TECHNISCHE UNIVERSITÄT DARMSTADT

Sharp-interface modeling of mass transfer in multicomponent two-phase fluid systems

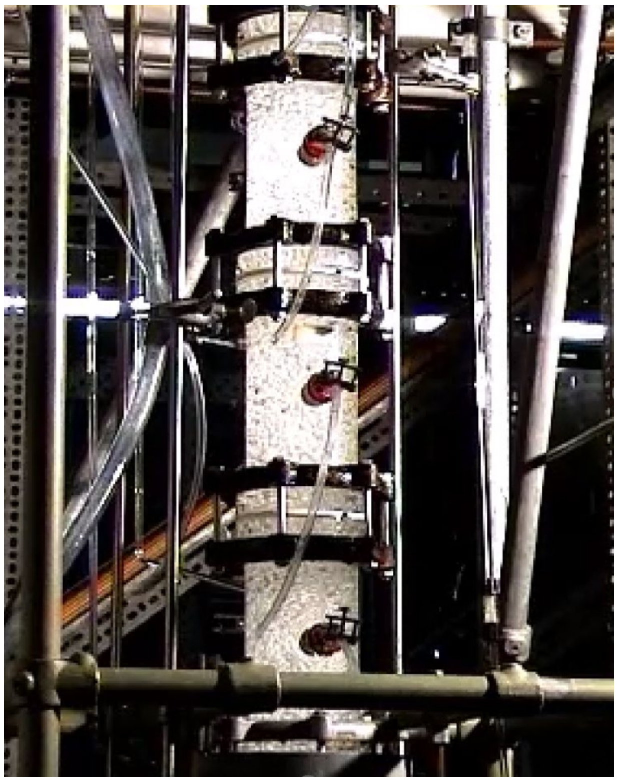
Dieter Bothe

Mathematical Modeling and Analysis

Mixtures: Modeling, Analysis & Computing

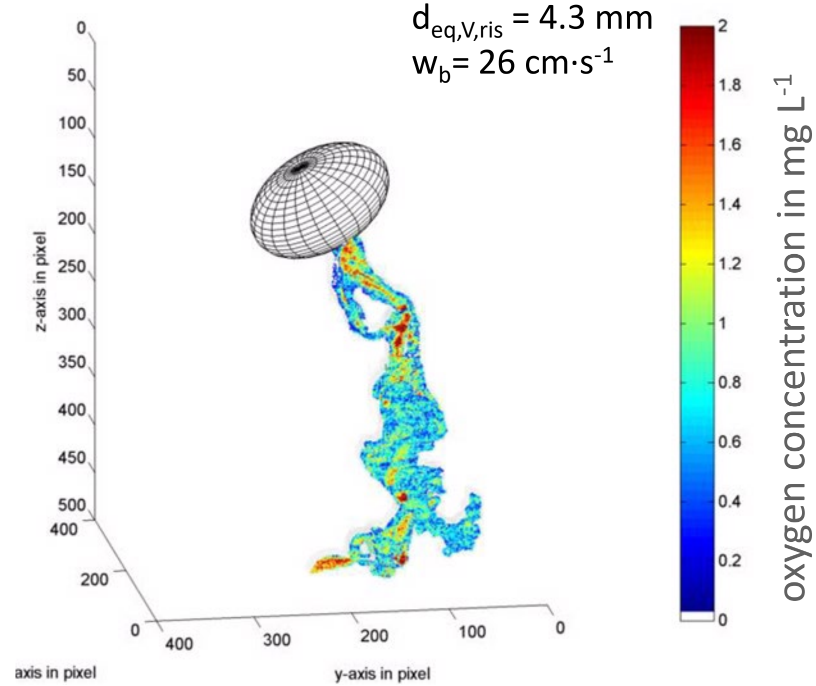
EMS Topical Activity Group *Mixtures*
Charles University, Prague, February 5-7, 2025

Motivation: Reactive Mass Transfer



Chemical Engineering Lab, U Paderborn

N_2-sat. dye solution/O_2
T = 20.2 °C
p = 1017.4 mbar
$d_{eq,V,ris}$ = 4.3 mm
w_b= 26 cm·s^{-1}



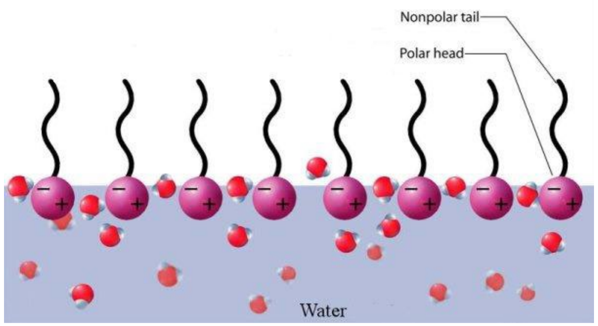
Time Resolved Scanning Laser Induced Fluorescence

