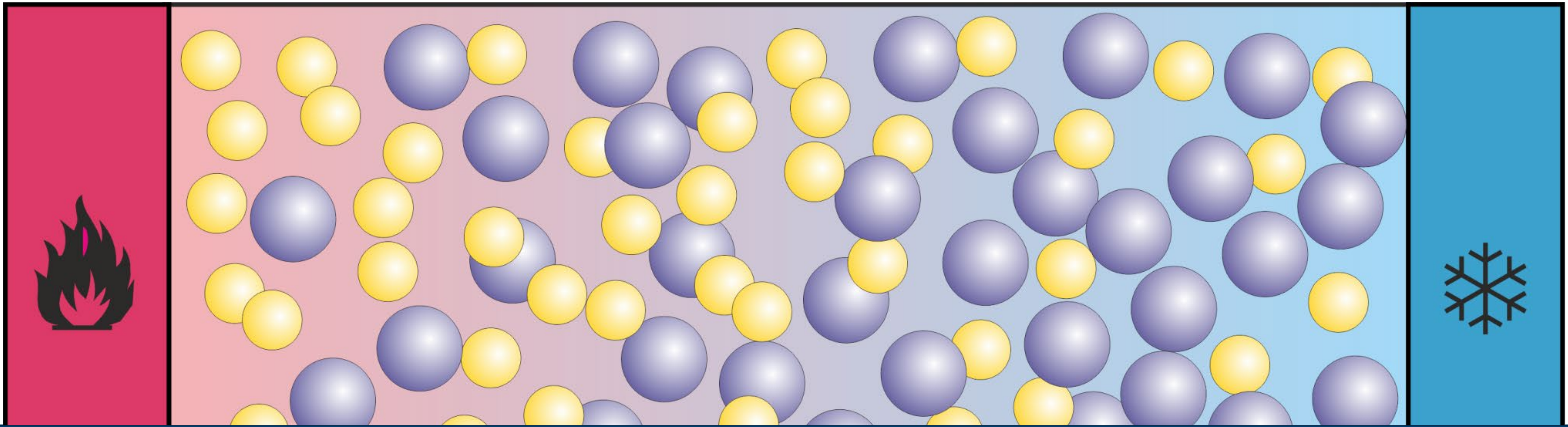


UNDERSTANDING THE MINIMUM OF SORET COEFFICIENT FOR ALKALI HALIDES IN WATER

22.06.2022 I SHILPA MOHANAKUMAR

MOTIVATION

Thermophoresis

- Motion of solute particles induced by thermal gradient.

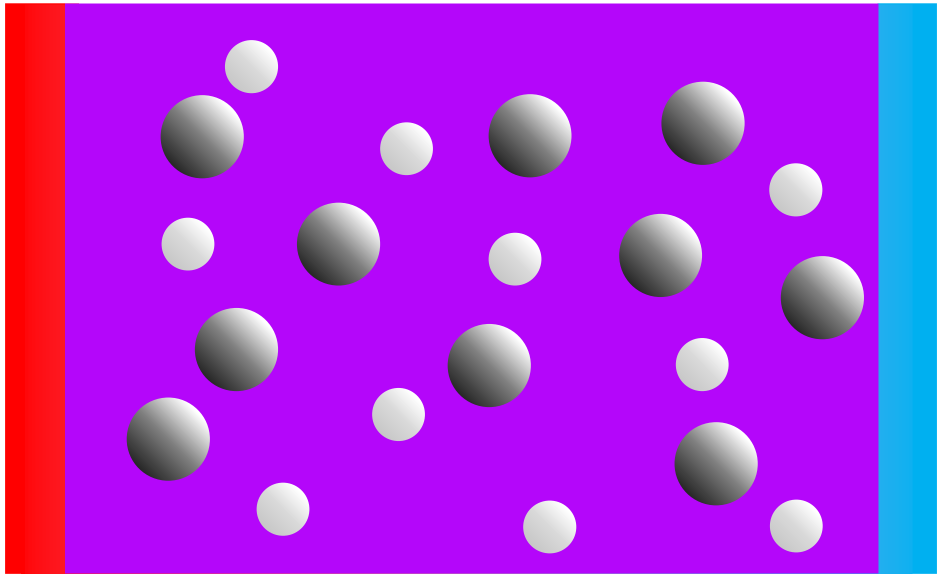
$$\vec{j} = -\rho D \vec{\nabla} w - w(1-w)\rho D_T \vec{\nabla} T$$

w	weight fraction
ρ	mass density
$\vec{j}$	flux
T	temperature

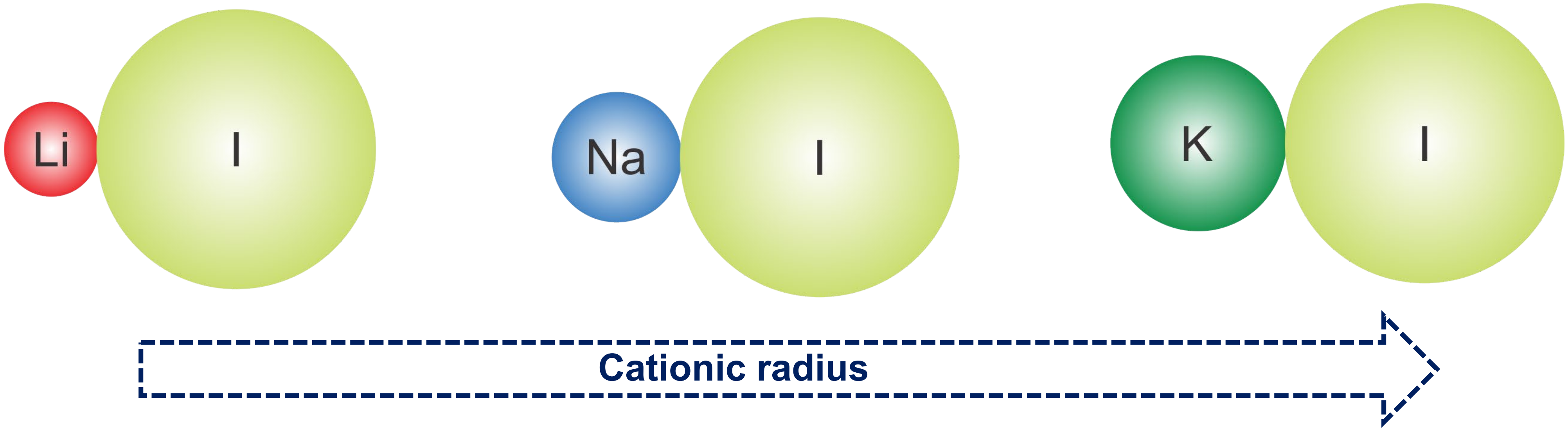
$$S_T \equiv \frac{D_T}{D} = -\frac{\vec{\nabla} w}{w(1-w)\vec{\nabla} T}$$

