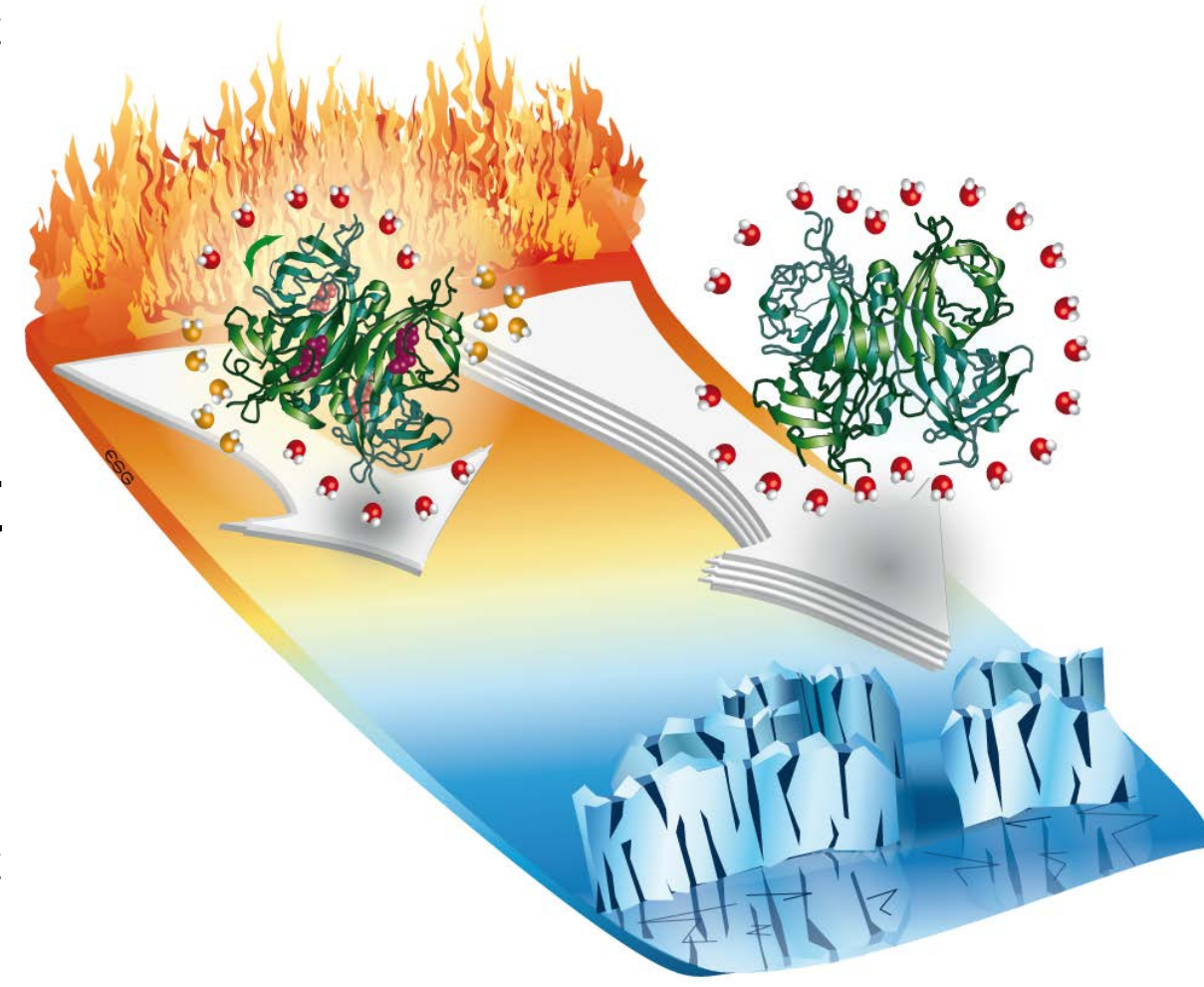
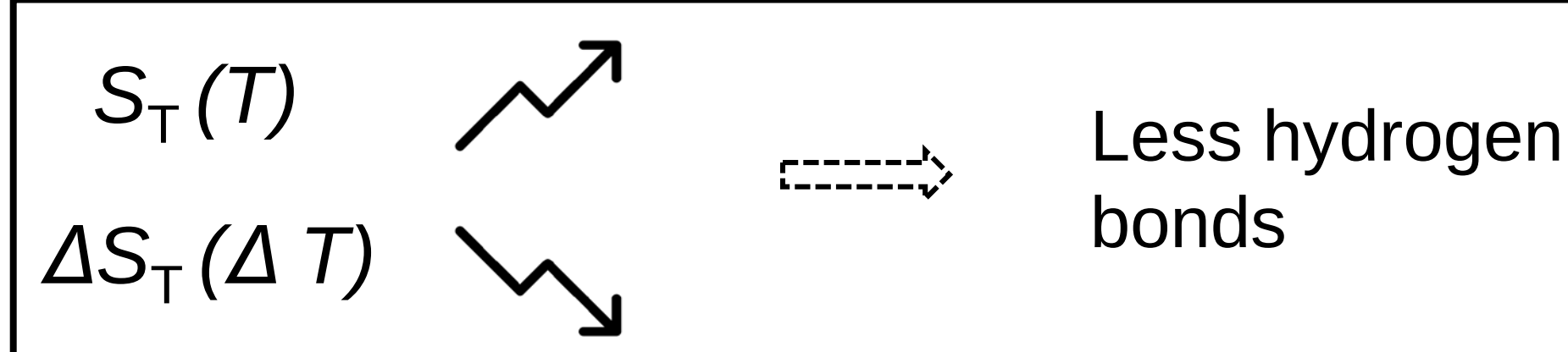


Motivation [1],[6],[7],[8]

- Long term goal:** Thermophoretic study of protein-ligand binding reactions
- Preliminary step:** Thermophoresis of salts, which are important components in buffer systems
- Do charge and hydration effects influence the thermophoretic behavior?
- Can the temperature dependence of S_T fitted using an empirical equation?



