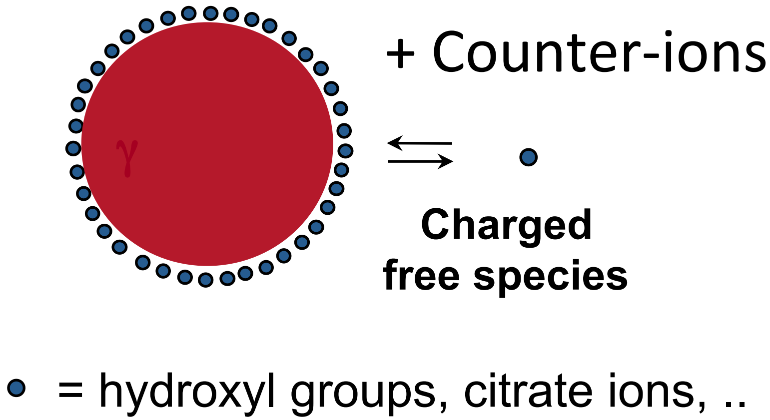
Under-field anisotropy of thermodiffusive and thermophoretic properties

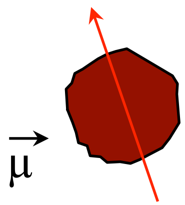




M. Kouyaté *et al Phys. Chem. Chem. Phys.* **21** (2019) 1895-1903

Ionic Magnetic Fluid in water





- d ~ 10 nm
- $\mu \sim 10^4 \mu_B$

ferrite nanoparticles

γ-Fe_2O_3, chemically synthesized by coprecipitation in alkaline media*

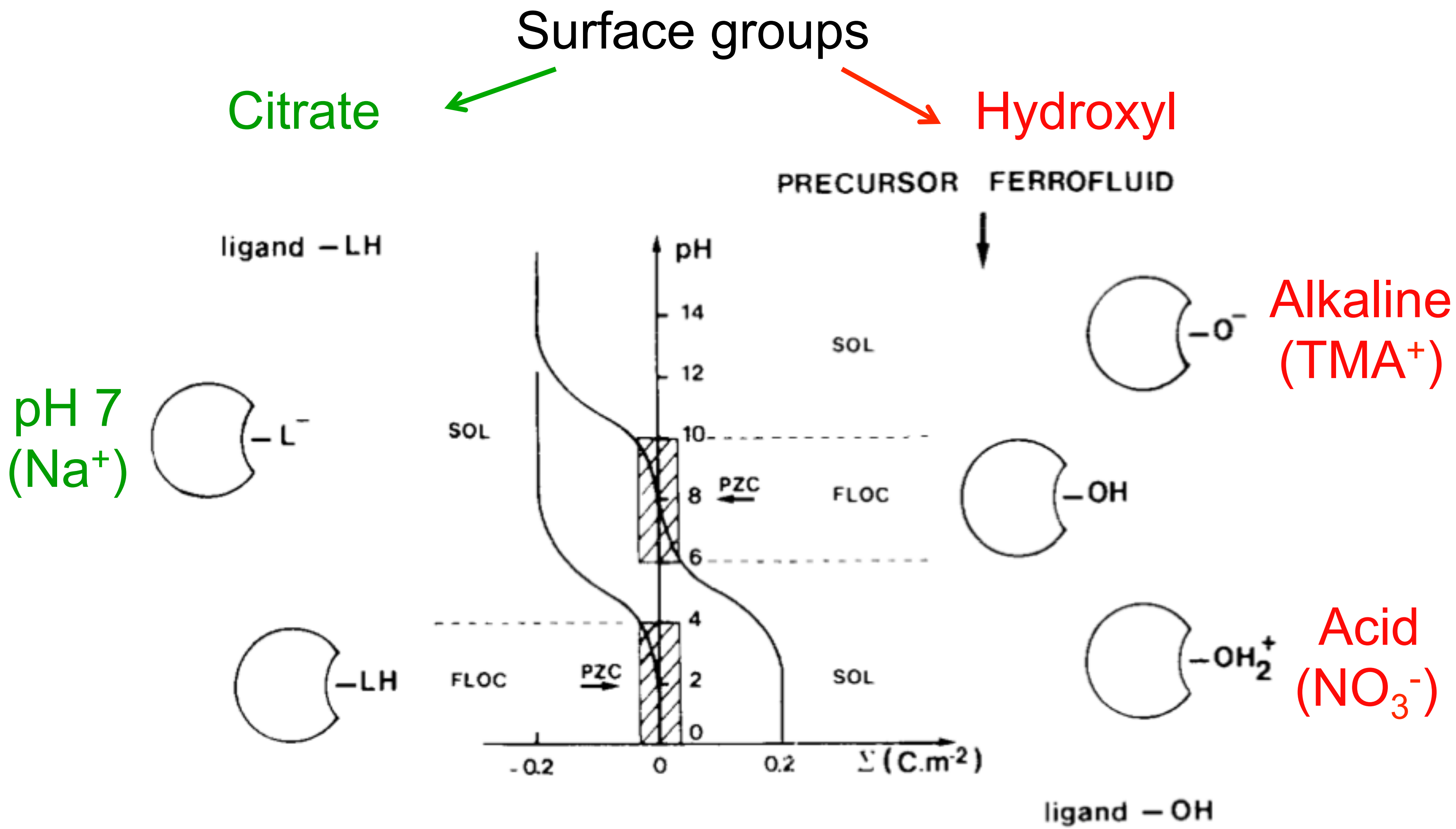
Ionic stabilization in water:

Electrostatic repulsion versus { van der Waals attraction and magnetic dipolar interaction

R. Massart I.E.E.E. Trans.Mag. Magn. ***17*** *(1981) 1247*
F. A. Tourinho et al J. Mat. Sci. ***25*** *(1990) 3249*

Aqueous dispersions of ferrite nanoparticles

Evolution of the structural charge with pH and coating



(+ counter-ions)

Synthesis method
for dispersing charged NPs
in polar solvents
(Molecular Solvents or Ionic Liquids)

What is needed in this study ?

(i) Prepare and stabilize FF in a reproducible manner, precisely controlling the nature and the quantity of ions in the solution

(ii) Prepare them in different media

(DMSO, various Ionic Liquids, ..),

(iii) Test different types of contreions

(… specific effects of counterions)

Ex.: in water

- Hofmeister series (protein solubility)
- Jones-Dole coefficients of ionic solution viscosity (ion-solvent interaction, chaotropic & kosmotropic nature of the ions),
- Eastman entropy of tranfer of the ions (*)

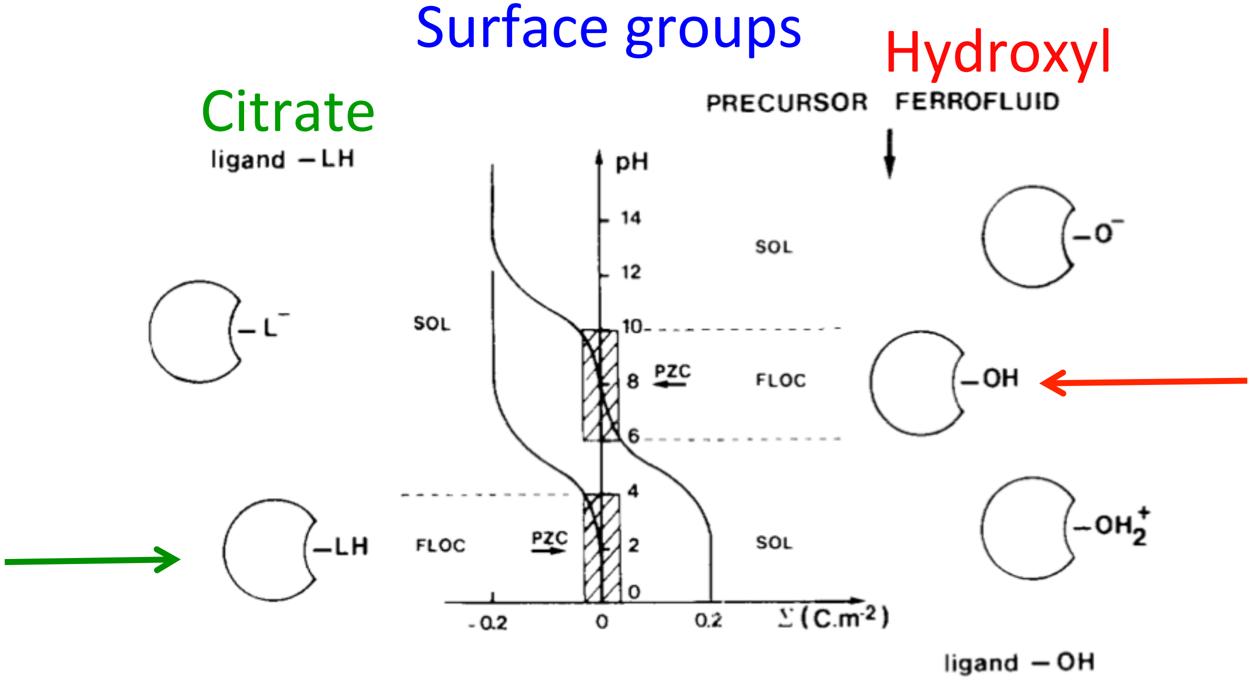
(ion-solvent interaction)

(*) J. Agar, C. Mou, J. Lin *J.Phys. Chem.* **93** (1989) 2079
N. Takeyama, K. Nakashima *J. Solution Chem.* **17** (1988) 305

Efficient method for exchanging solvent & counter-ions in polar molecular solvents (*)

- Starting from flocculated dispersion at PZC,
- Repeated washing out of free ions and removable water,
- Re-charging of the NPs in the chosen medium with the chosen counter-ions with a controlled and reproducible method

Surface groups



(*) C. L. Filomeno *et al J. Phys. Chem. C* **121** (2017) 5539-5550

It allows to change in a controlled way :

- the solvent (water, DMSO, EAN, other ILs)
- the counter-ions (broad spectrum)
- their global quantity

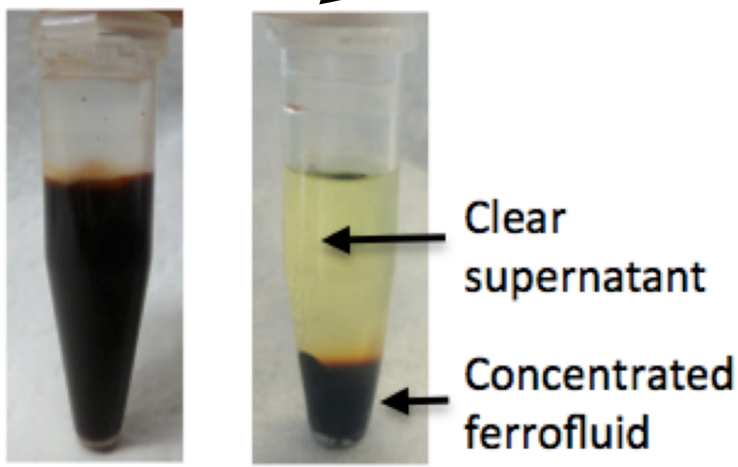
- Concentrated FF obtained by ultracentrifugation

- Conductivity measurements of the supernatant : $[\text{electrolyte}]_{\text{free}}$

- Comparison to the introduced quantity : structural NP charge

- Nano-ZS electrophoretic measurements + QELS in dilute sol : dynamic effective charge ξ_0 (in molecular solvents)

- SAXS – RFS



C. L. Filomeno et al J. Phys. Chem. C ***121*** *(2017) 5539-5550*

Coating	Counter-ions	Solvent	Φ-range	$\langle d_{NP} \rangle$ (nm)
hydroxide	ClO_4^-	Water	0.5-2.5% up to 80°C	9
hydroxide	ClO_4^-	DMSO and mixtures	0.5-2.5% up to 80°C	9
hydroxide	ClO_4^-	DMSO	0.5-3.5% Room T	6.7
citrate	$TBuA^+$ TMA^+ Na^+ Li^+	Water	0.5-5% Room T 1% up to 80°C	8.5
citrate	Na^+ Rb^+ Li^+	EAN	0.5-4% up to 105°C	7.4
hydroxide	$TFSI^-$ - $SMIM^{+/-}$	$EMIM^+$-TFS^-	1% up to 190°C	9.2

Small Angle Scattering* determination of interparticle interaction

(*) of neutrons SANS or of x-rays SAXS

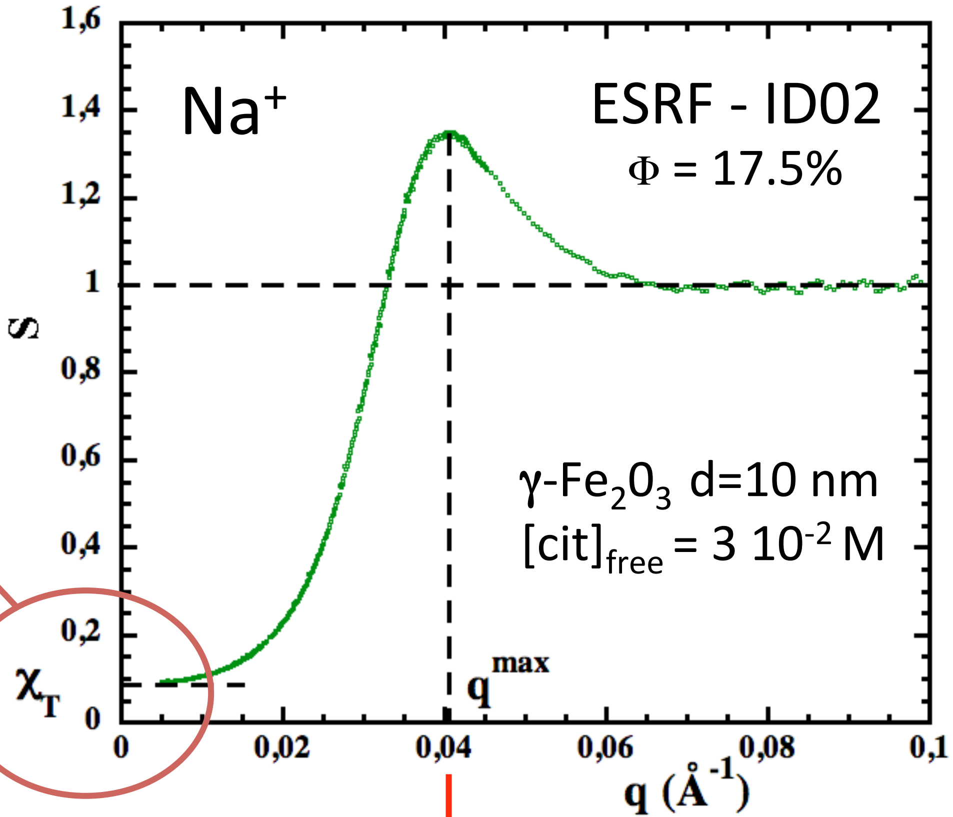
Typical *structure factor* of an assembly of nanoparticles with repulsive interparticle interaction, as obtained by *SAXS*

At low q's

$$S(q \to 0) = \chi = \frac{kT}{\frac{\partial \Pi v_{NP}}{\partial \Phi}}$$

Compressibility

Thermodynamic quantity



$$q^{\max} = \frac{2\pi}{d_0}$$

d_0 = most probable interparticle distance

*E. Wandersman et al Soft Matter **9** (2013) 11480*

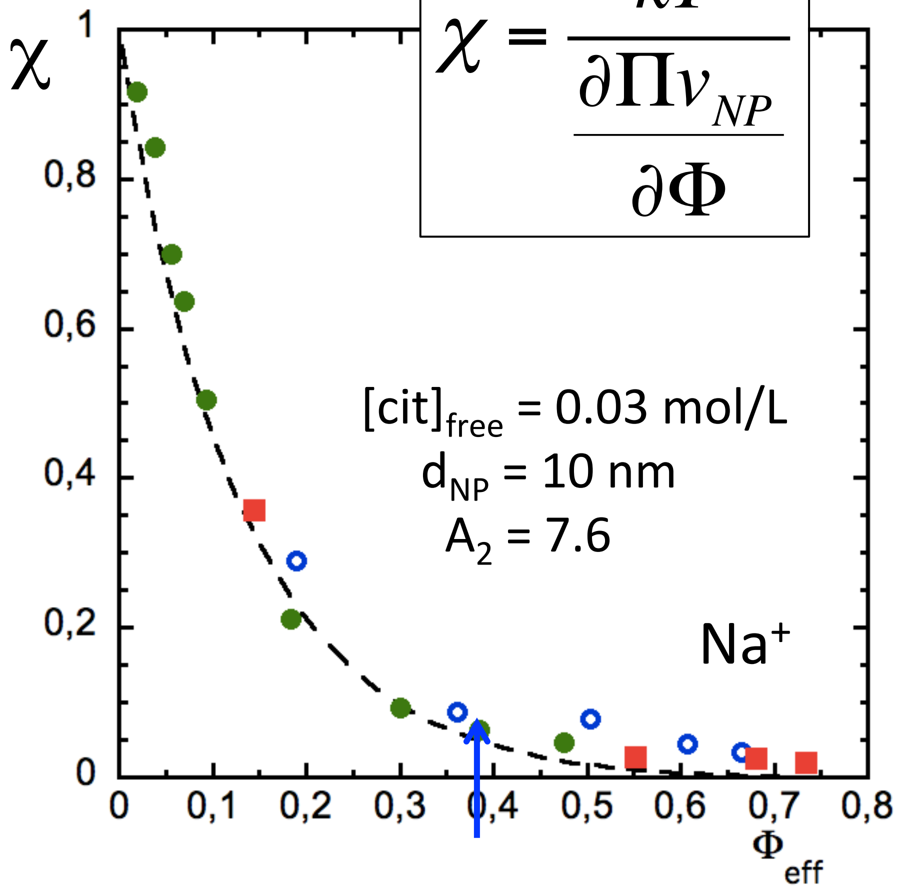
Small Angle X-ray or Neutron scattering

NP's compressibility c
given by the
Carnahan-Starling model of
effective Hard Spheres
(far from the glassy transition)

$$\chi = \frac{(1-\Phi_{eff})^4}{1+4\Phi_{eff}+4\Phi_{eff}^2-4\Phi_{eff}^3+\Phi_{eff}^4}$$

$$\frac{\Phi_{eff}}{\Phi} = \frac{A_2}{\underline{A_2^{HS}}} = \left(1+\frac{2\kappa^{-1}}{d_{NP}}\right)^3$$

Two bodies
interaction
coefficient



$$\chi = \frac{kT}{\dfrac{\partial \Pi v_{NP}}{\partial \Phi}}$$

Limit of validity
of Carnahan-Starling model

E. Wandersman et al *Soft Matter* **9** (2013)11480

Small Angle X-ray or Neutron scattering

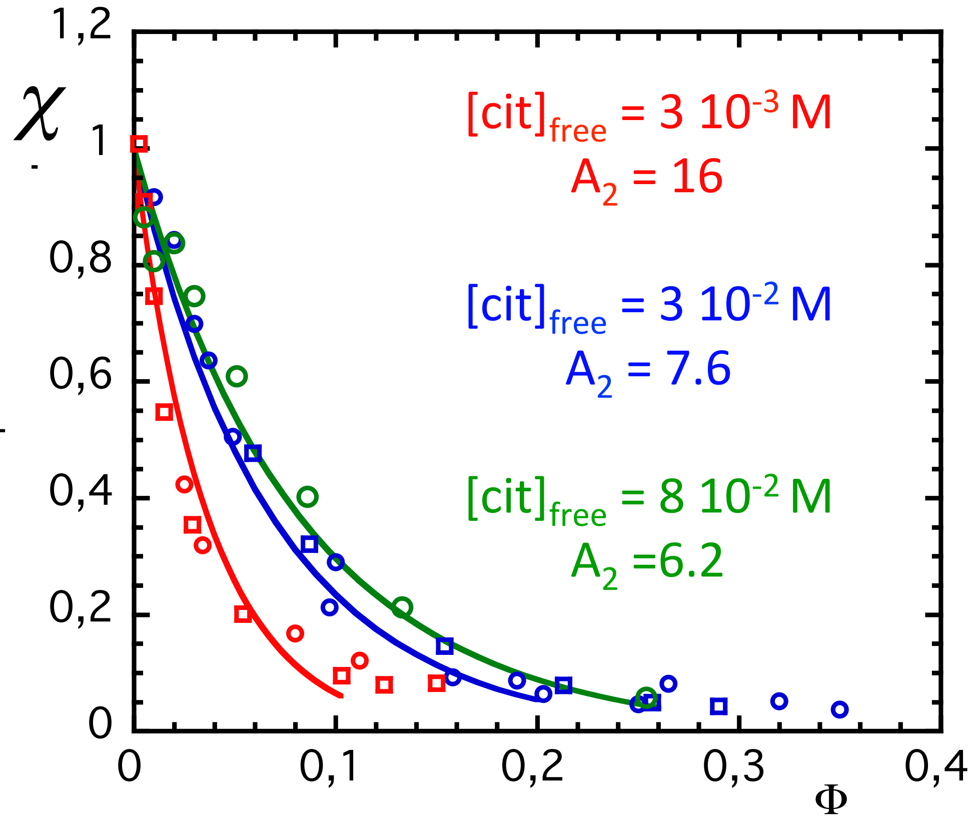
FF in water : citrated NPs with Na^+ counterions at ≠ [cit]

