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Simulating osmotic equilibria A new tool to calculate activity coefficients in solution

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M. Bley, Magali Duvail, Philippe Guilbaud, Jean-François Dufrêche. Simulating osmotic equilibria A new tool to calculate activity coefficients in solution. Les 17èmes Journées Scientifiques de Marcoule, Jun 2017, Bagnols Sur Ceze, France. CEA Marcoule, 2017. hal-02417800

HAL Id: hal-02417800

<https://hal.science/hal-02417800>

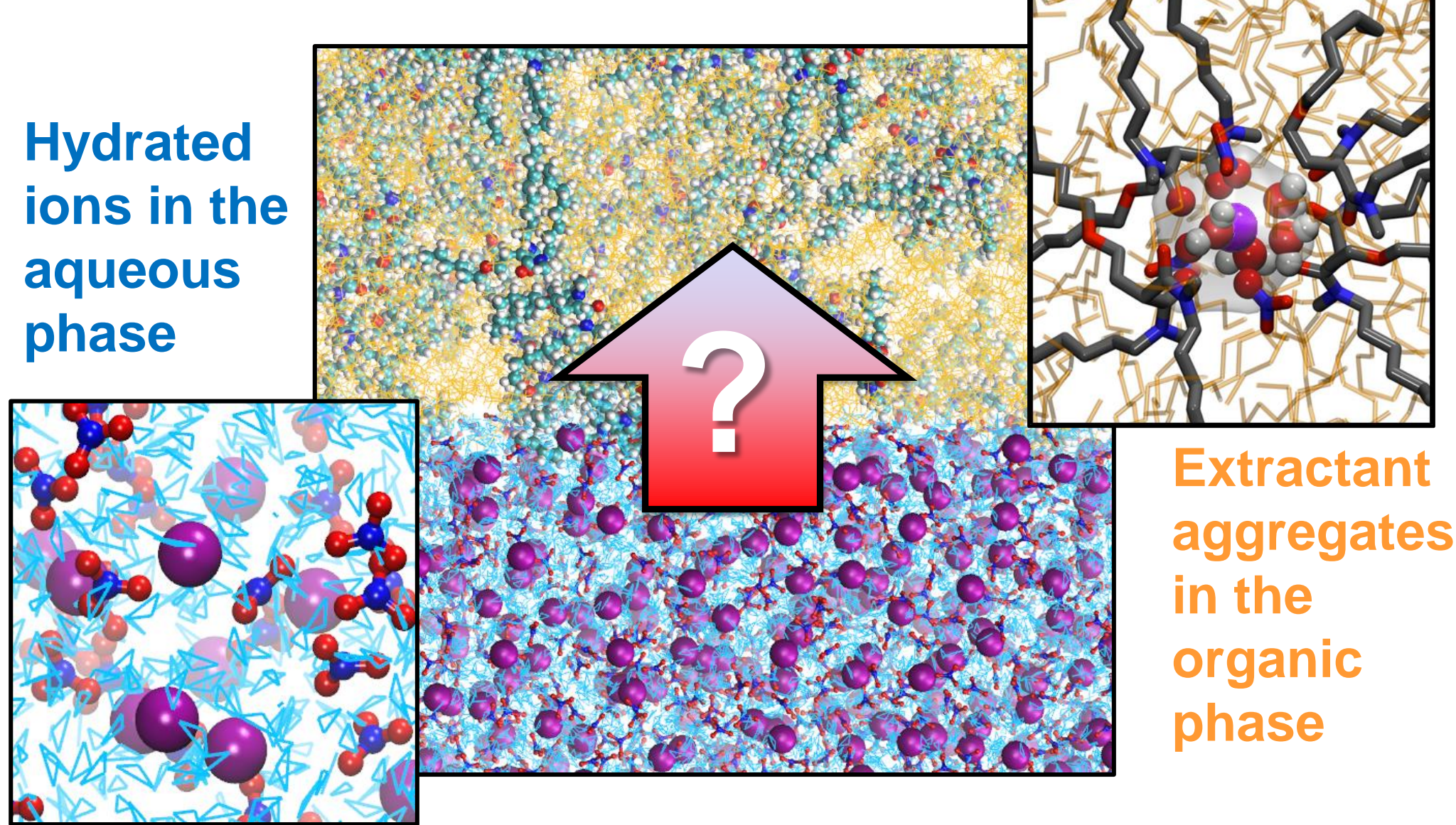
Submitted on 20 Feb 2020

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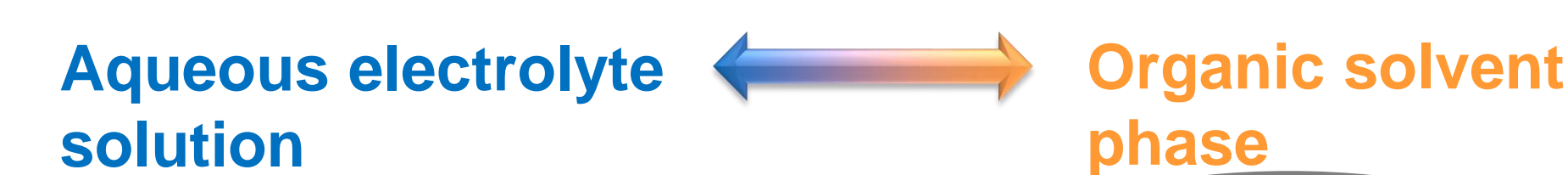
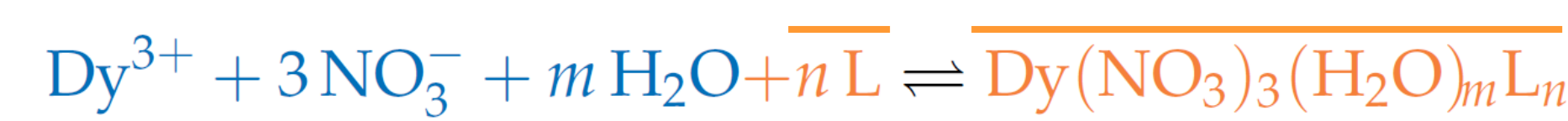
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Context