Michael Schlüter, IMS, TU Hamburg-Harburg

Rüttinger, Spille, Hoffmann, Schlüter,
ChemBioEng reviews 5.4 (2018): 253-269

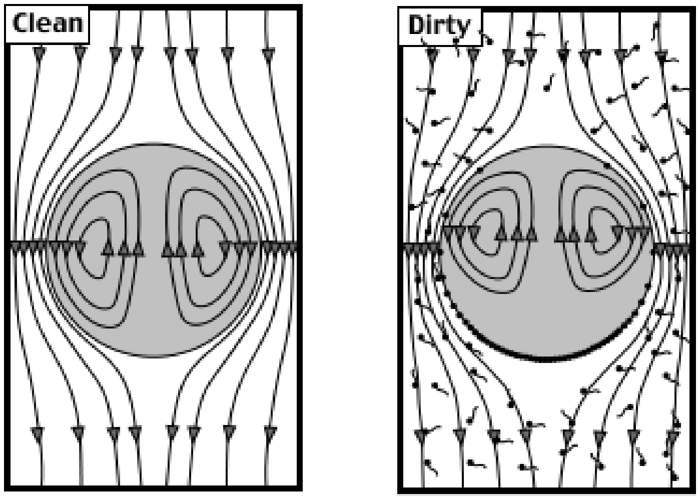
Surface Active Agents

surfactant = surface active agent



Interfacial concentration c_i^{Σ}

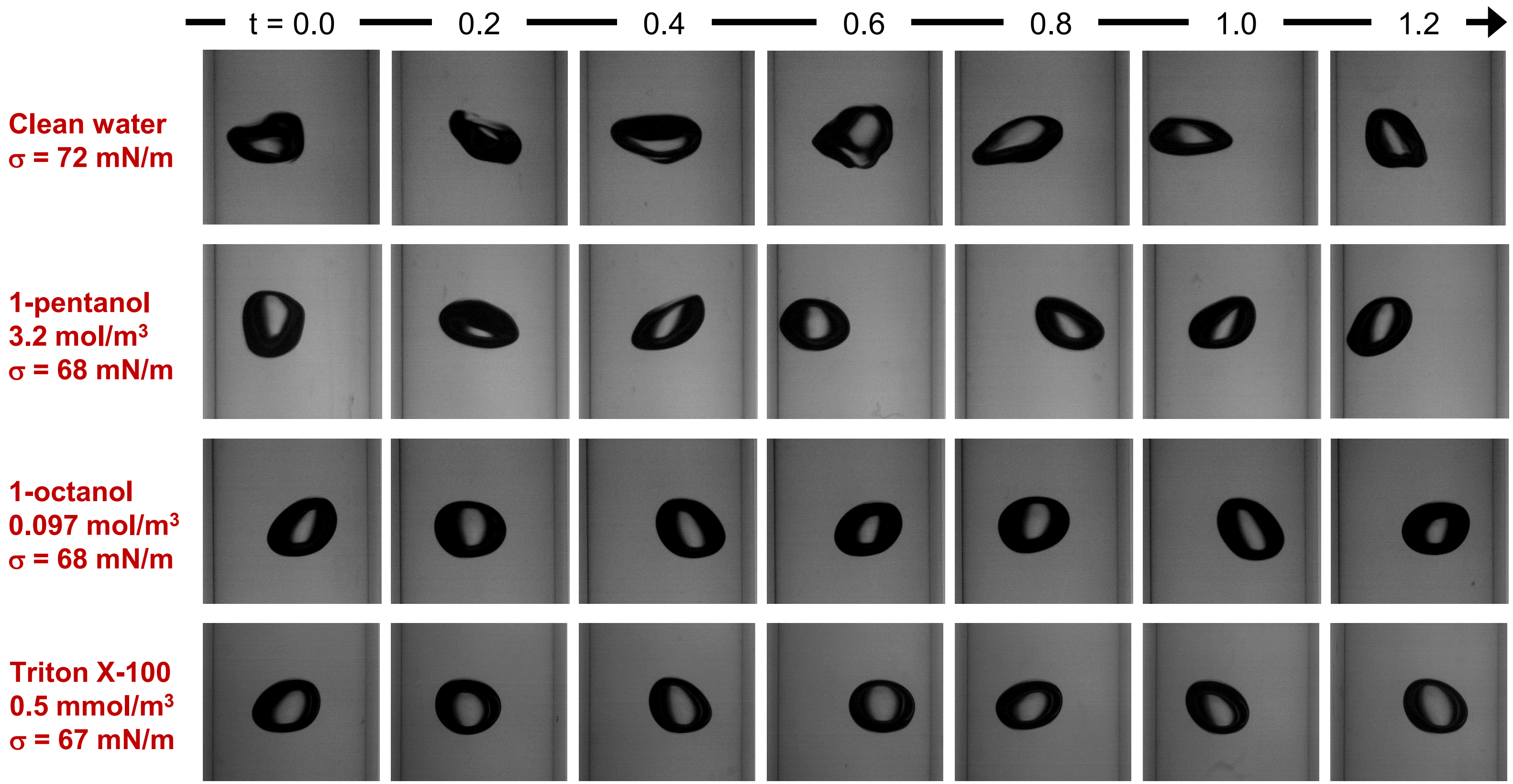
https://commons.wikimedia.org/wiki/File:Surfactant.jpg



http://www.bubbleology.com

- **Surface equation of state:** $$\sigma = \sigma(T, c_1^{\Sigma}, \ldots, c_N^{\Sigma})$$
- **Surface tension gradients induce Marangoni stress**
- **Surface coverage hinders mass transfer**

Dissolving CO_2 Bubbles in Surfactant Solutions



A. Tomiyama et al.,
Kobe University

Cf. Hori, B., Hayashi, Hosokawa, Tomiyama, Int. J. Multiph. Flow 124 (2020)

Experimental Findings by Akio Tomiyama et al.

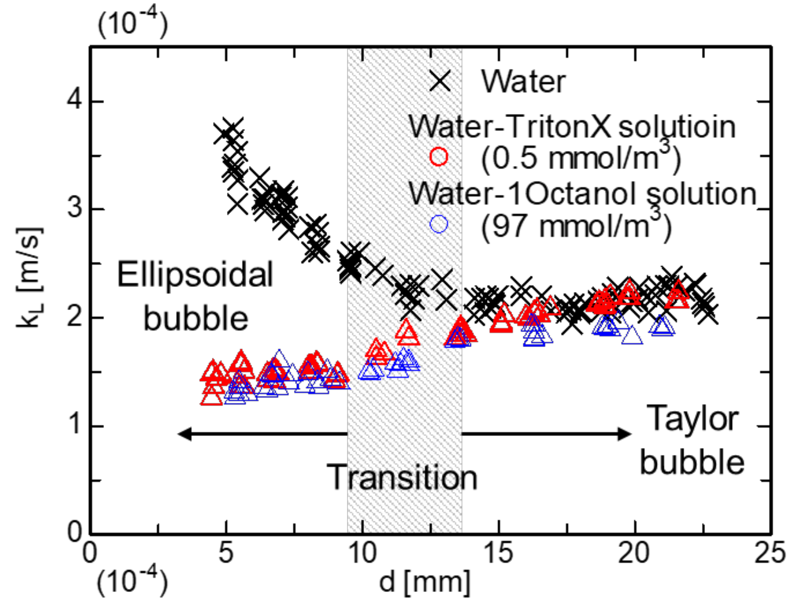
Triton X-100

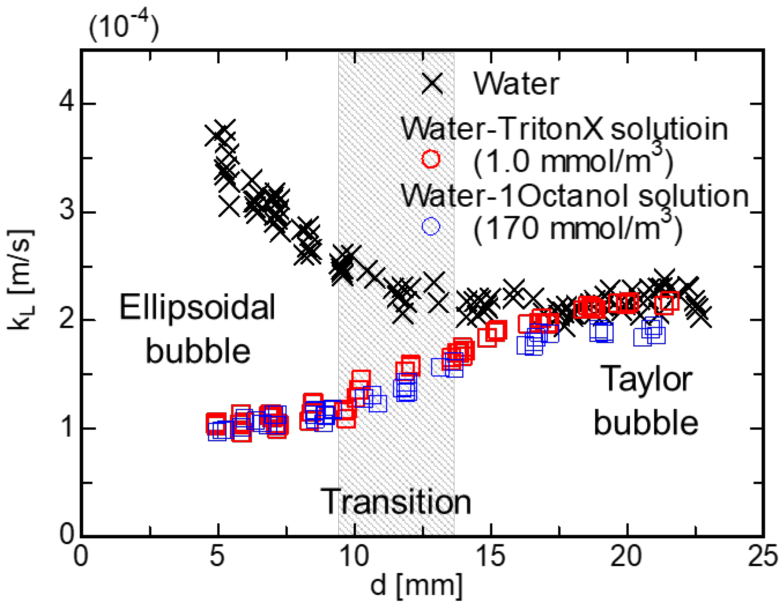
C_{sol} [mmol/m^3]	σ [mN/m]
0.5	68
1.0	65
10	52