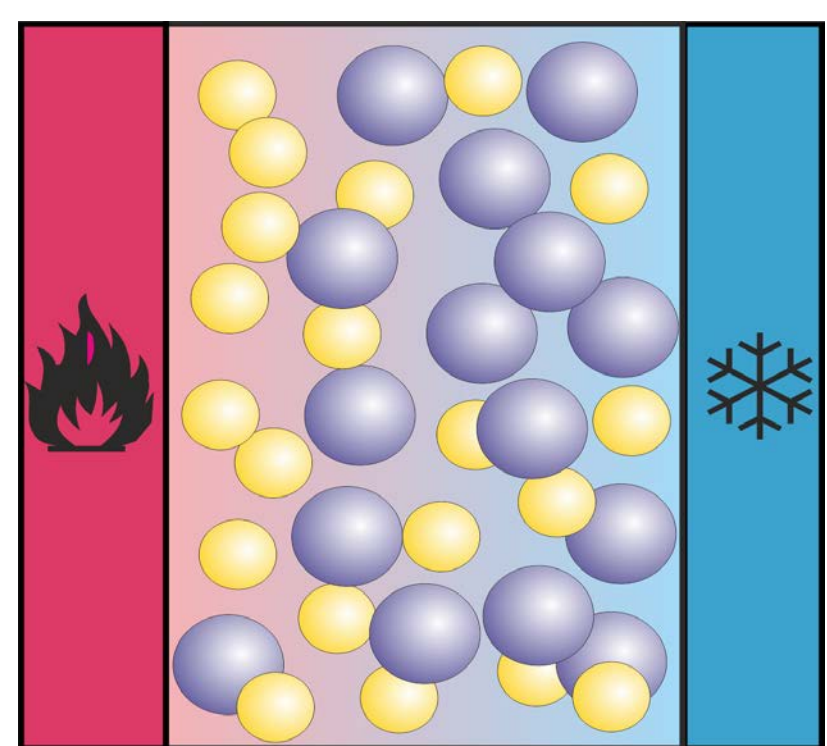
$$S_T(T) = S_T^\infty [1 - \exp\left(\frac{T^* - T}{T_0}\right)]$$



Typical for non-ionic solutes in water

- Is there a minimum of S_T with concentration as previously reported for salts like NaCl, KCl and LiCl?

Thermophoresis [2]