- Understanding **solvent extraction** – Recycling of rare earth elements and spent nuclear fuels



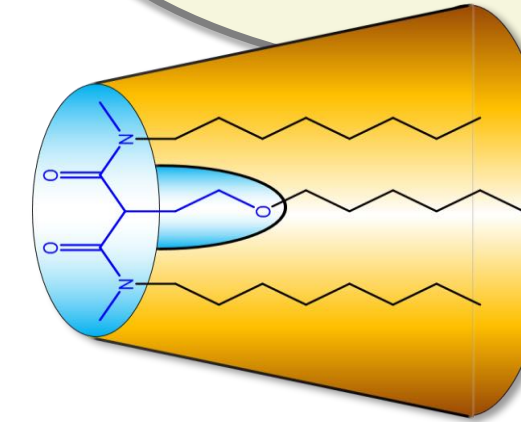
- The **equilibrium constant K^0** describes the extraction process and is given by the Mass Action Law



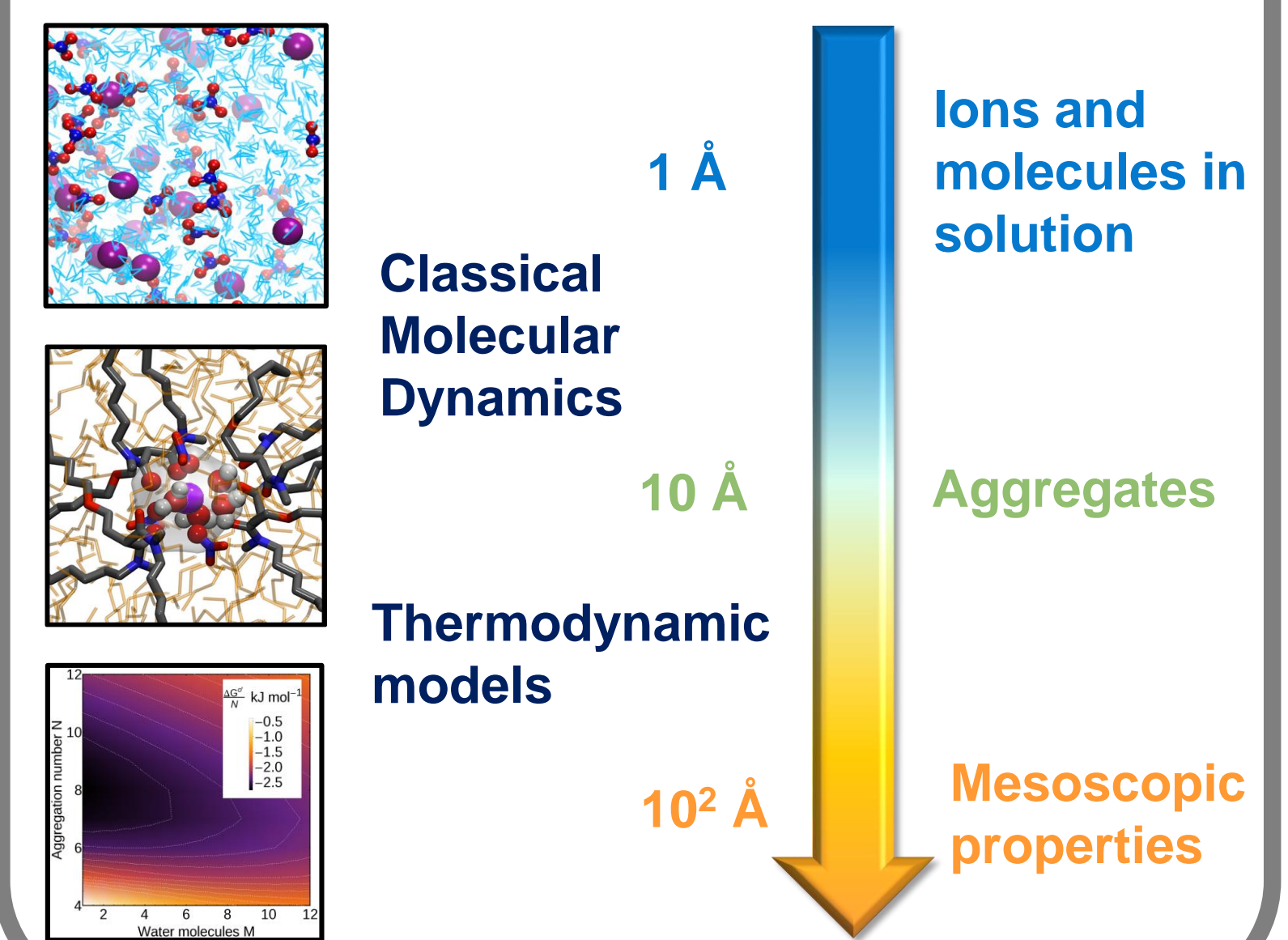
$$K^0 = \frac{c_{\text{Dy}(\text{NO}_3)_3(\text{H}_2\text{O})_m\text{L}_n}}{c_{\text{Dy}^{3+}} c_{\text{NO}_3^-}^3 c_{\text{H}_2\text{O}}^m c_{\text{L}}^n} \times \frac{\gamma_{\text{Dy}(\text{NO}_3)_3(\text{H}_2\text{O})_m\text{L}_n}}{\gamma_{\text{Dy}^{3+}} \gamma_{\text{NO}_3^-}^3 \gamma_{\text{H}_2\text{O}}^m \gamma_{\text{L}}^n}$$