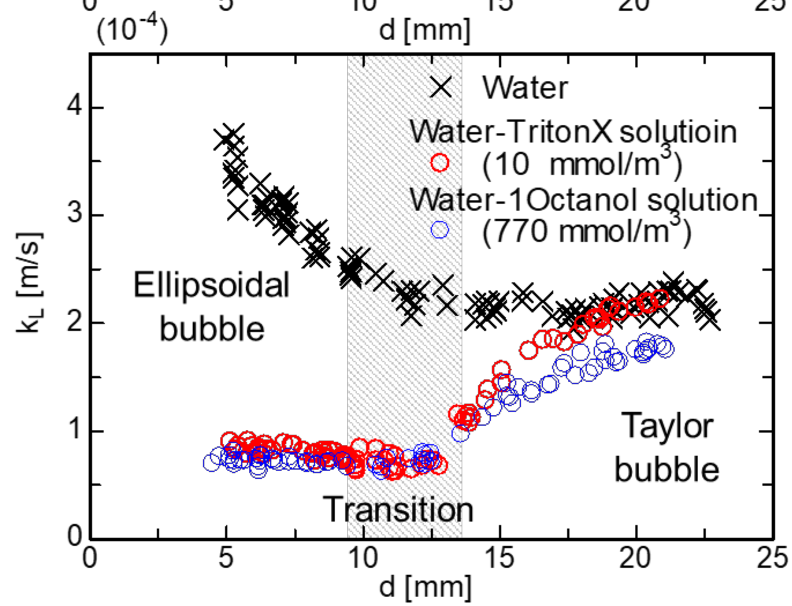
1-Octanol

C_{sol} [mmol/m^3]	σ [mN/m]
97	68
170	65
770	52

(C_{sol}: Surfactant concentration, σ:Surface tension)







Cf. Hori, B., Hayashi, Hosokawa, Tomiyama, Int. J. Multiph. Flow 124 (2020)

Effects of surface active agents on mass transfer

- **experimental findings**
  - surfactant coverage leads to local mass transfer hindrance
  - mass transfer reduction depends on the *reduction of surface tension* rather than on the surfactant concentration (type of surfactant seems irrelevant)

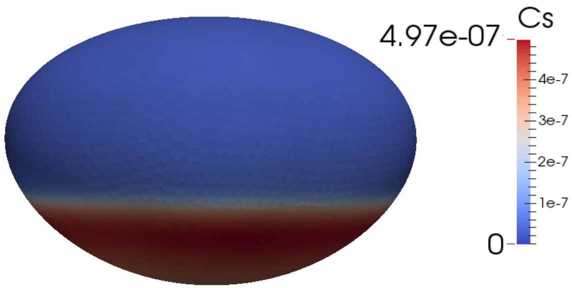
$$\dot{m}_i^{\mathrm{contam}} = \alpha(\sigma)\, \dot{m}_i^{\mathrm{clean}}$$

Thermodynamically consistent continuum model of hindered mass transfer?

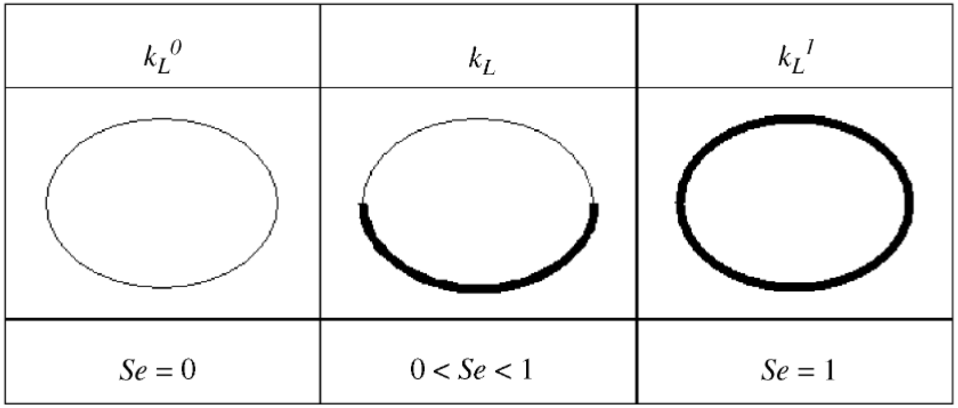
J. Aoki, et int., Tomiyama, Chem. Eng. Techn. 38 (2015)
Y. Hori, et int., Tomiyama, Int. J. Heat Mass Trans. 136 (2019)

Effects of surface active agents on mass transfer

- *hindrance* of mass transfer due to *surface coverage*



Surfactant surface concentration
$[C_s]$ = mol/m^2, t = 0.08 s.



surface coverage ratio

$$Se = \frac{\Gamma_{eq}}{\Gamma_\infty} = \frac{\beta C_{sol}}{\alpha + \beta C_{sol}}$$

Sardeing model : $Sh = (1 - Se)Sh_{clean} + Se Sh_{dirty}$

$$Sh_{clean} = 0.42[\Delta\rho g d^3 / \rho_L \nu_L^2]^{1/3} Sc^{1/2}$$

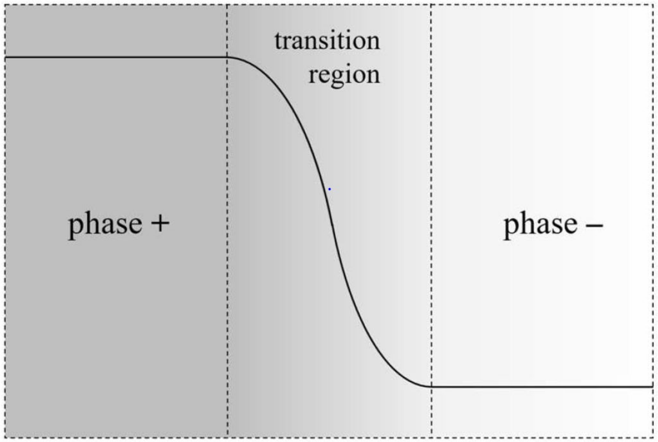
$$Sh_{dirty} = 0.54(\alpha/\beta)^{0.0837}(g d^3 / \nu_L^2)^{1/3} Sc^{1/3}$$

R. Sardeing et al., Chem. Eng. Sci. 61 (2006)

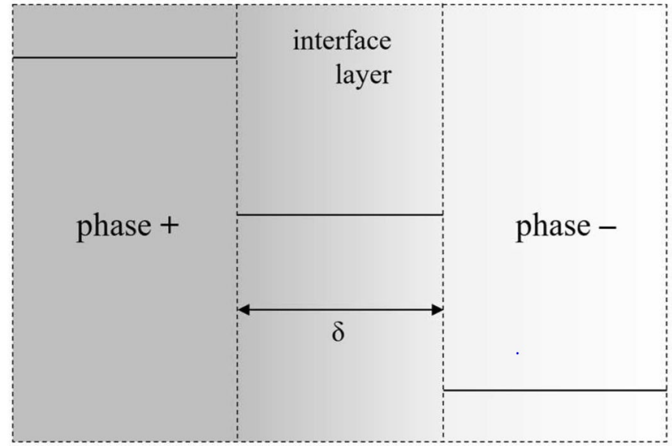
No quantitative match with experimental data (A. Tomiyama, Kobe Univ.)