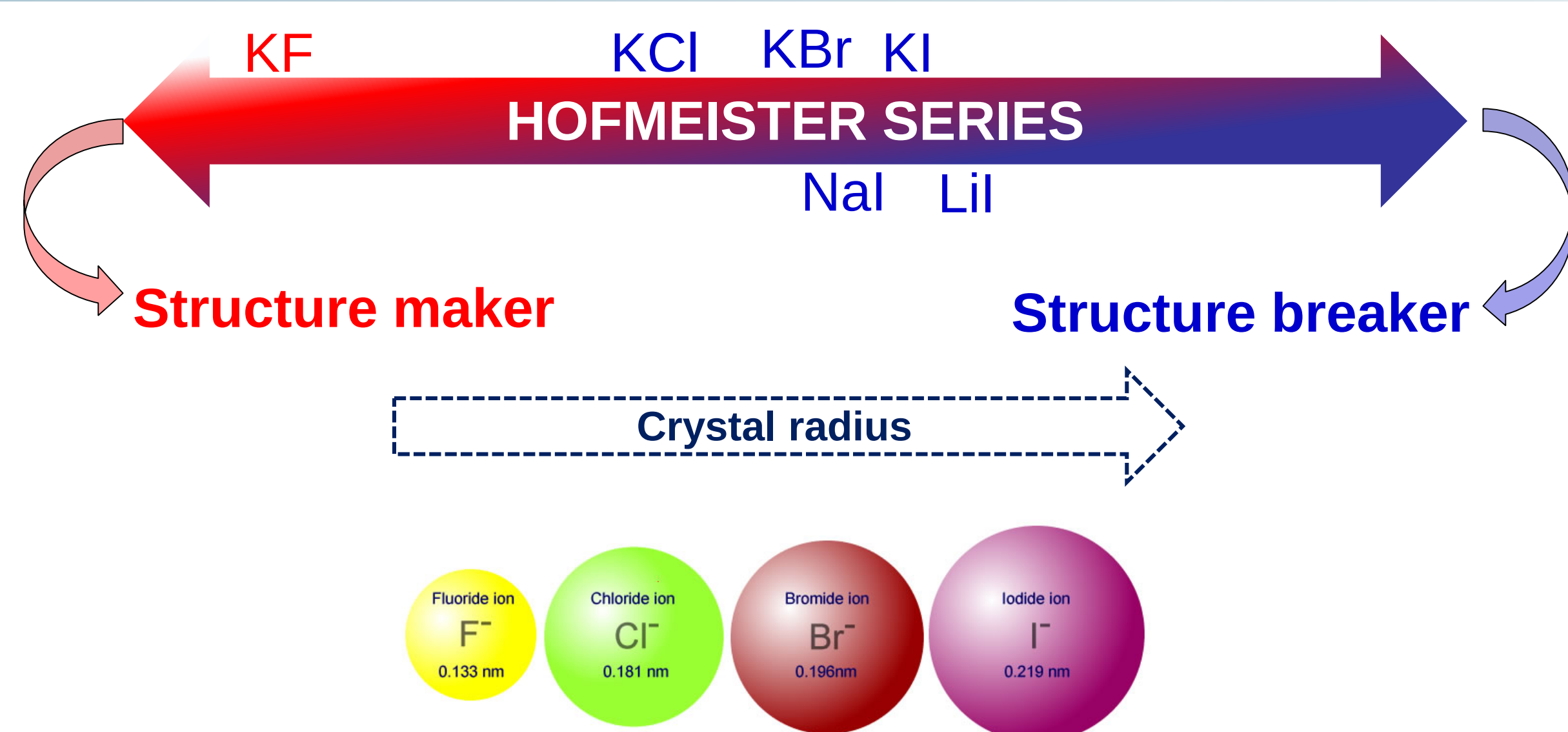


Flux $\vec{j}$ along a temperature gradient $\vec{\nabla}T$:
 (1) thermal diffusion D_T along a temperature gradient $\vec{\nabla}T$
 (2) Fickian diffusion D along the induced concentration gradient $\vec{\nabla}c$.

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

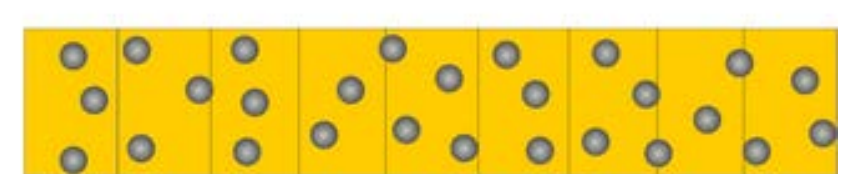
Steady state: $\vec{j} = 0$ $S_T \equiv \frac{D_T}{D} = -\frac{1}{c(1-c)} \frac{\Delta c}{\Delta T}$

Choice of systems [3]