Concentrations Activity coefficients

Ligand L:
DMDOHEMA

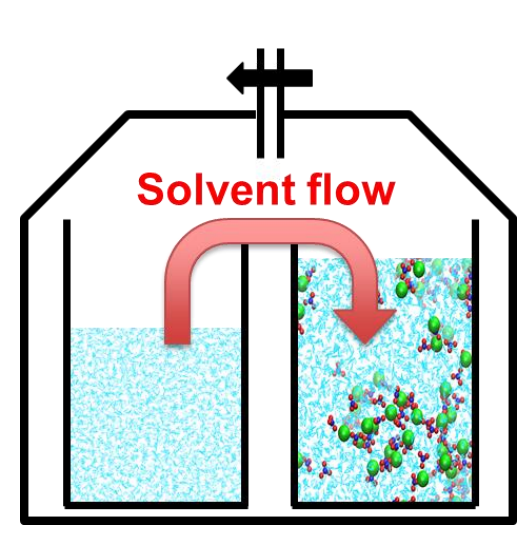


- A **multiscale approach** provides mesoscopic thermodynamic properties



Methods and concepts

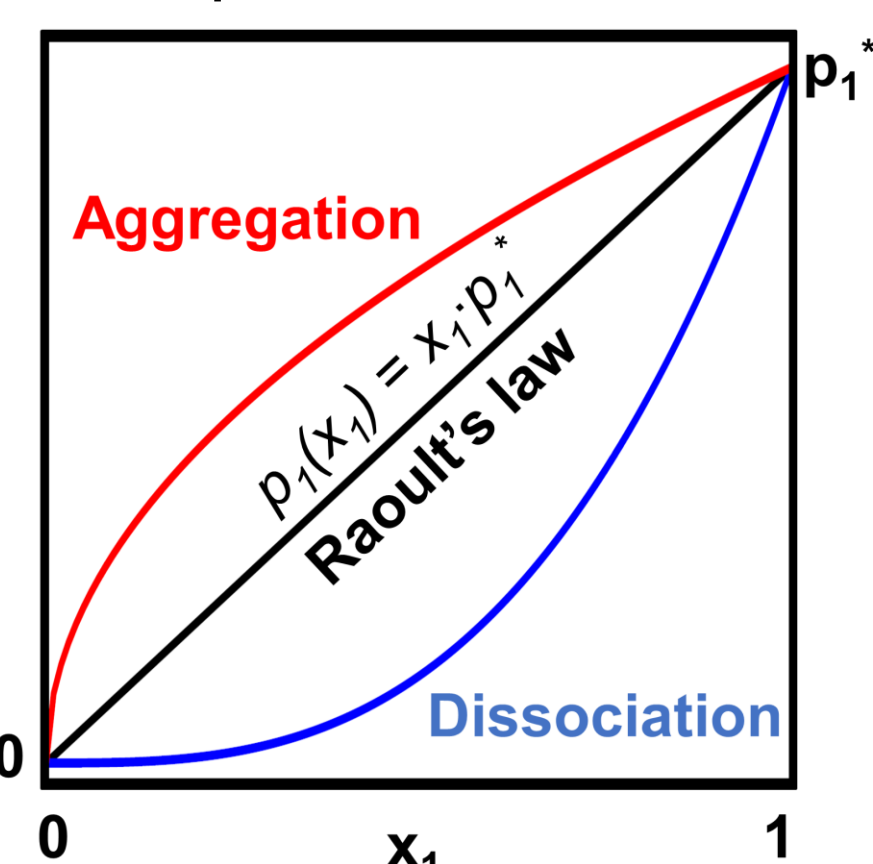
- Measuring** activity and the vapor pressure



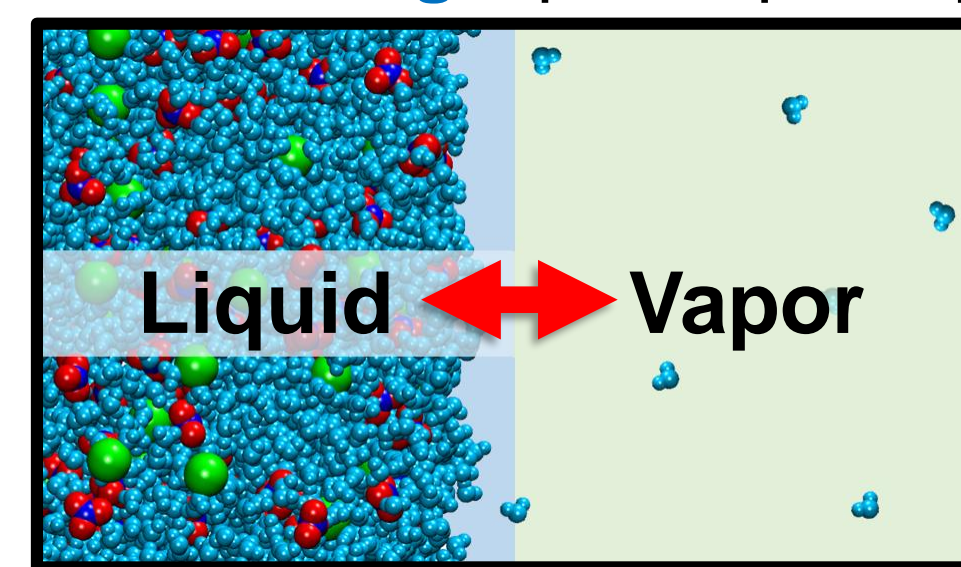
Isopiestic Measurements

- Solvent flow:** Vapor pressure of the pure solvent always higher than of a mixture
- Ideal case: Solvent vapor pressure by **Raoult's law**
- Otherwise: **Aggregation increases, dissociation decreases** solvent vapor pressure and thus activity