Carnahan-Starling model of effective Hard Spheres far from the glassy transition

$$\chi = \frac{(1-\Phi_{eff})^4}{1+4\Phi_{eff}+4\Phi_{eff}^2-4\Phi_{eff}^3+\Phi_{eff}^4}$$

$$\frac{\Phi_{eff}}{\Phi} = \frac{A_2}{A_2^{HS}} = \left(1+\frac{2\kappa^{-1}}{d_{NP}}\right)^3$$

Two bodies interaction coefficient



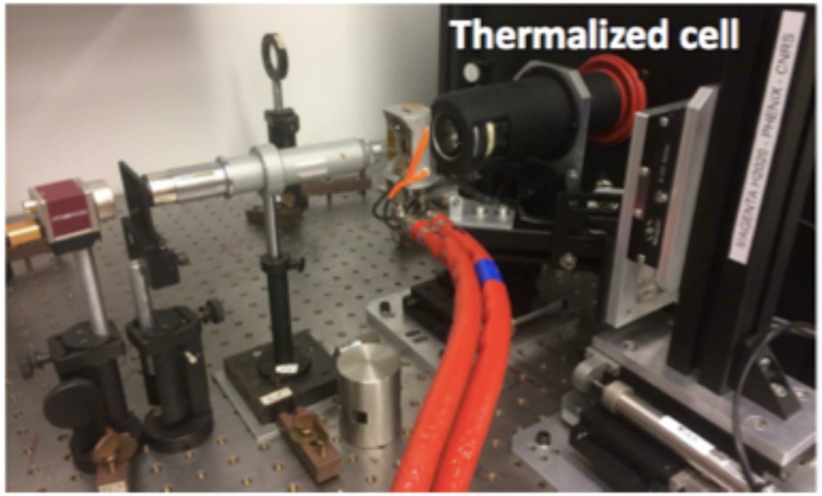
SANS, ILL, Grenoble, France

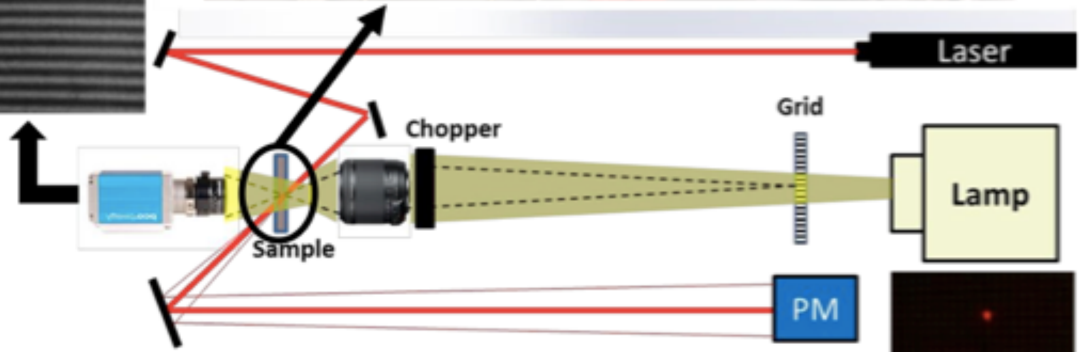
R. Cabreira Gomes *et al Phys. Chem. Chem. Phys*. **20** (2018) 16402-16413

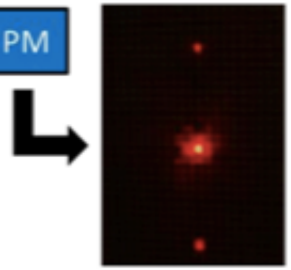
Forced Rayleigh Scattering (FRS)

RFS device

Spatial modulations of temperature
⇨ Spatial modulations of concentration (Soret effect)



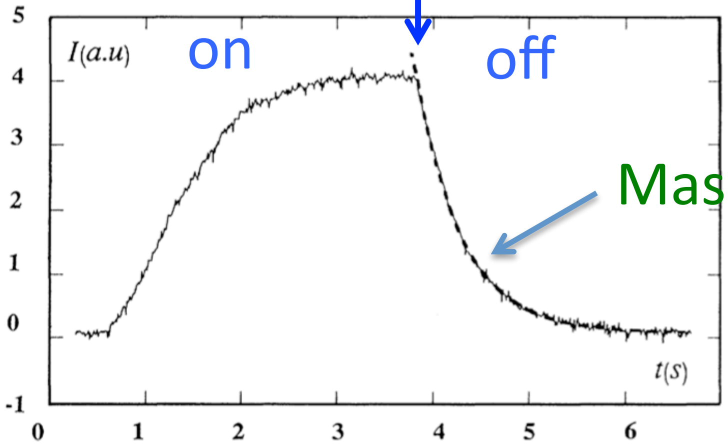




Heating beam

on

off



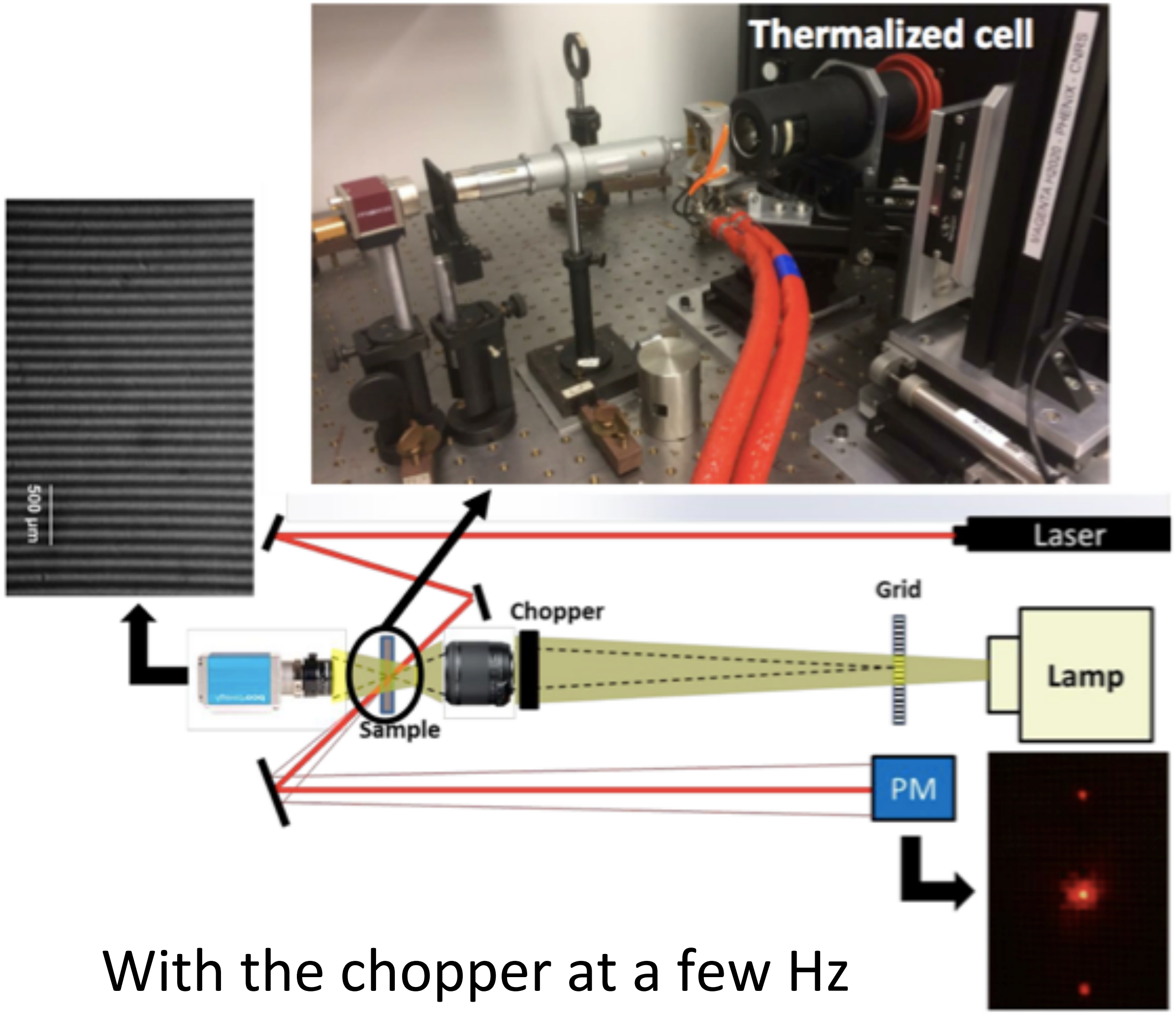
Mass diffusion coefficient D_m

Without chopper

RFS device

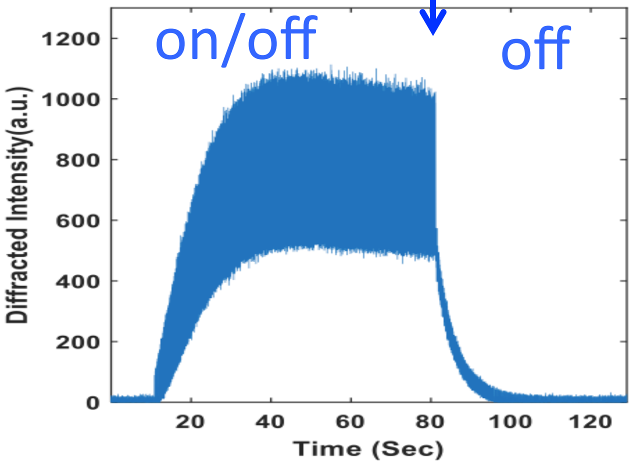
Spatial modulations of temperature

⇨ Spatial modulations of concentration (Soret effect)



Heating beam on/off

off



With the chopper at a few Hz

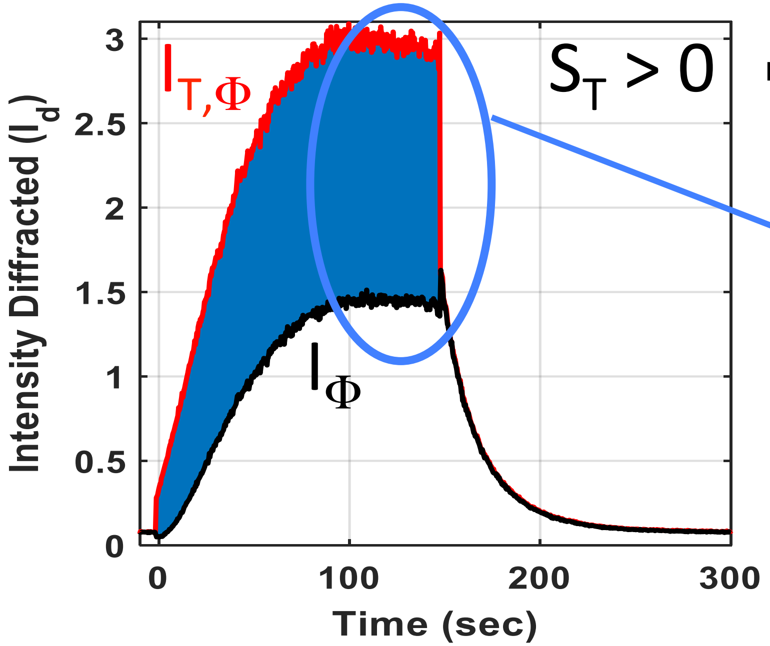
+ Temporal modulations of temperature

In stationary conditions : $\vec{\nabla}\Phi = -\Phi S_T \vec{\nabla} T$

Soret coefficient

$S_T < 0$: NPs migrate towards hot regions

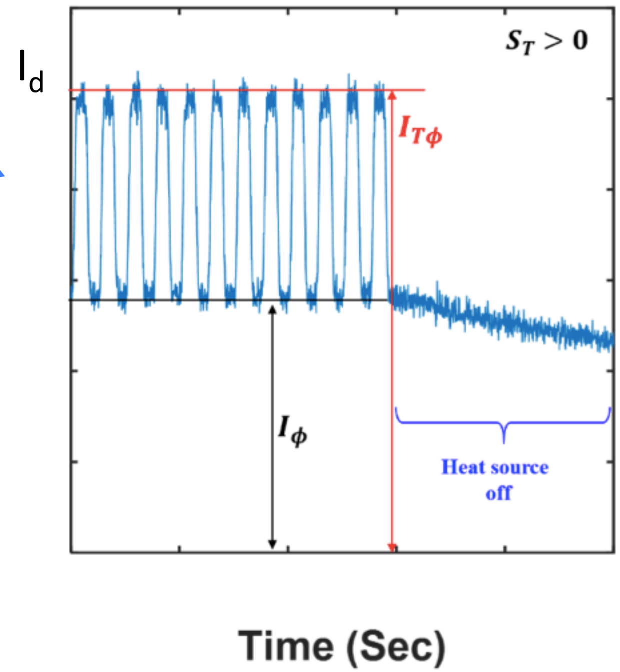
$S_T > 0$: NPs migrate towards cold regions



⇨ $I_\Phi < I_{T,\Phi}$

$I_d \ \alpha \ \Delta n^2$

$\Delta n_{T,\Phi} = \Delta n_\Phi + \Delta n_T$



Thermal grating : $\Delta n_T \ \alpha \ \sqrt{I_{T,\Phi}} - \sqrt{I_\Phi}$

Concentration grating : $\Delta n_\Phi \ \alpha \ \sqrt{I_\Phi}$

In stationary conditions : $\vec{\nabla}\Phi = -\Phi S_T \vec{\nabla} T$

Soret coefficient

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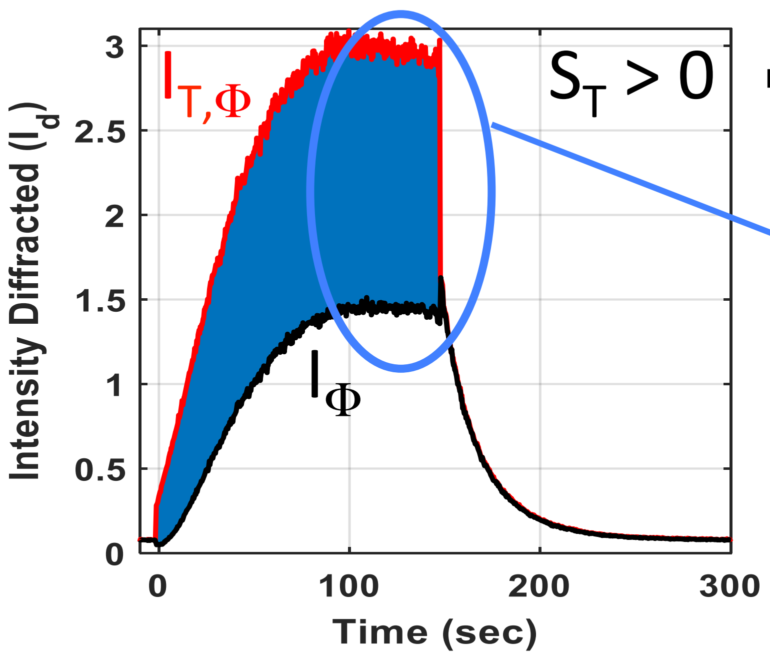

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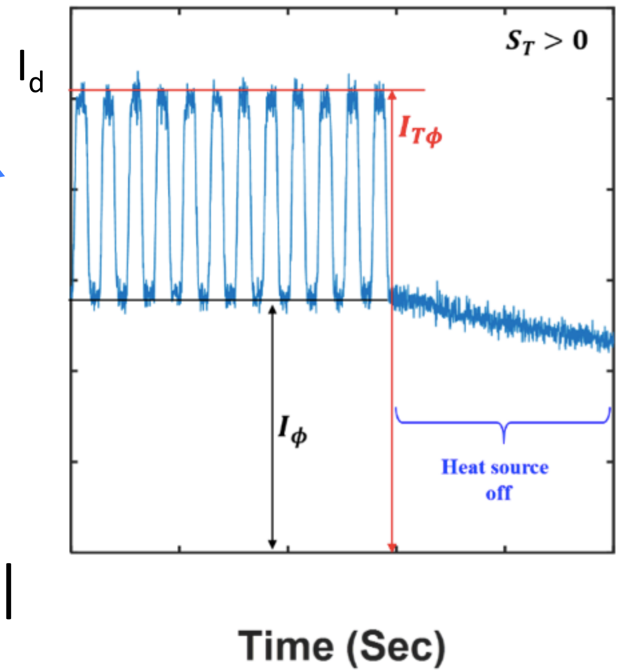


Thermal grating : $\Delta T = |\Delta n_T| / |\delta n/\delta T|$

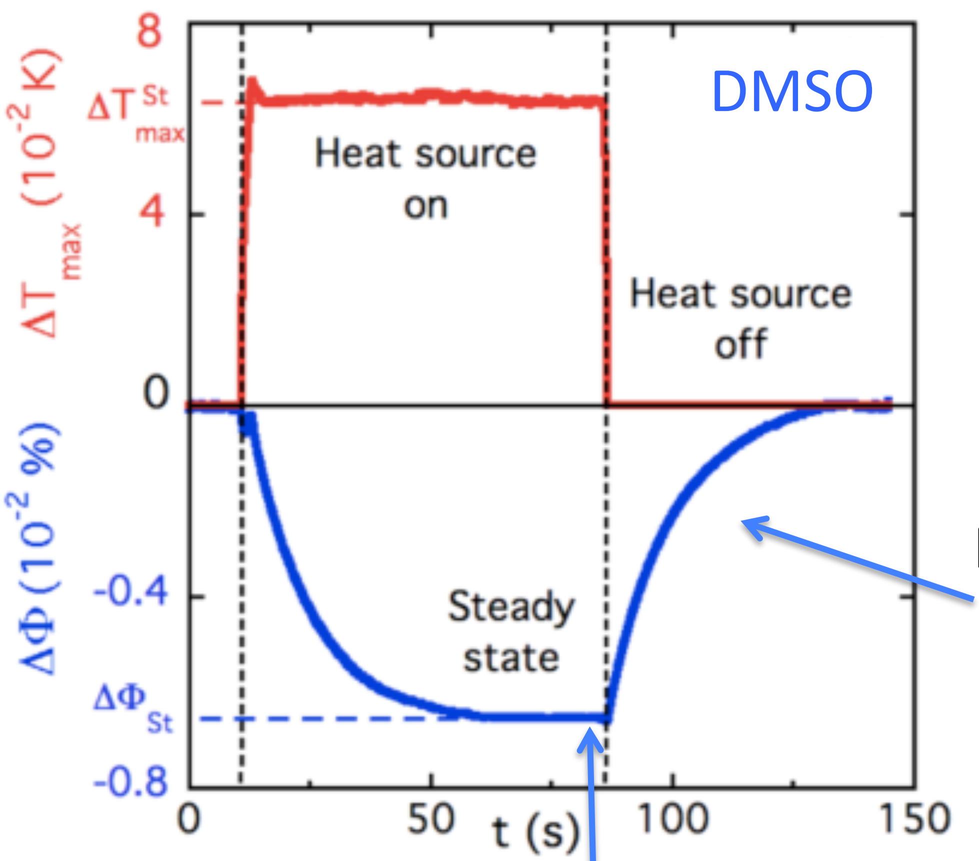
Concentration grating : $|\Delta\Phi| = |\Delta n_\Phi| / |\delta n/\delta\Phi|$

Example : FF in DMSO at T= 295 K

- hydroxyl-coated NPs with $[H^+] \approx 10^{-2}$ mole.L^{-1}
- ClO_4^- counter-ions