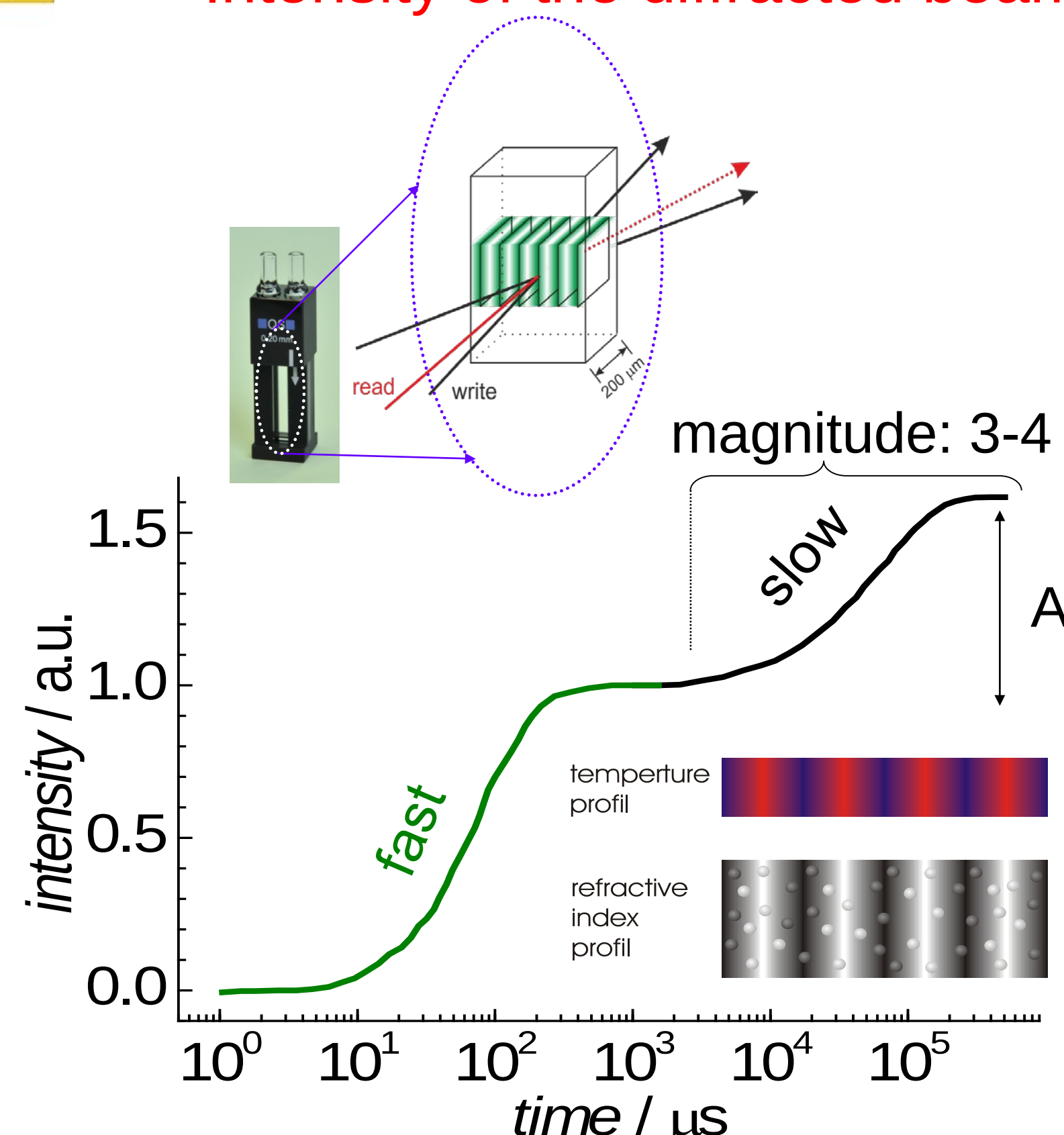
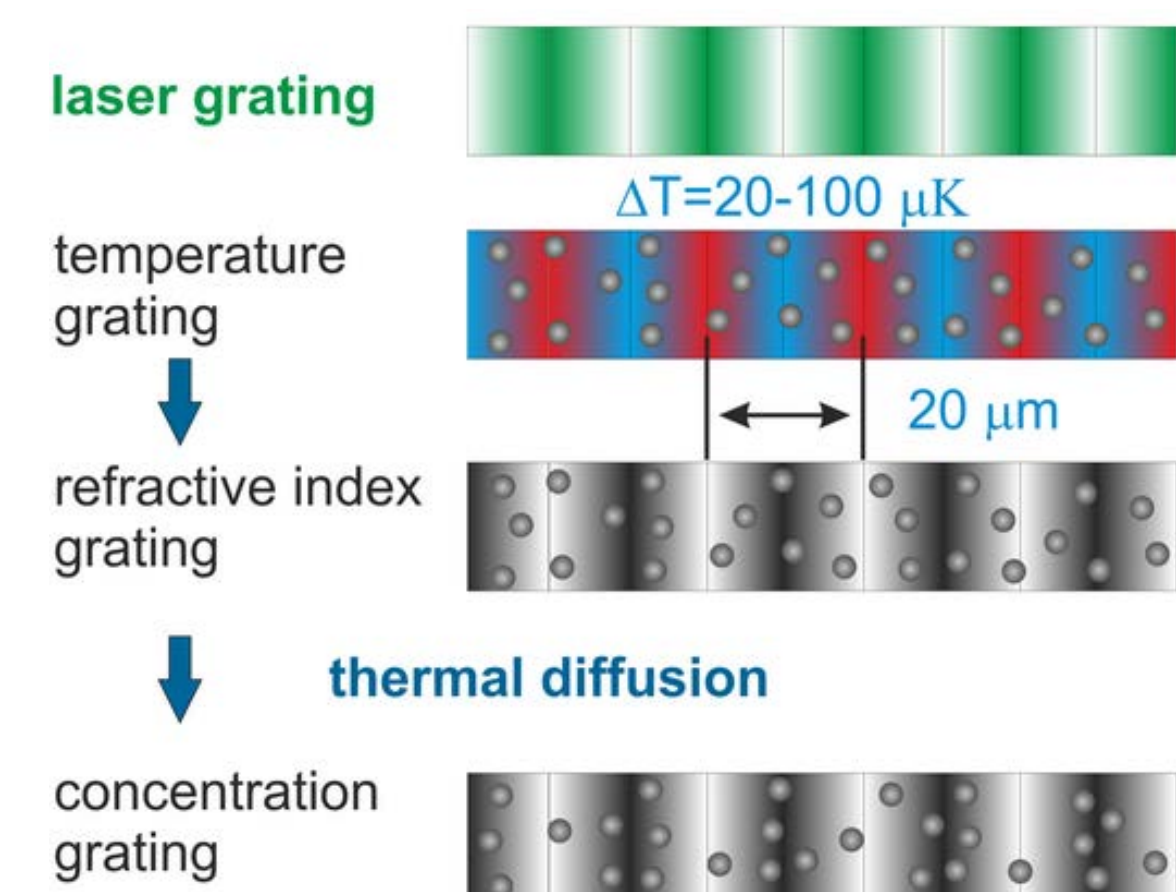
