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## Modelling phase transfer of electrolytes in emulsified microemulsions

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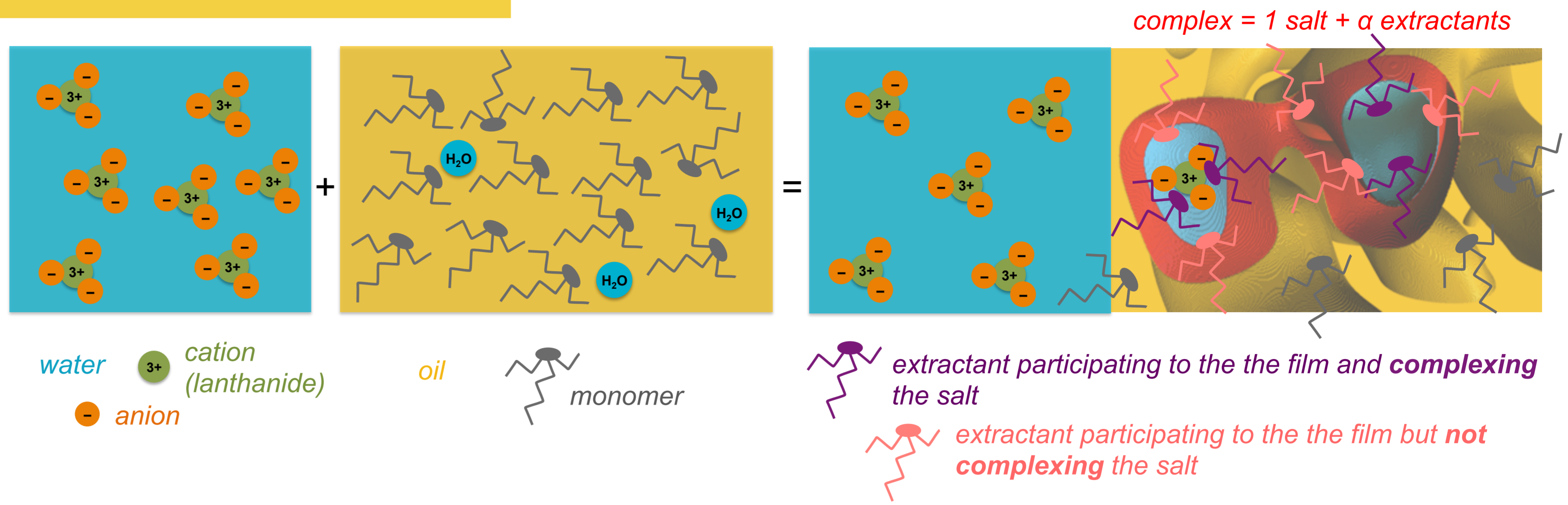
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## Introduction

- ✓ **Thermodynamics model** for describing the free energy differences of salts transfer from water to microemulsions.
- ✓ The system is composed of **two macroscopic phases**: a solvent phase assimilated to a **microemulsion** and an **aqueous phase**
- ✓ Between the two macroscopic phases, **ions and water may be exchanged**, thus the potential reads:

$$B = G - N_{\text{salt}}\mu_{\text{salt}} + N_{\text{water}}\mu_{\text{water}}$$

$B$  = generalized semi-grand potential,  $G$  = Gibbs free energy,  $\mu$  = chemical potential, and  $N$  = number of molecules



## Theory

- ✓ **Three levels of approximation** for calculating the free energy:

### Langmuir-like model for ion complexation by curved surfaces

All extractants form the highly curved film in the water-poor microemulsion, there is no monomer to film equilibria (CAC = 0).