At stationary state,

$$\boxed{S_T \propto \frac{\Delta w}{\Delta T}}$$



THERMOPHORESIS OF SALT SYSTEMS

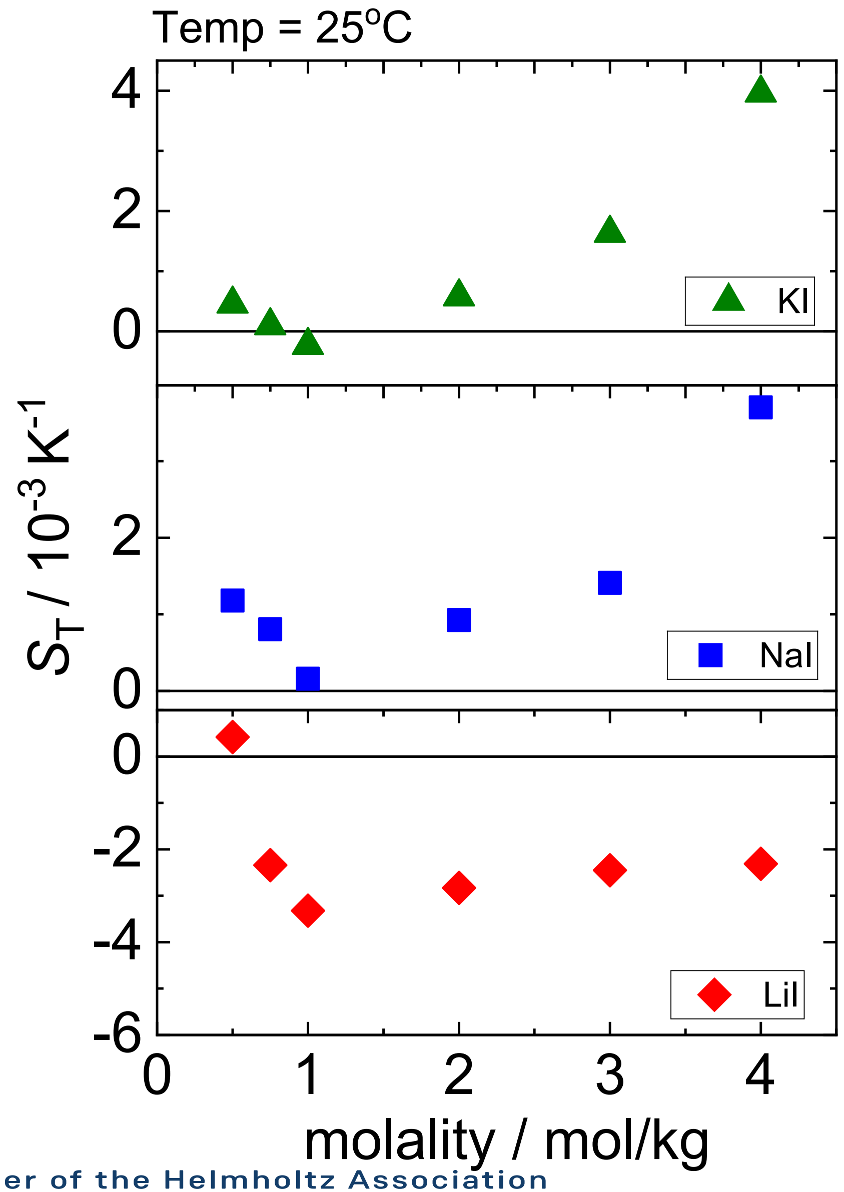


Cationic radius

Ion	Radius (Å)
Li^+	0.74
Na^+	1.02
K^+	1.38
I^-	2.2

R. Heyrovsả, *Chem. Phys. Lett.*, **163**(1989), 207

CONCENTRATION DEPENDENCE OF S_T

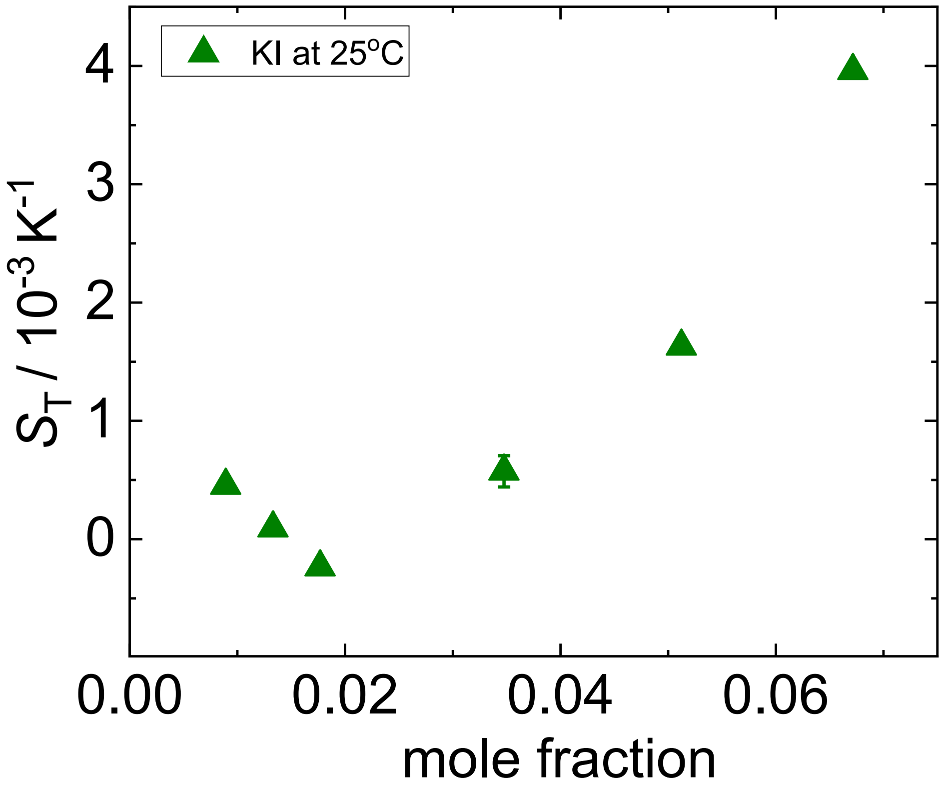


- S_T shows a minimum with concentration for all the studied systems
- Below the minimum, we observe linear behaviour

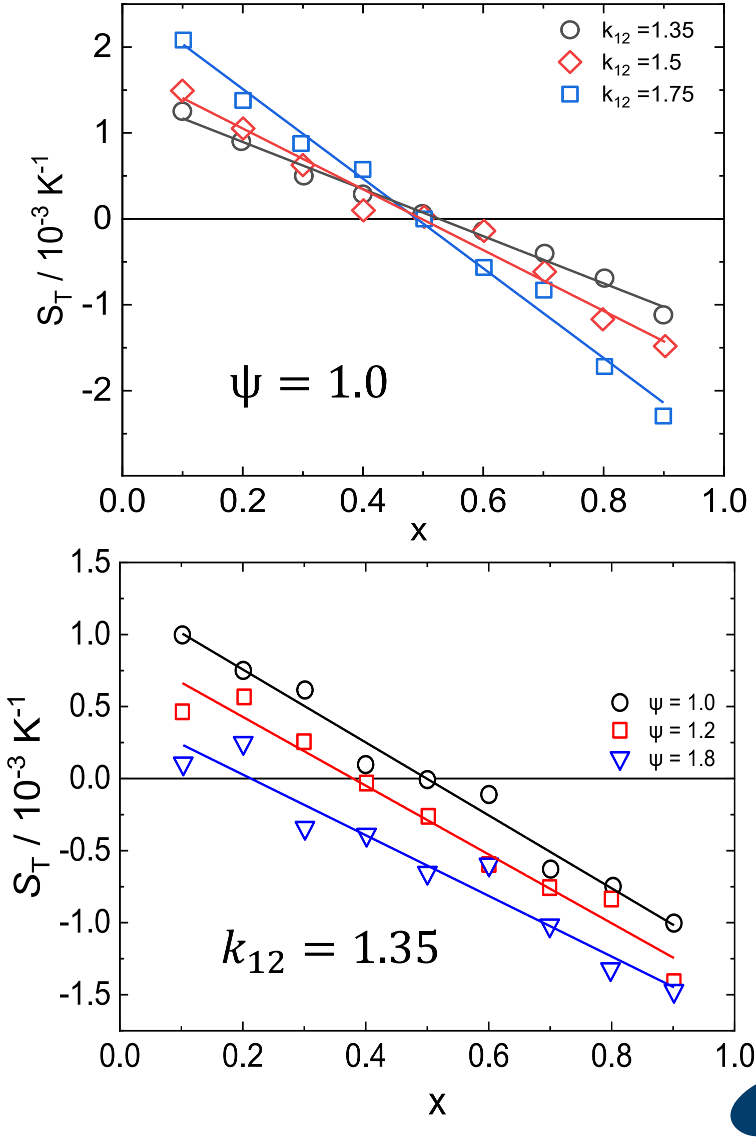
What is the reason for this minimum?

CAN WE MAP TO LJ FOR DILUTED SOLUTIONS?

Experimental results:



Artola et al., Phys Rev Lett 98, 2007, 125901



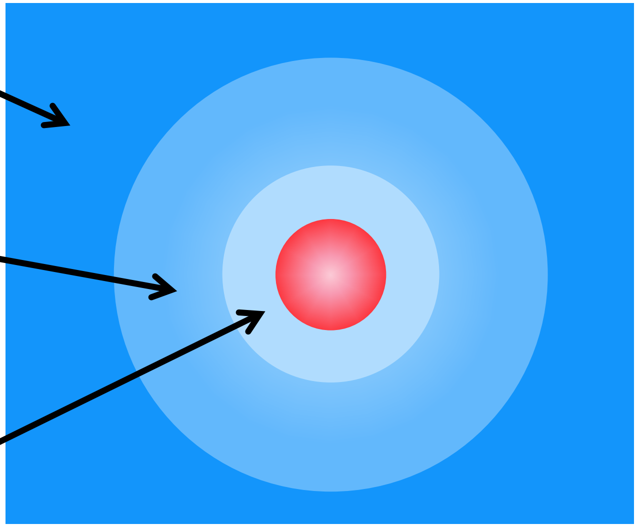
Simulation results:

$$k_{12} = \frac{\varepsilon_{12}}{\sqrt{\varepsilon_{11}\varepsilon_{22}}}$$

$$\psi = \frac{\varepsilon_{22}}{\varepsilon_{11}}$$

WHAT IS THE REASON FOR THIS MINIMUM?

Structure of water near the salt molecule is different from bulk water



Bulk water

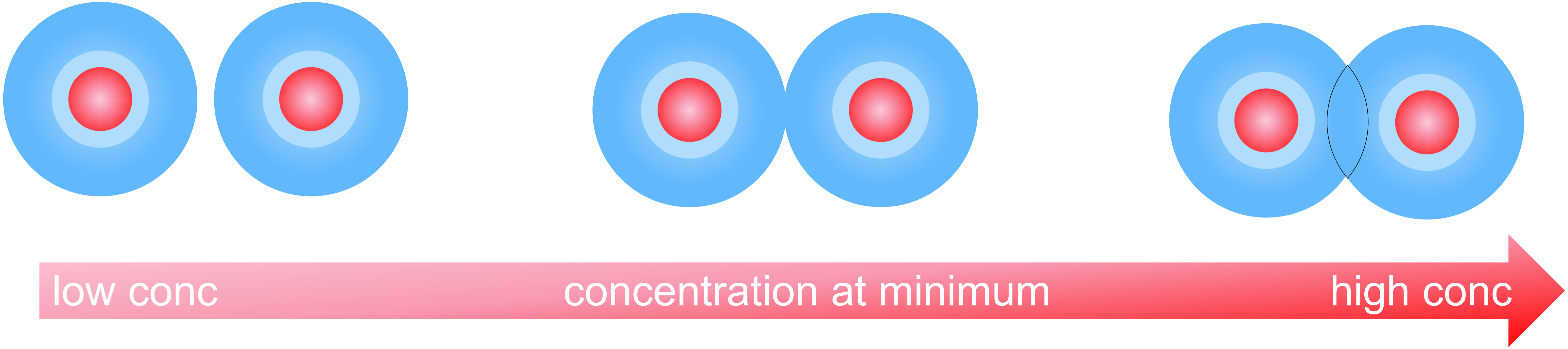
Perturbed water molecules

Immobilized water molecules close to the solute

Show the salt pairs

- At low concentrations, salt molecules are surrounded by immobilized and perturbated water
- With increasing concentration the perturbated water layers start to touch
- Up to this point we assume that S_T decays monotonously

CHANGE WITH CONCENTRATION



- Perturbed water molecules start to touch at minimum and overlap beyond minimum
- Salt-salt contribution to the energy of the system is;

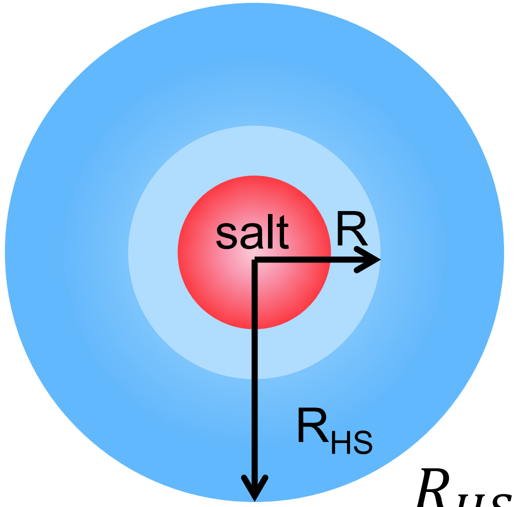
$$E_{SS}^{real} = \sum_{i<j}^{N_S} \varepsilon_{SS}^{bare} \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^{6} \right] - \sum_{i<j}^{N_S} \kappa \frac{1}{4} H_{ij}^2 (3 - H_{ij})$$

HYPOTHESIS: RANDOM CLOSE PACKING AT THE MINIMUM

What is the Radius of the hydrated salt molecules?