Contents

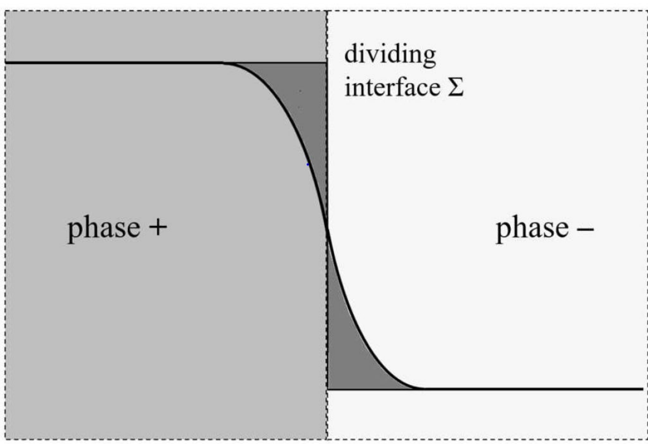
Various Interface Conceptions



Diffuse interface



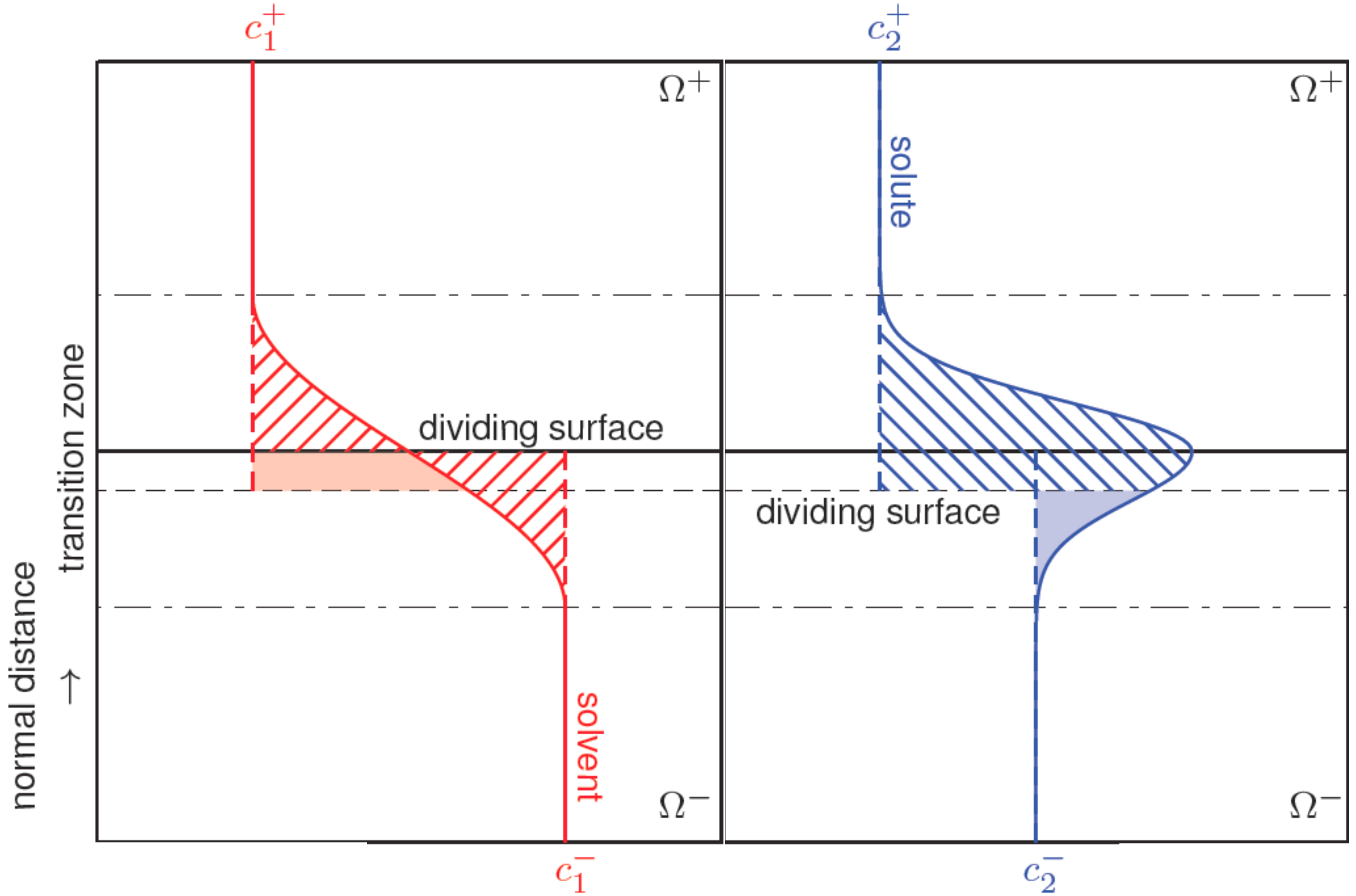
Guggenheim's interface layer



Gibbs' dividing interface

Chosing the Interface Position

Gibbs‘ construction of a dividing interface

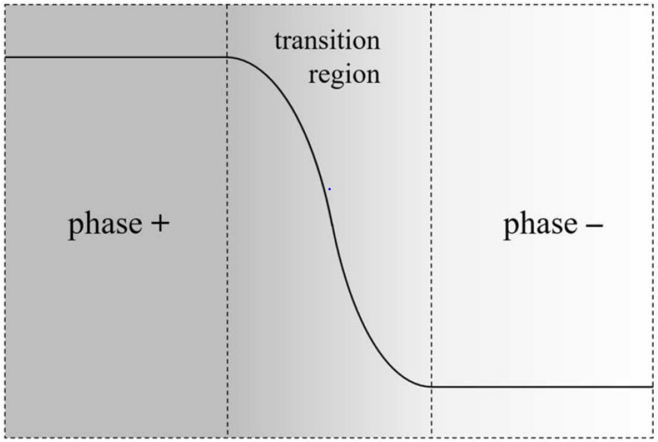


- **replace steep gradient by discontinuous field**
- **introduce excess quantities to conserve (partial) mass**

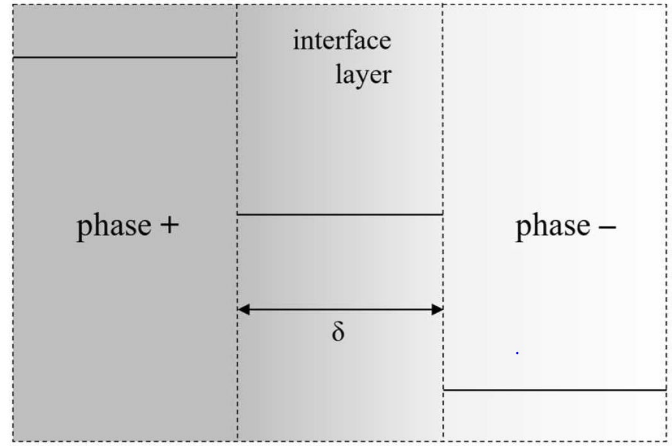
Chosing the Interface Concept

- **Gibbs‘ construction tricky for multicomponent systems**
  - excess concentrations can become negative
  - components appear/disappear on Σ depending on position of Σ
  - modified construction of van den Tempel / Lucassen-Reynders: positive excess, but interface can be shifted far away
- **Is a transfer species like CO_2 present on the interface ?**
  - answer depends on the modeling approach !
  - in diffuse interface models, any species is present in the transition layer
  - unspecified in the Gibbs construction
  - model by Guggenheim keeps the interface layer