$\xi_0 > 0$

$\Phi = 2.5\%$



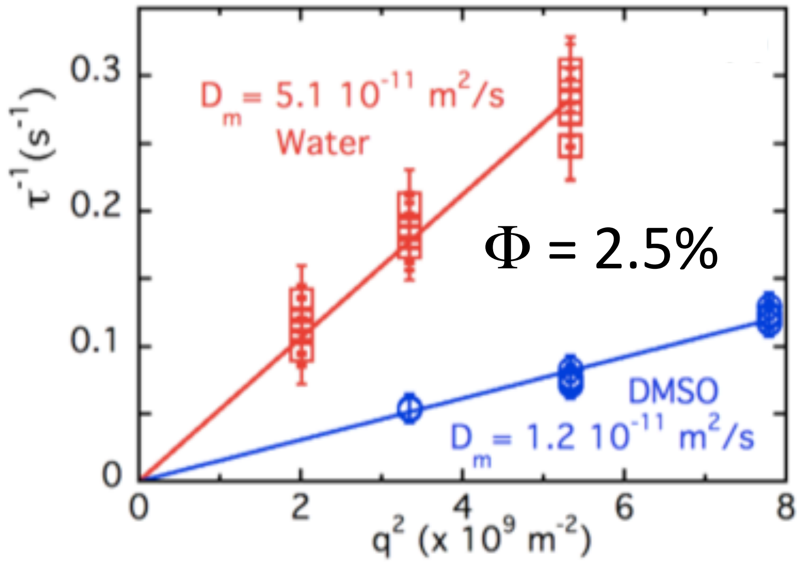
Relaxation of $\Delta\Phi$

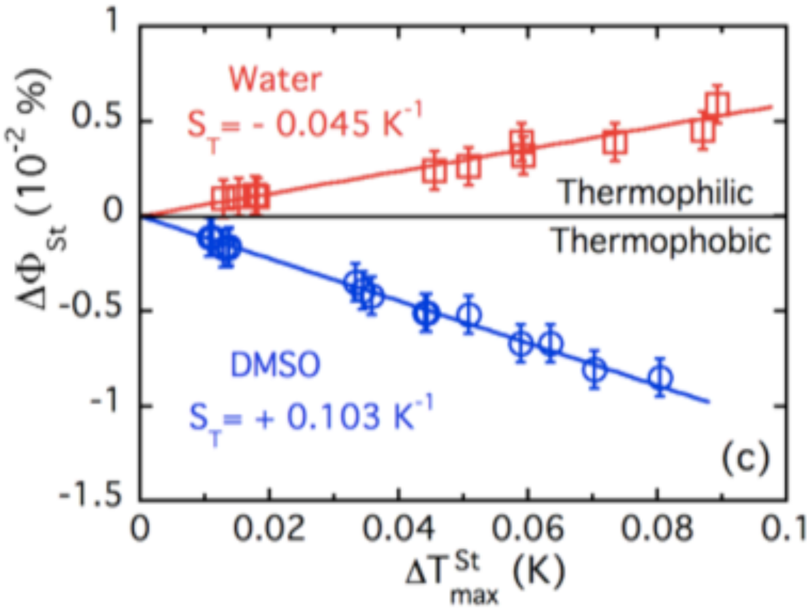
$$\tau^{-1} = D_m q^2$$

$$\Delta\Phi_{St} = -\Phi S_T \frac{\Delta T_{max}^{St}}{2}$$

FF in water and in DMSO at T= 295 K

- Same hydroxyl-coated NPs with $[H^+] \approx 10^{-2}$ mole.L^{-1} $\xi_0 > 0$
- Same ClO_4^- counter-ions





$$\tau^{-1} = D_m q^2$$

$$\Delta\Phi_{St} = -\Phi S_T \frac{\Delta T^{St}_{\max}}{2}$$

M. Sarkar *et al (submitted for publication)*

Thermodiffusive and thermophoretic properties

FF in molecular solvents*
at room temperature

(*) water, DMSO and their mixtures

FF in water-DMSO mixtures at T = 295 K

- Same hydroxyl-coated NPs with $[H^+] \approx 10^{-2}$ mole.L^{-1} $\xi_0 > 0$
- Same ClO_4^- counter-ions

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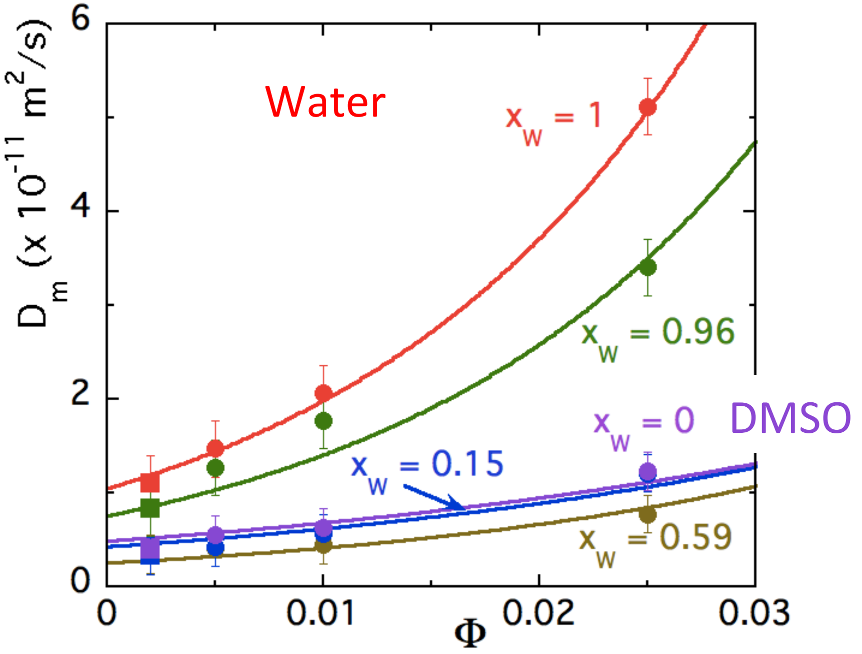
FF in water-DMSO mixtures at T = 295 K

- Same hydroxyl-coated NPs with $[H^+] \approx 10^{-2}$ mole.L^{-1} $\xi_0 > 0$
- Same ClO_4^- counter-ions

Mass diffusion coefficient

$$D_m = \frac{k_B T}{3\pi\eta d_H \chi}$$



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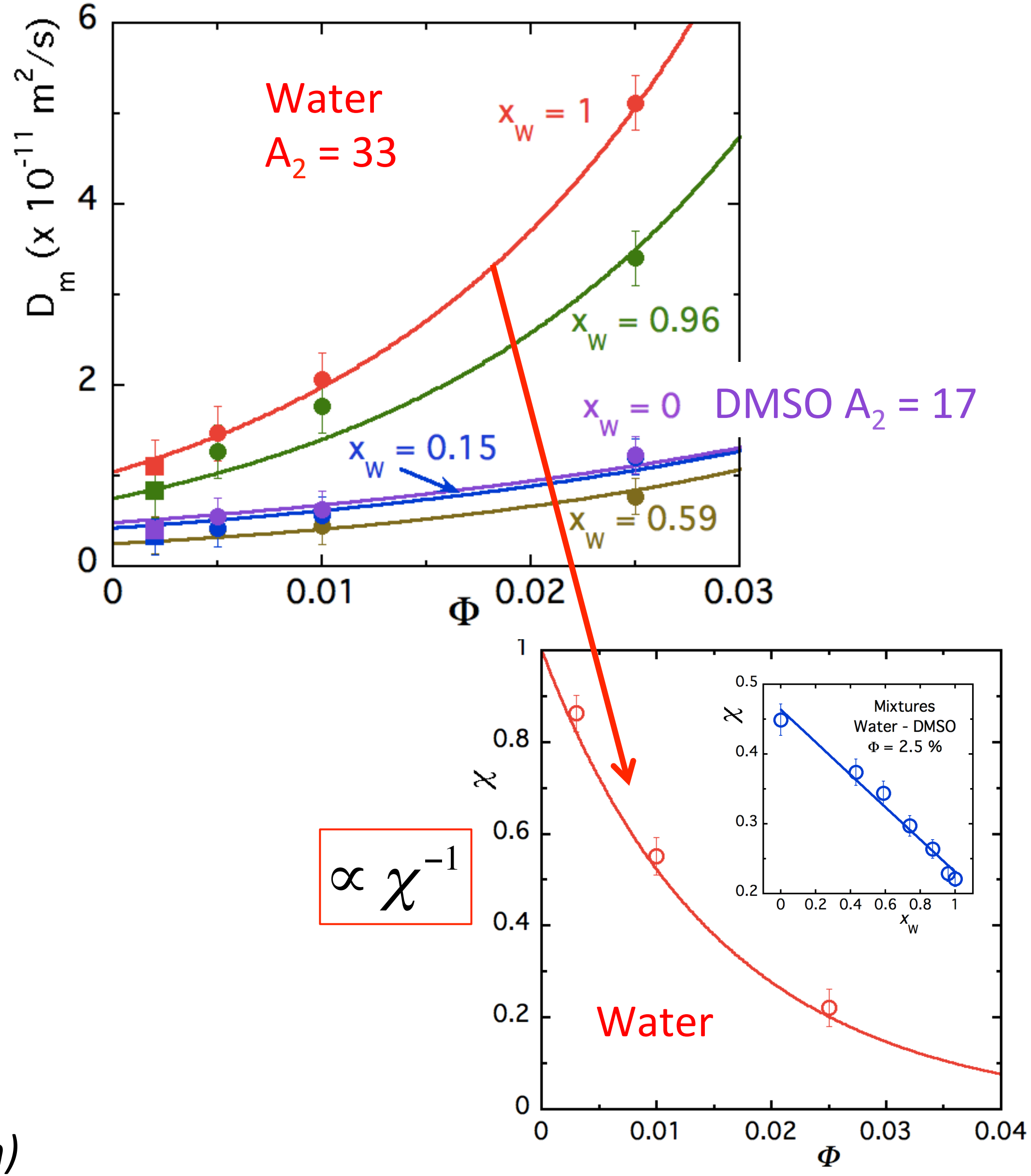

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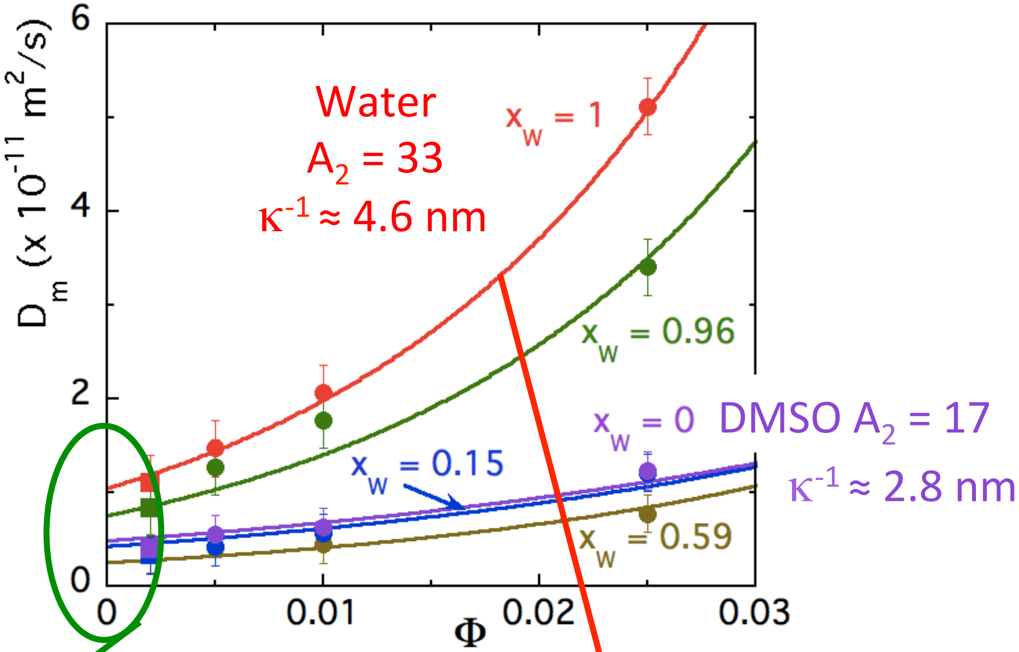
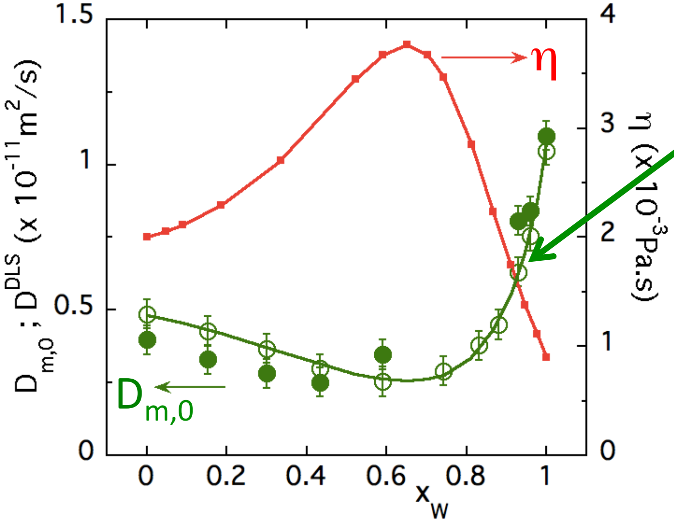
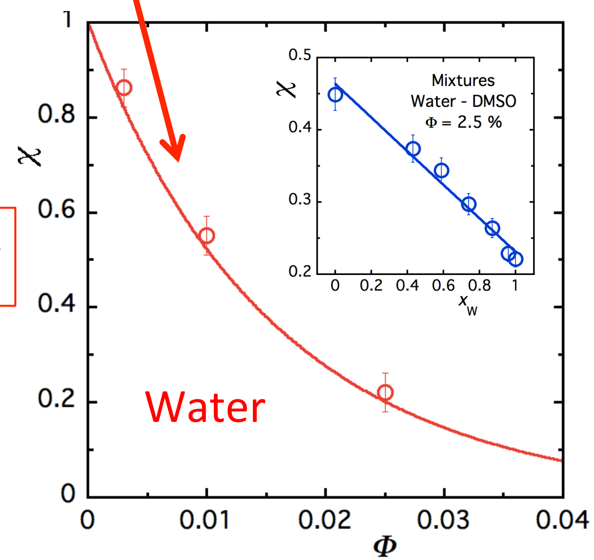


$\propto \eta^{-1}$

$\propto \chi^{-1}$





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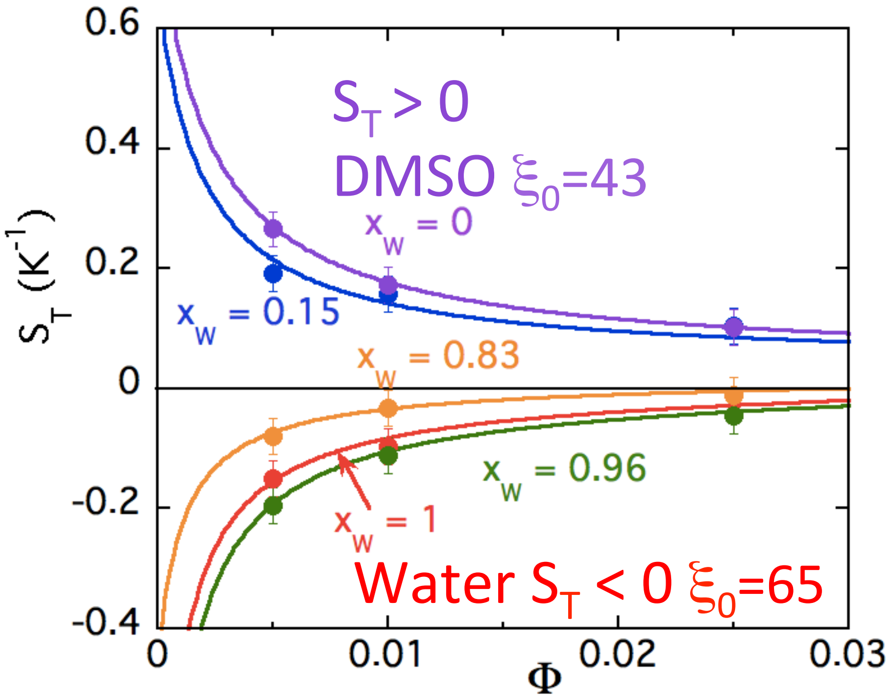
FF in water-DMSO mixtures at T = 295 K

- Same hydroxyl-coated NPs with $[H^+] \approx 10^{-2}$ mole.L^{-1} $\xi_0 > 0$
- Same ClO_4^- counter-ions

$$S_T = \frac{\chi}{k_B T}\left(\hat{S}_{NP} - e\xi_0 S_e^{st}\right)$$

→ Soret coefficient



$$eS_e^{st} = \frac{n_+\hat{S}_+ - n_-\hat{S}_- + Zn\chi\hat{S}_{NP}}{n_+ + n_- + Zn\chi\xi_0}$$

→ Seebeck coefficient for monovalent ions

ξ_0 : Electrophoretic charge

$Zn + n_+ = n_-$

$\hat{S}_{NP}$, $\hat{S}_+$, $\hat{S}_-$: Eastman entropy of transfer of the charged species

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FF in water at pH = 7 and T = 295 K

- Same citrate-coated NPs $\xi_0 < 0$
- Different counter-ions : $TBuA^+$, TMA^+, Na^+, Li^+

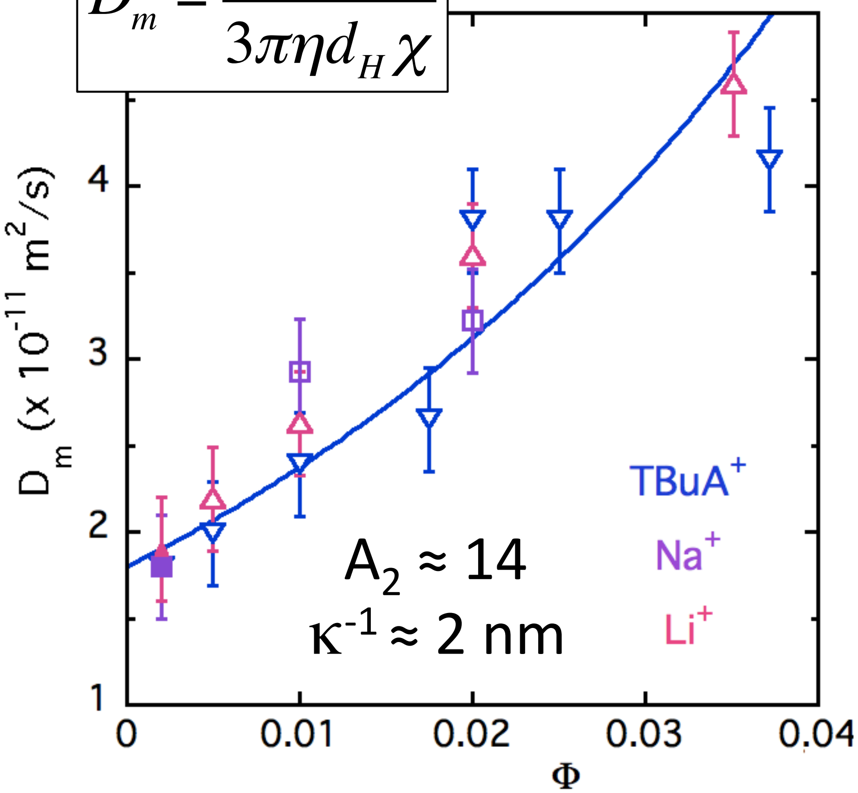
Another method in water to modulate
the sign of Soret coefficient S_T

FF in water at pH=7 and T = 295 K

- Same citrate-coated NPs
- Different counter-ions : $TBuA^+$, TMA^+, Na^+, Li^+

$-40 \leq \xi_0 < -28$

$$D_m = \frac{k_B T}{3\pi\eta d_H \chi}$$



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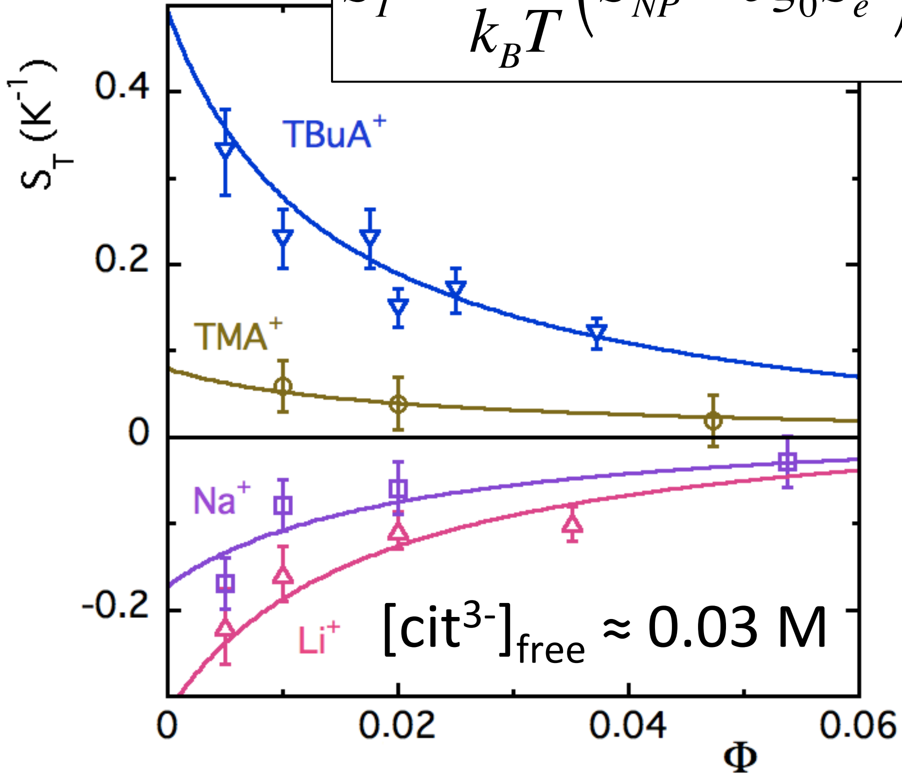