p_1^* : Vapor pressure of pure solvent



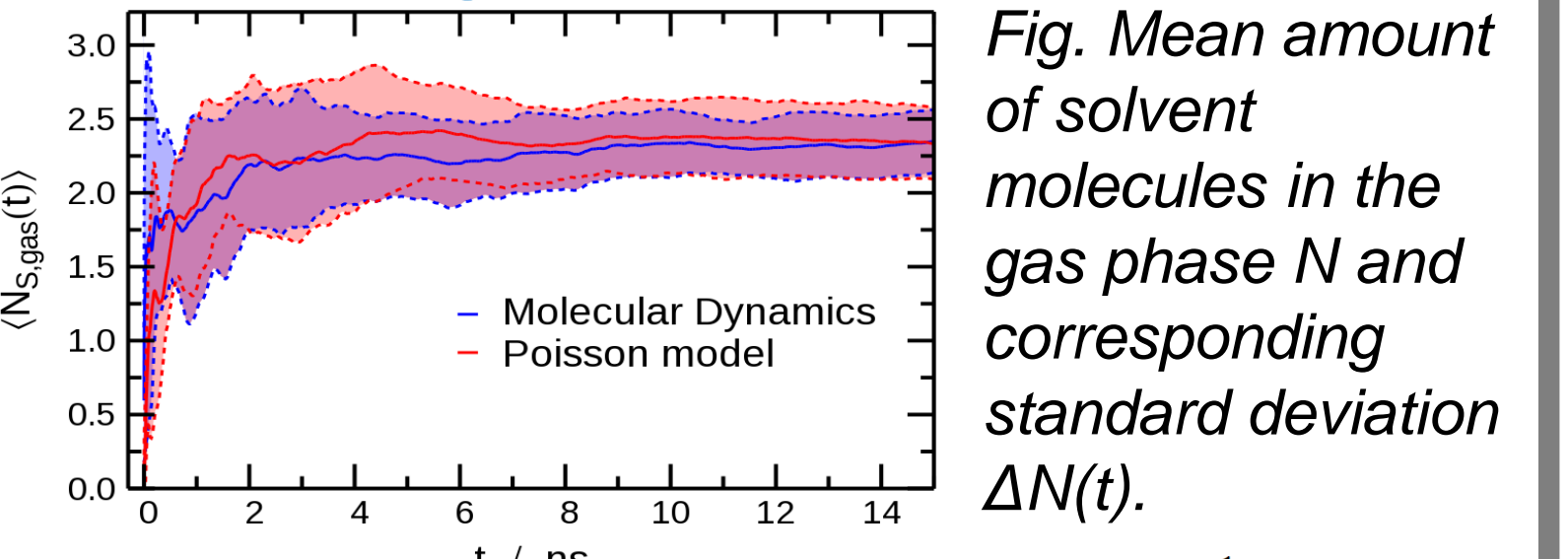
- Simulating** liquid-vapor equilibria⁽¹⁾



- Molecular Dynamics using **explicit polarization**^(2,3) at 298.15 K for 15 ns

$$a_s = \frac{p}{p^*} = \frac{\rho}{\rho^*} = \frac{N \times V_{\text{gas}}^*}{N^* \times V_{\text{gas}}} = \frac{\lambda \times V_{\text{gas}}^*}{\lambda^* \times V_{\text{gas}}}$$

- Controlling** the error of the method



$$N = \langle \tau_x \rangle \times \lambda \quad \delta_N(t) = \frac{1}{\sqrt{\lambda \times t}}$$