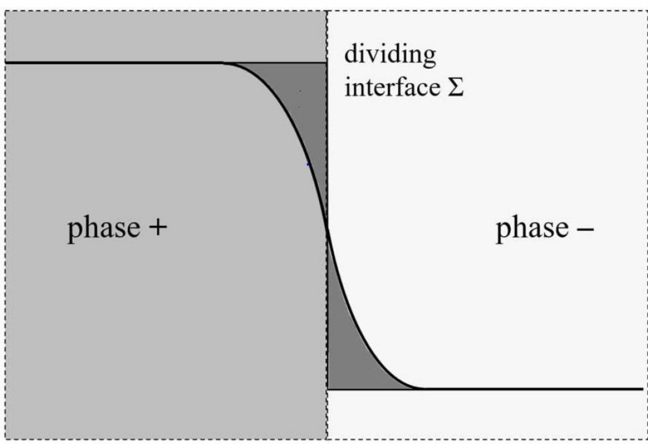
Various Interface Conceptions



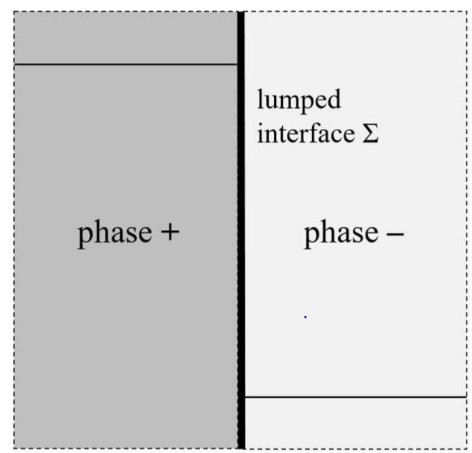
Diffuse interface



Guggenheim's interface layer



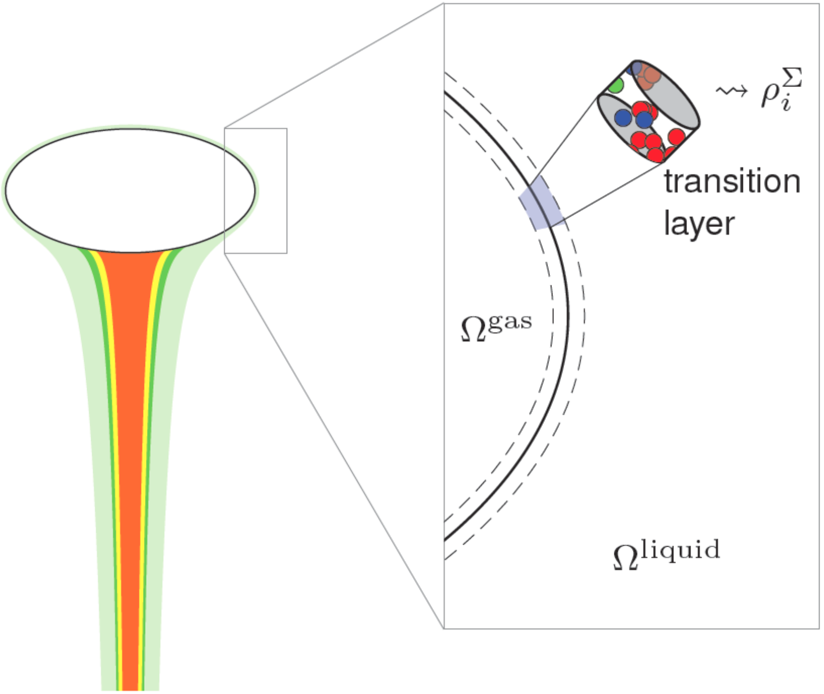
Gibbs' dividing interface



lumped interface layer

Effects of surface active agents on mass transfer

- sharp-interface continuum thermodynamics of multi-component fluid systems with ***non-vanishing interfacial mass densities*** for all constituents !



Aim: Thermodynamically consistent theory of local mass transfer resistance

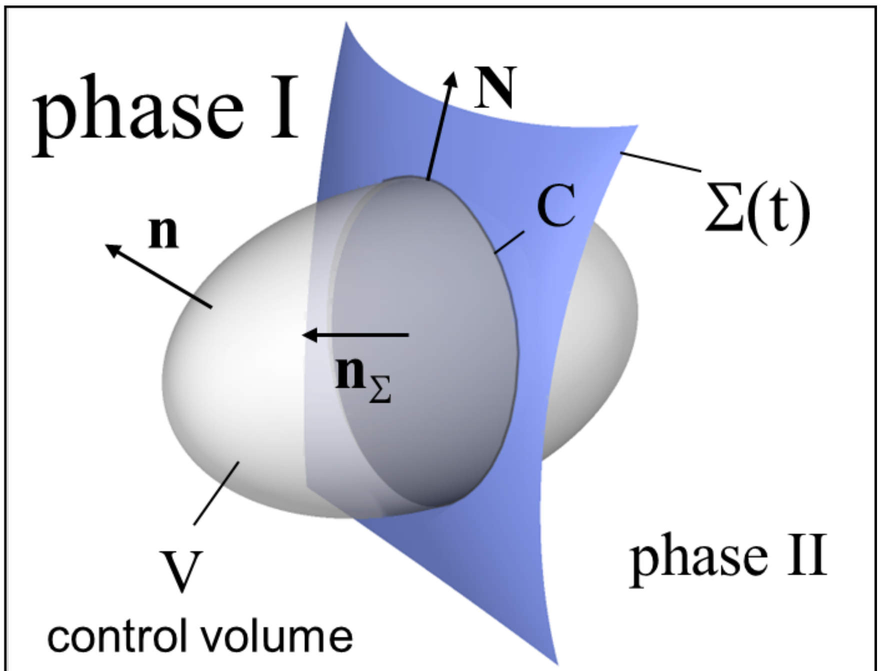
D. Bothe: Sharp-interface continuum thermodynamics of multicomponent fluid systems with interfacial mass. Int. Journal of Engineering Science **179**, 103731 (2022).

D. Bothe: Multi-velocity sharp-interface continuum thermodynamics of fluid systems with adsorption. arXiv:2502.00906 (2025).