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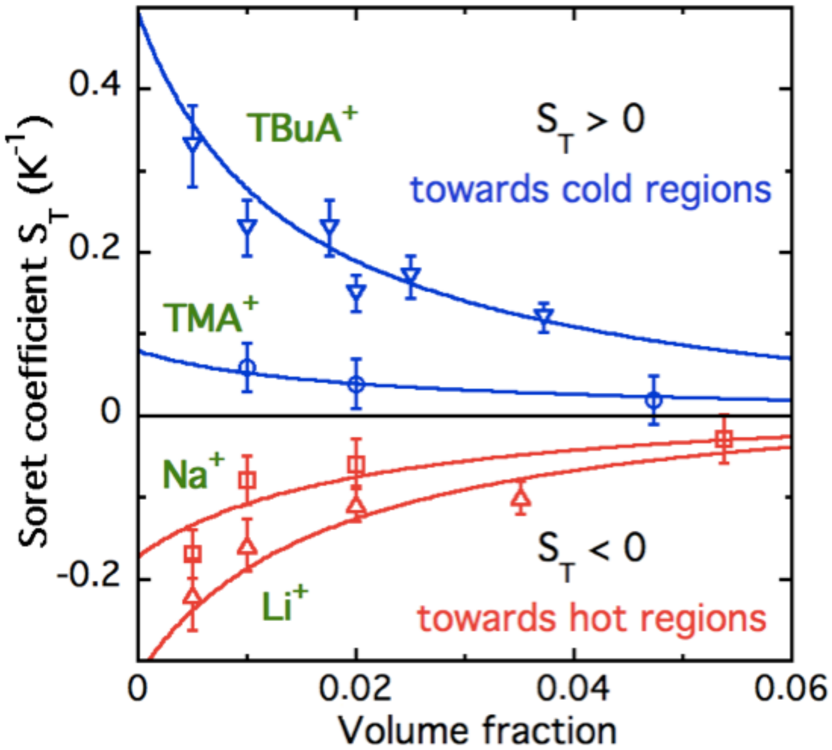

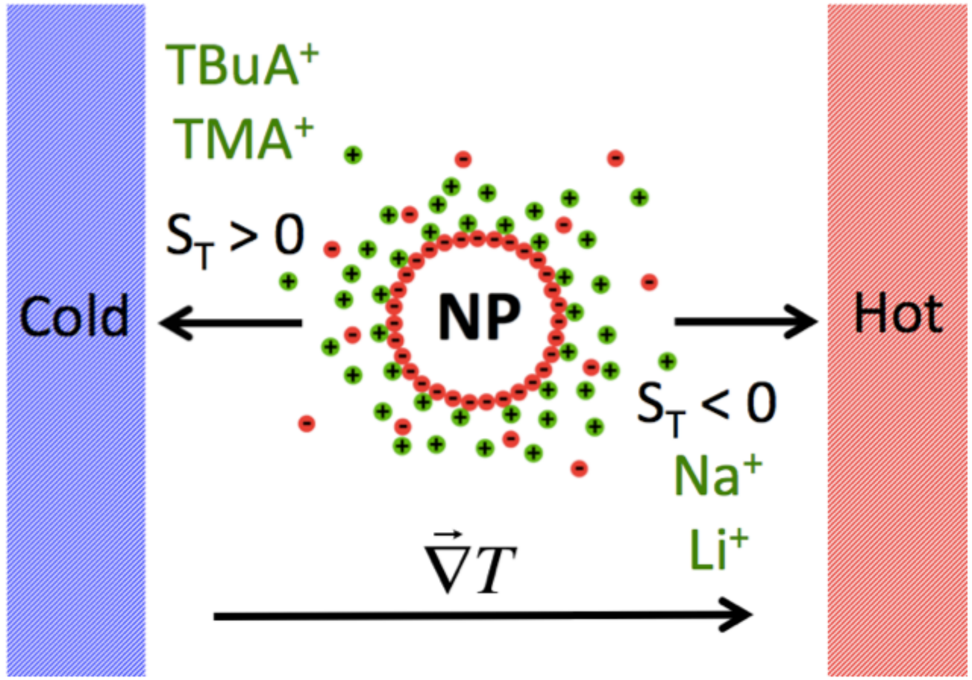

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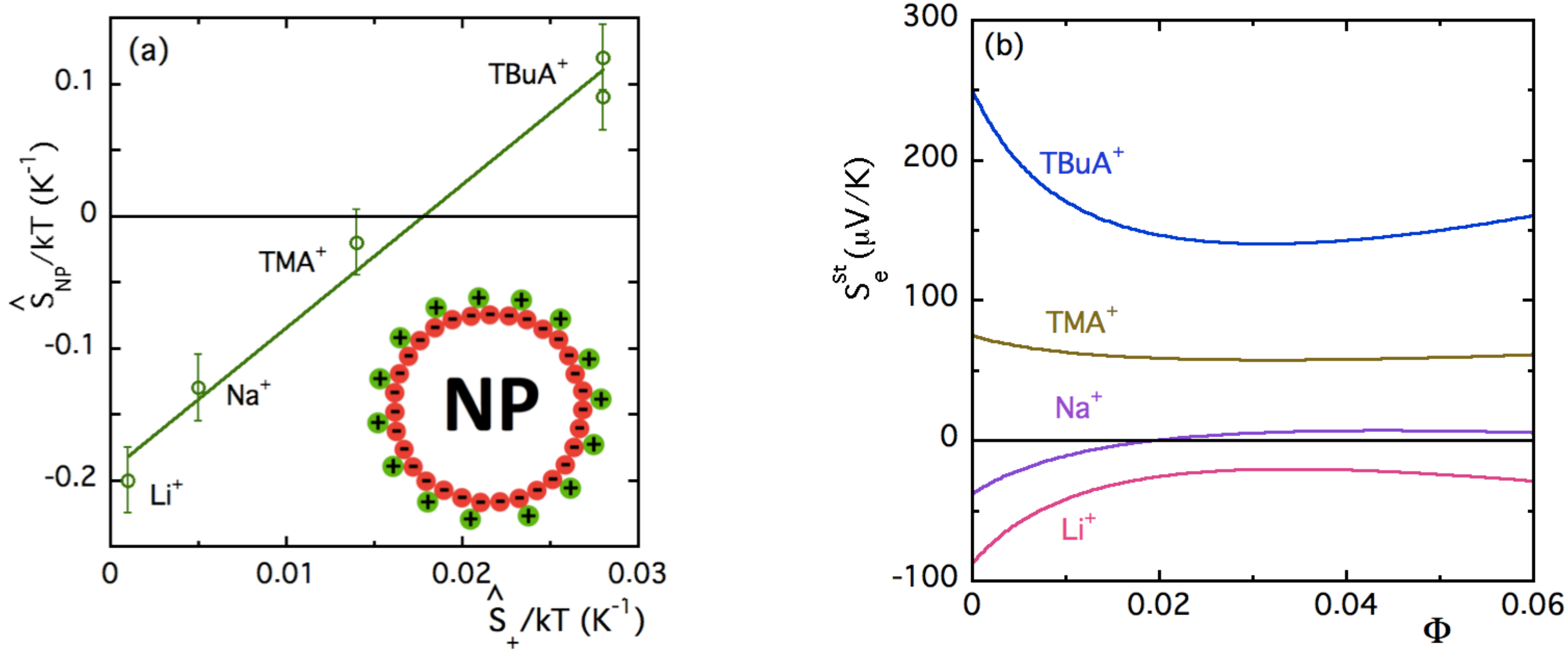
FF in water at pH=7 and T = 295 K

- Same citrate-coated NPs
- Different counter-ions : $TBuA^+$, TMA^+, Na^+, Li^+

$\xi_0 < 0$

$$S_T = \frac{\chi}{k_B T}\left(\hat{S}_{NP} - e\xi_0 S_e^{st}\right) \qquad S_e^{st} = \frac{n_+\hat{S}_+ - n_-\hat{S}_- + Z n \chi \hat{S}_{NP}}{n_+ + n_- + Z n \chi \xi_0}$$

Hyp $Z = \xi_0$ - Here the only unknown parameter is $\hat{S}_{NP}$



N. Takeyama, K. Nakashima *J. Solution Chem.* **17** (1988) 305

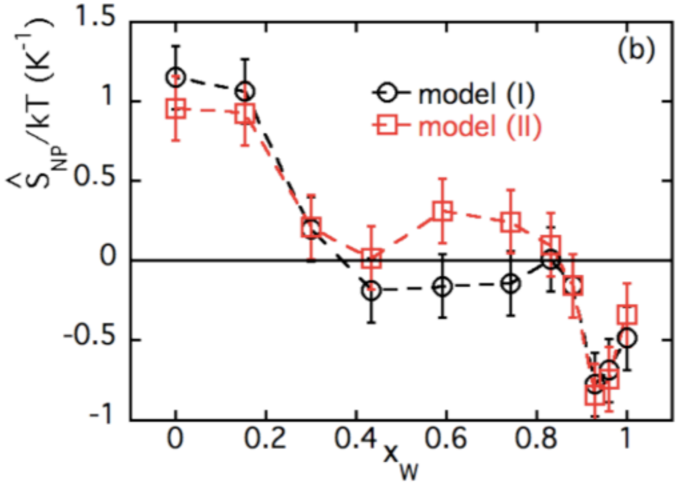
M. Kouyaté *et al Phys. Chem. Chem. Phys*. **21** (2019) 1895-1903

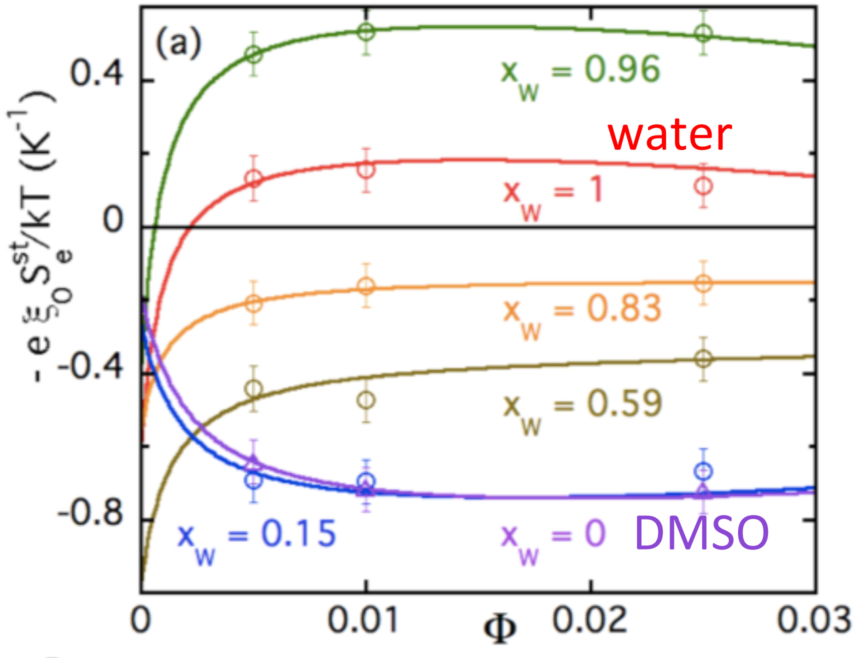
Backwards analysis of FF in water-DMSO mixtures

$\hat{S}_{ion}$ deduced from: (I) Born model and (II) Enthalpy transfer model

$$\hat{S}_{ion}(x_w) = \hat{S}_{ion}^{water} - \frac{\Delta_t H_{ion}^o(x_w)}{T N_a}$$

$$S_T = \frac{\chi}{k_B T}\left(\hat{S}_{NP} - e\xi_0 S_e^{st}\right)$$





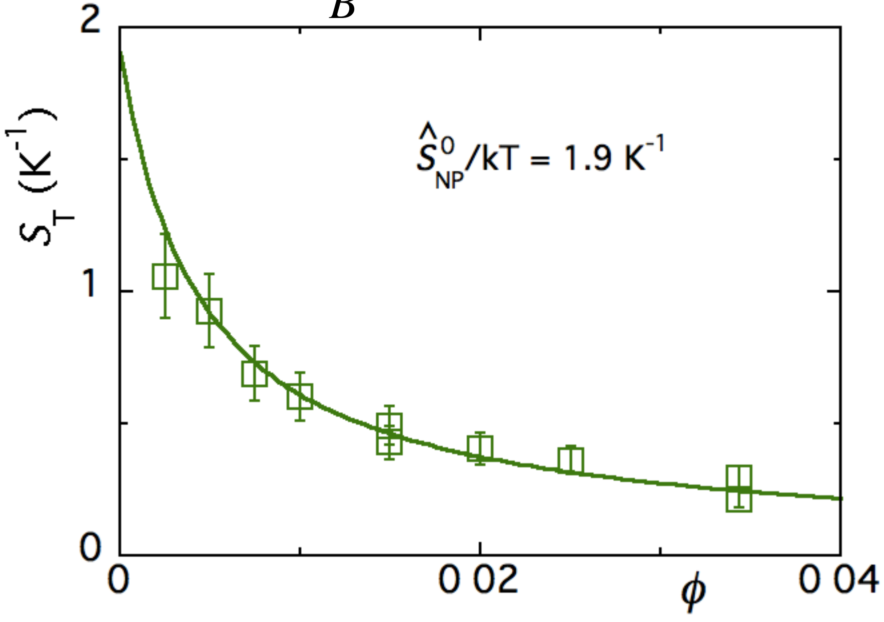
In our range of Φ measurements $-e\xi_0 S_e/kT$ is almost constant but there is a large variation at lower Φ's

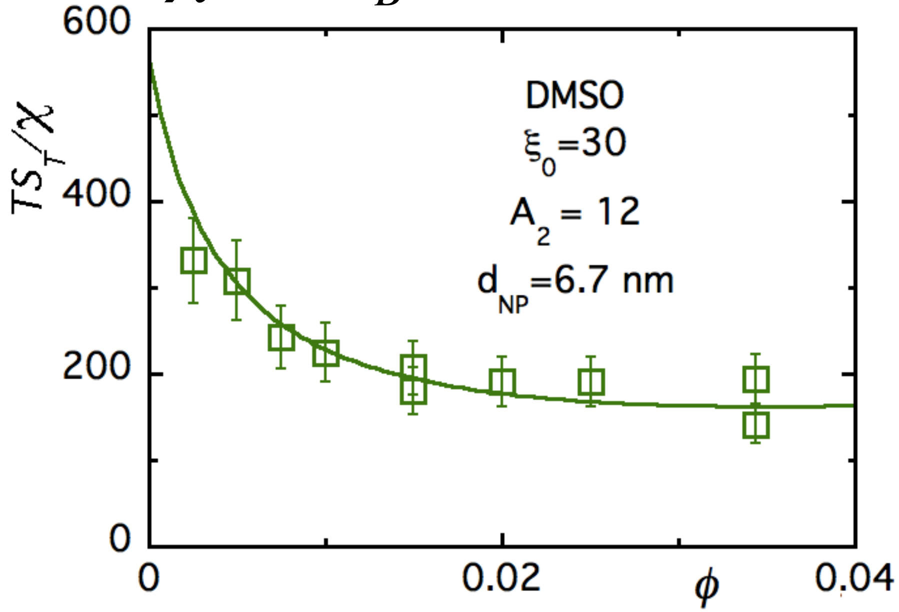
M. Sarkar *et al (submitted for publication)*

Illustrated with another FF sample in pure DMSO

(smaller NPs, smaller ξ_0)

$$S_T = \frac{\chi}{k_B T}\left(\hat{S}_{NP} - e\xi_0 S_e^{st}\right) \qquad \frac{TS_T}{\chi} = \frac{1}{k_B}\left(\hat{S}_{NP} - e\xi_0 S_e^{st}\right)$$



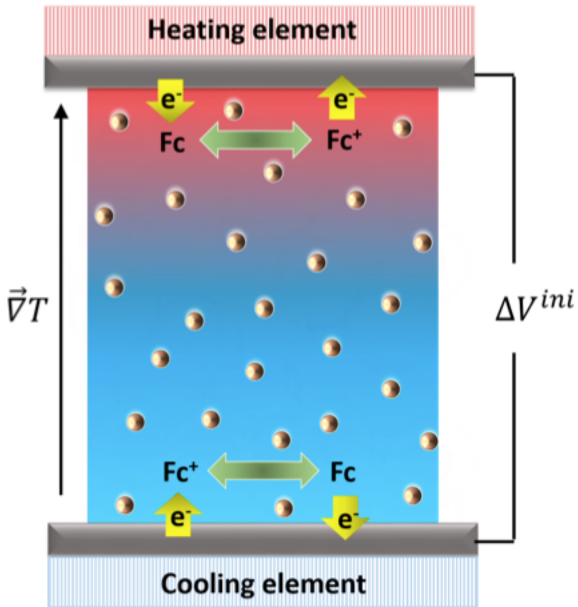


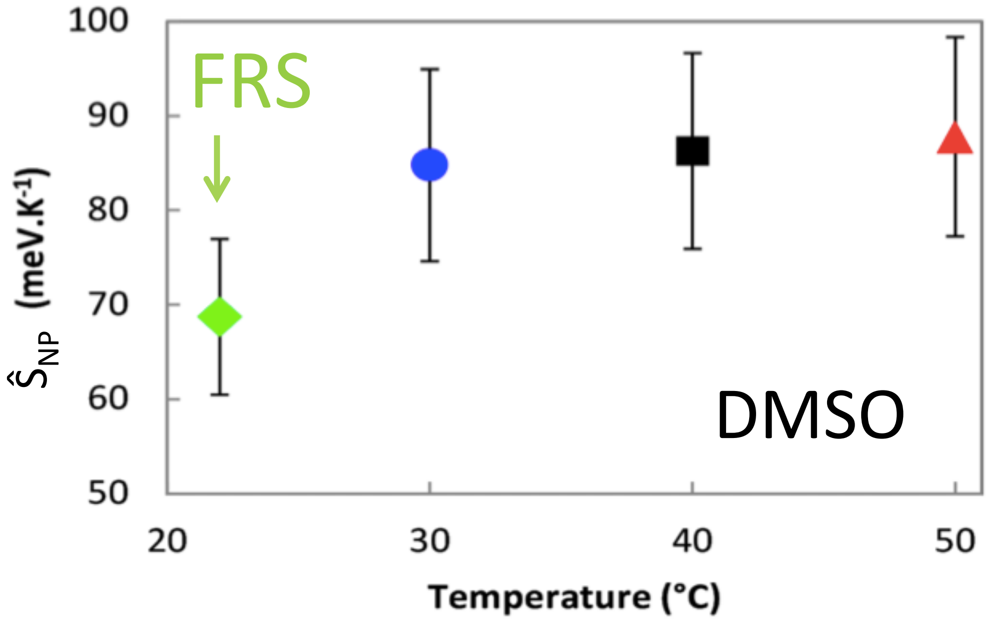
TS_T/χ is almost constant in the range $1\% \leq \Phi \leq 4\%$

but there is a large variation at lower Φ's

T. Salez et al (submitted) ; B. Huang et al J. Chem. Phys 2015

Thermoelectric measurements (*) on a similar FF sample in pure DMSO





Same order of magnitude of $\hat{S}_{NP}$ is found by both determinations : FRS and thermoelectric measurements in the initial regime

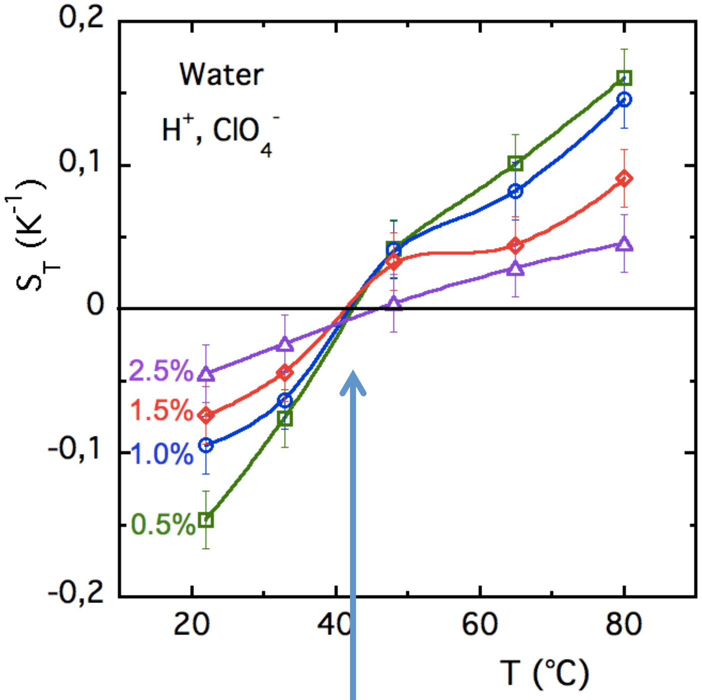
(*) B. Huang *et al J. Chem. Phys* 143 (2015) 054902 – see Sawako Nakamae presentation