$$\emptyset_{random\ close\ packing} = 0.64$$

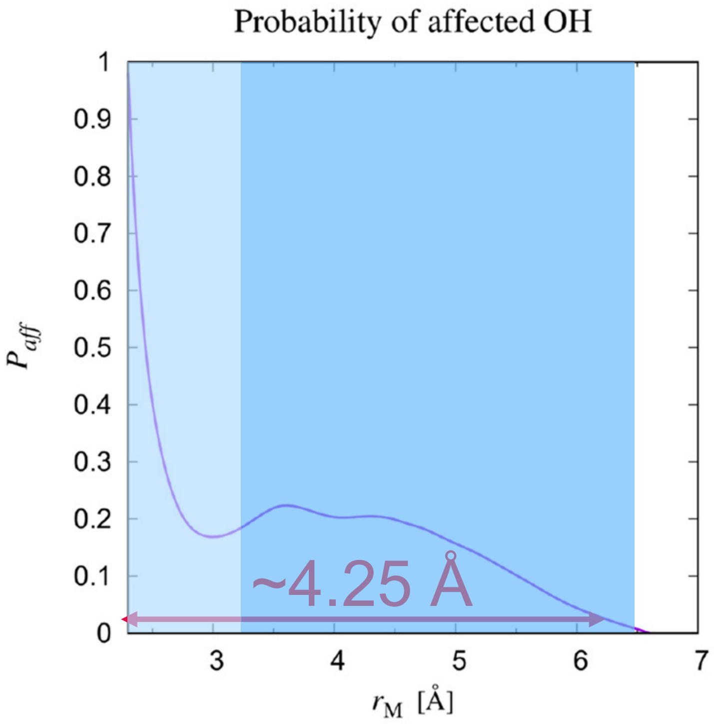
$$\emptyset^{random\ close\ packing} = Molarity(@min) * N_A * V^{hydrated\ salt}$$



$$R^{hydrated\ salt} = 6.3\ \text{Å}$$

Hydration layer thickness ~ 4.1Å

$$R_{HS} = 2 * R$$

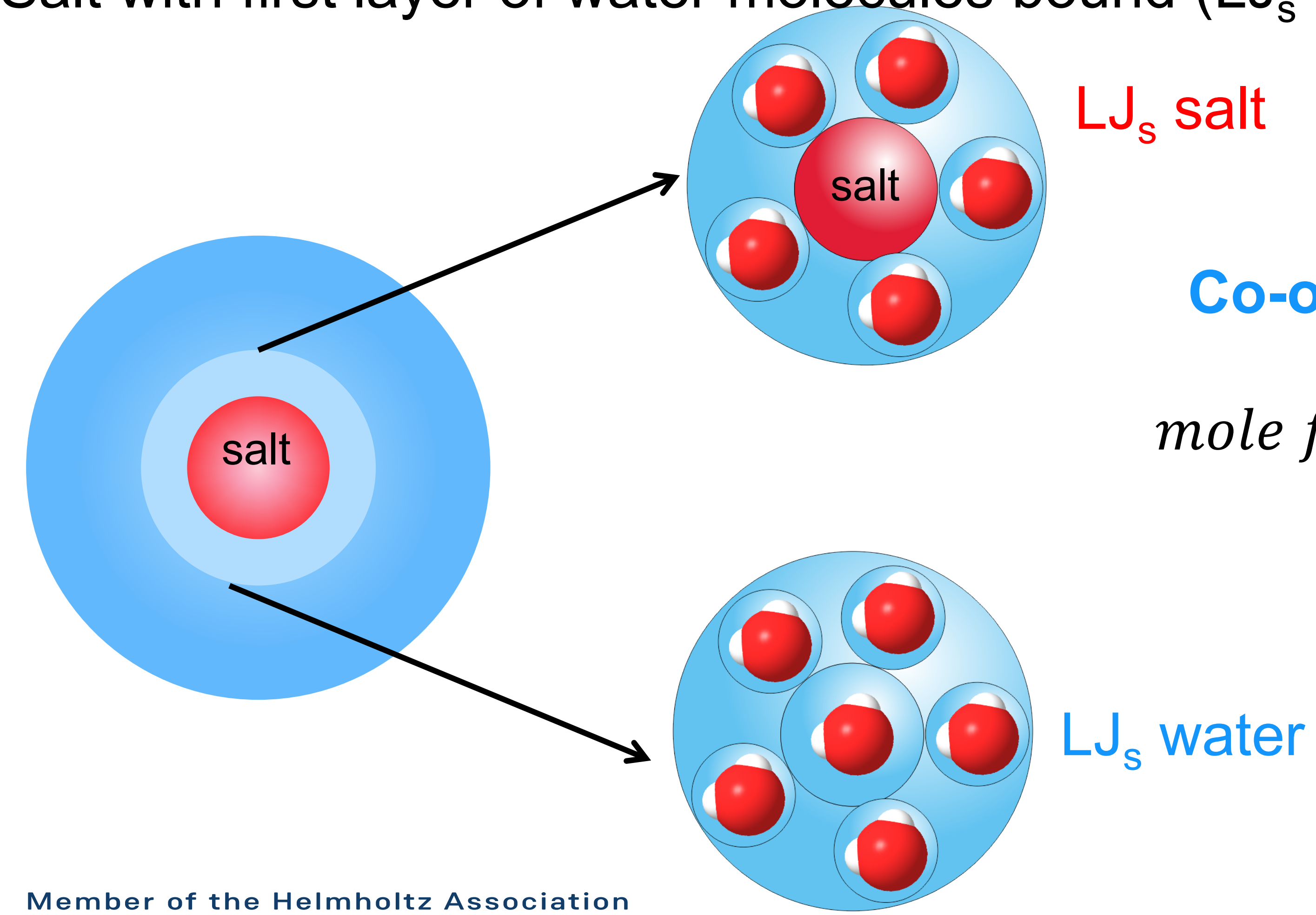


G. D. Scott and D. M. Kilgour, J. Phys. D **2**, 863 (1969).
P. D. Mitev, W. J. Briels, and K. Hermansson, J. Phys. Chem. B 125, 13886 (2021).

LET'S FOCUS ON DILUTED SOLUTIONS

Molecular dynamic simulations of LJ mixtures

Salt with first layer of water molecules bound (LJ_s particle)



Co-ordination number, Z=5!

$$mole\ fraction_{LJ}(salt) = \frac{(Z+1)m}{m_0 + m}$$

m_0- No of moles of water

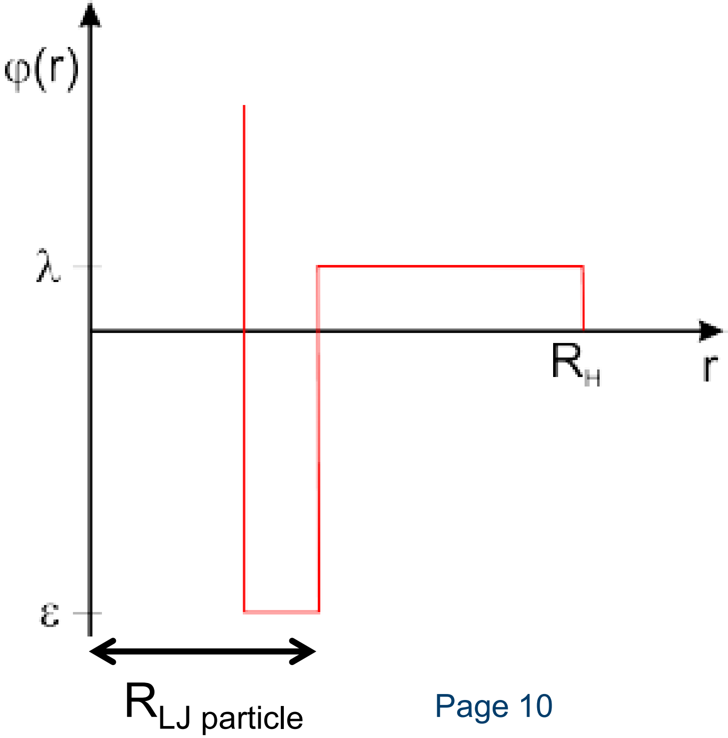
INTERACTION MODEL

Three interactions:

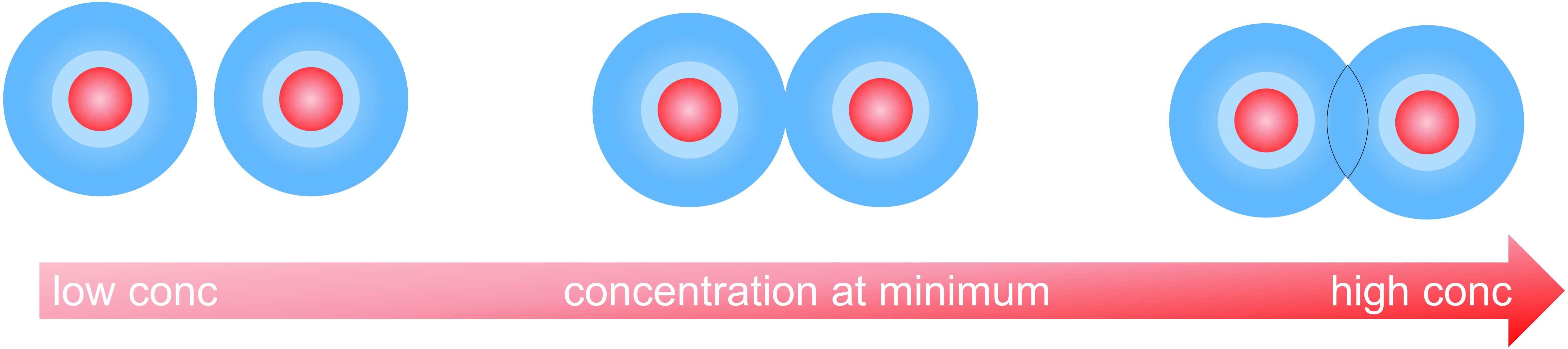
- Salt-salt (ε_{ss}) → Changes with concentration of salt solution
- Salt-water (ε_{sw})
- Water-water(ε_{ww})

We assume these to be constant as function of concentration

How does a salt molecule interact with water?