Extractants at the interface:

- free (e1)
- complexed to the salt (e2)

Gibbs energy

$$G = N_{\text{oil}}\mu_{\text{oil}} + N_{\text{water}}\mu_{\text{water}} + N_{e1}\mu_{e1} + N_{e2}\mu_{e2}$$

Semi-grand potential

$$B = N_{\text{oil}}\mu_{\text{oil}} + N_{e1}\mu_{e1} + N_{e2}\mu_{e2} - N_{\text{salt}}\mu_{\text{salt}}$$

Langmuir-like equation

$$\frac{N_{e2}}{N_{e1} + N_{e2}} = \frac{K^0 a_s^{1/\alpha}}{1 + K^0 a_s^{1/\alpha}}$$

Mass Action Law constant

$$K^0 = \exp\left(\frac{\mu_{e2}^0 - \mu_{e1}^0 - \mu_{\text{salt}}^0/\alpha}{k_B T}\right)$$

### Dissolved monomers to interfacial film equilibrium of the extractant

We considered the monomer to film equilibria which is experimentally known to be driven by the transfer of species from water to oil [1].

The extractant molecules are shared between the surface (free e1 and complexed e2) and the oily part (dissolved monomer ef).

Gibbs energy

$$G = N_{\text{oil}}\mu_{\text{oil}} + N_{\text{water}}\mu_{\text{water}} + N_{e1}\mu_{e1} + N_{e2}\mu_{e2} + N_{ef}\mu_{ef}$$

Semi-grand potential

$$B = N_{\text{oil}}\mu_{\text{oil}} - N_{\text{salt}}\mu_{\text{salt}} + N_{e1}\mu_{e1} + N_{e2}\mu_{e2} + N_{ef}\mu_{ef}$$

Critical aggregation concentration (CAC)

$$\text{CAC} = \frac{\overline{\text{CAC}}}{1 + K^0 a_s^{1/\alpha}} \quad \overline{\text{CAC}} = \text{CAC without extracted salt}$$

### Variation of microstructure induced by complexation

In addition to the monomer to film equilibria we also took into account the variation of the microemulsion microstructure (area, curvature and packing).

The microemulsion microstructure yields a contribution to the Gibbs energy and is solved by a random Gaussian Field model [2].

Gibbs energy

$$G = N_{\text{oil}}\overline{\mu_{\text{oil}}} + N_{\text{water}}\overline{\mu_{\text{water}}} + N_{e1}\overline{\mu_{e1}} + N_{e2}\overline{\mu_{e2}} + N_{ef}\overline{\mu_{ef}} + G^{\text{Helfrich}}(N_{e1}, N_{e2}, N_{\text{water}})$$

with

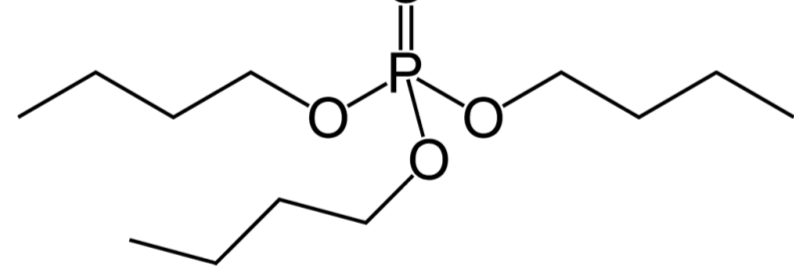
$$\mu_i = \overline{\mu}_i + \frac{\partial G^{\text{Helfrich}}}{\partial N_i}$$

and where the molecular packing parameters [3] have been converted into the Helfrich formalism [4]

$$H_0 = \frac{p_0 - 1}{L_{\text{extractant}}} \quad p_0: \text{spontaneous packing parameter}, H_0^c: \text{spontaneous curvature}$$