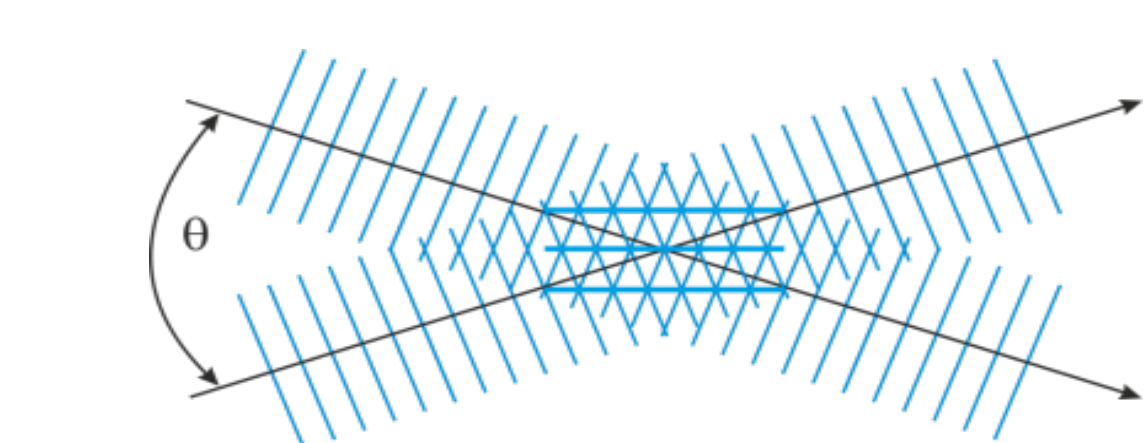