Contents

Two-phase integral balance equations

$$\frac{\mathrm{d}}{\mathrm{d}t}\left(\int_V \phi\,\mathrm{d}x + \int_{\Sigma_V} \phi^\Sigma\,\mathrm{d}o\right) = -\int_{\partial V} \mathbf{j}\cdot\mathbf{n}\,\mathrm{d}o + \int_V f\,\mathrm{d}x - \int_{\partial\Sigma_V} \mathbf{j}^\Sigma\cdot\mathbf{N}\,\mathrm{d}s + \int_{\Sigma_V} f^\Sigma\,\mathrm{d}o$$



- $\Omega^+(t), \Omega^-(t)$ bulk phases
- $\mathbf{n}_\Sigma$ unit interface normal (into Ω^-)
- $\mathbf{n}$ outer unit normal to V
- $\Sigma(t)$ interface, $\Sigma_V(t) := \Sigma(t) \cap V$
- $\partial\Sigma_V$ boundary curve of Σ_V
- $\mathbf{N}$ outer unit normal to $\partial\Sigma_V$, $\mathbf{N} \perp \mathbf{n}_\Sigma$

Balance equations for mass, momentum, energy

partial mass balance

$$\partial_t \rho_i + \operatorname{div}\left(\rho_i \mathbf{v} + \mathbf{j}_i\right) = M_i r_i$$

$$\partial_t^\Sigma \rho_i^\Sigma + \operatorname{div}_\Sigma\left(\rho_i^\Sigma \mathbf{v}^\Sigma + \mathbf{j}_i^\Sigma\right) + [\![\rho_i(\mathbf{v} - \mathbf{v}^\Sigma) + \mathbf{j}_i]\!] \cdot \mathbf{n}_\Sigma = M_i r_i^\Sigma$$

momentum balance

$$\partial_t(\rho \mathbf{v}) + \operatorname{div}\left(\rho \mathbf{v} \otimes \mathbf{v} - \mathbf{S}\right) = \rho \mathbf{b},$$

$$\partial_t^\Sigma(\rho^\Sigma \mathbf{v}^\Sigma) + \nabla_\Sigma \cdot (\rho^\Sigma \mathbf{v}^\Sigma \otimes \mathbf{v}^\Sigma - \mathbf{S}^\Sigma) + [\![\rho \mathbf{v} \otimes (\mathbf{v} - \mathbf{v}^\Sigma) - \mathbf{S}]\!] \cdot \mathbf{n}_\Sigma = \rho^\Sigma \mathbf{b}^\Sigma$$

internal energy balance

$$\partial_t(\rho e) + \nabla \cdot (\rho e \mathbf{v} + \mathbf{q}) = \nabla \mathbf{v} : \mathbf{S} + \sum_{i=1}^N \mathbf{j}_i \cdot \mathbf{b}_i$$

$$\partial_t^\Sigma(\rho^\Sigma e^\Sigma) + \nabla_\Sigma \cdot (\rho^\Sigma e^\Sigma \mathbf{v}^\Sigma + \mathbf{q}^\Sigma) + [\![\dot{m}\left(e + \frac{(\mathbf{v} - \mathbf{v}^\Sigma)^2}{2}\right)]\!]$$

$$- [\![(\mathbf{v} - \mathbf{v}^\Sigma) \cdot (\mathbf{S}\,\mathbf{n}_\Sigma)]\!] + [\![\mathbf{q} \cdot \mathbf{n}_\Sigma]\!] = \nabla_\Sigma \mathbf{v}^\Sigma : \mathbf{S}^\Sigma + \sum_{i=1}^N \mathbf{j}_i^\Sigma \cdot \mathbf{b}_i^\Sigma$$

Entropy Balance for Bulk-Interface

integral entropy balance

$$\frac{\mathrm{d}}{\mathrm{d}t}\Big(\int_{V(t)} \rho s \,\mathrm{d}x + \int_{A(t)} \rho^\Sigma s^\Sigma \,\mathrm{d}o\Big) = -\int_{\partial V(t)} \mathbf{\Phi}\cdot\mathbf{n}\,\mathrm{d}o + \int_{V(t)} \zeta\,\mathrm{d}x$$

$$-\int_{\partial A(t)} \mathbf{\Phi}^\Sigma \cdot \mathbf{N}\,\mathrm{d}s + \int_{A(t)} \zeta^\Sigma\,\mathrm{d}o$$

$$\zeta \geq 0 \qquad \zeta^\Sigma \geq 0$$

local entropy balance

$$\partial_t(\rho s) + \nabla\cdot(\rho s\mathbf{v} + \mathbf{\Phi}) = \zeta \quad \text{in } \Omega\setminus\Sigma$$

$$\partial_t^\Sigma(\rho^\Sigma s^\Sigma) + \nabla_\Sigma\cdot(\rho^\Sigma s^\Sigma \mathbf{v}^\Sigma + \mathbf{\Phi}^\Sigma) + [\![\rho s(\mathbf{v}-\mathbf{v}^\Sigma) + \mathbf{\Phi}]\!]\cdot\mathbf{n}_\Sigma = \zeta^\Sigma \quad \text{on } \Sigma$$

$$[\![\phi]\!](t,\mathbf{x}) := \lim_{h\to 0+}\big(\phi(t,\mathbf{x}+h\mathbf{n}_\Sigma) - \phi(t,\mathbf{x}-h\mathbf{n}_\Sigma)\big)$$

Interfacial Entropy Production

Reduced interfacial entropy production (zero interfacial viscosities):

$$
\begin{aligned}
\zeta^\Sigma = {} & \mathbf{q}^\Sigma \cdot \nabla_\Sigma \frac{1}{T^\Sigma} - \sum_{i=1}^{N} \mathbf{j}_i^\Sigma \cdot \left(\nabla_\Sigma \frac{\mu_i^\Sigma}{T^\Sigma} - \frac{\mathbf{b}_i^\Sigma}{T^\Sigma} \right) - \frac{1}{T} \sum_{a=1}^{N_R^\Sigma} R_a^\Sigma \mathcal{A}_a^\Sigma \\
& - \frac{1}{T^\Sigma} (\mathbf{v}^+ - \mathbf{v}^\Sigma)_{||} \cdot (\mathbf{S}^+ \mathbf{n}^+)_{||} - \frac{1}{T^\Sigma} (\mathbf{v}^- - \mathbf{v}^\Sigma)_{||} \cdot (\mathbf{S}^- \mathbf{n}^-)_{||} \\
& + \left(\frac{1}{T^\Sigma} - \frac{1}{T^+} \right) \left(\dot{m}^{+,\Sigma} (e^+ + \frac{p^+}{\rho^+}) + \mathbf{q}^+ \cdot \mathbf{n}^+ \right) \\
& + \left(\frac{1}{T^\Sigma} - \frac{1}{T^-} \right) \left(\dot{m}^{-,\Sigma} (e^- + \frac{p^-}{\rho^-}) + \mathbf{q}^- \cdot \mathbf{n}^- \right) \\
& + \sum_{i=1}^{N} \dot{m}_i^{+,\Sigma} \left(\frac{\mu_i^+}{T^+} - \frac{\mu_i^\Sigma}{T^\Sigma} + \frac{1}{T^\Sigma} \left(\frac{(\mathbf{v}^+ - \mathbf{v}^\Sigma)^2}{2} - \mathbf{n}^+ \frac{\mathbf{S}^{+,\mathrm{irr}}}{\rho^+} \mathbf{n}^+ \right) \right) \\
& + \sum_{i=1}^{N} \dot{m}_i^{-,\Sigma} \left(\frac{\mu_i^-}{T^-} - \frac{\mu_i^\Sigma}{T^\Sigma} + \frac{1}{T^\Sigma} \left(\frac{(\mathbf{v}^- - \mathbf{v}^\Sigma)^2}{2} - \mathbf{n}^- \frac{\mathbf{S}^{-,\mathrm{irr}}}{\rho^-} \mathbf{n}^- \right) \right)
\end{aligned}
$$

Interfacial Entropy Production - Literature

Kovac, J.: Non-equilibrium thermodynamics of interfacial systems, Physica A **86**, 1-24 (1977).