## Practical case of TriButylPhosphate

### Physical parameters used for TBP



Chain length of TBP

$$L_{\text{extractant}} = 1 \text{ nm}$$

Spontaneous packing parameter

$$p_0 = 3.5$$

Polar head area

$$a_0 = 0.8 \text{ nm}^2$$

Rigidity constant

$$\kappa = 2.4 k_B T / \text{molecule}$$

Volume

$$V = 0.45 \text{ nm}^3 / \text{molecule} = 270 \text{ cm}^3 \text{ mol}^{-1}$$

Polar fraction

$$\Phi_{\text{polar}} = 0.16$$

Critical Aggregation Concentration

$$\text{CAC} = 0.4 \text{ mol L}^{-1}$$

Number of extractants per salt

$$\alpha = 2$$

### Predictions of the model

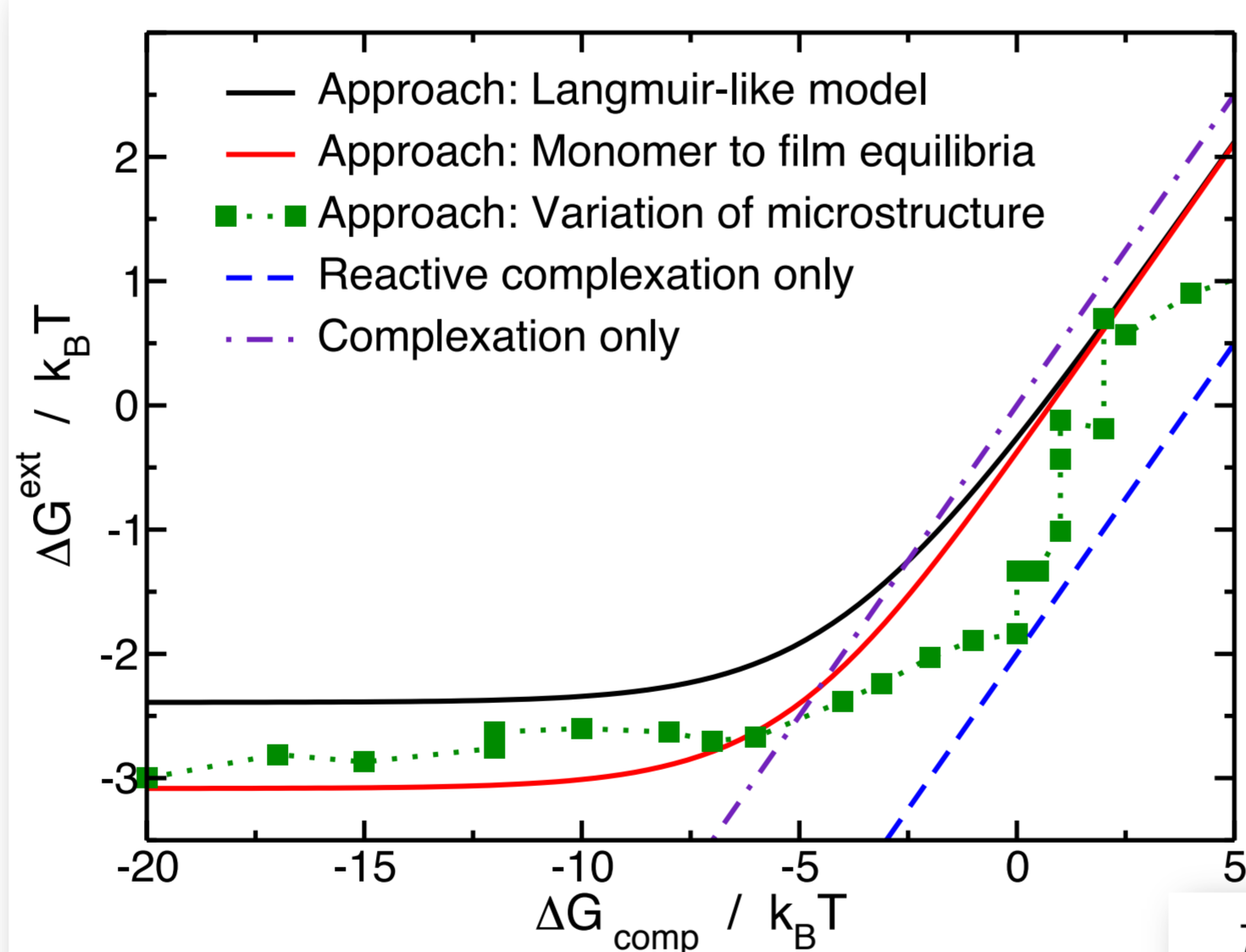


Fig.: Free energy of water-oil transfer as a function of the free energy of complexation as predicted by our model using the different levels of approximation for the calculation of the free energy.