INTERACTION MODEL



- Perturbed water molecules start to touch at minimum and overlap beyond minimum
- Salt-salt contribution to the energy of the system is;

$$E_{ss}^{real} = \sum_{i<j}^{N_s} \varepsilon_{ss}^{bare} [\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}] - \sum_{i<j}^{N_s} \kappa \frac{1}{4} H_{ij}^2 (3 - H_{ij})$$

MAPPING OUR SYSTEM TO SIMULATIONS

Experiment:

$$E_{ss}^{real} = \sum_{i<j}^{N_s} \varepsilon_{ss}^{bare} \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^{6} \right] - \sum_{i<j}^{N_s} \kappa \frac{1}{4} H_{ij}^{2} (3 - H_{ij})$$

⇓

Simulation:

$$E_{ss}^{real} = \sum_{i<j}^{N_s} \varepsilon_{ss}^{effective} \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^{6} \right]$$

MAPPING OUR SYSTEM TO SIMULATIONS

Using Gibbs-Bogoliubov inequality

$$A^{real} \leq A^{LJ} + \left\langle E^{real} - E^{LJ} \right\rangle_{LJ}$$

Data by Artola and Rousseau is summarized as;

$$S_T = -\frac{1}{140}[k(M) - 1][x - x_0(M)]$$

- $k(M)$ and $x_0(M)$ in our case depends on concentration since ε_{ss} changes with concentration

PROCEDURE

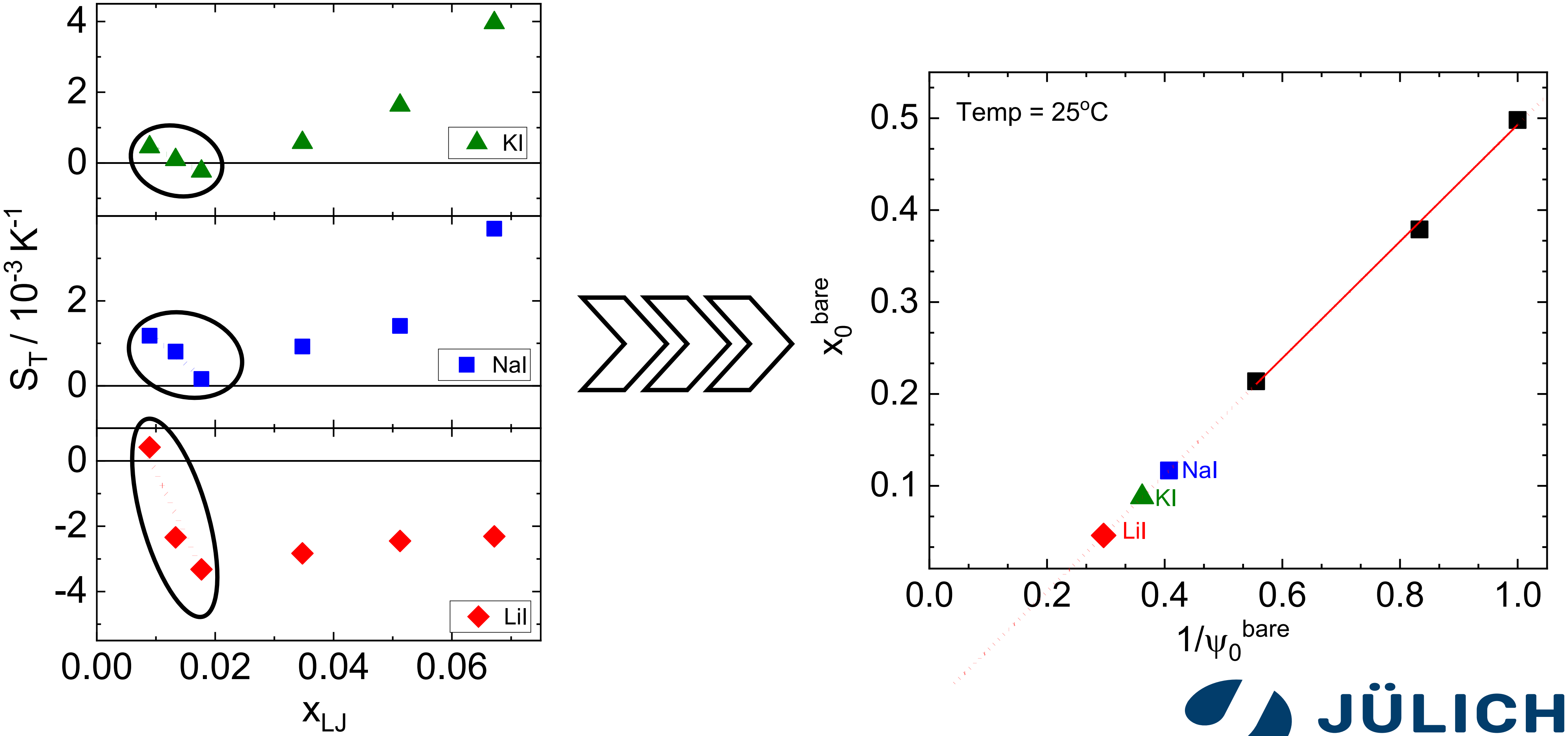
Fit data below minimum and obtain k^{bare} and x_0^{bare}

For concentrations beyond minimum, calculate H as a function of concentration

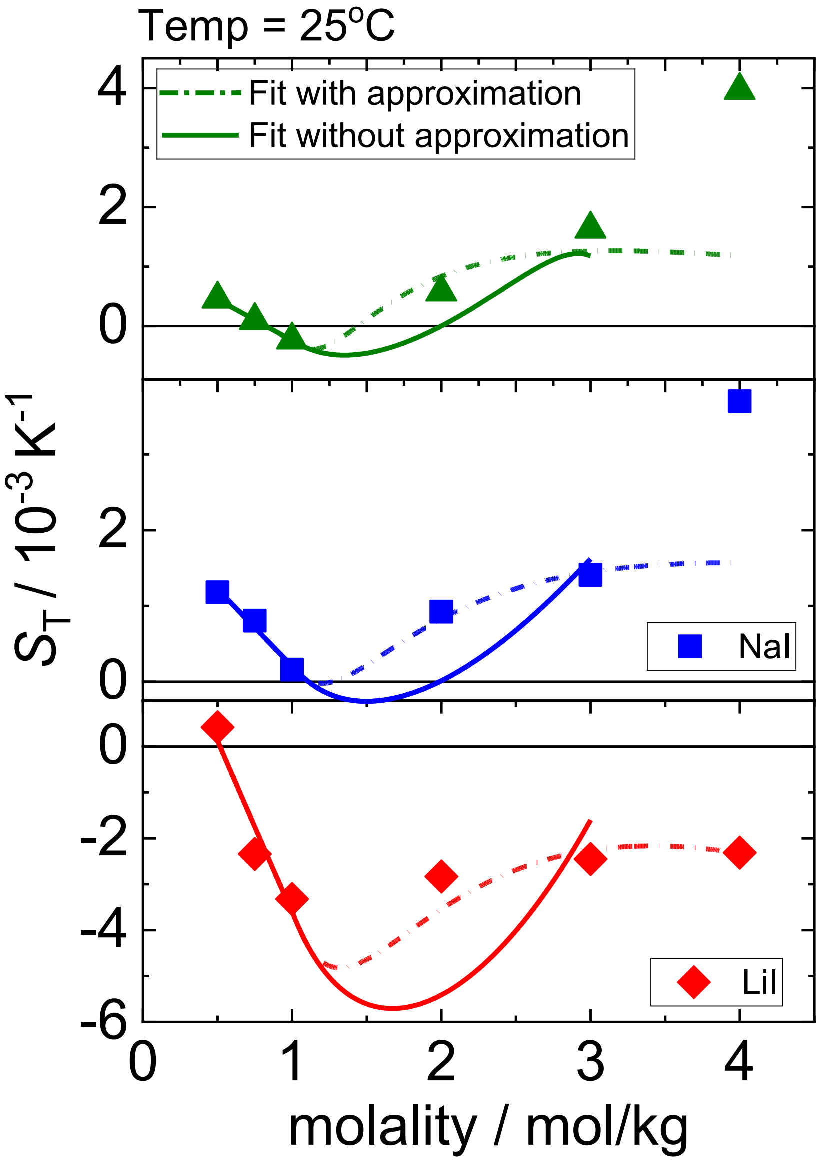
Calculate k and x_o as a function of concentration