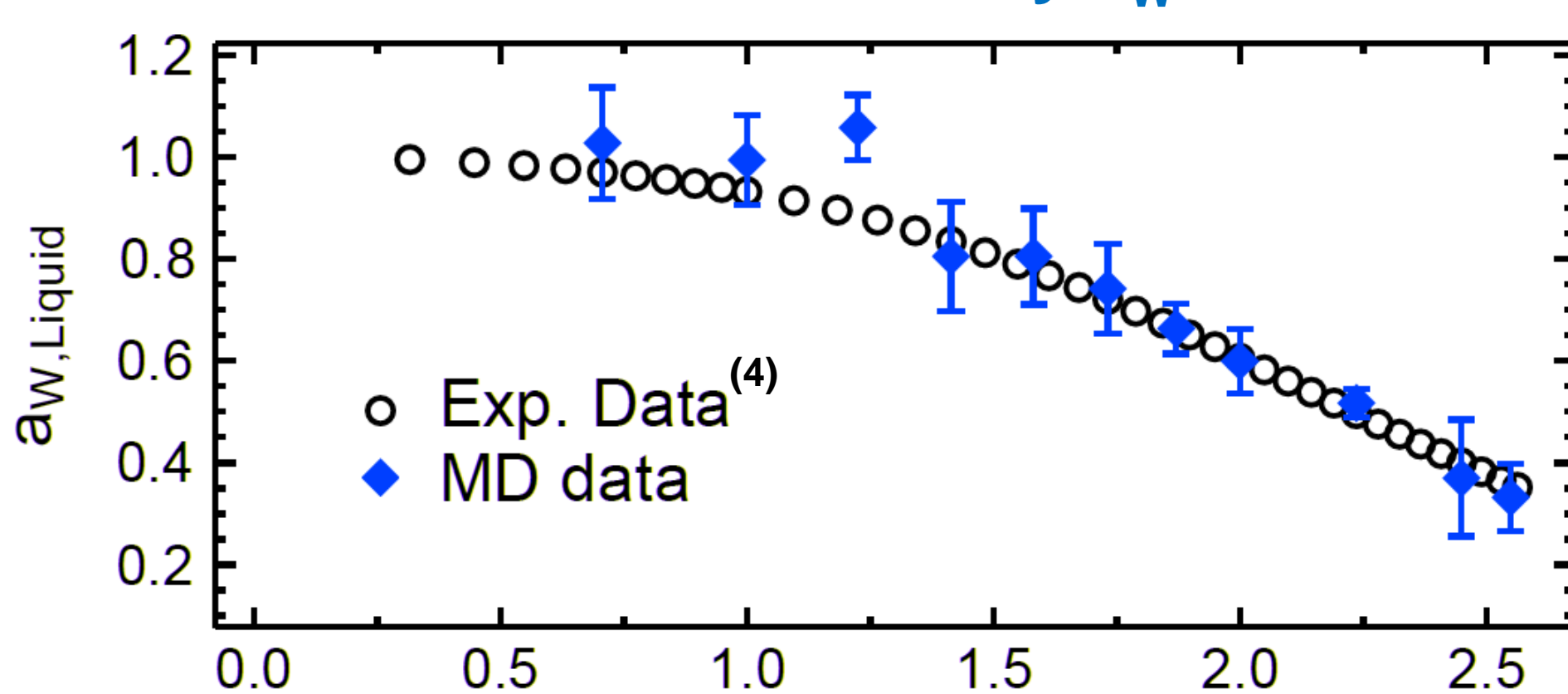
λ : Evaporation rate $\langle \tau_x \rangle$: Time of flight

$\delta_N(t)$: Relative error of the method

a_s : Solvent activity

Aqueous dysprosium nitrate $\text{Dy}(\text{NO}_3)_3$ solutions

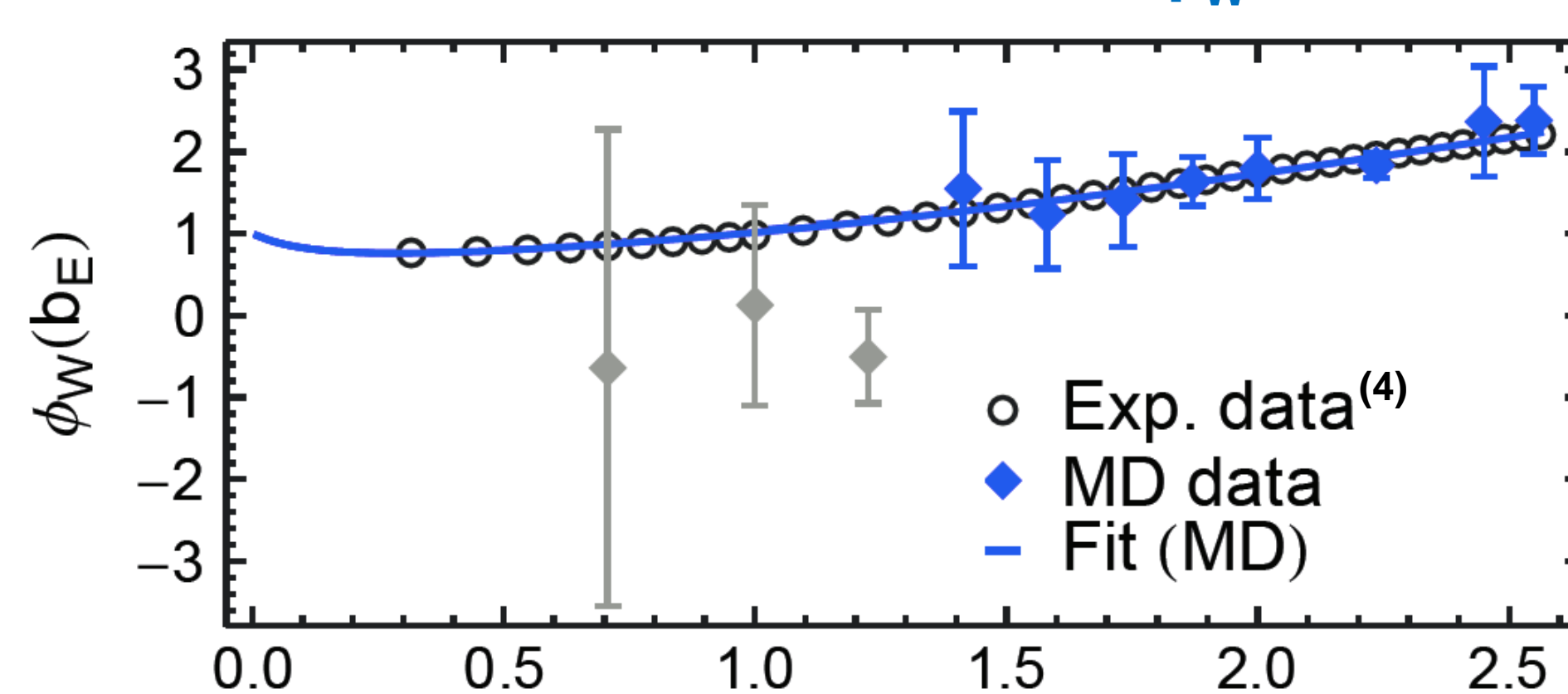
Water activity a_w



Salt concentration: $b_E^{1/2} / \text{mol}^{1/2} \text{kg}^{-1/2}$

$$a_w(b_E) = \frac{p_{\text{gas}}(b_E)}{p_{\text{gas}}^*} = \frac{\rho_{\text{gas}}(b_E)}{\rho_{\text{gas}}^*}$$