Fig.: Effective selectivity between a small and a big salt as a function of the free energy of complexation ( $C_{\text{extractant}} = 1 \text{ mol L}^{-1}$ ).

$$\Delta G^{\text{ext}} = -k_B T \ln\left(\frac{[\text{salt}]_{\text{org}}}{a_{\text{salt}}}\right)$$

$$\text{Selectivity} = \frac{K_{\text{app,ext}}^{\text{small}}}{K_{\text{app,ext}}^{\text{big}}}$$

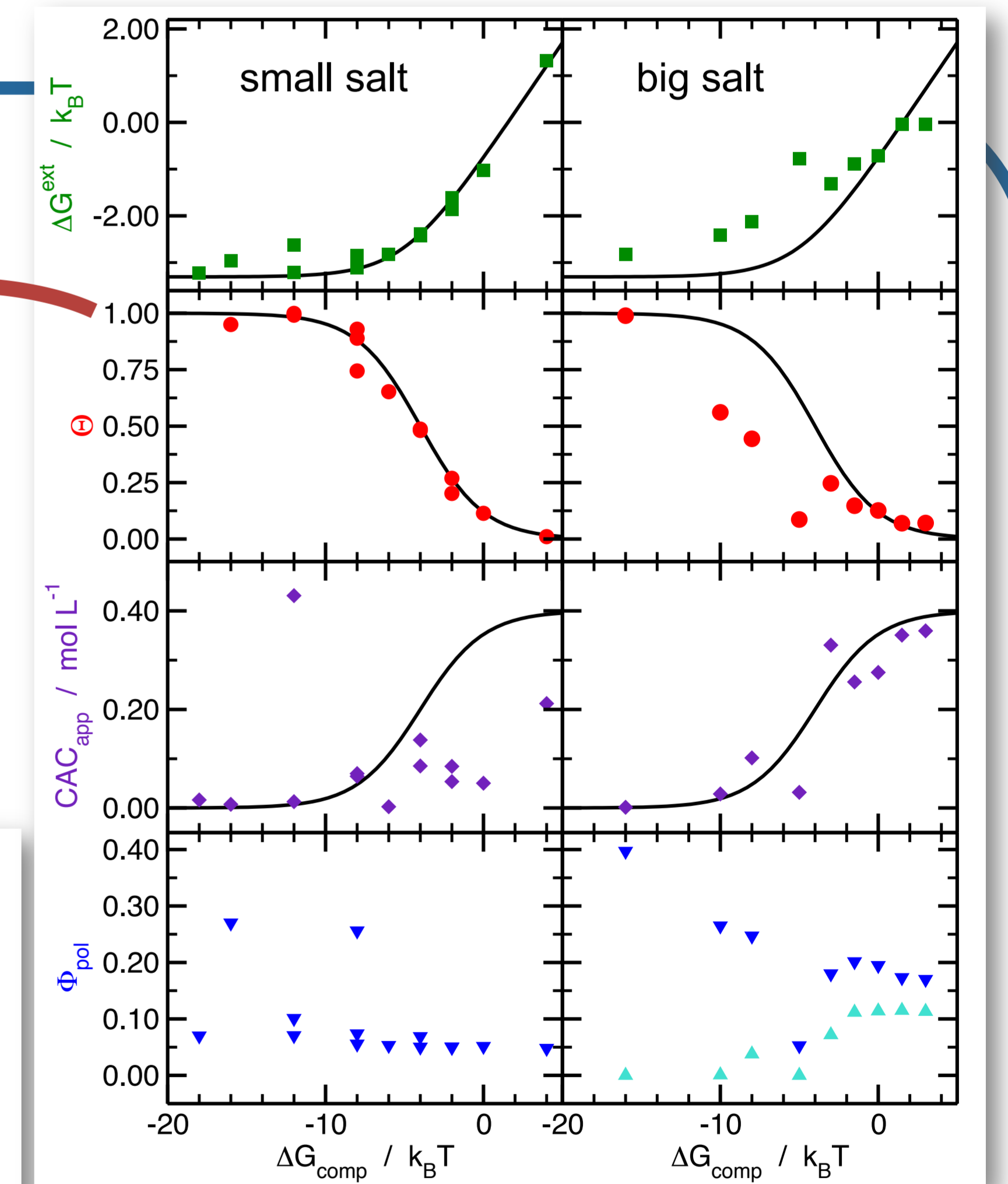
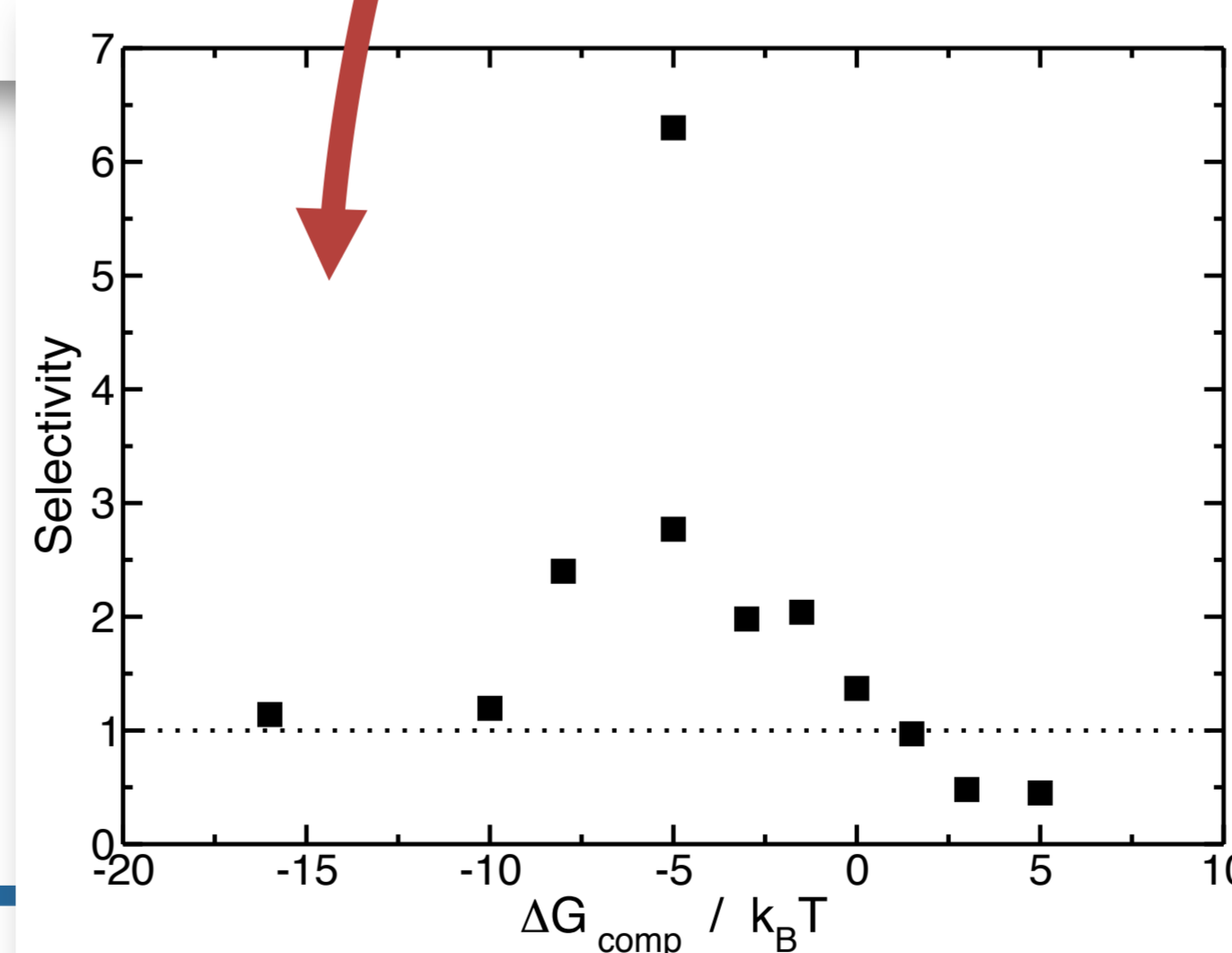