Bedeaux, D.: Nonequilibrium thermodynamics and statistical physics of surfaces, pp. 47-109 in *Advance in Chemical Physics* **64** (I. Prigogine, S.A. Rice, eds), Jon Wiley & Sons 1986.

Slattery, J.C.: *Interfacial Transport Phenomena*. Springer, New York 1990.

Sagis, L.M.C.: Dynamic behavior of interfaces: Modeling with nonequilibrium thermodynamics, Adv. Colloid & Interf. Sci. **206**, 328-343 (2014).

Dreyer, W., Guhlke, C., Müller, R.: Bulk-surface electrothermodynamics and applications to electrochemistry, Entropy **20**, 939,1-44 (2018).

Bothe, D.: Sharp-interface continuum thermodynamics of multicomponent fluid systems with interfacial mass*, Int. J. Eng. Sci. **179**, 103731 (2022).

six different contributions six different results...

*based on conference proceedings: D.B. IBW7 (2015), D.B. RIMS (2016)

Interfacial Entropy Production

Reduced interfacial entropy production (zero interfacial viscosities):

$$\zeta^\Sigma = \mathbf{q}^\Sigma \cdot \nabla_\Sigma \frac{1}{T^\Sigma} - \sum_{i=1}^{N} \mathbf{j}_i^\Sigma \cdot \left(\nabla_\Sigma \frac{\mu_i^\Sigma}{T^\Sigma} - \frac{\mathbf{b}_i^\Sigma}{T^\Sigma} \right) - \frac{1}{T} \sum_{a=1}^{N_R^\Sigma} R_a^\Sigma \mathcal{A}_a^\Sigma$$

$$- \frac{1}{T^\Sigma} (\mathbf{v}^+ - \mathbf{v}^\Sigma)_{||} \cdot (\mathbf{S}^+ \mathbf{n}^+)_{||} - \frac{1}{T^\Sigma} (\mathbf{v}^- - \mathbf{v}^\Sigma)_{||} \cdot (\mathbf{S}^- \mathbf{n}^-)_{||}$$

$$+ \left(\frac{1}{T^\Sigma} - \frac{1}{T^+} \right) \left(\dot{m}^{+,\Sigma} (e^+ + \frac{p^+}{\rho^+}) + \mathbf{q}^+ \cdot \mathbf{n}^+ \right)$$

$$+ \left(\frac{1}{T^\Sigma} - \frac{1}{T^-} \right) \left(\dot{m}^{-,\Sigma} (e^- + \frac{p^-}{\rho^-}) + \mathbf{q}^- \cdot \mathbf{n}^- \right)$$

$$+ \sum_{i=1}^{N} \dot{m}_i^{+,\Sigma} \left(\frac{\mu_i^+}{T^+} - \frac{\mu_i^\Sigma}{T^\Sigma} + \frac{1}{T^\Sigma} \left(\frac{(\mathbf{v}^+ - \mathbf{v}^\Sigma)^2}{2} - \mathbf{n}^+ \frac{\mathbf{S}^{+,\mathrm{irr}}}{\rho^+} \mathbf{n}^+ \right) \right)$$

$$+ \sum_{i=1}^{N} \dot{m}_i^{-,\Sigma} \left(\frac{\mu_i^-}{T^-} - \frac{\mu_i^\Sigma}{T^\Sigma} + \frac{1}{T^\Sigma} \left(\frac{(\mathbf{v}^- - \mathbf{v}^\Sigma)^2}{2} - \mathbf{n}^- \frac{\mathbf{S}^{-,\mathrm{irr}}}{\rho^-} \mathbf{n}^- \right) \right)$$

Class I

are these terms grouped correctly?

Interfacial Entropy Production – Class II

$$
\begin{aligned}
\zeta^\Sigma =& \frac{1}{T^\Sigma}\sum_{i=1}^{N}\nabla_\Sigma \mathbf{S}_i^{\Sigma,\circ} : \mathbf{D}_i^{\Sigma,\circ} + \frac{1}{T^\Sigma}\sum_{i=1}^{N}\pi_i^\Sigma \nabla_\Sigma\cdot\mathbf{v}_i^\Sigma + \mathbf{q}^\Sigma\cdot\nabla_\Sigma\frac{1}{T^\Sigma} - \frac{1}{T^\Sigma}\sum_a R_a^\Sigma \mathcal{A}_a^\Sigma \\
&- \sum_{i=1}^{N}\mathbf{u}_i^\Sigma\cdot\Big(\rho_i^\Sigma\nabla_\Sigma\frac{\mu_i^\Sigma}{T^\Sigma} + \frac{1}{T^\Sigma}\big(\mathbf{f}_i^\Sigma - r_i^\Sigma(\mathbf{v}_i^\Sigma - \frac{\mathbf{u}_i^\Sigma}{2}) - \nabla_\Sigma p_i^\Sigma\big)\Big) \\
&- \frac{1}{T^\Sigma}\sum_{i=1}^{N}(\mathbf{v}_i^+ - \mathbf{v}_i^\Sigma)_{||}\cdot(\mathbf{S}_i^{+,\mathrm{irr}}\mathbf{n}^+)_{||} - \frac{1}{T^\Sigma}\sum_{i=1}^{N}(\mathbf{v}_i^- - \mathbf{v}_i^\Sigma)_{||}\cdot(\mathbf{S}_i^{-,\mathrm{irr}}\mathbf{n}^-)_{||} \\
&- \Big(\frac{1}{T^+} - \frac{1}{T^\Sigma}\Big)(\dot m^{+,\Sigma} h^+ + \mathbf{q}^+\cdot\mathbf{n}^+) - \Big(\frac{1}{T^-} - \frac{1}{T^\Sigma}\Big)(\dot m^{-,\Sigma} h^- + \mathbf{q}^-\cdot\mathbf{n}^-) \\
&+ \sum_{i=1}^{N}\dot m_i^{+,\Sigma}\Big(\frac{\mu_i^+}{T^+} - \frac{\mu_i^\Sigma}{T^\Sigma} + \frac{1}{T^\Sigma}\Big(\frac{(\mathbf{v}_i^+ - \mathbf{v}_i^\Sigma)^2}{2} - \mathbf{n}^+\cdot\frac{\mathbf{S}_i^{+,\mathrm{irr}}}{\rho_i^+}\mathbf{n}^+\Big)\Big) \\
&+ \sum_{i=1}^{N}\dot m_i^{-,\Sigma}\Big(\frac{\mu_i^-}{T^-} - \frac{\mu_i^\Sigma}{T^\Sigma} + \frac{1}{T^\Sigma}\Big(\frac{(\mathbf{v}_i^- - \mathbf{v}_i^\Sigma)^2}{2} - \mathbf{n}^-\cdot\frac{\mathbf{S}_i^{-,\mathrm{irr}}}{\rho_i^-}\mathbf{n}^-\Big)\Big),
\end{aligned}
$$