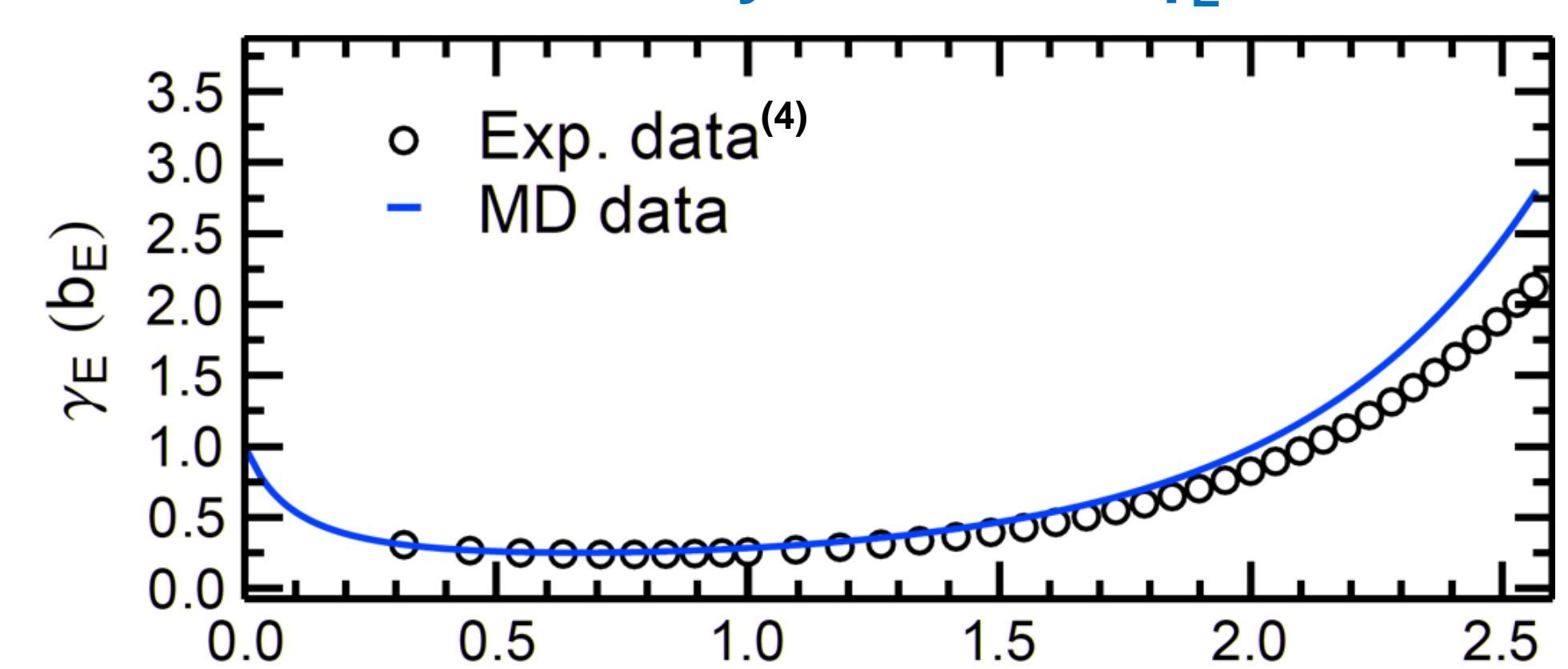
Osmotic coefficient ϕ_w



$b_E^{1/2} / \text{mol}^{1/2} \text{kg}^{-1/2}$

$$\phi_w(b_E) = \frac{-\ln a_w(b_E)}{\nu M_W b_E}$$

Activity coefficient γ_E



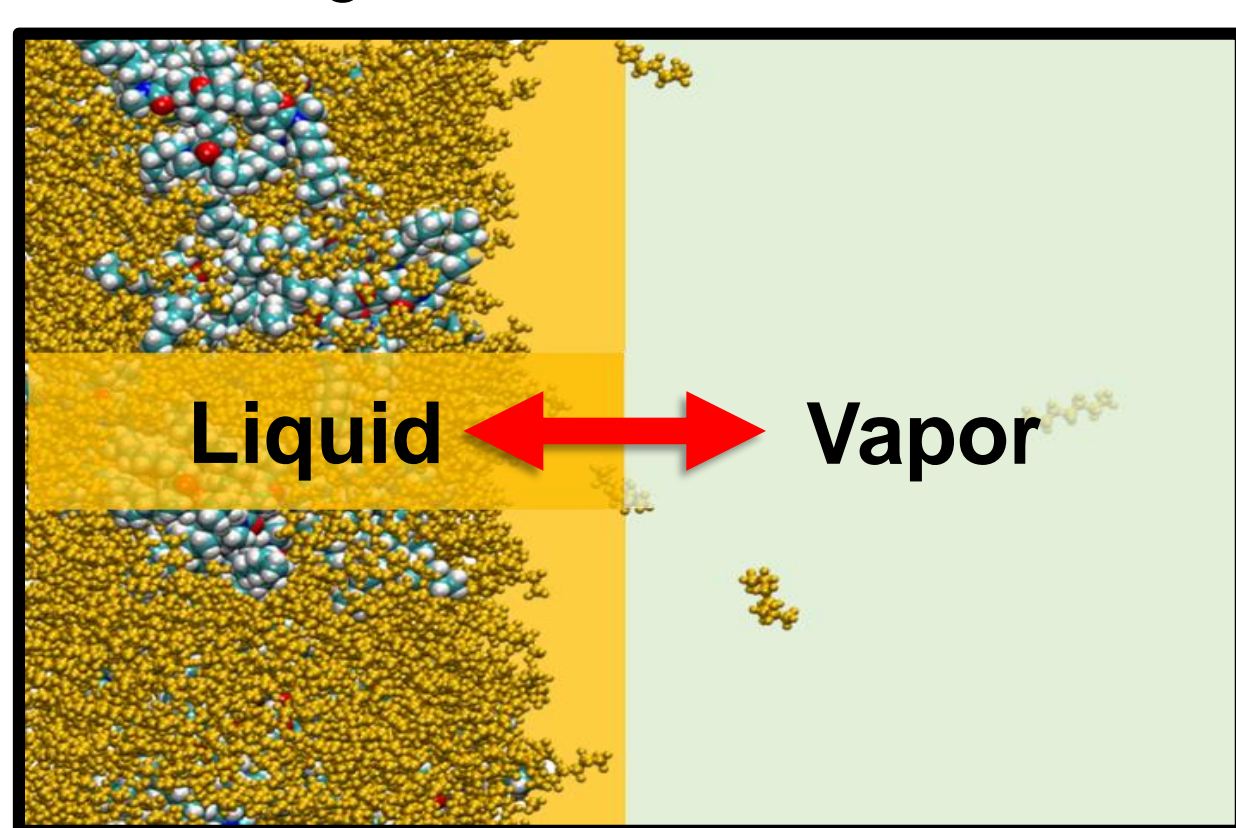
$b_E^{1/2} / \text{mol}^{1/2} \text{kg}^{-1/2}$

$$\ln \gamma_E(b_E) = \phi_w(b_E) - 1 + \int_{b=0}^{b=b_E} \frac{\phi_w(b) - 1}{b} db$$

Gibbs-Duhem relation

Organic phases

- Molecular dynamics simulation of liquid-vapor equilibria of organic solvent phases containing:



Pure solvent
+ Extractant
+ Water
+ Ionic species

Increasing computational cost

- Aggregation of DMDOHEMA in the organic phase relies on the availability of water

DMDOHEMA amphiphilic extractant

n-heptane volatile solvent

Solvent mixtures

- Ethanol-Water mixtures:** Risk of phase separation because of too weak ethanol-water interaction, but good qualitative results compared to experimental findings.