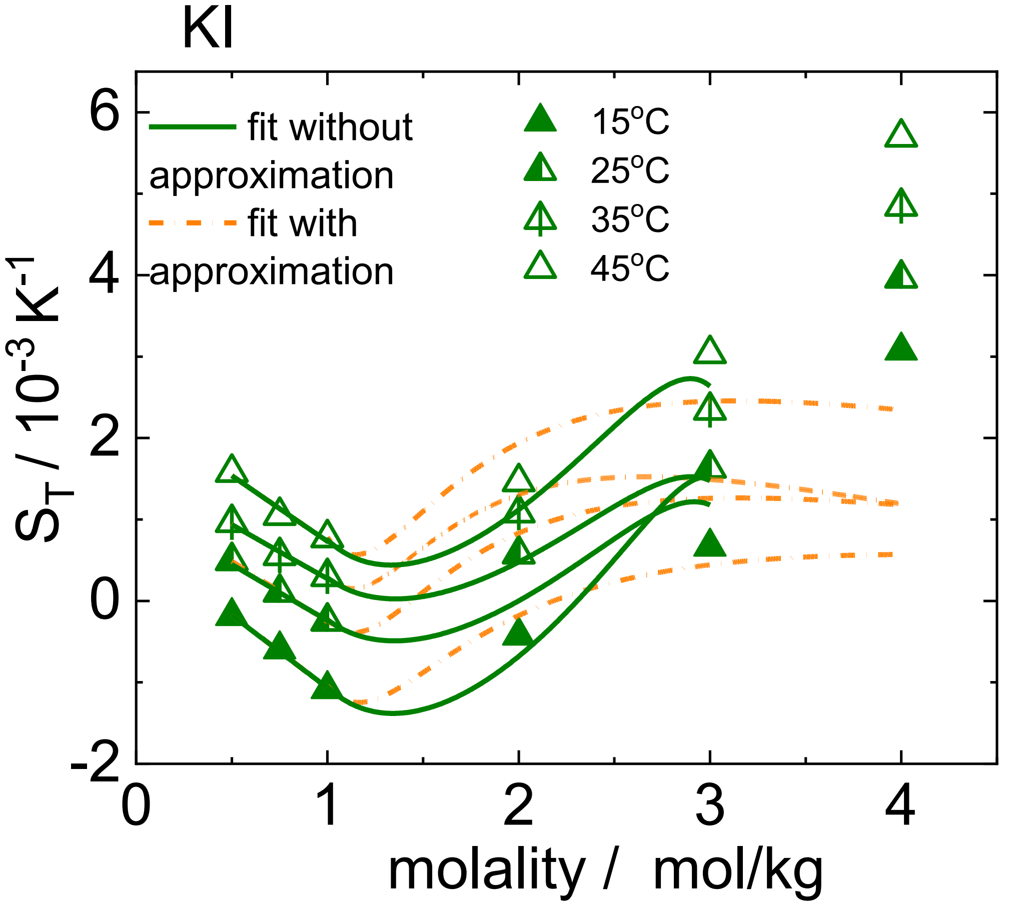
Calculate S_T beyond minimum

LET'S FOCUS ON DILUTED SOLUTIONS



RESULTS

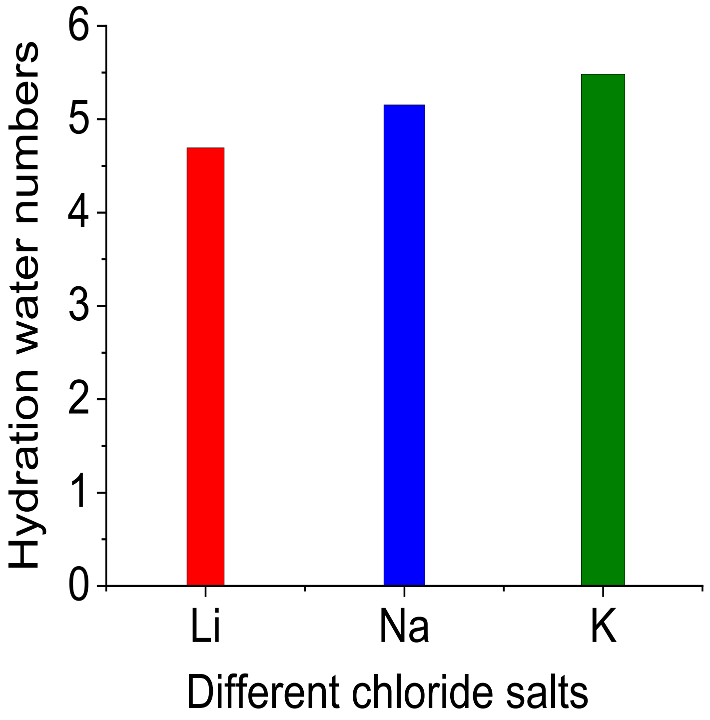




- Proposed theory deviates at higher concentrations
- At higher concentrations, there are chances of cluster formation, which are not covered in our model

SUMMARY

- Procedure was followed for KI and NaI assuming Z=5
- KI and NaI showed a good agreement between experimental and fitted values
- For LiI, Z=4 was used to get a better agreement



G. Schwaab et al., *Angew Chem Int Edit*, 2019, 58 (10), 3000–3013

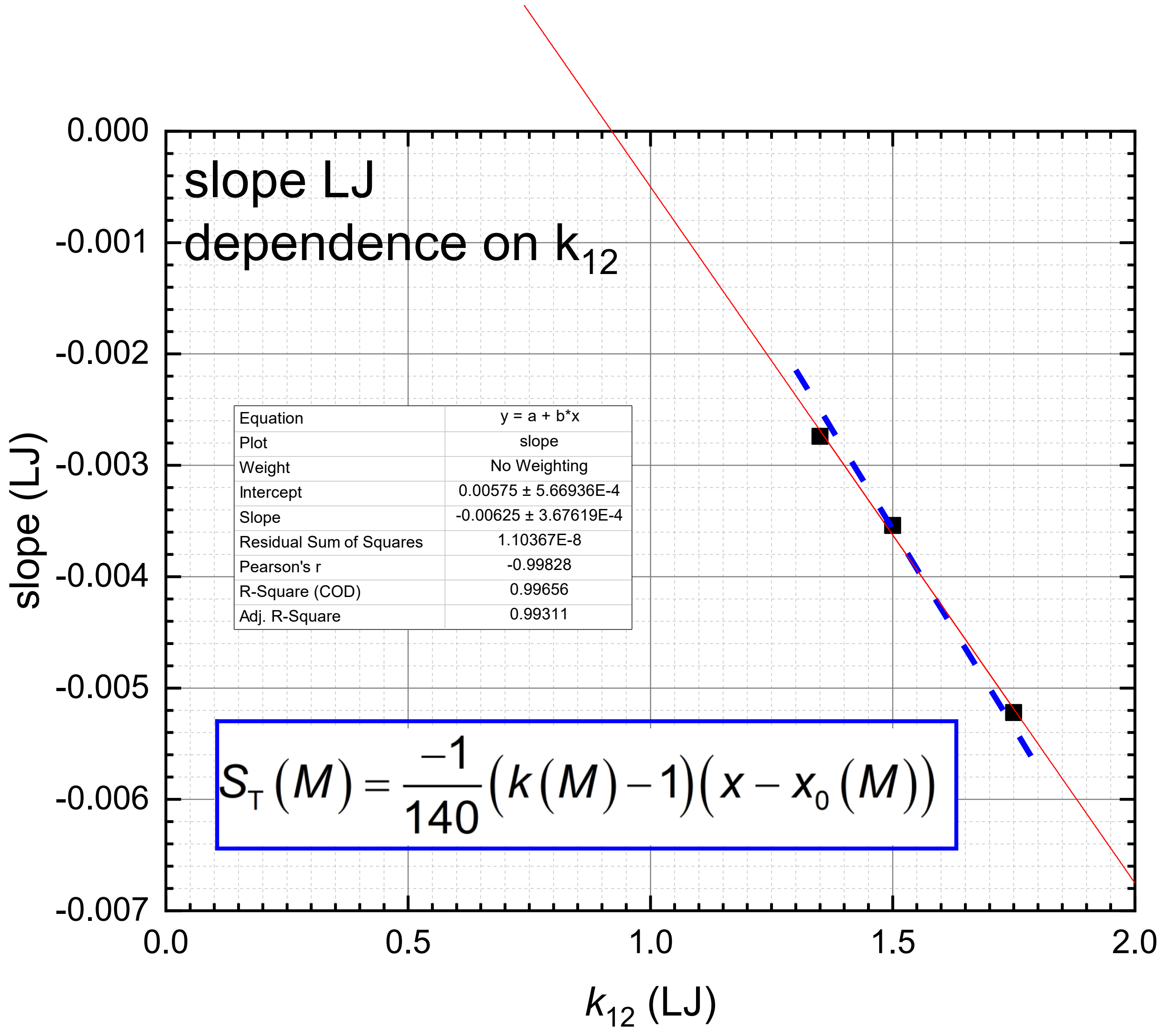
CONCLUSION

- S_T of the KI, NaI and LiI shows a minimum with concentration at all measured temperatures
- We provided arguments that the minimum is related to overlapping hydration layers
- Mapping that we used is not exact, but identifies the most important free energy components that are responsible for the minimum
- We observe deviations at higher concentrations which are due to cluster formation not covered by the model

ACKNOWLEDGEMENT

- Simone Wiegand and Wim Briels
- Hartmut Kriegs, Jan K.G. Dhont and Annette Schmidt
- The whole IBI-4

FITTING OF DATA BY ARTOLA



Equation	y = a + b*x
Plot	slope
Weight	No Weighting
Intercept	0.00575 ± 5.66936E-4
Slope	-0.00625 ± 3.67619E-4
Residual Sum of Squares	1.10367E-8
Pearson's r	-0.99828
R-Square (COD)	0.99656
Adj. R-Square	0.99311

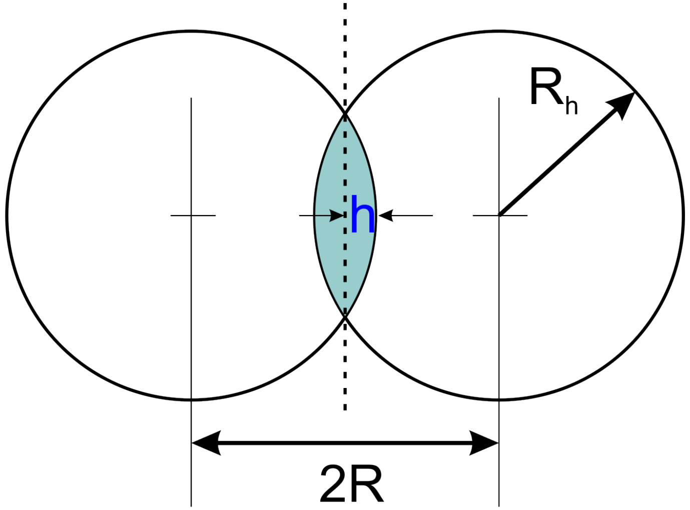
$$S_T(M) = \frac{-1}{140}\left(k(M)-1\right)\left(x-x_0(M)\right)$$

MAPPING OUR SYSTEM INTO SIMULATIONS

$$\varepsilon_{ss}^{effective} = \varepsilon_{ss}^{bare} + \Delta\varepsilon_{ss}$$

$$A^{real} - A^{LJ} \leq [\langle E^{real} - E^{LJ} \rangle_{LJ}]$$

Gibb’s-Bogoliubov
inequality : to estimate $\Delta\varepsilon_{ss}$



$$H = 1 - \frac{R}{R_h}$$

MAPPING OUR SYSTEM TO SIMULATIONS

$$\varepsilon_{ss}^{effective} = \varepsilon_{ss}^{bare} + \Delta\varepsilon_{ss}$$