IR-TDFRS: Setup [4], [5]

homogeneous temperature and particle distribution

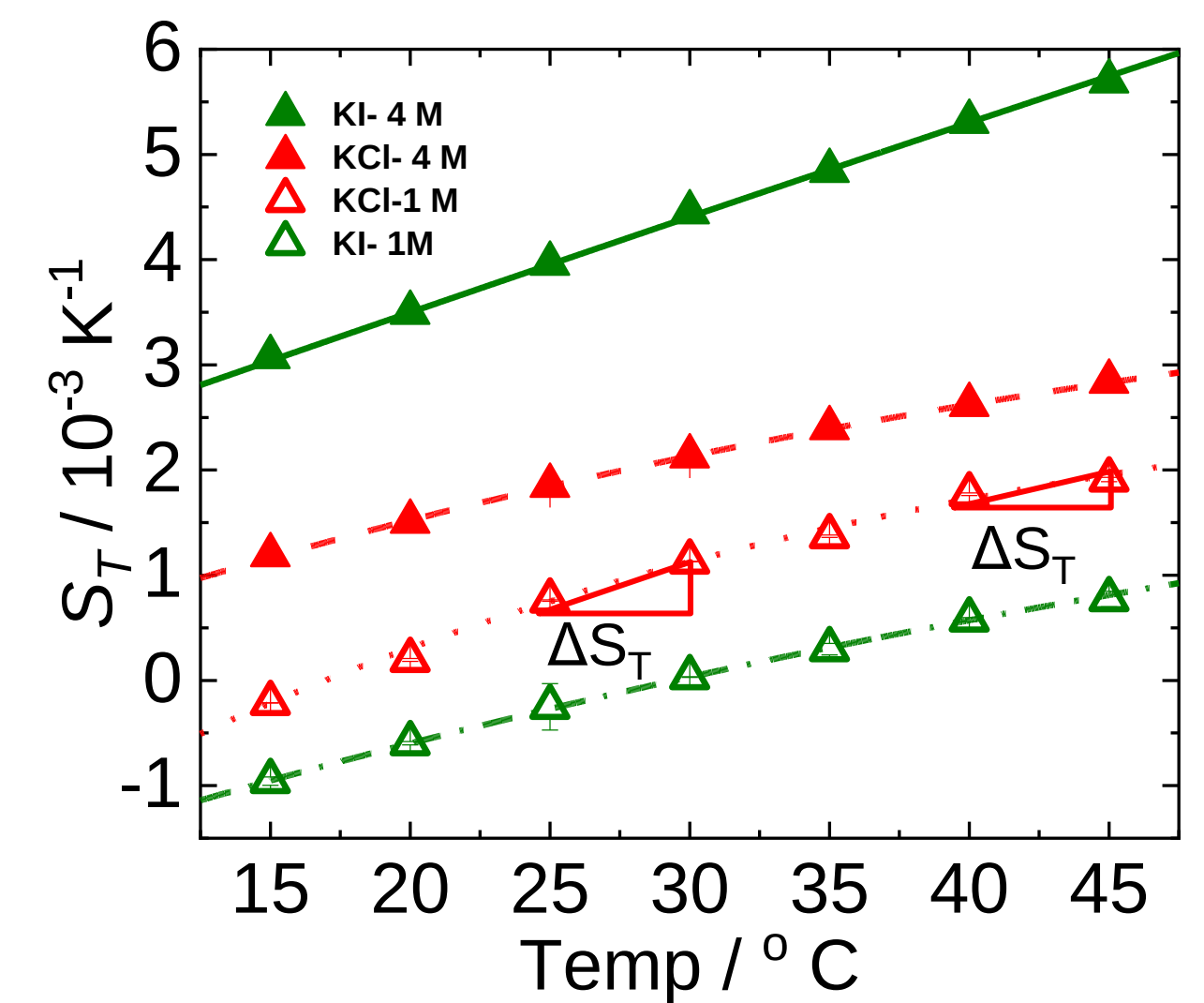
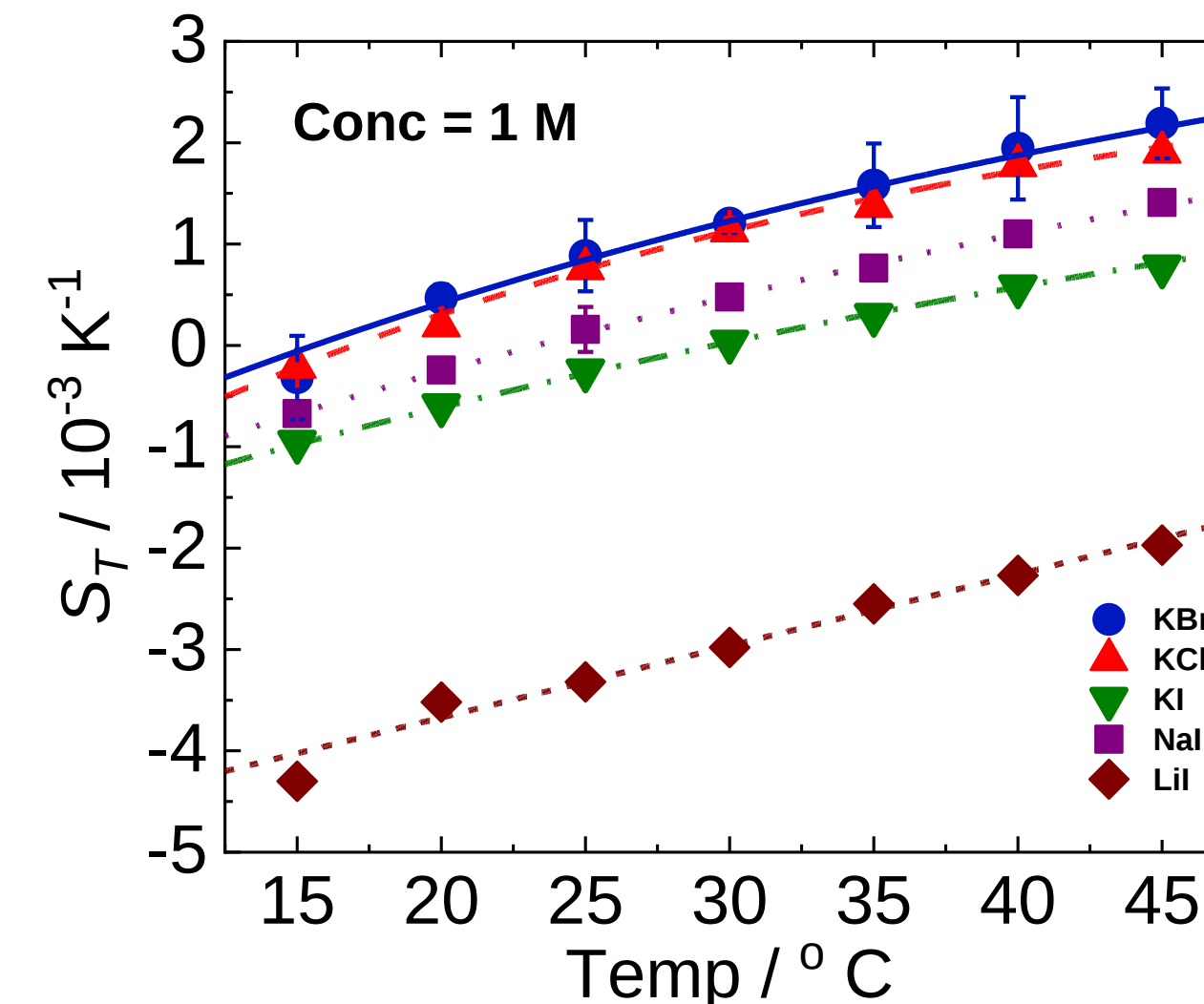


