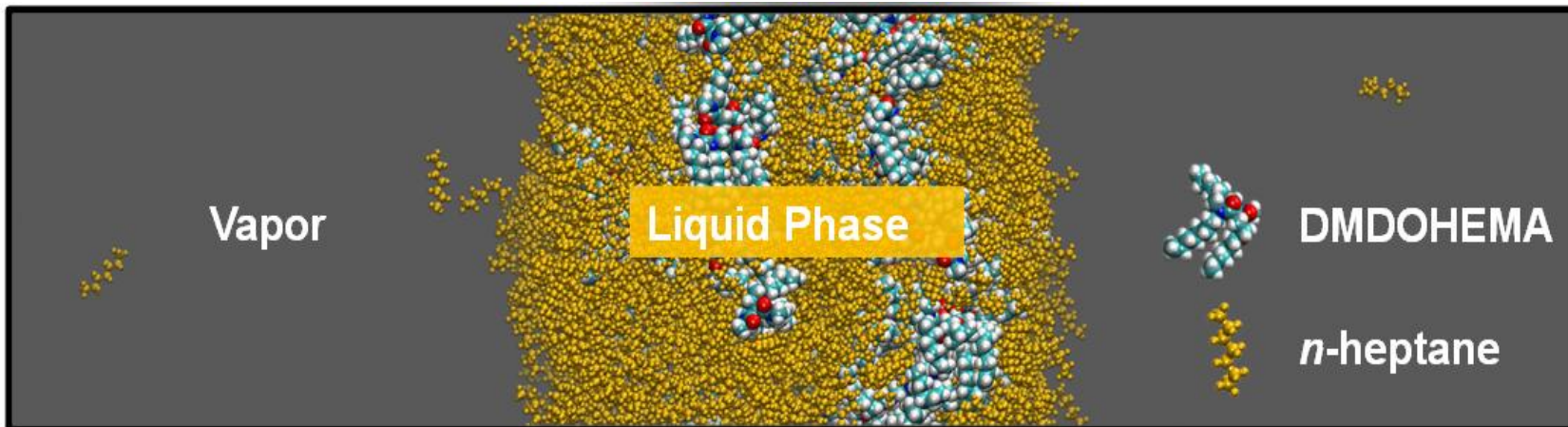




Activity Coefficients from Vapor-Liquid Interfaces: A Molecular Dynamics Approach for Separation Chemistry



- **Molecular Dynamics simulations** of a vapor-liquid equilibrium at 298.15 K with $\sim 10^4 - 10^5$ atoms for more than 10 ns
- **Solvent activity a_s directly** from the amount of solvent molecules in the gas phase
$$a_W(b_E) = \frac{p_W(b_E)}{p_W^*} = \frac{n_W(b_E)}{n_W^*}$$
- **Advantage:** Error of the method determined entirely by the evaporation rate of the solvent and the total simulation time

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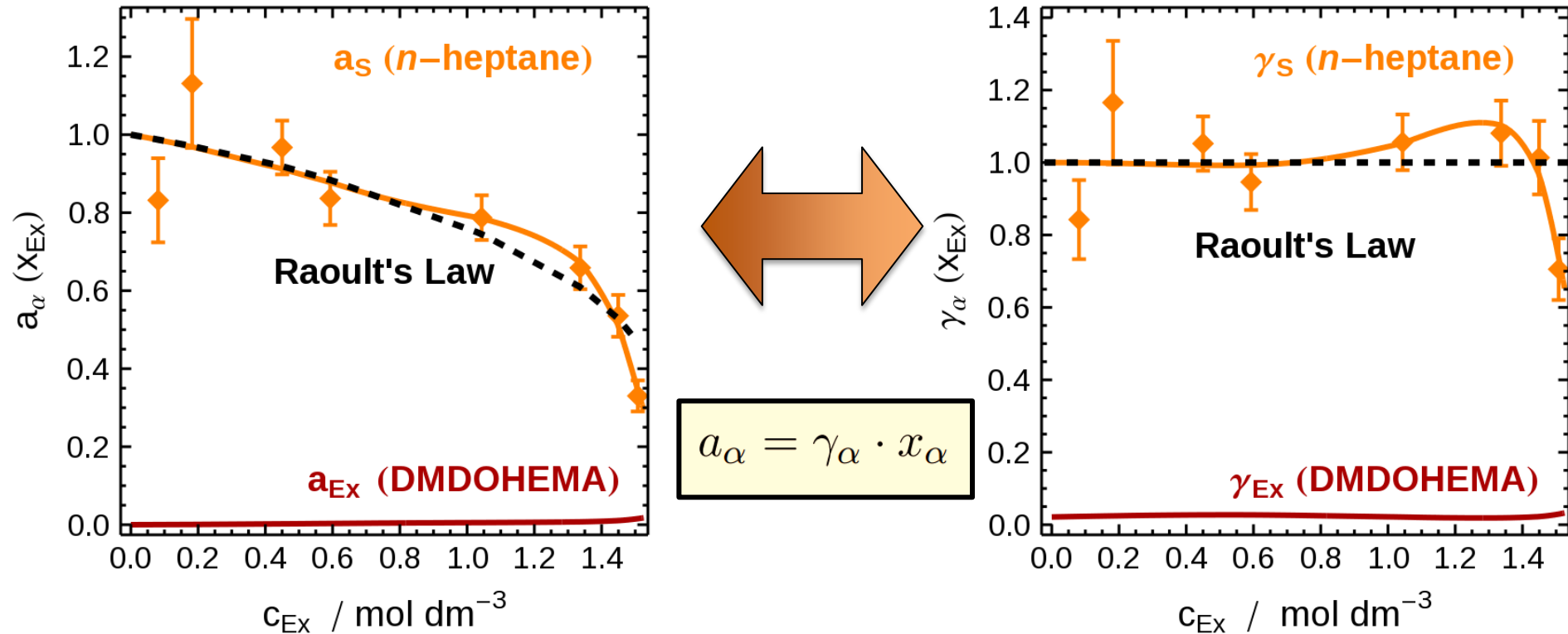
Binary Mixtures of *n*-heptane and DMDOHEMA



Calculated solvent activities fitted with the **Redlich-Kister activity model**:

$$\ln \gamma_S(x_{EX}) = x_{EX}^2 [B + C(4x_{EX} - 3) + D(2x_{EX} - 1)(6x_{EX} - 5)]$$

Solvent follows **Raoult's Law** ($a_S = 1 - x_{EX}$ and $\gamma_S \approx 1$) in good agreement



- **Mean aggregation number** taking into account monomers:

$$\bar{N} = \frac{\sum_{j=1} n_i N_{n_i}}{\sum_{j=1} N_{n_i}}$$

- *n*-heptane activities fitted with the **Van-Laar activity model**:

$$\ln \gamma_S(x_{\text{Ex}}) = B \left(\frac{Ax_{\text{Ex}}}{Ax_{\text{Ex}} + B(1 - x_{\text{Ex}})} \right)^2$$

➔ **Aggregation properties and solvent activities** in complex organic phases