Fig.: Comparison of free energy of extraction, complexed fraction, apparent CAC and polar fraction as a function of the free energy of complexation calculated for a small and a big salt ( $C_{\text{extractant}} = 1 \text{ mol L}^{-1}$ ).

### Water/Oil/Extractant Microstructures

Without extraction of salt

Extraction of small salt

Extraction of big salt

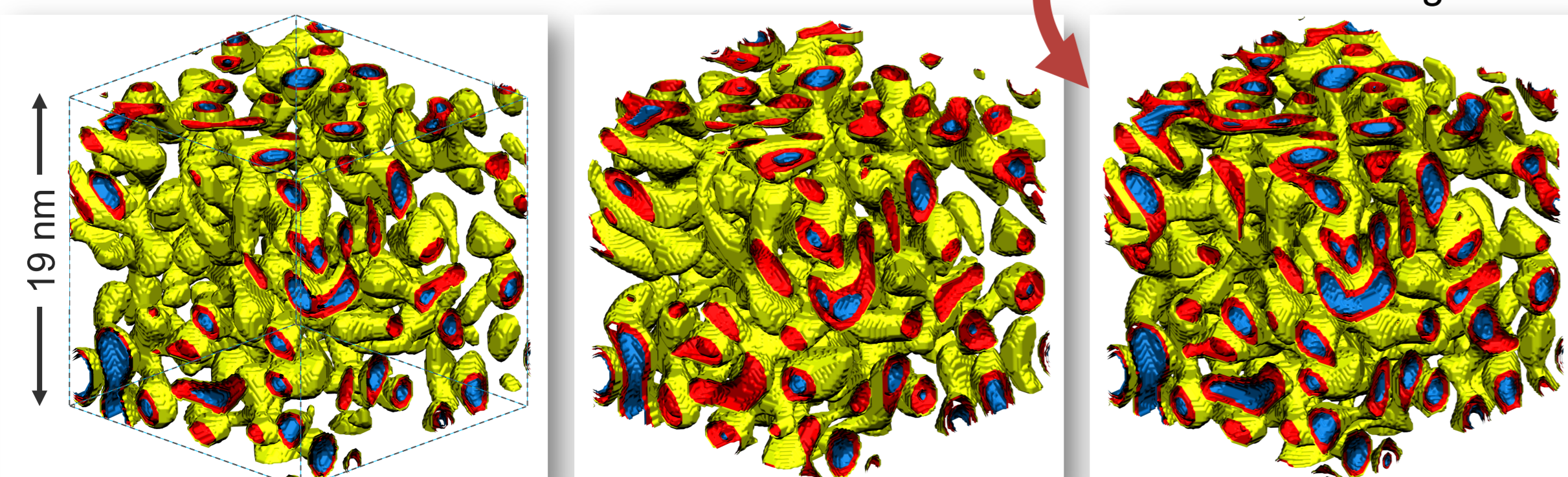


Fig.: 3D field projections of the direct space representation predicted by the Gaussian random field model.