Measured quantity: Intensity of the diffracted beam



TDFRS: results [4]

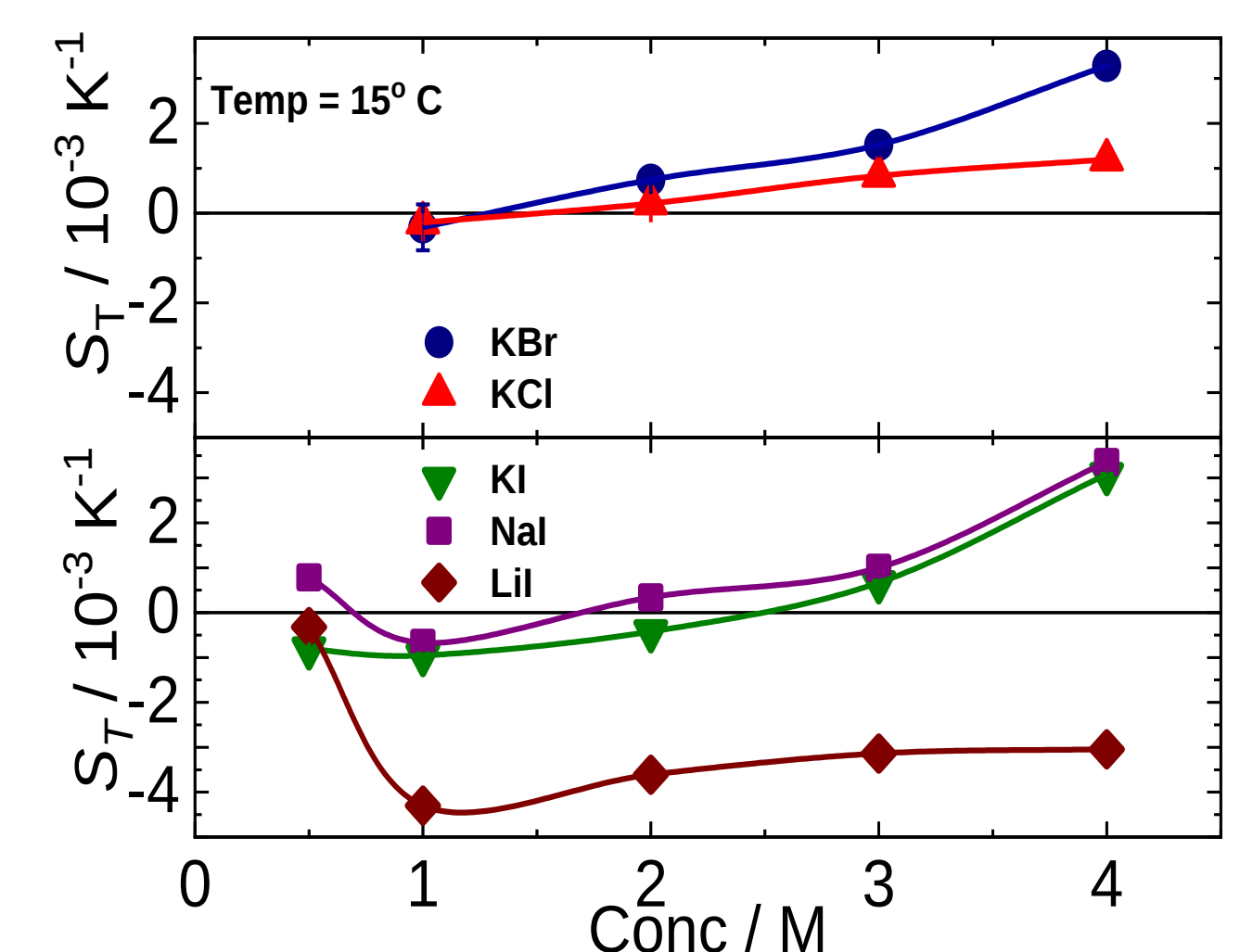
1. Temperature dependence of S_T



- Curves are fitted using the empirical equation.
- KCl, KBr, NaI and LiI behave like non-ionic water soluble solutes.
- KI deviates at higher concentrations.

2. Concentration dependence of S_T

- Minimum: KI, NaI, LiI
- No minimum: KCl, KBr
- Minimum was observed at all temperatures for iodide salts