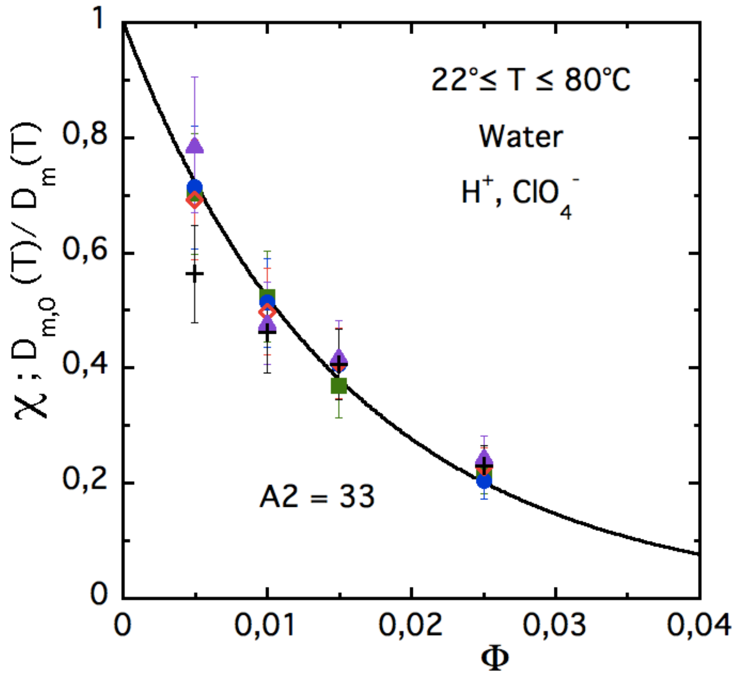
Thermodiffusive and thermophoretic properties of FF in molecular solvents* at $T \geq 295K$

(*) acidic NPs in water and DMSO

Acid FF in water at T ≥ 295 K

- Same hydroxyl-coated NPs with $[H^+] \approx 10^{-2}$ mole.L^{-1} $\xi_0 > 0$
- Same ClO_4^- counter-ions





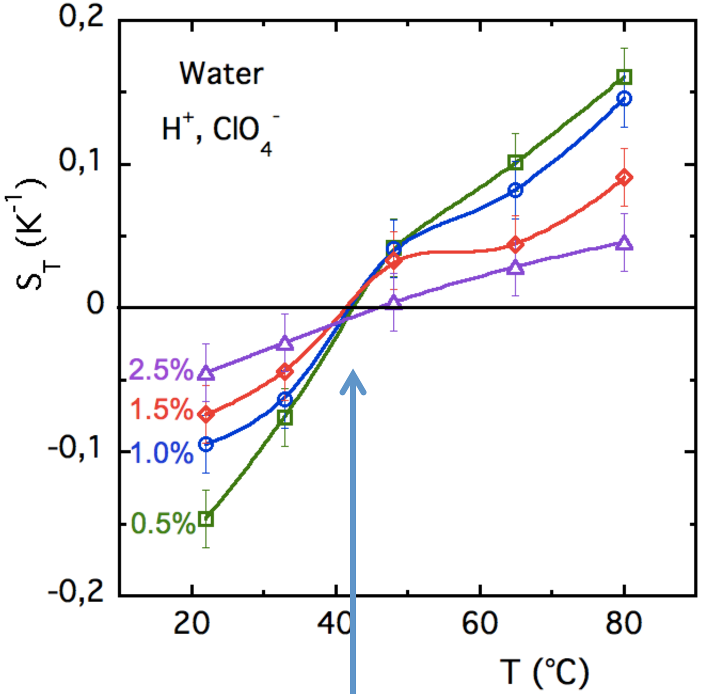
S_T changes its sign whatever Φ

From $D_m(\Phi)$:
χ indt of T
for 20°C ≤ T ≤ 80°C

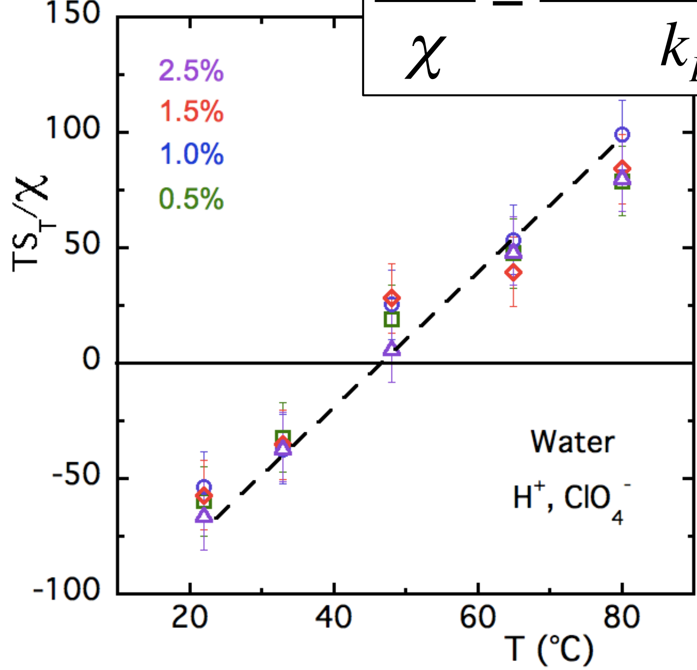
Acid FF in water at T ≥ 295 K

- Same hydroxyl-coated NPs with $[H^+] \approx 10^{-2}$ mole.L^{-1} $\xi_0 > 0$
- Same ClO_4^- counter-ions

$$\frac{TS_T}{\chi} = \frac{\hat{S}_{NP} - e\xi_0 S_e^{st}}{k_B}$$



S_T changes its sign whatever Φ



Reference values at 295K :

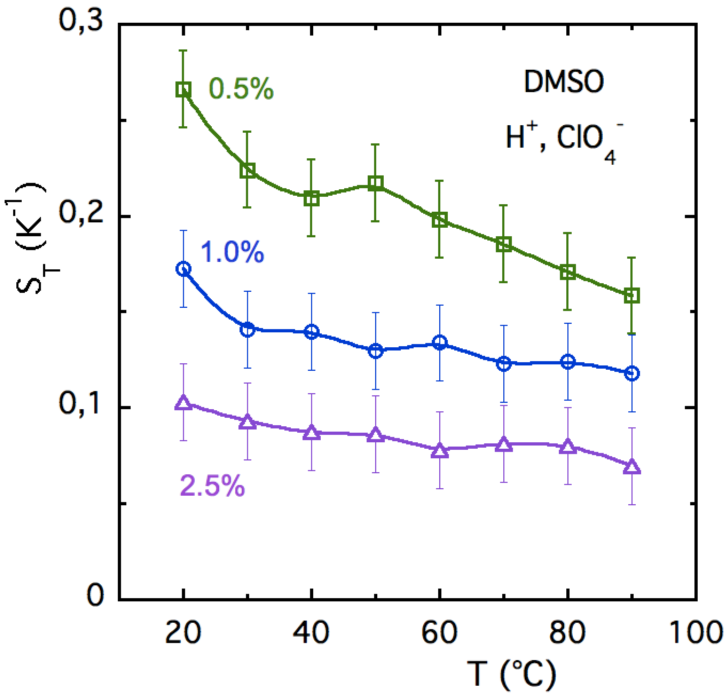
$\hat{S}_{NP}/k \approx -100$

$-e\xi_0 S_e/k \approx +35$

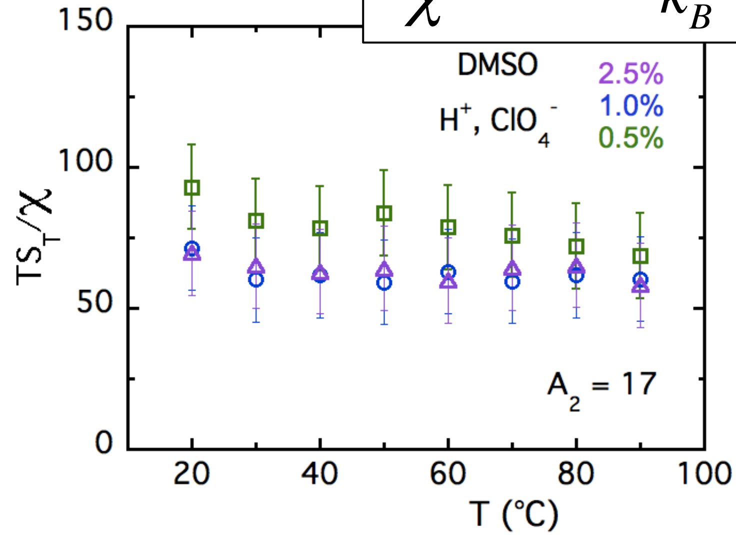
Contr. Ions at $\Phi = 0$: -180

Acid FF in DMSO at T ≥ 295 K

- Same hydroxyl-coated NPs with $[H^+] \approx 10^{-2}$ mole.L^{-1} $\xi_0 > 0$
- Same ClO_4^- counter-ions



$$\frac{TS_T}{\chi} = \frac{\hat{S}_{NP} - e\xi_0 S_e^{st}}{k_B}$$



$S_T > 0$ whatever Φ and T
$TS_T/\chi \approx$ cst with T

Reference values at 295K :

$\hat{S}_{NP}/k \approx +280$

$-e\xi_0 S_e/k \approx -205$

Contr. Ions at $\Phi = 0$: - 45

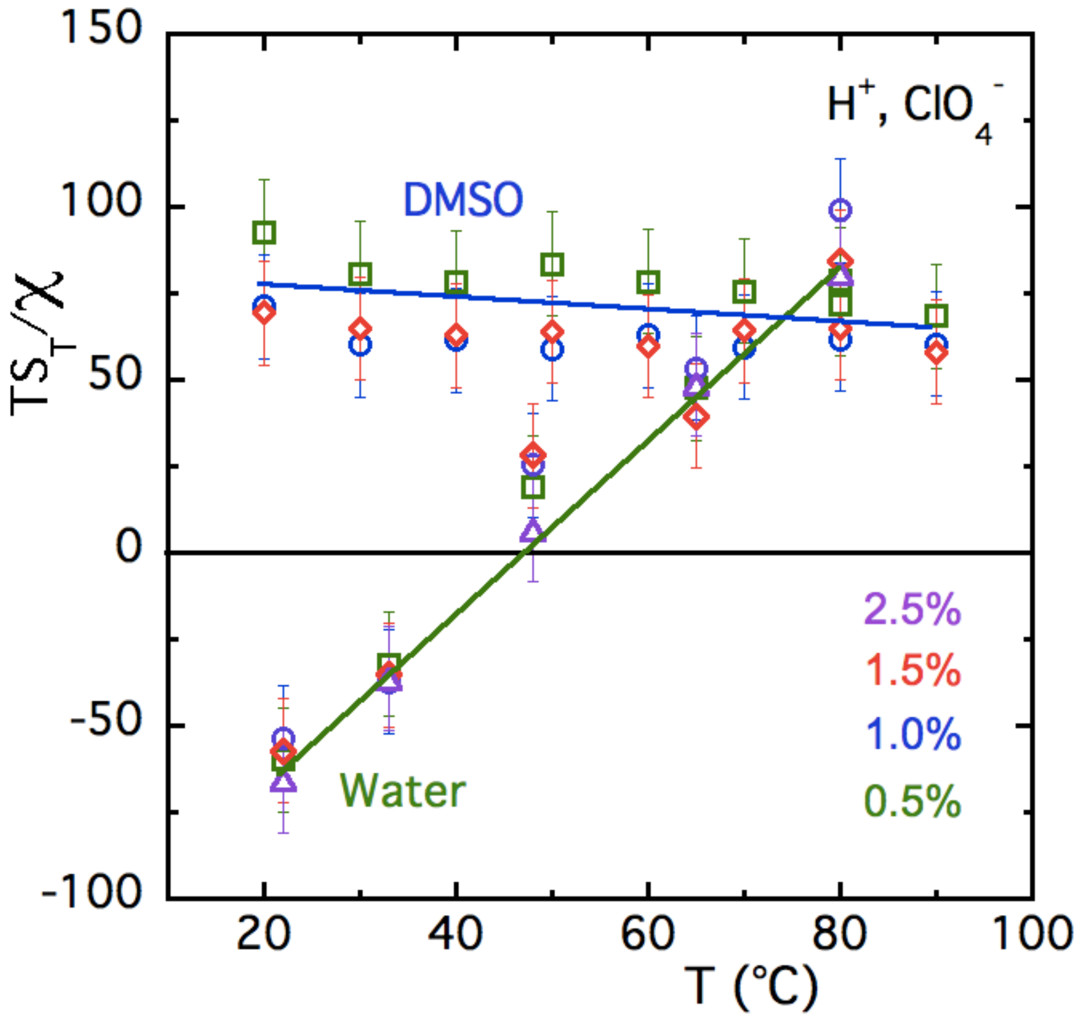
Acid FF in water and DMSO at T ≥ 295 K

- Same hydroxyl-coated NPs with $[H^+] \approx 10^{-2}$ mole.L^{-1} $\xi_0 > 0$
- Same ClO_4^- counter-ions

$$\frac{TS_T}{\chi} = \frac{\hat{S}_{NP} - e\xi_0 S_e^{st}}{k_B}$$

At room T,
TS_T/χ results
from the balance
of two large terms
of opposite sign.

For $\Phi \to 0$,
$TS_T/\chi \to$ larger values
+ 235 in DMSO
-280 in water



FF in water at pH=7 and $T \geq 295$ K

- Same citrate-coated NPs

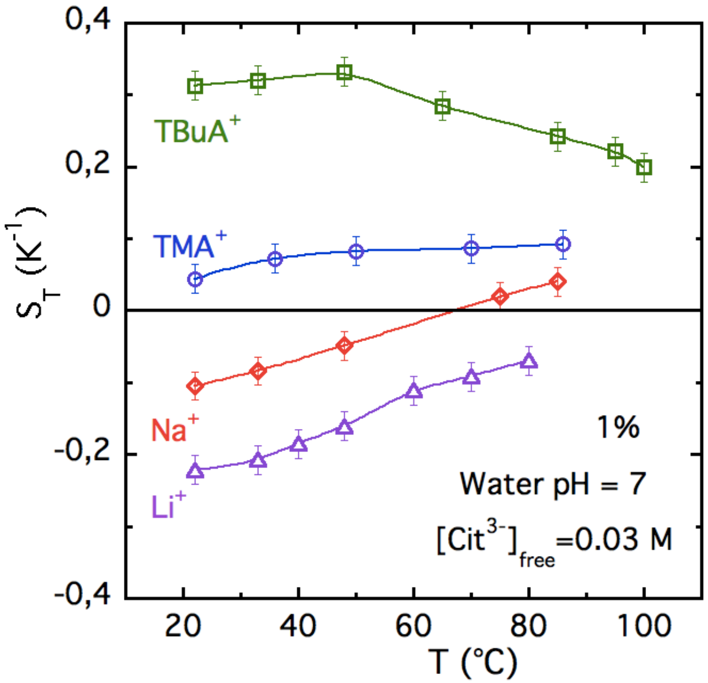
$\xi_0 < 0$

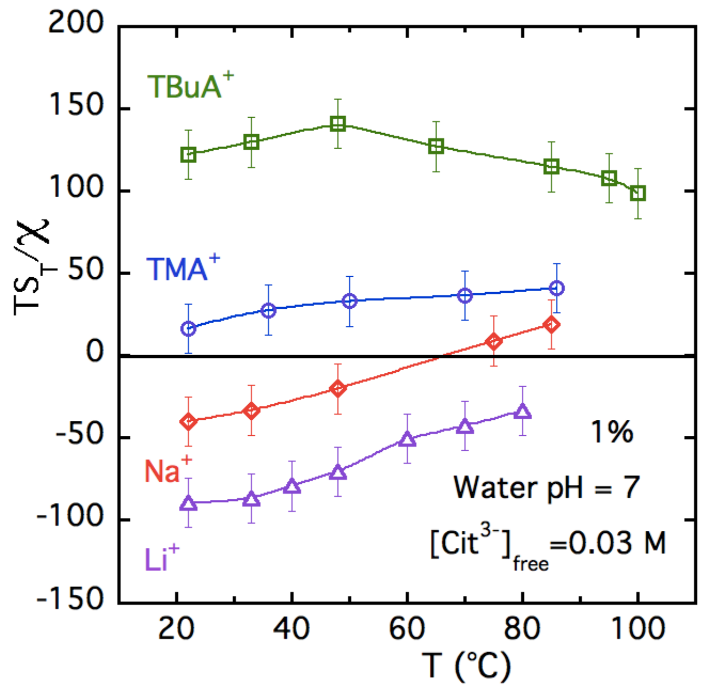
- Different counter-ions : $TBuA^+$, TMA^+, Na^+, Li^+

FF in water at pH=7 and T ≥ 295 K

- Same citrate-coated NPs
- Different counter-ions : $TBuA^+$, TMA^+, Na^+, Li^+

$\xi_0 < 0$





Here also the T-dependence of $\hat{S}_+$, $\hat{S}_-$ and ξ_0 are unknown,

Hyp χ indt of T

Reference values at 295K :

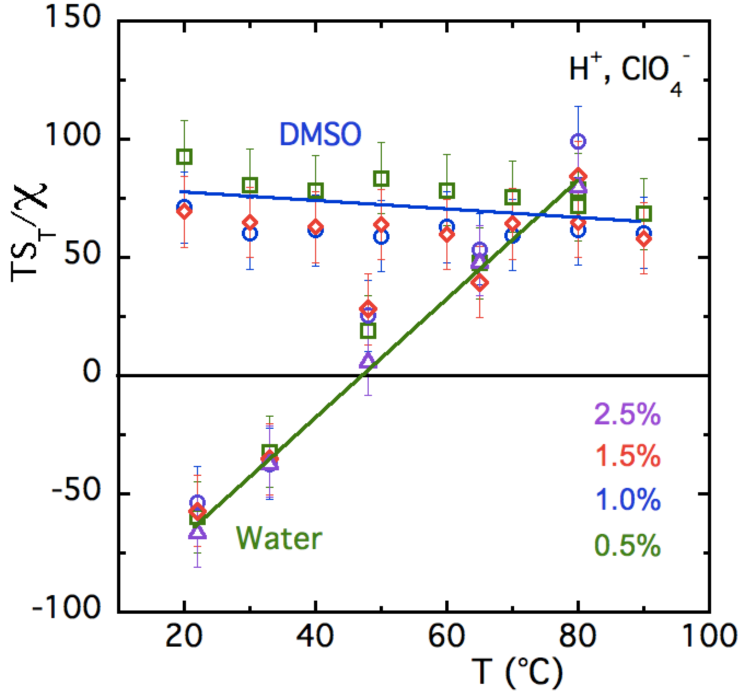
$TBuA^+$: $\hat{S}_{NP}/k \approx$ + 30, $-e\xi_0 S_e/k \approx$ + 80

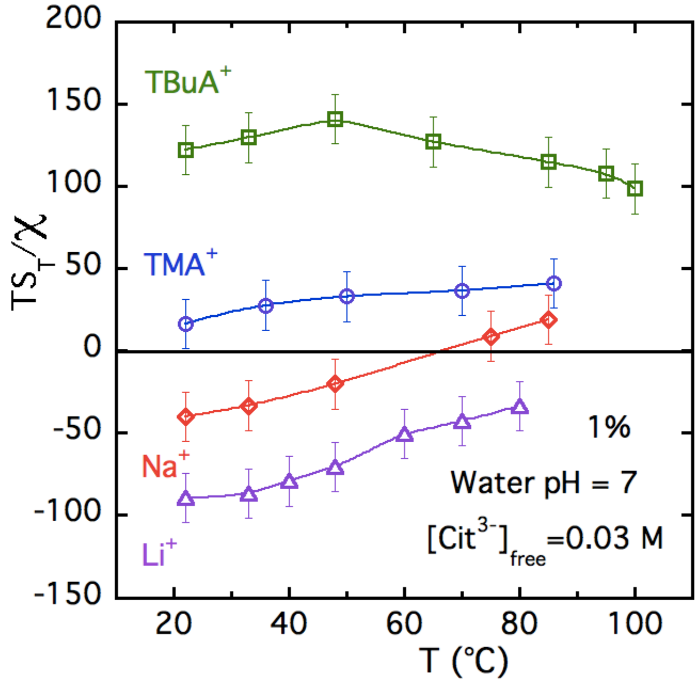
TMA^+ : $\hat{S}_{NP}/k \approx$ - 6, $-e\xi_0 S_e/k \approx$ + 25