Using Gibbs-Bogoliubov inequality

$$A^{real} \leq A^{LJ} + \left\langle E^{real} - E^{LJ} \right\rangle_{LJ}$$

This gives;

$$\Delta\varepsilon_{ss} = \kappa \sum_{n=0}^{3} a_n H^n$$

After some additions and rearrangements

where, $\frac{\varepsilon_{ss}}{\varepsilon_{ww}} = \frac{1}{\psi}$

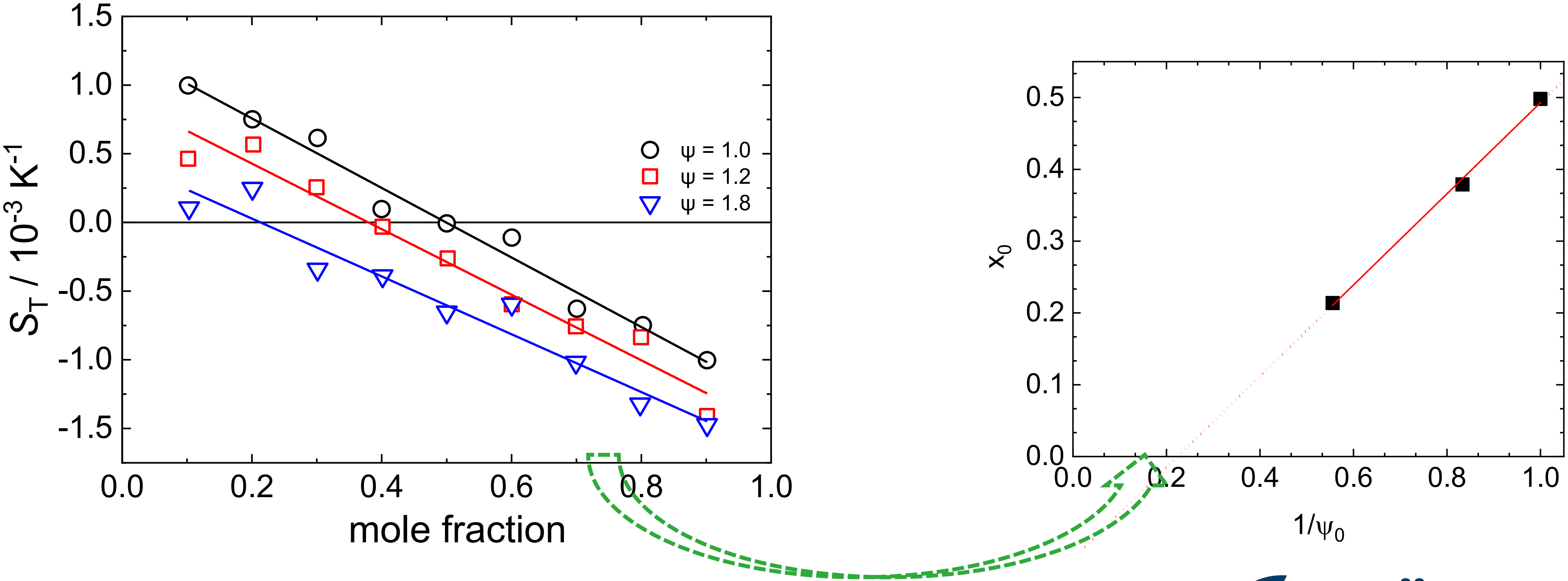
$$\frac{1}{\psi} = \frac{1}{\psi^{bare}} + \Lambda H^2(3 - H)$$

JÜLICH
Forschungszentrum

LET'S FOCUS ON DILUTED SOLUTIONS

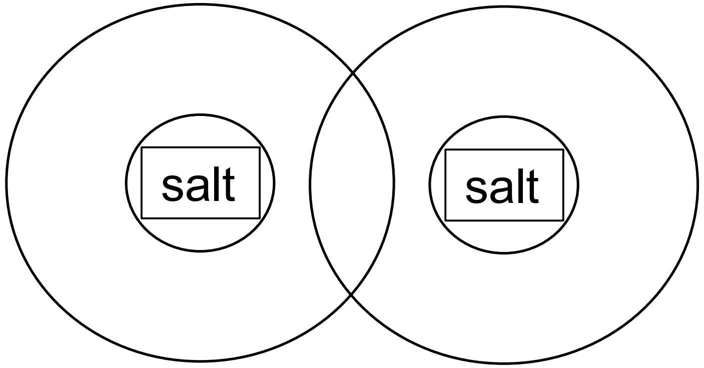
Molecular dynamic simulations of LJ mixtures

Backup slide



Artola et al., Phys Rev Lett 98, 2007, 125901

WHAT ARE WE TRYING TO UNDERSTAND?



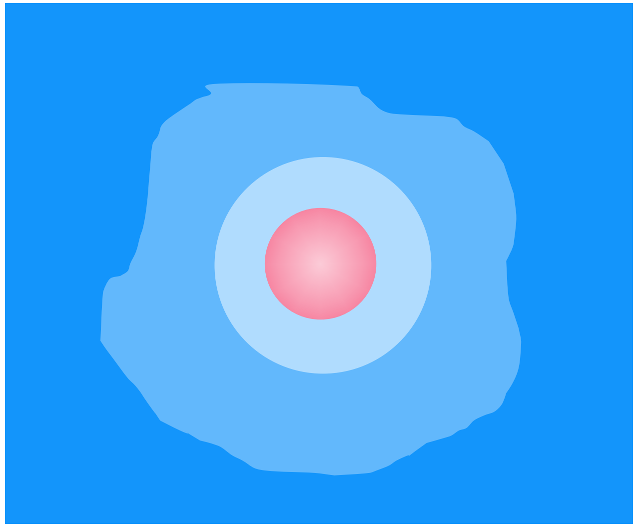
- What is the reason for the occur
minimum?
- How does the arrangement of w
with increasing salt concentratio

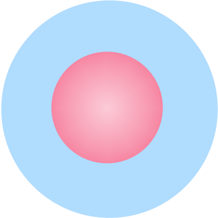
LET‘S FOCUS ON DILUTED SOLUTIONS

Molecular dynamic simulations of LJ mixtures

Mapping of our system into LJ mixture of Artola and Rousseau

Salt with perturbed water molecules : hydrated salt molecule





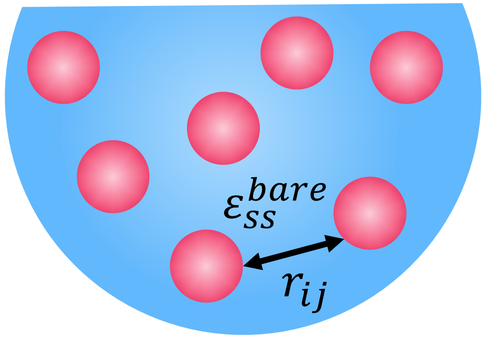
$$\phi = N_A * molality * \boxed{Volume_{HS}}$$

R_{HS}

$$R_{HS} = 6.3\ A^0$$

Not so clear us the equation from the maple script:

HOW DOES INTERACTION BETWEEN SALT MOLECULES CHANGE?

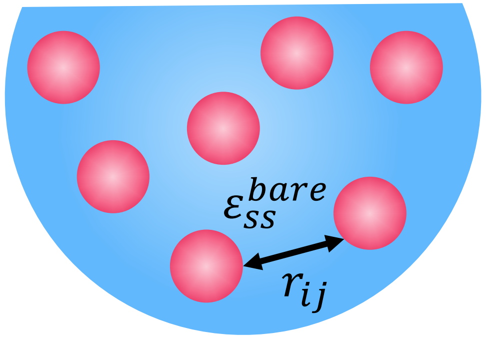


E_i^{self} : Energy released when one salt molecule is dissolve

N_s : Number of salt molecules

$$\sum_{i=1}^{N_s} E_i^{self} = N_s E^0 - \sum_{i<j}^{N_s} \kappa \frac{1}{4} H_{ij}^2 (3 - H_{ij}) \qquad H_{ij} = 1 - \frac{r_{ij}}{2R_{HS}}$$

HOW DOES INTERACTION BETWEEN SALT MOLECULES CHANGE?