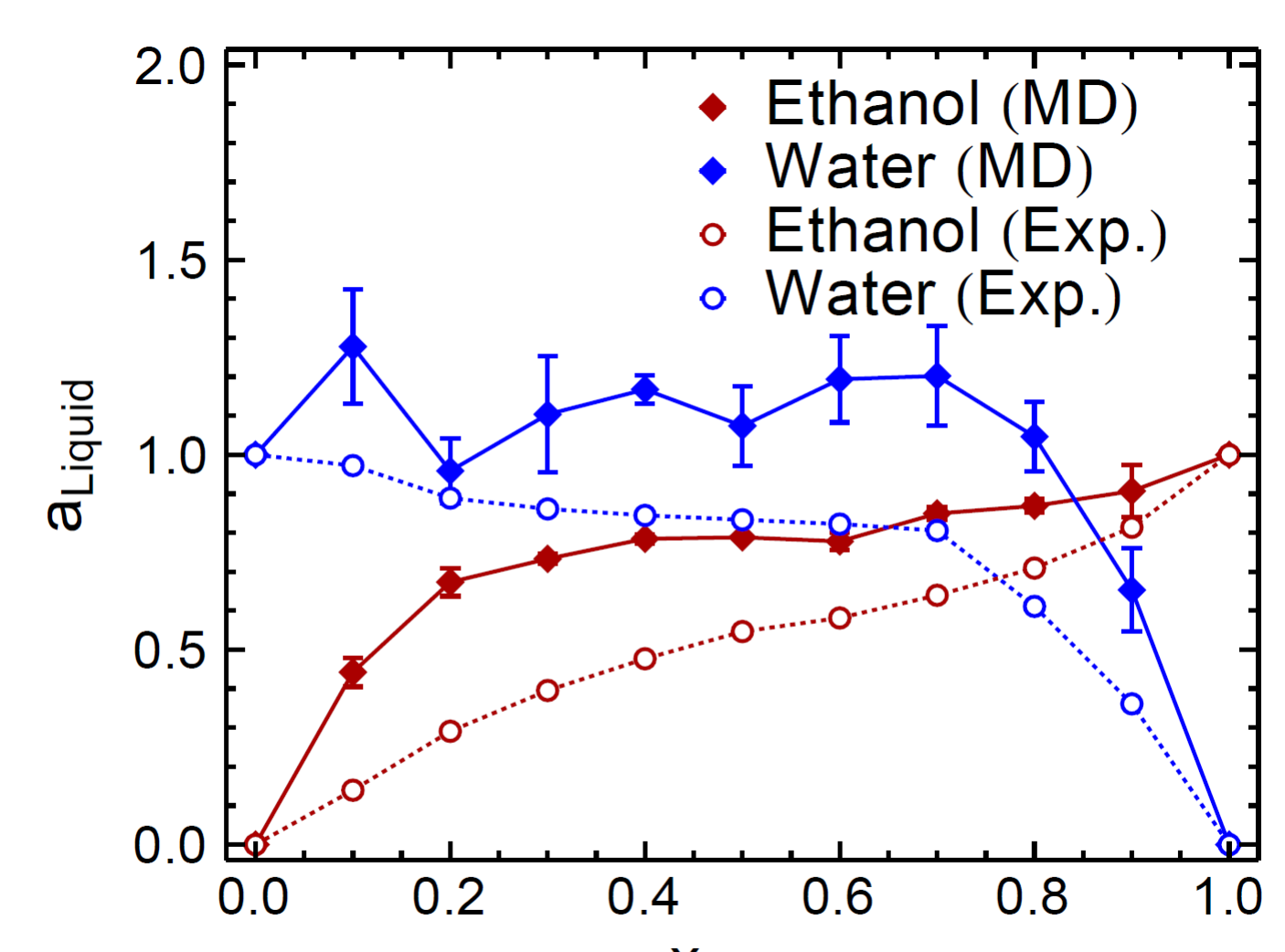
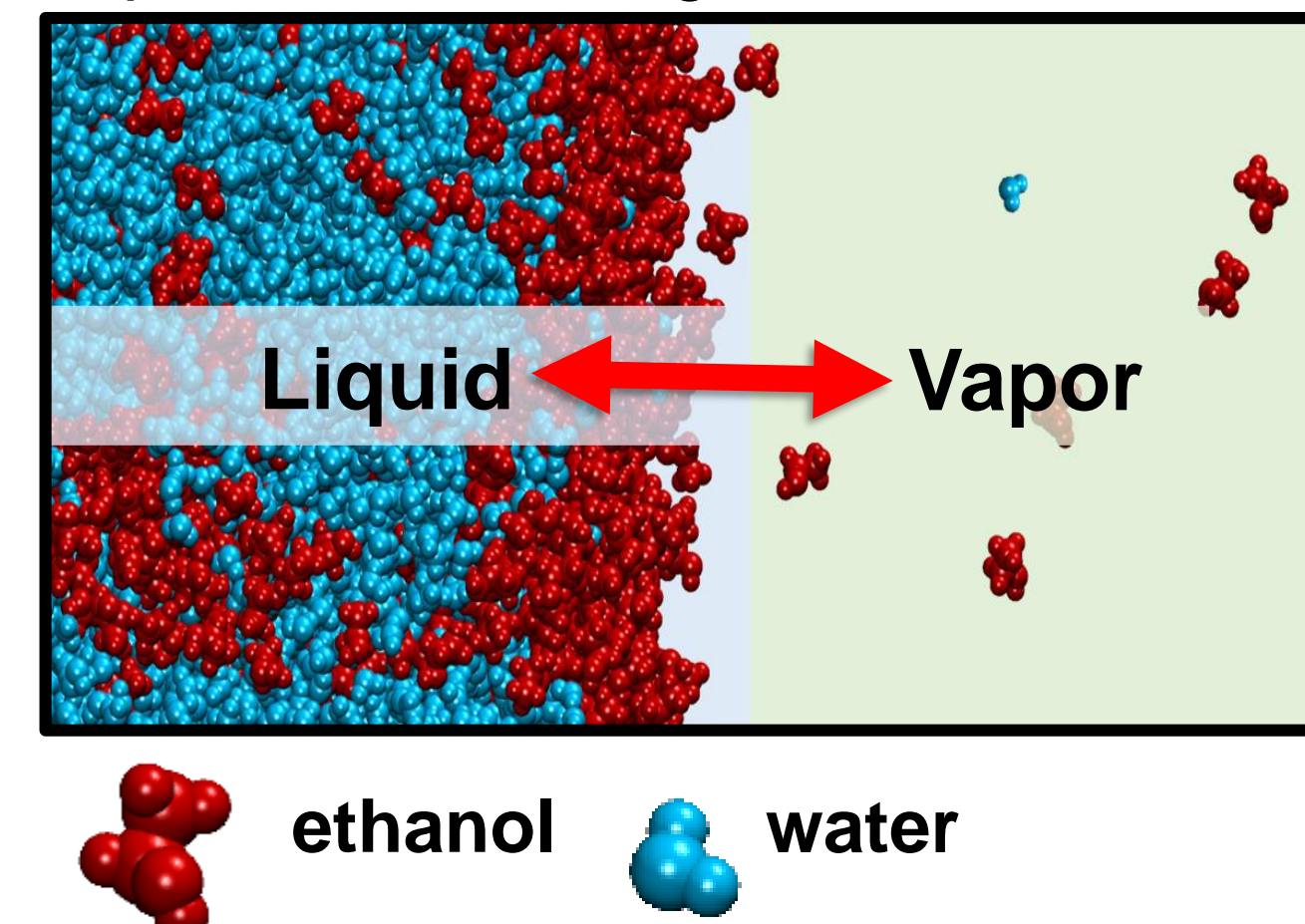


Fig. Simulated and experimental⁽⁵⁾ water and ethanol activities a_{Liquid}

Outlook and conclusion

- Aqueous salt solutions:** Results from molecular dynamics simulation are in good agreement with experimental data. Validation of the method for aqueous solutions of different cationic species and their mixtures is necessary.
- Organic Phases:** Analysis of organic solvent phases containing non-ionic extractant molecules (e.g. *n*-heptane and DMDOHEMA) for understanding their behavior.
- Solvent mixtures:** The intermolecular interactions between two different solvents require adjustments for obtaining a proper description of the liquid-vapor equilibrium.

- Simulation of activity coefficients of **complex solutions with volatile solvents** for understanding solvent extraction

References

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Acknowledgements

M. Bley would like to thank B. Siboulet, M. Spadina, A. Coste, C. Penisson, and S. Gourdin for fruitful discussions. This work was made possible thanks to the high performance computing facilities of TGCC/CCRT and the computing center of CEA Marcoule.