Na^+ : $\hat{S}_{NP}/k \approx$ - 40, $-e\xi_0 S_e/k \approx$ - 5

Li^+ : $\hat{S}_{NP}/k \approx$ - 60, $-e\xi_0 S_e/k \approx$ - 20

Summary of FRS results in molecular solvents at T ≥ 295 K





$$\frac{TS_T}{\chi} = \frac{\hat{S}_{NP} - e\xi_0 S_e^{st}}{k_B}$$

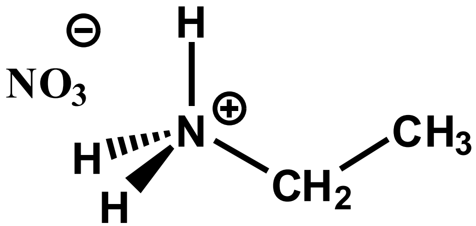
At room T, TS_T/χ results from the balance of two large terms either in competition of sign or with the same sign

Thermodiffusive and thermophoretic properties of FF in Ionic Liquids* at T ≥ 295K

(*) Two examples in EAN (several counter-ions) and in EMIM-TFSI

FF based on EAN

Ethyl ammonium nitrate EAN

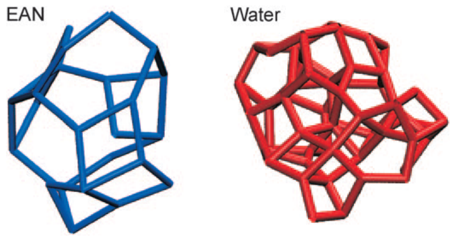


Home made

Melting Point = 14 °C η= 35 cP at 300K

Similar to water

H-bonded network



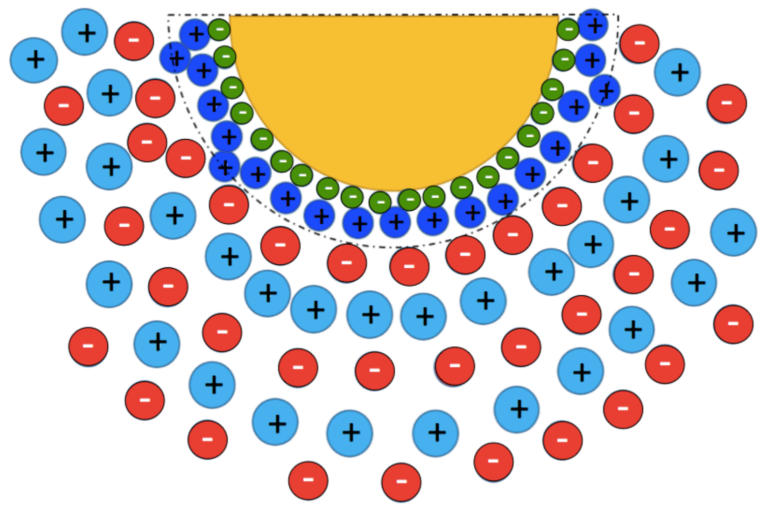
Protic Ionic Liquid

$EtNH_3^+ + NO_3^- \leftrightarrows EtNH_2 + HNO_3$

acidic   neutral   basic

0   5   10   pH

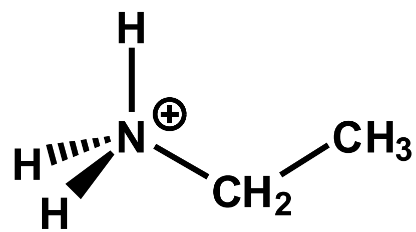
Water content < 0.3% w/w



Negative citrate surface species

various counterions

NO_3^-



Ethylammonium $^+$

M. Mamusa et al, *Soft Matter* **10** (2014) 1097-1101; *Faraday Discuss.* **181** (2015) 193-209

FF based on EAN at 295K – SAXS measurements

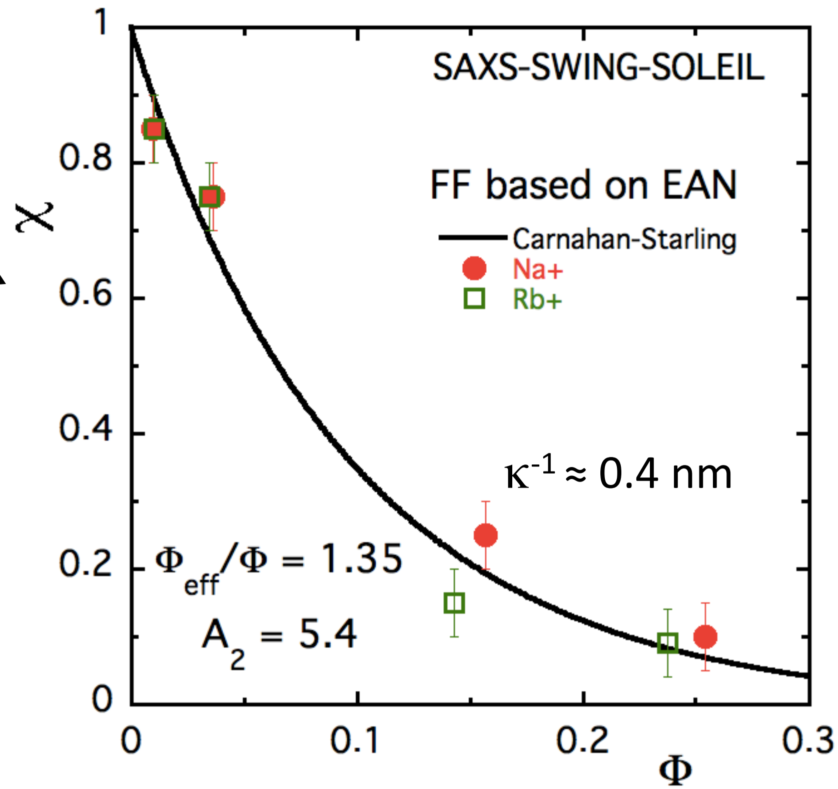
Nature of the counter-ions in the mother-solution influence

- the colloidal stability of the dispersion
- the interparticle interaction

Na^+, Rb^+ } Repulsion $A_2 > 0$

Li^+ Attraction $A_2 < 0$

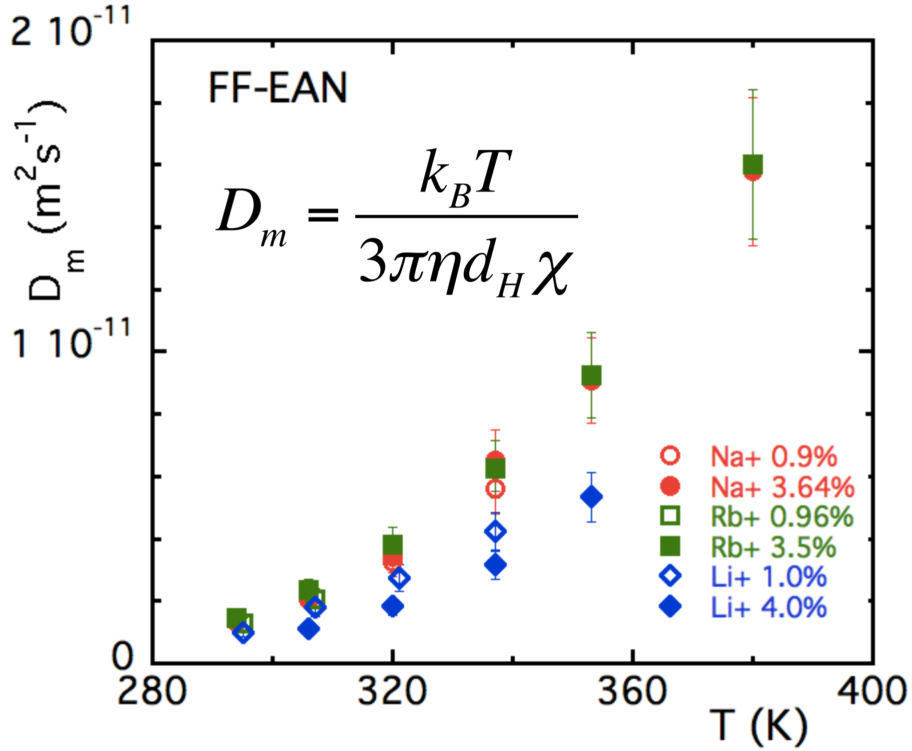
$S(q=0)>1$

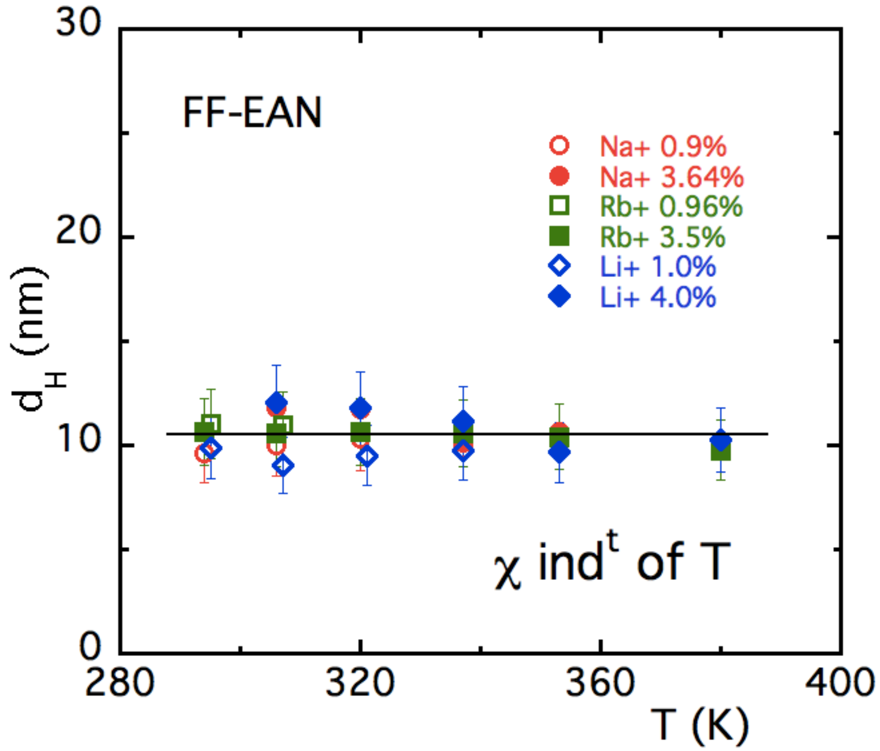


In case of repulsion: some counter-ions remain close to the NPs surface (chemical titration, ASAXS)

M. Sarkar *et al (to be submitted for publication)*

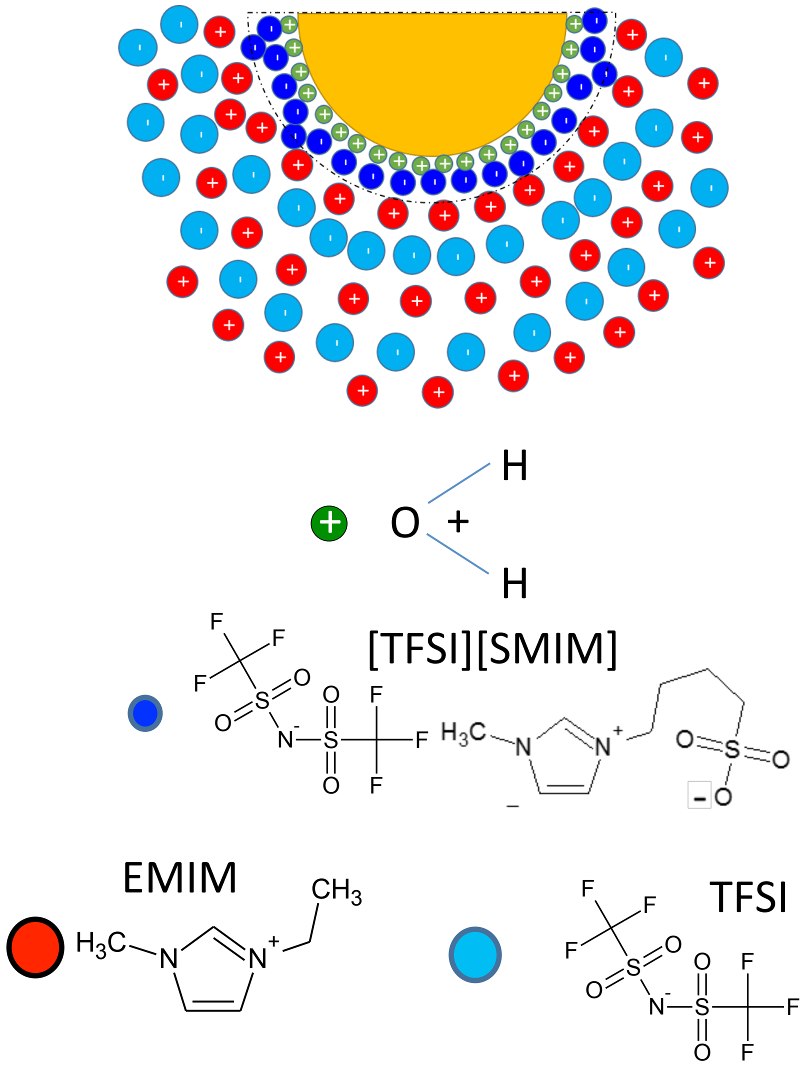
FF based on EAN at T≥ 295K

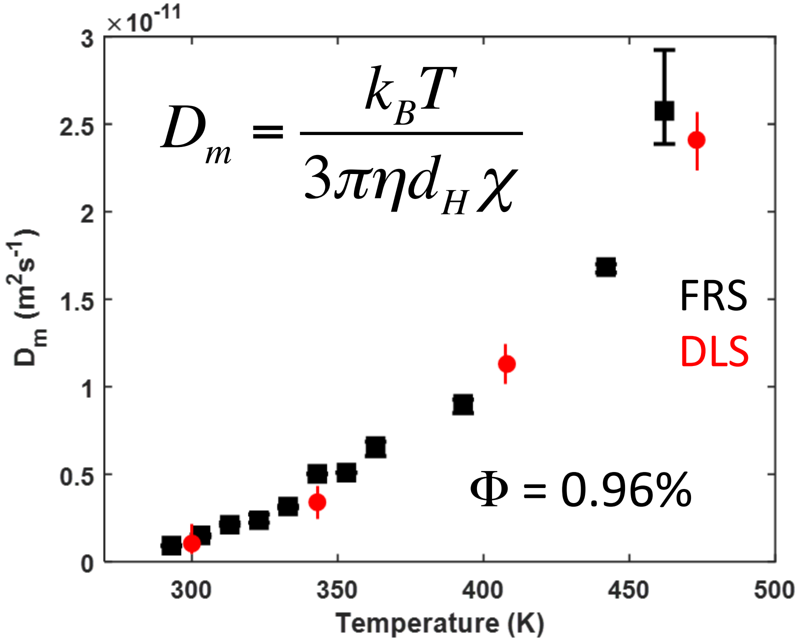


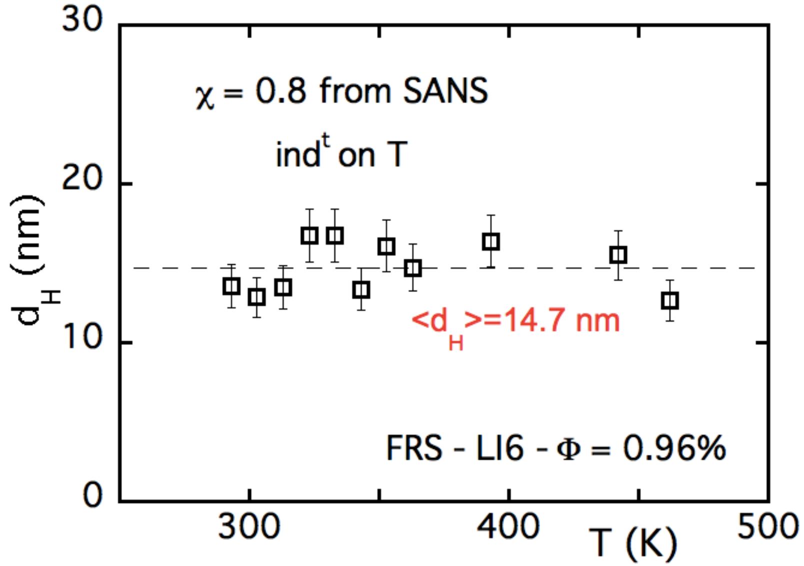


In the Φ-range 1-4%, diffusion coefficient D_m is ruled by viscosity η(T) and interparticle interaction χ(Φ) at 295K

FF based on EMIM-TFSI at T≥ 295K



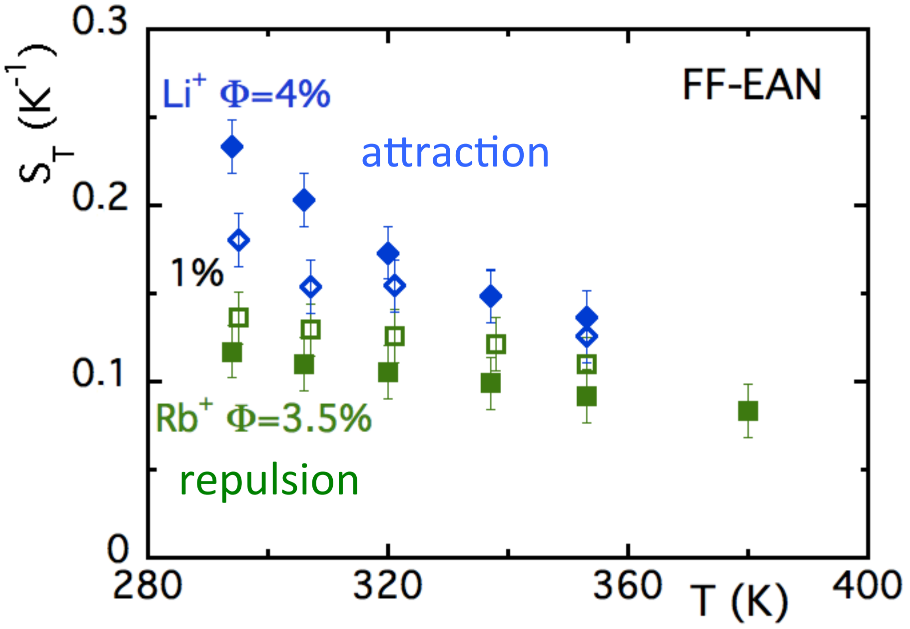


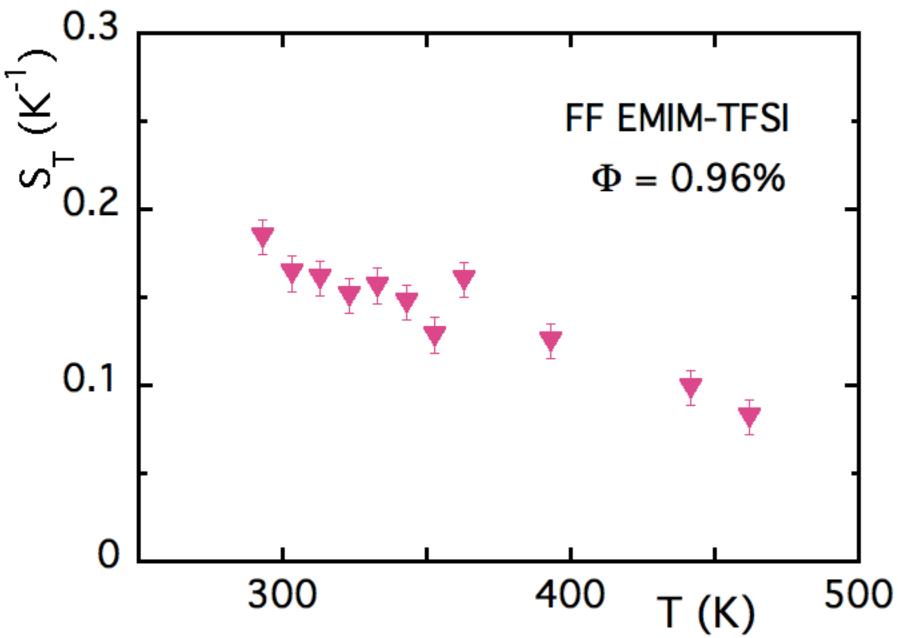


M. Sarkar et al – Communication to INCF 2019 – Castello – Spain – June 26-28, 2019

IL-FF based on
NEA or EMIM-TFSI

$$S_T = \frac{\chi}{k_B T}\left(\hat{S}_{NP} - e\xi_0 S_e^{st}\right)$$



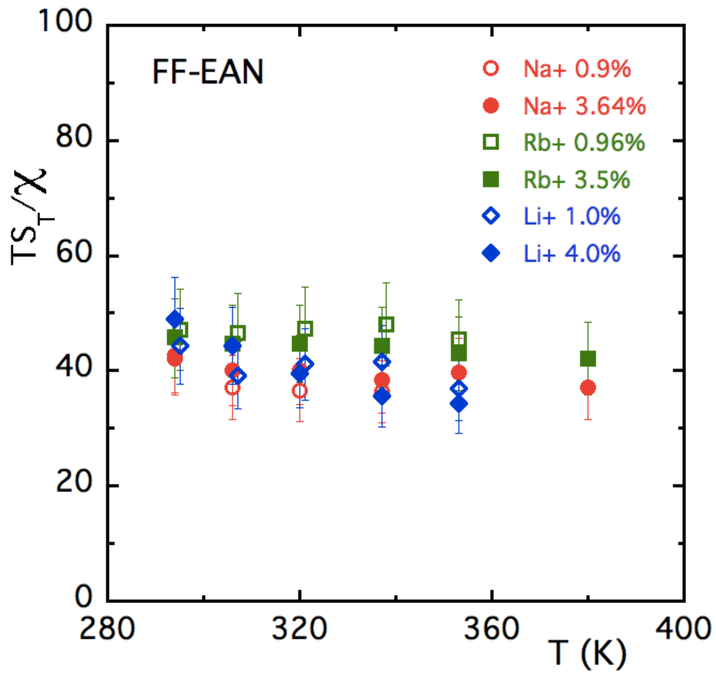


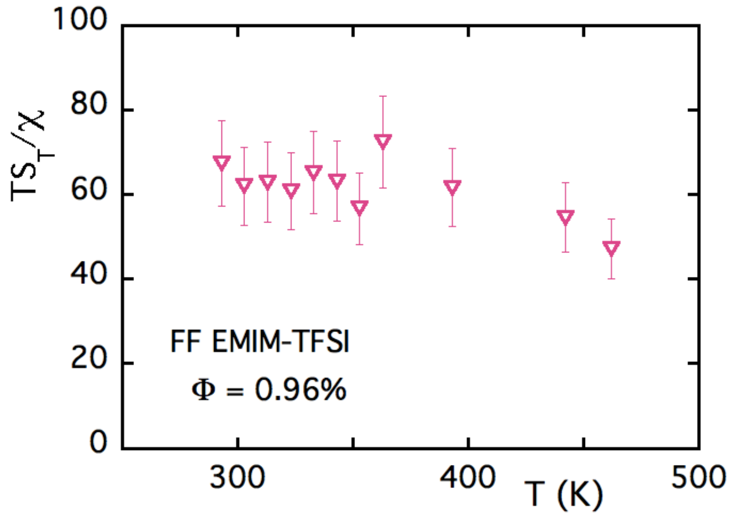
IL-FF based on NEA or EMIM-TFSI

$$\frac{TS_T}{\chi} = \frac{\hat{S}_{NP} - e\xi_0 S_e^{st}}{k_B}$$

$$S_e^{st} = \frac{n_+\hat{S}_+ - n_-\hat{S}_- + Z n \chi \hat{S}_{NP}}{n_+ + n_- + Z n \chi \xi_0}$$