E_i^{self}: Energy released when one salt molecule is dissolved

N_s : Number of salt molecules

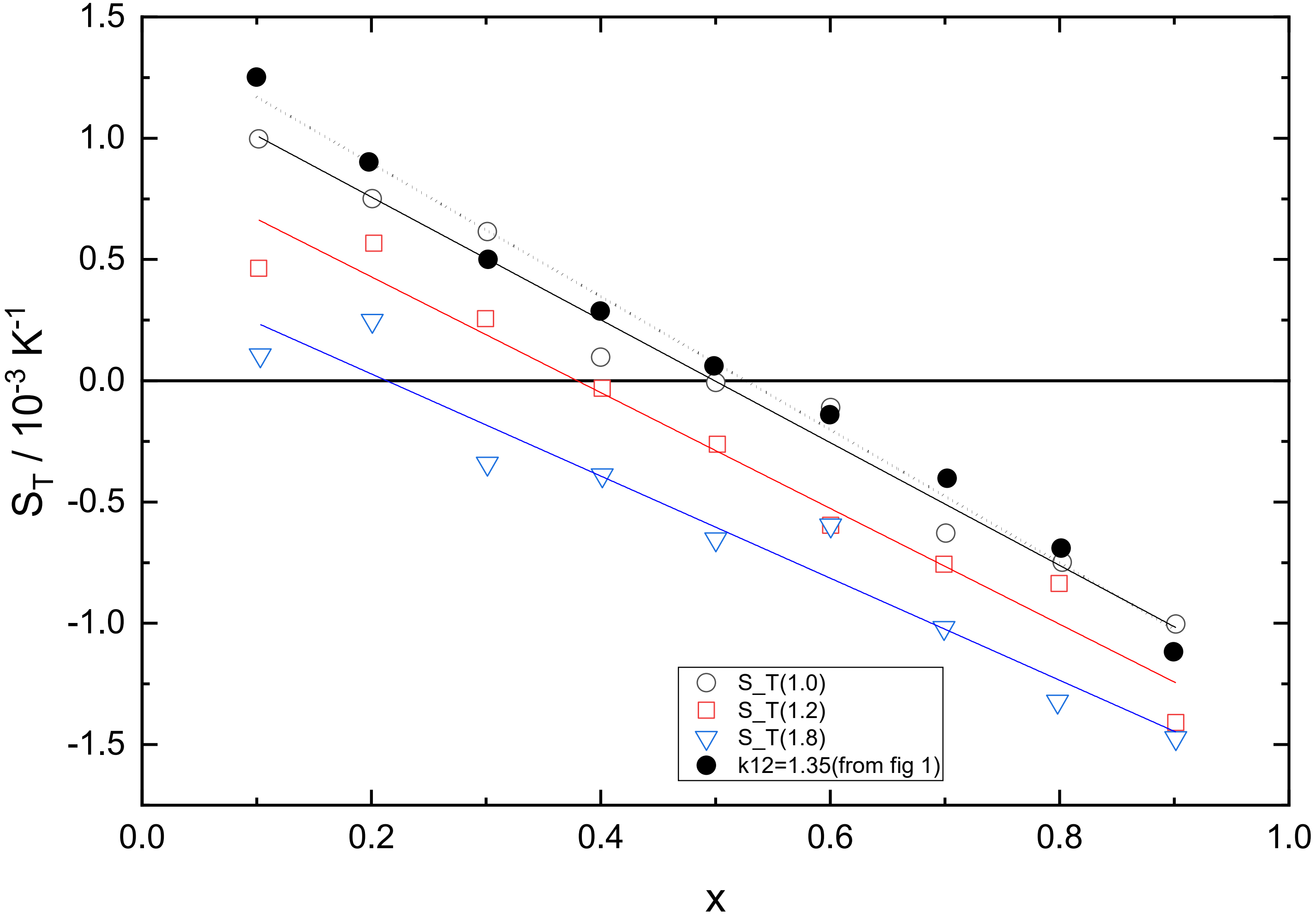
This gives the total interaction energy

$$\varepsilon_{ss} = \varepsilon_{bare} + 16\kappa H^2(3 - H)$$

Dividing this equation by ε_{ww}, thus expressing in terms of ψ,

$$\frac{1}{\psi} = \frac{1}{\psi_{bare}} + \Lambda H^2(3 - H)$$

MOLECULAR DYNAMIC SIMULATIONS OF LJ MIXTURES



Constant decrease in S_T with concentration for different k_{12}

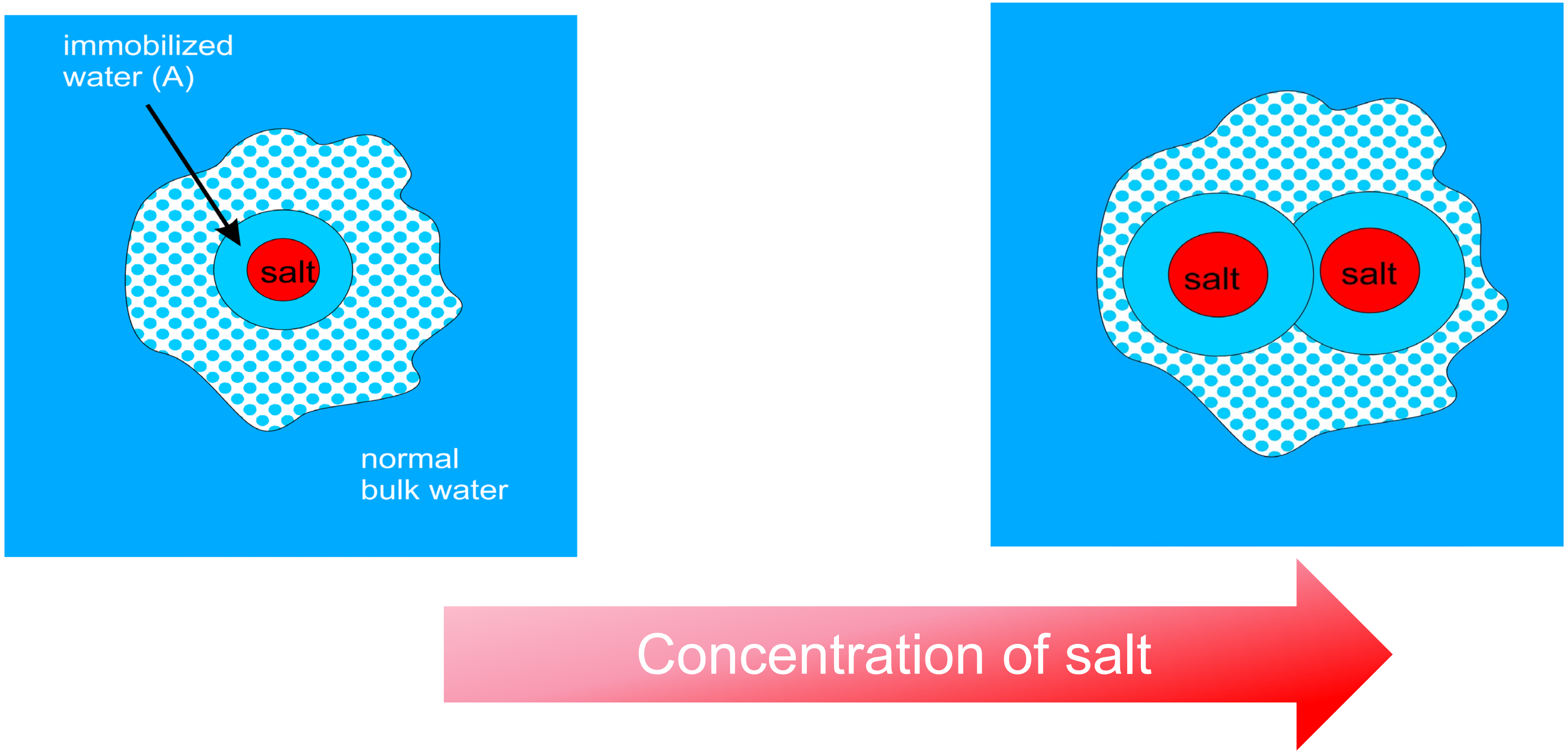
Include more water to the salt

Mole fraction spans over a higher range compared to our mole fraction

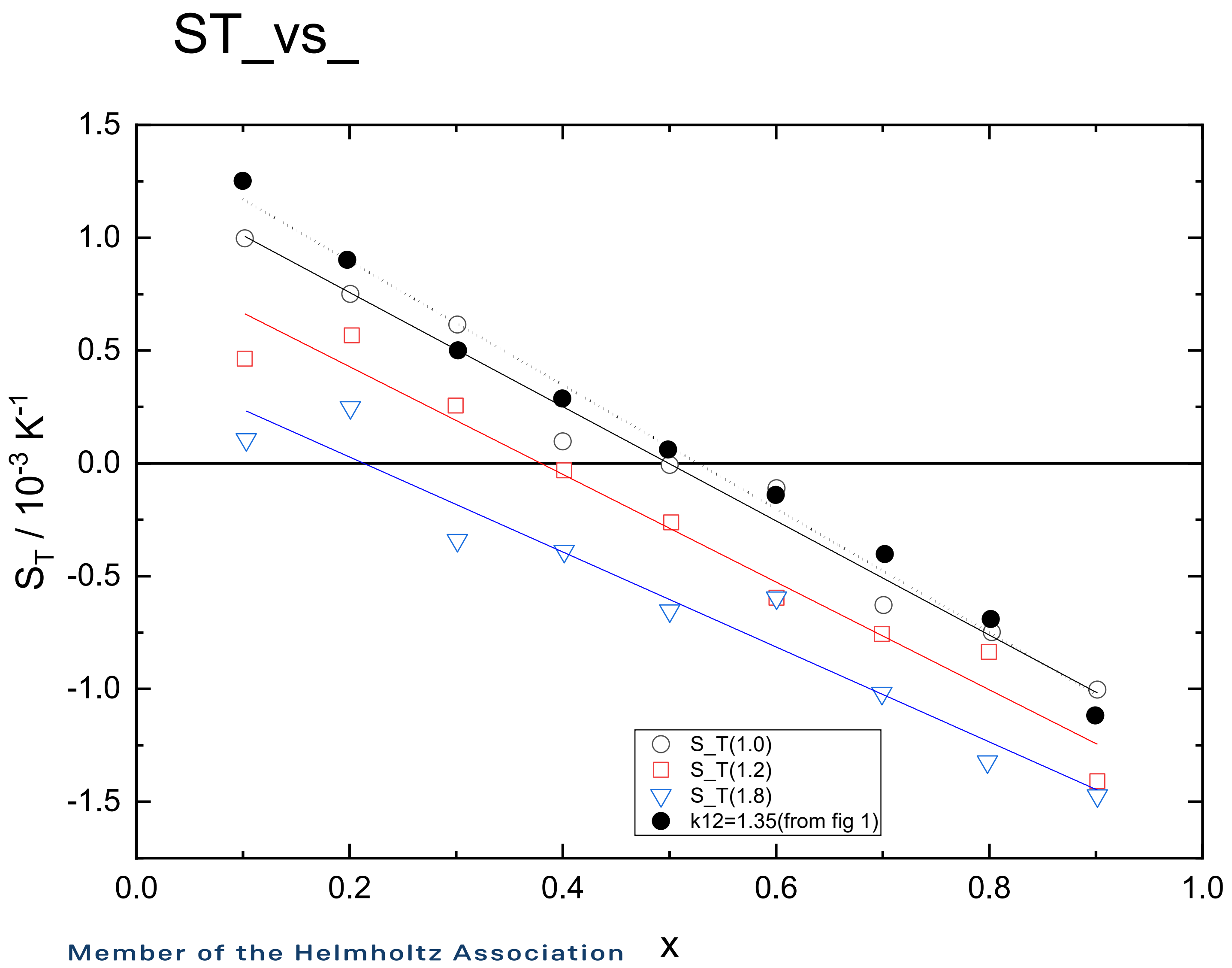
Psi dependence

No theoretical concepts

HOW DOES SALT INTERACT WITH WATER?