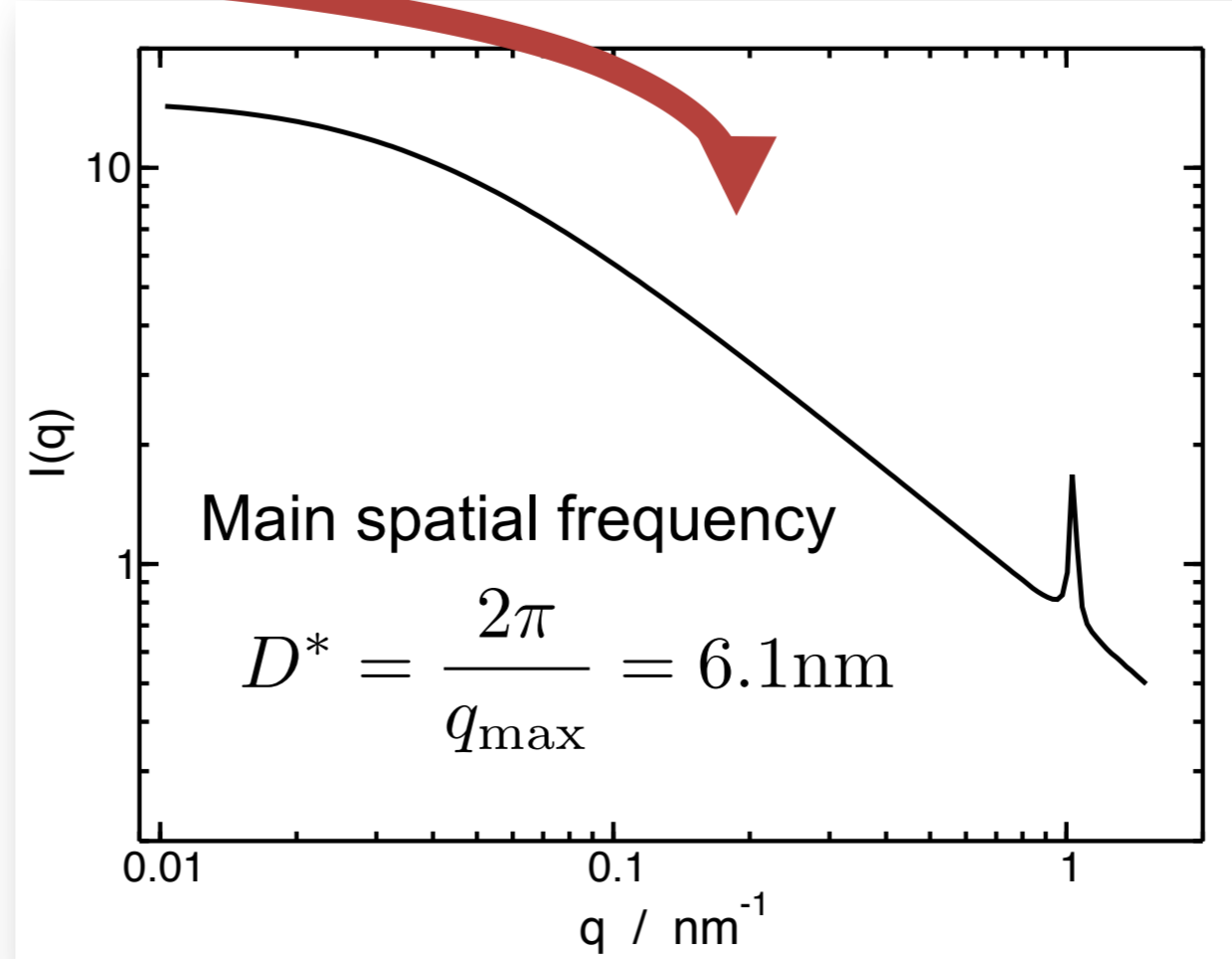


Fig.: Corresponding scattering function predicted by the Gaussian random field model.

## References

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