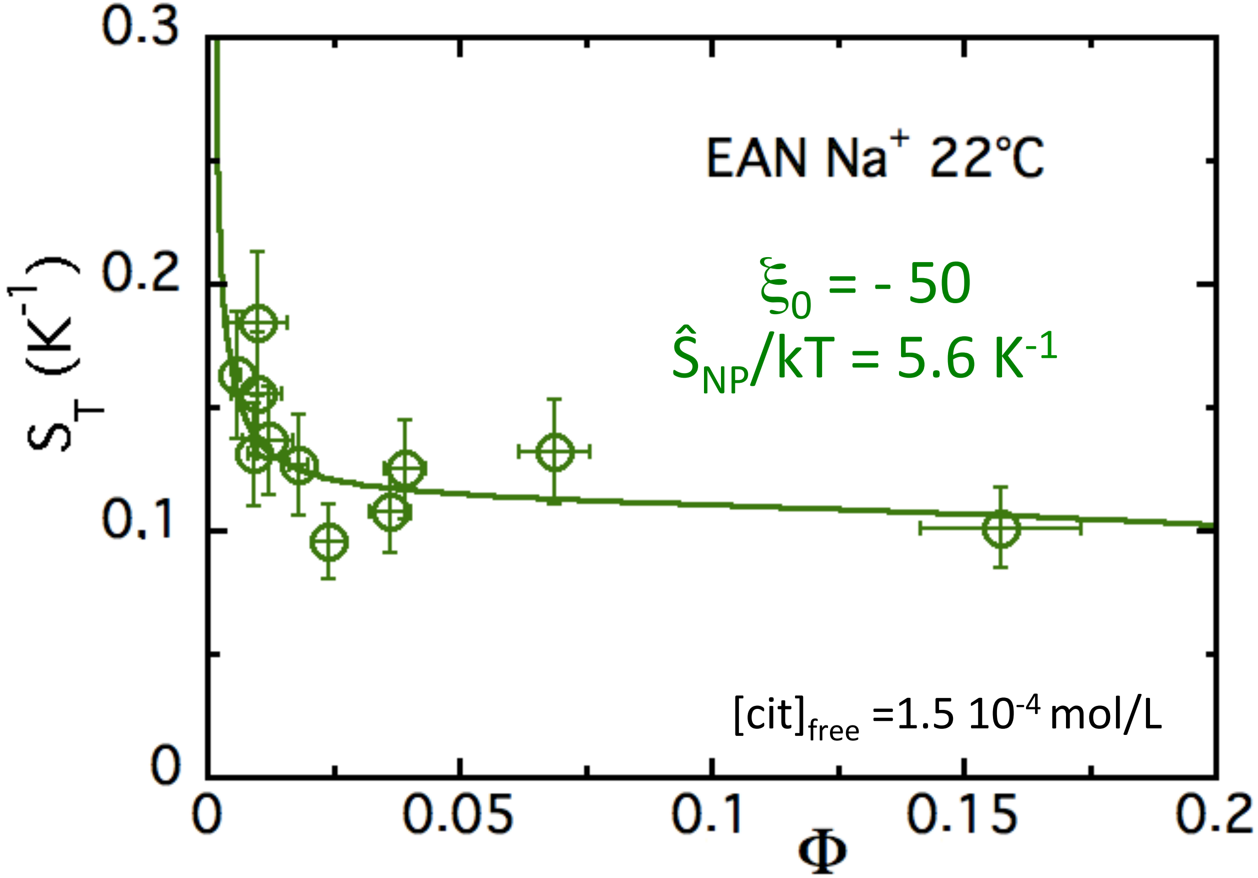
To go further
we need measurements
at larger concentrations
.. They are in progress





M. Sarkar et al – Communication to INCF 2019 – Castello – Spain – June 26-28, 2019

An example of Φ-dependence at room temperature for FF based on EAN with Na^+ counterions

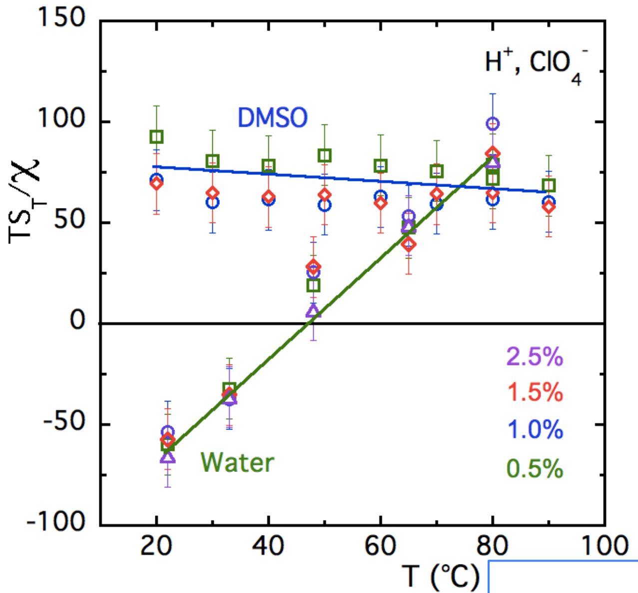


Tentative adjustment neglecting $\hat{S}_+$ and $\hat{S}_-$ in front of $\hat{S}_{NP}$

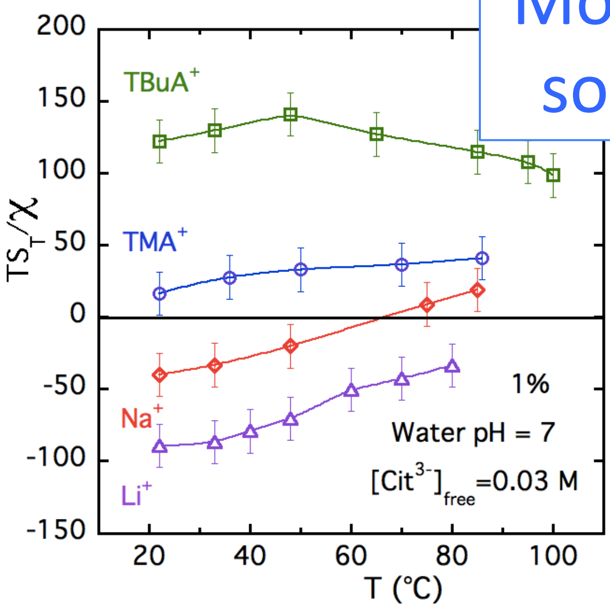
Summary

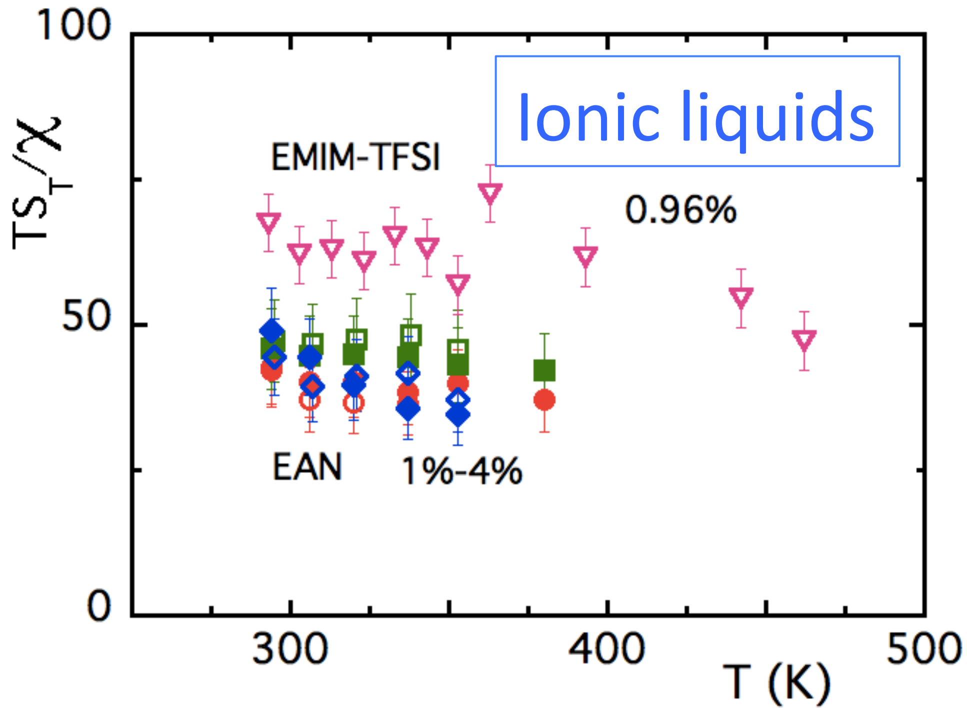
T-dependences of

$$\frac{TS_T}{\chi} = \frac{\hat{S}_{NP} - e\xi_0 S_e^{st}}{k_B}$$



Molecular solvents





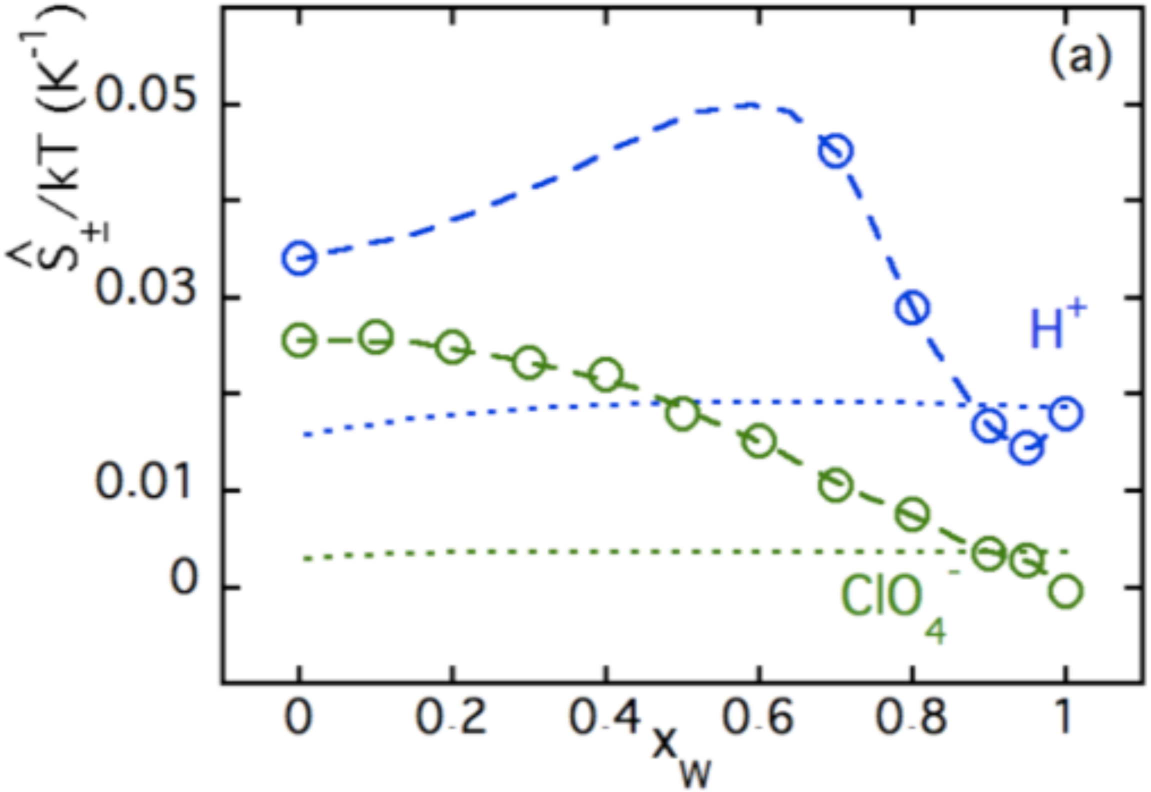
Thank you for your attention

We acknowledge :

- Synchrotron SOLEIL for time-allocation at the SWING beam-line,
- Horizon 2020 FET-PROACTIVE project, MAGENTA, associated with the Grant n° 731976,

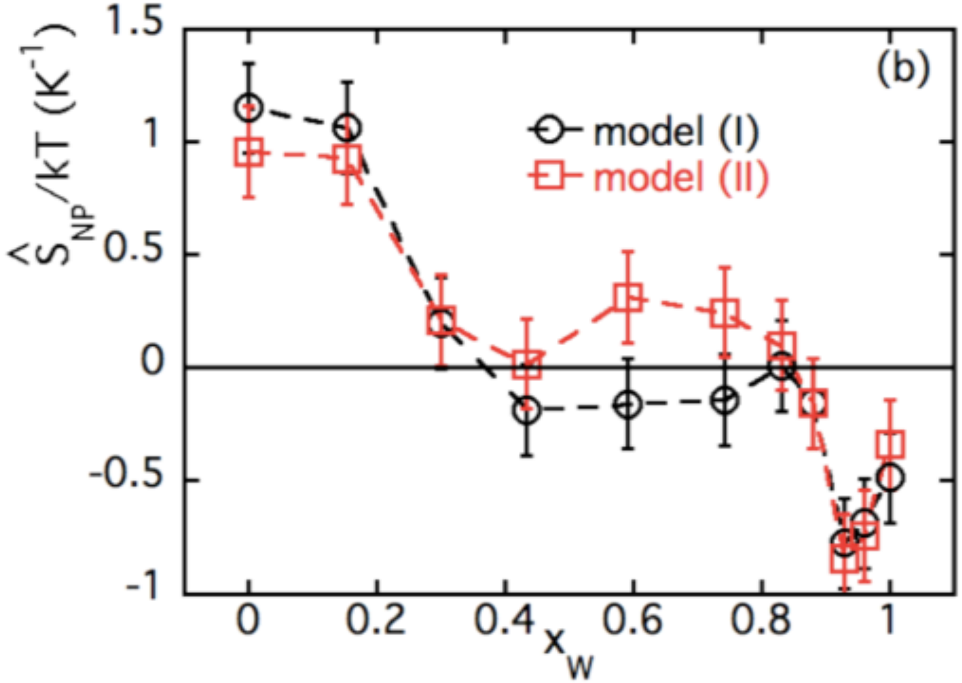
Contributions Ŝ+ and Ŝ- (of ions H+ and ClO4-) in mixtures of water and DMSO deduced from:

- Born model (dotted lines)
- Enthalpy transfer model (dashed lines) $\hat{S}_{ion}(x_w) = \hat{S}_{ion}^{water} - \frac{\Delta_t H_{ion}^o(x_w)}{T N_a}$