MOLECULAR DYNAMIC SIMULATIONS OF LJ MIXTURES

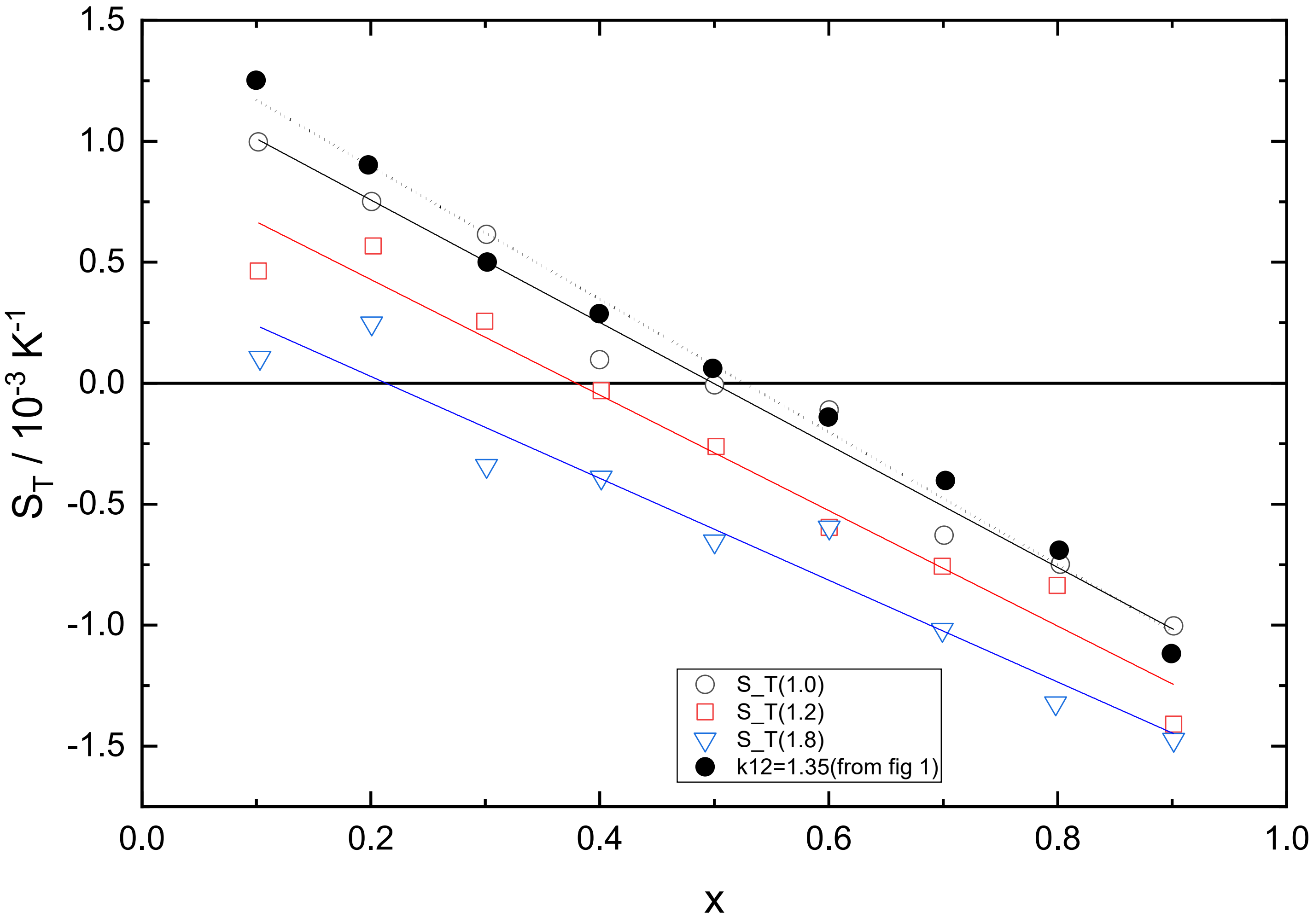


Constant decrease in S_T with concentration for different k_{12}

Mole fraction spans over a higher range compared to our mole fraction

K12 : parameter to define cross interaction

MOLECULAR DYNAMIC SIMULATIONS OF LJ MIXTURES



Sign change conc changes with psi

Finding a psi_0 corresponding to x0 where the sign change happens

Add xo for the salts to the 1/psi0 plot

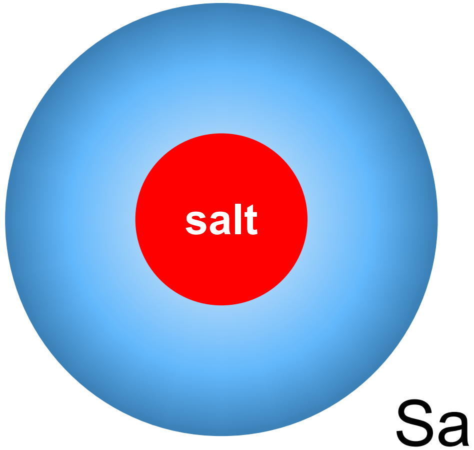
Show the relation between psi and x

MOLECULAR DYNAMIC SIMULATIONS OF LJ MIXTURES

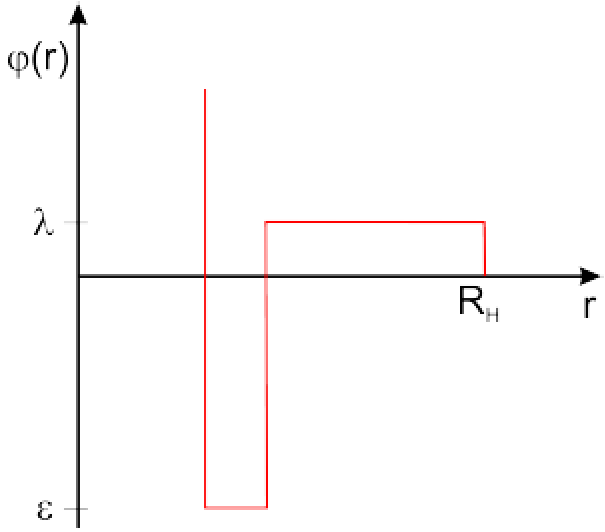
Interaction model

Three major interactions:
- Salt-salt
- Salt-water
- Water-water

Interaction energy of molecule with water has different contributions:
- Strongly bound first layer
- Repulsive in the transition zone
- Gradual transitior to the bulk water



Depends on the conc



Salt with the strongly bound water layer is considered as a single LJ particle

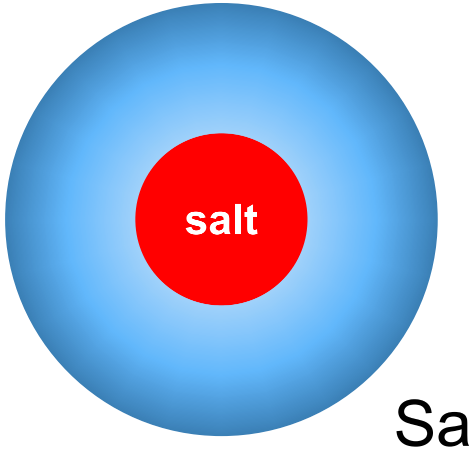
MOLECULAR DYNAMIC SIMULATIONS OF LJ MIXTURES

Interaction model

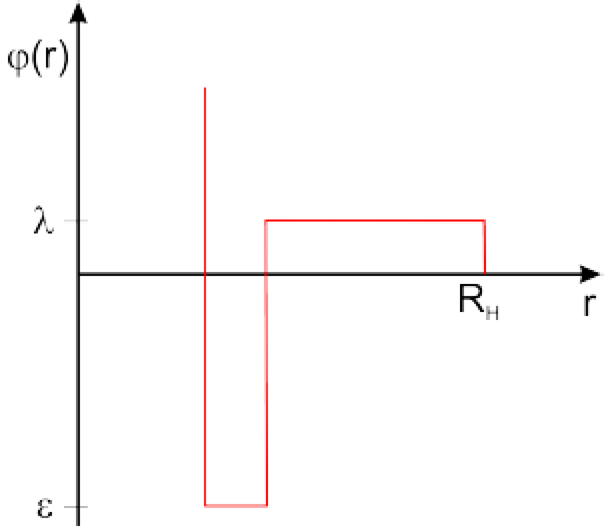
Three major interactions:
- Salt-salt
- Salt-water
- Water-water

Interaction energy of molecule with water has different contributions:

- Strongly bound first layer
- Repulsive in the transition zone
- Gradual transition that happens from first layer to the bulk water



Depends on the conc



Salt with the strongly bound water layer is considered as a single LJ particle

MOLECULAR DYNAMIC SIMULATIONS OF LJ MIXTURES

Assumption 2 : Beyond minimum concentration, water layers of salt molecules overlap

1/psi equation

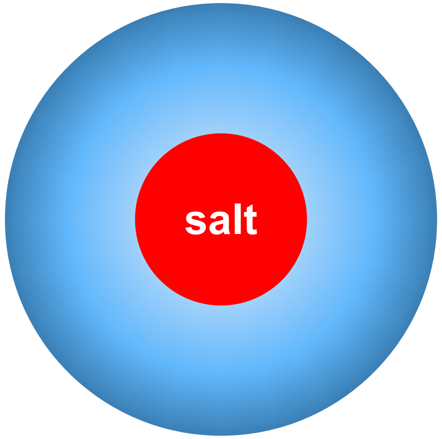
MOLECULAR DYNAMIC SIMULATIONS OF LJ MIXTURES

Interaction model

Three major interactions:

- Salt-salt
- Salt-water
- Water-water

Dissolve one salt molecule in water

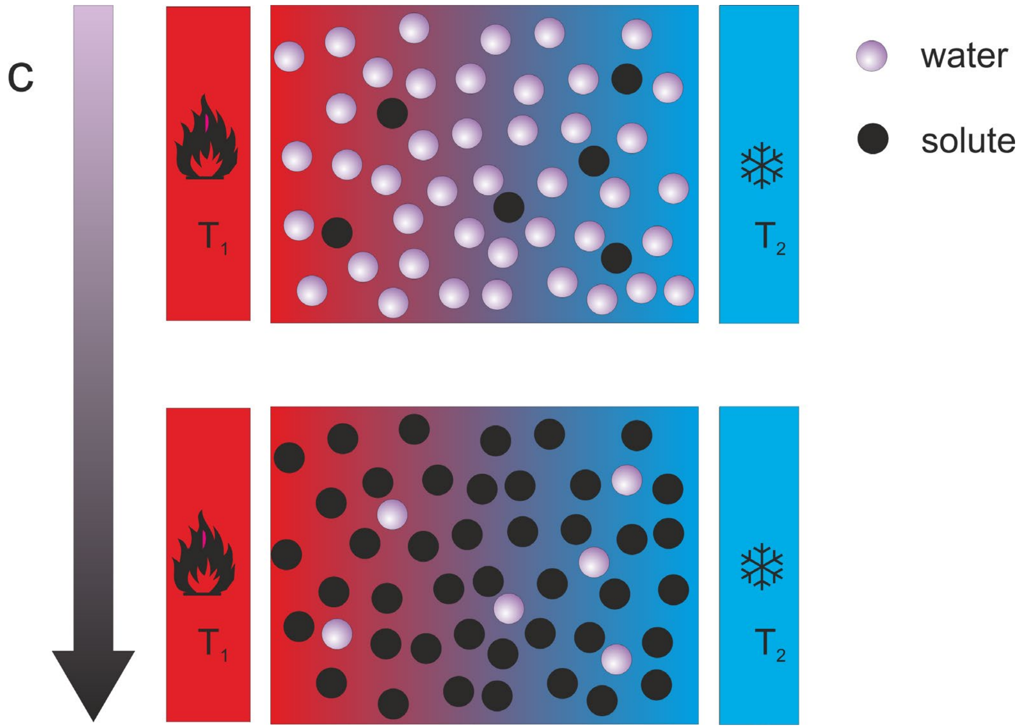


Interaction energy of molecule with water has different contributions:

- Strongly bound first layer
- Gradual transition that happens from first layer to the bulk water

PRIGOGINE‘S ARGUMENT

If the cross interactions are stronger than the pure interaction ...



$$\varepsilon_{12} > \varepsilon_{11}$$

$$\varepsilon_{12} > \varepsilon_{22}$$

$$T_1 > T_2$$

$$\Rightarrow \underbrace{e^{-\varepsilon_{12}/kT_1}}_{\propto E(T_1)} > \underbrace{e^{-\varepsilon_{12}/kT_2}}_{\propto E(T_2)}$$

For energetic reasons most mixed interaction take place on the cold side

... Minority component goes to the cold side

I. Prigogine et al., *Physica,* **16** (1950), 851