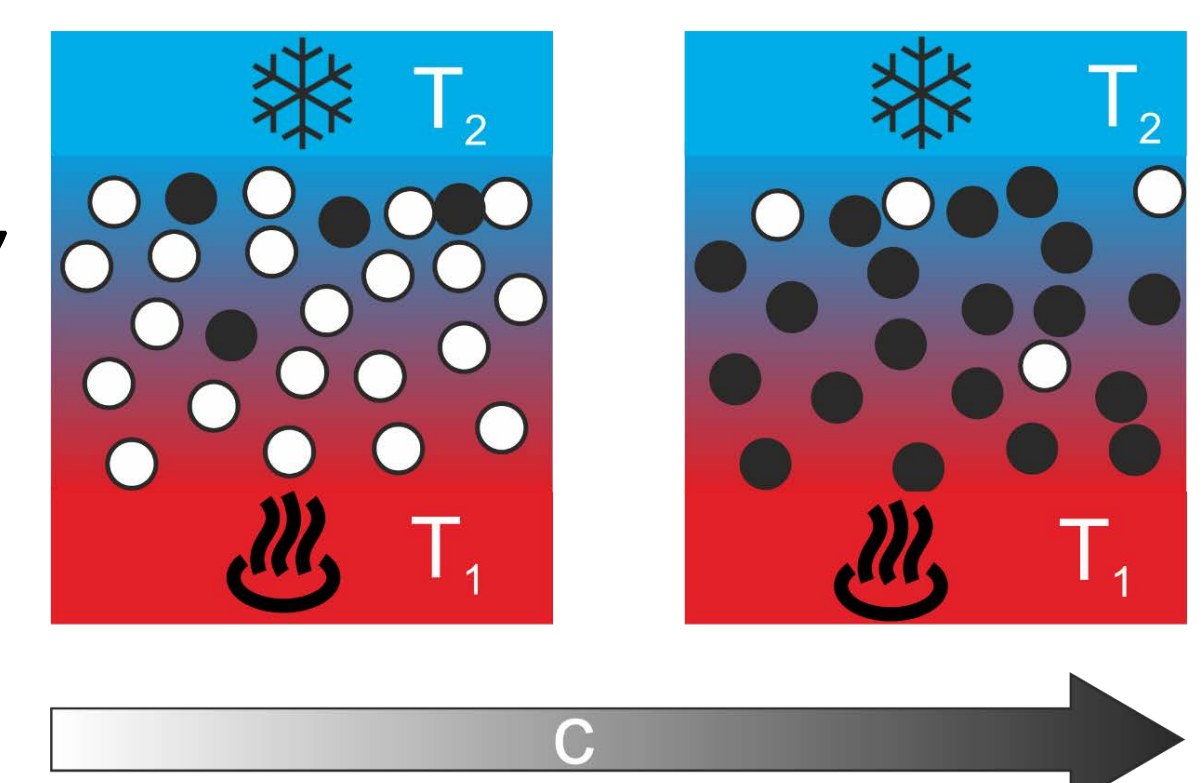


Prigogine predicts sign change of S_T with concentration

$$\epsilon_{sw} > \epsilon_{ss}; \epsilon_{sw} > \epsilon_{ww}$$

$$T_1 > T_2$$

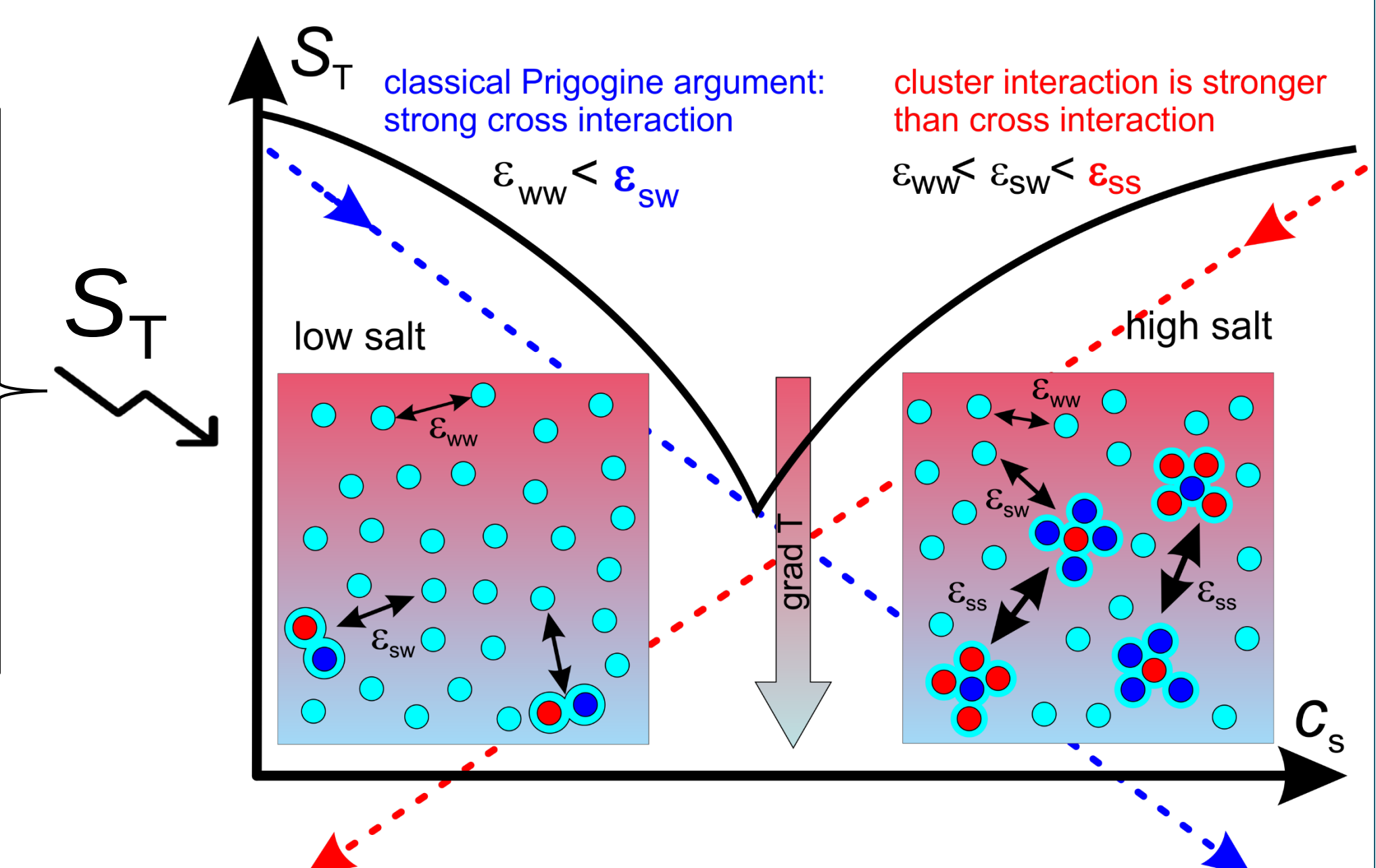
$$\frac{e^{-\frac{\epsilon_{sw}}{kT_1}}}{\propto E(T_1)} > \frac{e^{-\frac{\epsilon_{sw}}{kT_2}}}{\propto E(T_2)}$$



○ component 1
● component 2

Minority component goes to the cold

- Low c_s :**
 ϵ_{sw} dominates
 $c_s \nearrow \rightarrow$ fewer ϵ_{sw} interactions
- High c_s :**
 ϵ_{ss} dominates
 $c_s \nearrow \rightarrow$ fewer ϵ_{ss} interactions



Microscopic explanation: Work under progress

Conclusion [5],[6],[7]

- KCl, KBr, NaI and LiI depict a similar T -dependence of S_T as non-ionic solutes
- Probably structural changes, in particular the hydrogen bonding network influence the thermophoretic behavior

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