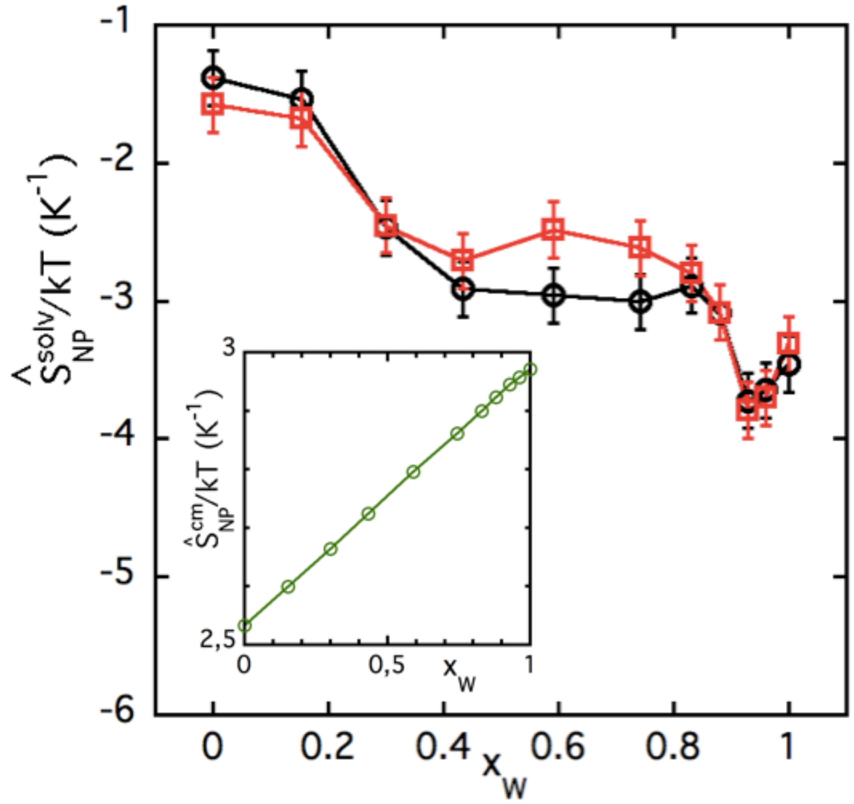


N. Takeyama, K. Nakashima *J. Solution Chem.* **17** (1988) 305

Y. Marcus, *Ion properties* (Marcel Dekker, New York 1997).

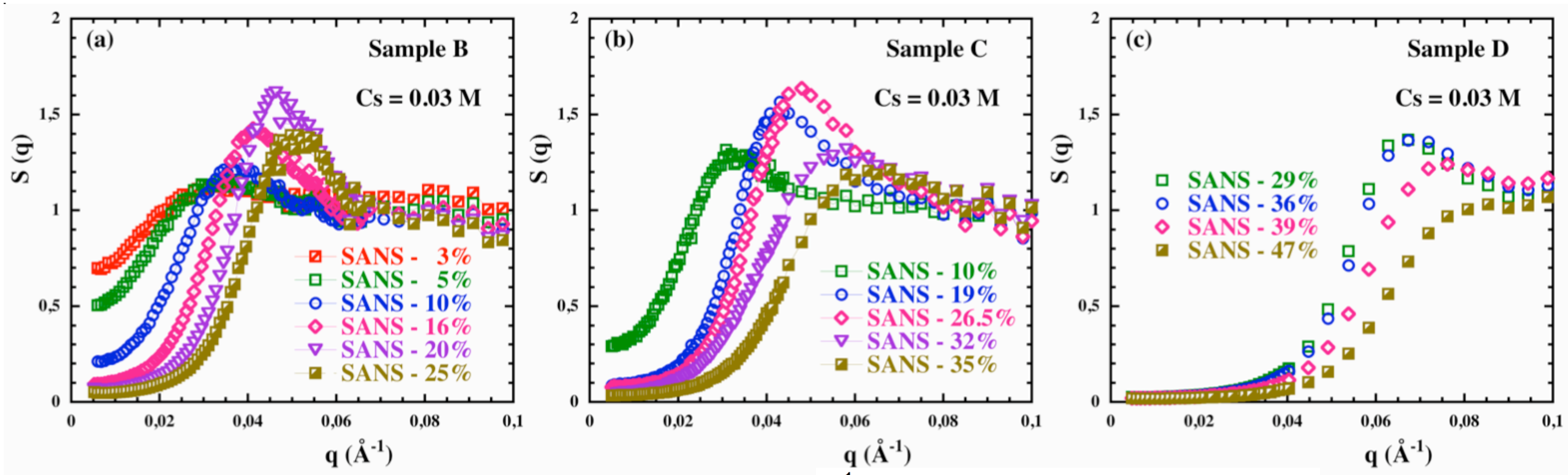


$$\hat{S}_{NP} = \hat{S}_{NP}^{cm} + \hat{S}_{NP}^{solv}$$

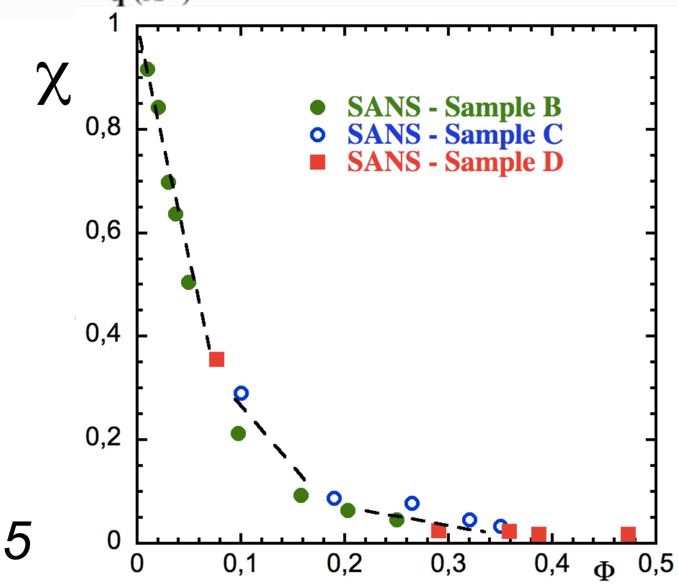


Influence of volume fraction Φ on the structure factor

SANS (LLB – ILL) d_{NP} ~10 nm [cit]$_{free}$ = 0.03 mol/L



and on the compressibility

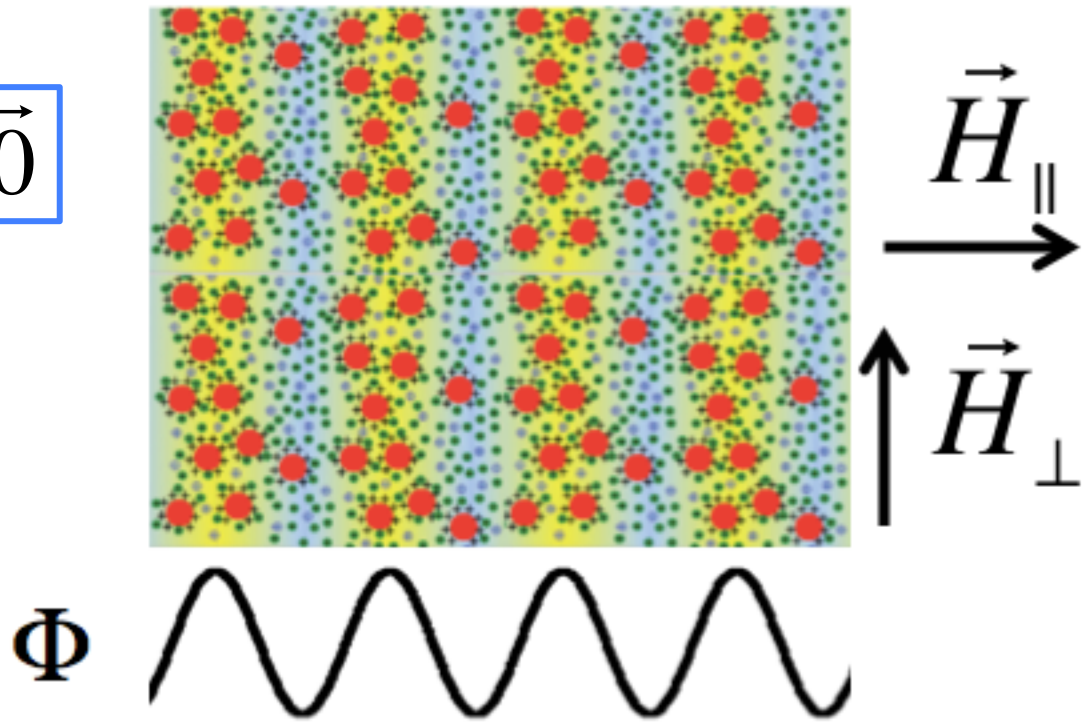


G. Mériguet et al
Magnetohydrodynamics 48 (2012) 415

Na$^+$

Relaxation of the concentration grating under magnetic field

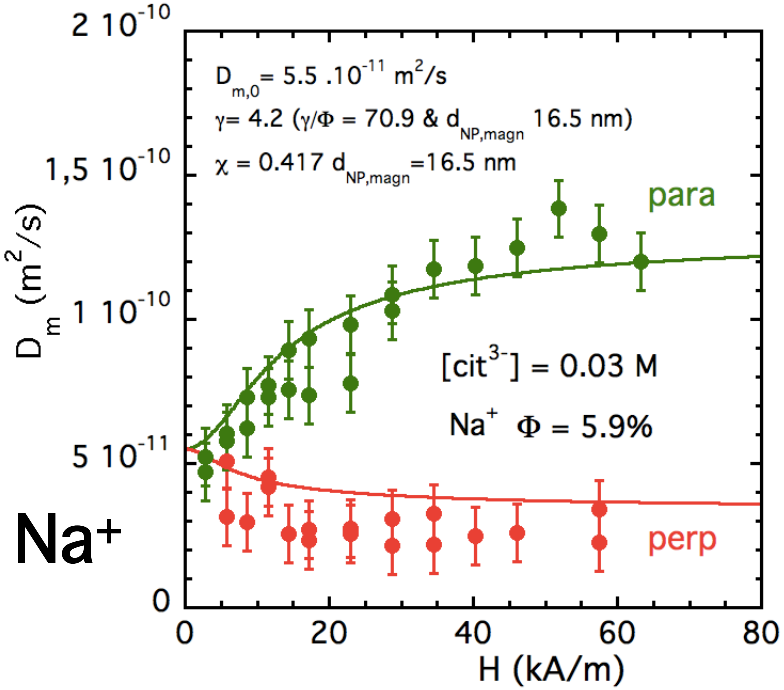
$$\vec{\nabla} T = \vec{0}$$



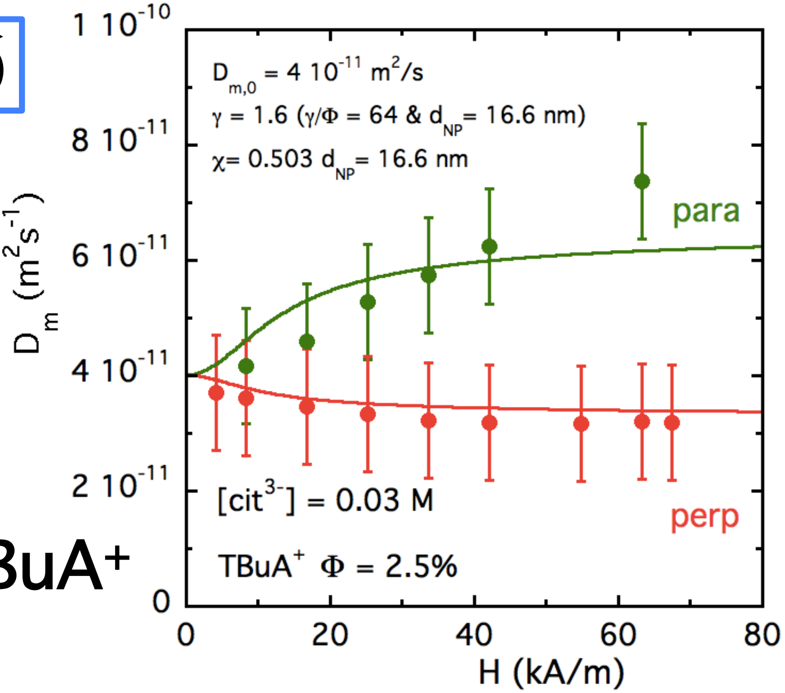
Under-field anisotropy of the diffusion coefficient

$$\vec{\nabla} T = \vec{0}$$

Na+



TBuA+



$$D_m^{\vec{H}_\perp} = \frac{kT}{\zeta}\left(\frac{1}{\chi} - \alpha_\lambda\right)$$

$$D_m^{\vec{H}_\parallel} = \frac{kT}{\zeta}\left(\frac{1}{\chi} + \beta_\lambda - \alpha_\lambda\right)$$

with

$$\alpha_\lambda = \frac{\lambda \gamma L^2(\xi_e)}{1 - \lambda \gamma L'(\xi_e)}$$

$$\beta_\lambda = \frac{\gamma L^2(\xi_e)}{\left(1 - \lambda \gamma L'(\xi_e)\right)\left(1 + (1-\lambda)\gamma L'(\xi_e)\right)}$$

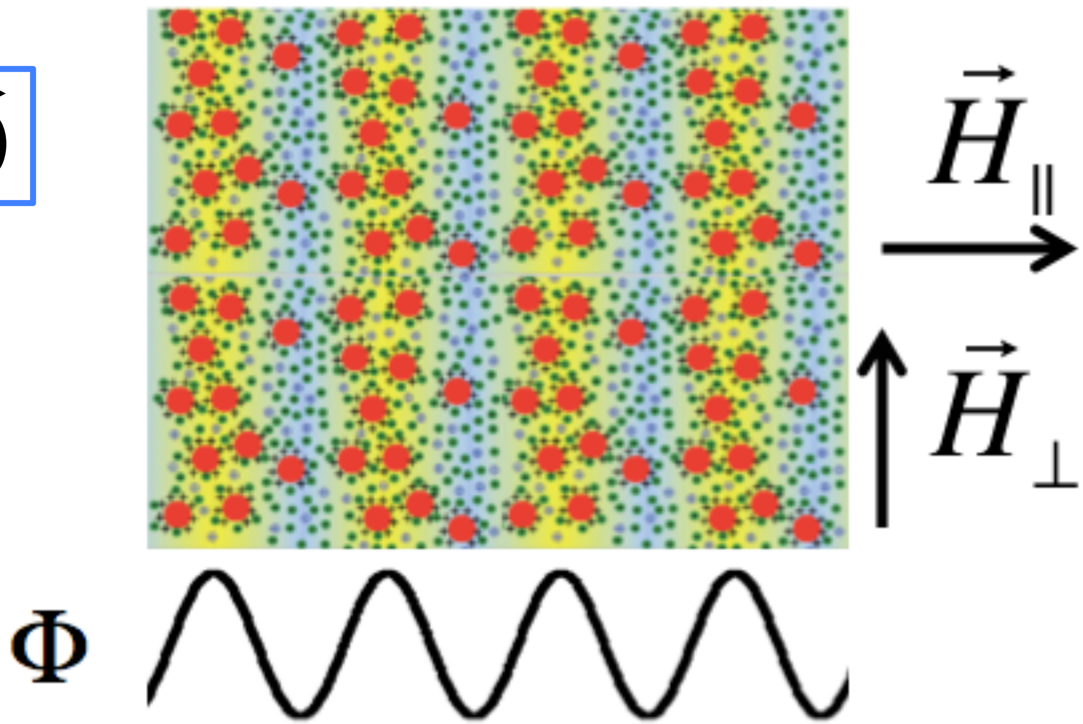
$$\xi_e = \xi + \lambda \gamma L(\xi_e) \qquad \xi = \mu_0 \frac{m_S v_{NP} H}{kT} \qquad L(\xi) = \coth \xi - 1/\xi \qquad \gamma = \mu_0 \frac{m_S^2 v_{NP} \Phi}{kT}$$

J.-C. Bacri et al *Phys. Rev. Lett.* **74** (1995) 5232-5035; *Phys. Rev. E* **52** (1995) 3936-3942

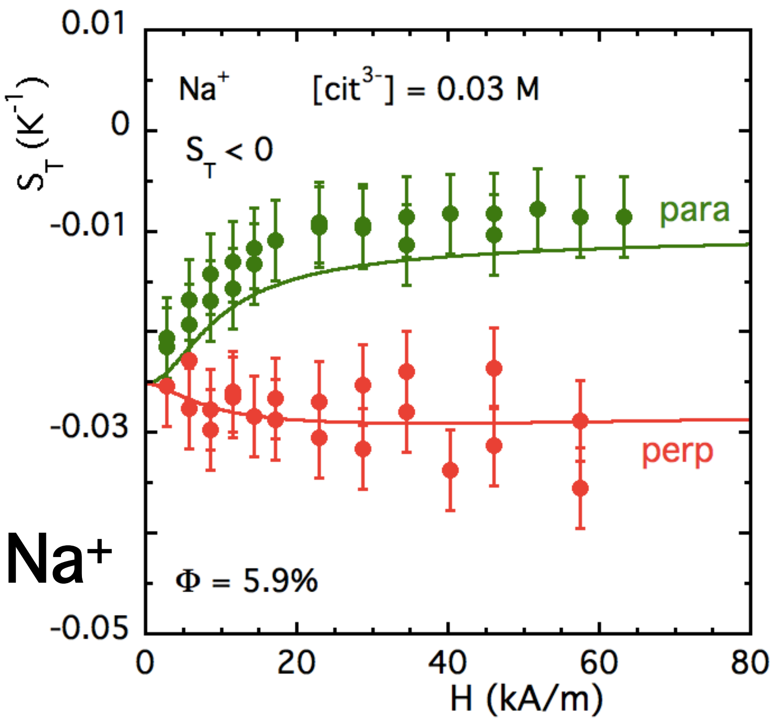
Soret coefficient measurements under magnetic field (in stationary conditions)

Local $\vec{\nabla}T$ either in phase or out-of-phase with respect to $\vec{\nabla}\Phi$ depending on S_T sign

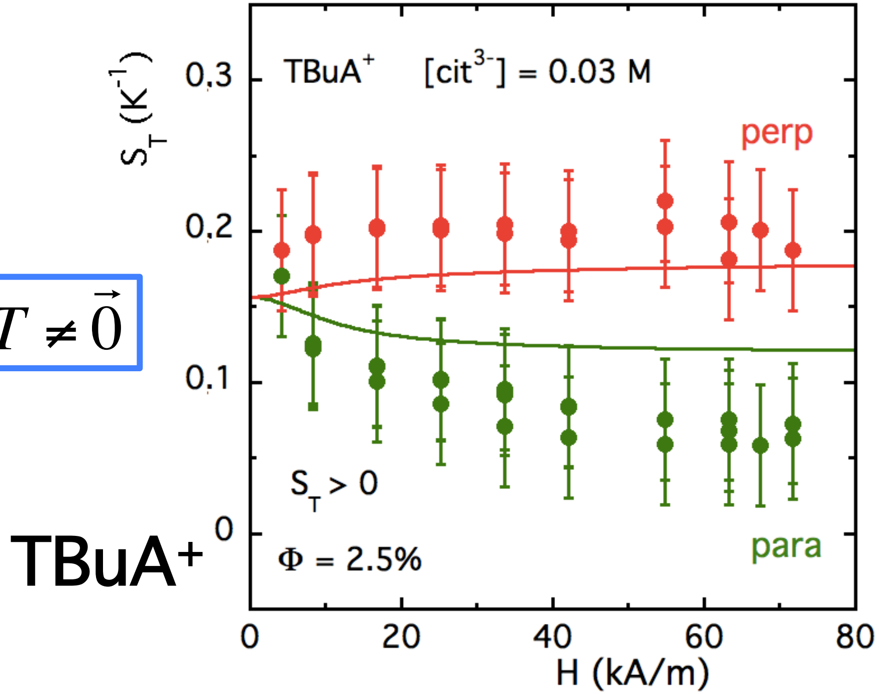
$$\vec{\nabla}T \neq \vec{0}$$



Under-field anisotropy of the Soret coefficient



$$\vec{\nabla} T \neq \vec{0}$$



$$S_T^{\vec{H}_\perp} = \frac{1}{kT\left(\frac{1}{\chi} - \alpha_\lambda\right)}\left[\frac{1}{n}\frac{\partial \Pi_{H=0}}{\partial T} + \hat{S}_{NP} - e\xi_0 S_e^{st} + k\,S_1\right]$$

$$S_1 = \frac{\xi_e L(\xi_e)}{1 - \lambda\gamma L'(\xi_e)} - \ln\frac{sh\,\xi_e}{\xi_e}$$

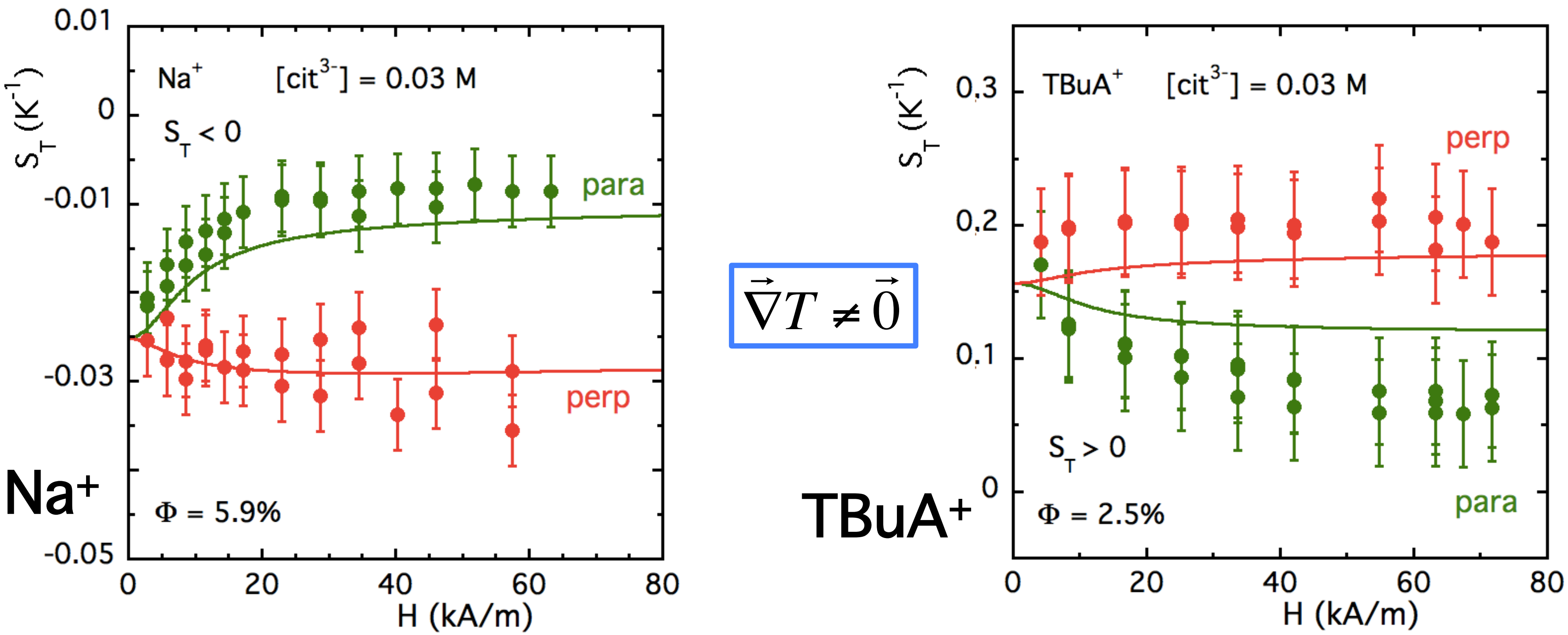
$$S_T^{\vec{H}_\parallel} = \frac{1}{kT\left(\frac{1}{\chi} + \beta_\lambda - \alpha_\lambda\right)}\left[\frac{1}{n}\frac{\partial \Pi_{H=0}}{\partial T} + \hat{S}_{NP} - e\xi_0 S_e^{st} + k\left(S_1 - S_2\right)\right]$$

with

$$S_2 = \beta_\lambda \frac{\xi_e L'(\xi_e)}{L(\xi_e)}$$

T. Salez et al *Entropy* 20 (2018) 405 1-27

Under-field anisotropy of the Soret coefficient



The ordering between $S_T^{H_\perp}$ and $S_T^{H_\parallel}$ depends on the sign of $S_T^{H=0}$ thus on the nature of the counterions

Increasing Soret coefficient by field application may allows increasing thermoelectric energy conversion in thermocells (*).

(*) T. Salez et al *Phys. Chem. Chem. Phys.* **19** (2017) 9409