Class II

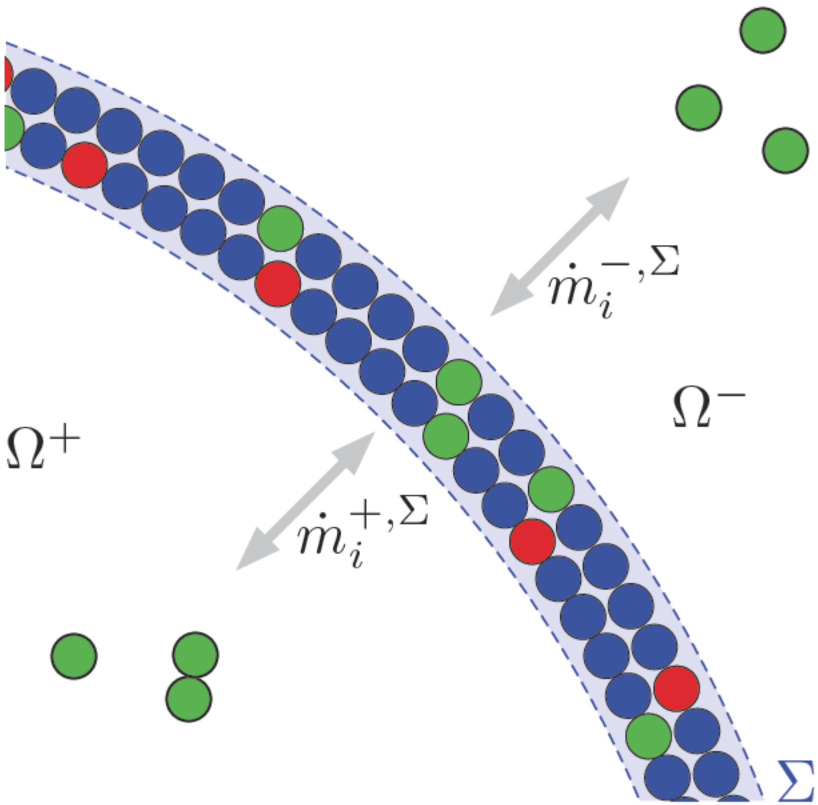
$\Rightarrow$ **correctly grouped !**

D. Bothe: Multi-Velocity Sharp-Interface Continuum Thermodynamics of Fluid Systems with Adsorption. arXiv:2502.00906 (2025).

Contents

One-sided Mass Transfer Processes in Series

- mass transfer as a sequence of „ad- and desorption“ processes



- transfer species pass through the force field of the other (adsorbed) constituents

Mass Transfer Entropy Production

Reduced interfacial entropy production (zero interfacial viscosities):

$$\zeta^\Sigma = \mathbf{q}^\Sigma \cdot \nabla_\Sigma \frac{1}{T^\Sigma} - \sum_{i=1}^{N} \mathbf{j}_i^\Sigma \cdot \left(\nabla_\Sigma \frac{\mu_i^\Sigma}{T^\Sigma} - \frac{\mathbf{b}_i^\Sigma}{T^\Sigma} \right) - \frac{1}{T} \sum_{a=1}^{N_R^\Sigma} R_a^\Sigma \mathcal{A}_a^\Sigma$$

$$- \frac{1}{T^\Sigma} (\mathbf{v}^+ - \mathbf{v}^\Sigma)_{||} \cdot (\mathbf{S}^+ \mathbf{n}^+)_{||} - \frac{1}{T^\Sigma} (\mathbf{v}^- - \mathbf{v}^\Sigma)_{||} \cdot (\mathbf{S}^- \mathbf{n}^-)_{||}$$

$$+ \left(\frac{1}{T^\Sigma} - \frac{1}{T^+} \right) \left(\dot{m}^{+,\Sigma} (e^+ + \frac{p^+}{\rho^+}) + \mathbf{q}^+ \cdot \mathbf{n}^+ \right)$$

$$+ \left(\frac{1}{T^\Sigma} - \frac{1}{T^-} \right) \left(\dot{m}^{-,\Sigma} (e^- + \frac{p^-}{\rho^-}) + \mathbf{q}^- \cdot \mathbf{n}^- \right)$$

$$+ \sum_{i=1}^{N} \dot{m}_i^{+,\Sigma} \left(\left(\frac{\mu_i^+}{T^+} - \frac{\mu_i^\Sigma}{T^\Sigma} \right) + \frac{1}{T^\Sigma} \left(\frac{(\mathbf{v}^+ - \mathbf{v}^\Sigma)^2}{2} - \mathbf{n}^+ \frac{\mathbf{S}^{+,\mathrm{irr}}}{\rho^+} \mathbf{n}^+ \right) \right)$$

$$+ \sum_{i=1}^{N} \dot{m}_i^{-,\Sigma} \left(\left(\frac{\mu_i^-}{T^-} - \frac{\mu_i^\Sigma}{T^\Sigma} \right) + \frac{1}{T^\Sigma} \left(\frac{(\mathbf{v}^- - \mathbf{v}^\Sigma)^2}{2} - \mathbf{n}^- \frac{\mathbf{S}^{-,\mathrm{irr}}}{\rho^-} \mathbf{n}^- \right) \right)$$

Mass Transfer Closure

Interfacial mass transfer: decompose into ad- and desorption

$$\dot{m}_i^{+,\Sigma} = s_i^{\mathrm{ad},+} - s_i^{\mathrm{de},+}, \qquad \dot{m}_i^{-,\Sigma} = s_i^{\mathrm{ad},-} - s_i^{\mathrm{de},-}$$

Mass transfer entropy production (simplified):

$$\zeta^{\pm}_{\mathrm{TRANS}} = \frac{1}{T} \sum_{i=1}^{N} (s_i^{\mathrm{ad},\pm} - s_i^{\mathrm{de},\pm})(\mu_i^{\pm} - \mu_i^{\Sigma})$$

Closure of sorption kinetics: analogous to chemical reactions!

$$\ln \frac{s_i^{\mathrm{ad},\pm}}{s_i^{\mathrm{de},\pm}} = \frac{a_i^{\pm}}{RT}(\mu_i^{\pm} - \mu_i^{\Sigma}) \quad \text{with} \quad a_i^{\pm} \geq 0$$

Desorption modeled explicitly, adsorption follows: ($a_i^{\pm}$ set to 1)

$$s_i^{\mathrm{de},\pm} = k_i^{\mathrm{de},\pm} x_i^{\Sigma}, \qquad s_i^{\mathrm{ad},\pm} = k_i^{\mathrm{de},\pm} x_i^{\Sigma} \exp\left(\frac{\mu_i^{\pm} - \mu_i^{\Sigma}}{RT} \right)$$

Mass Transfer Closure

Simple mixture assumption:

$$\mu_i^{\pm}(T, p, x_1, \ldots, x_{N-1}) = g_i^{\pm}(T, p) + RT \ln x_i^{\pm}$$
$$\mu_i^{\Sigma}(T, p, x_1^{\Sigma}, \ldots, x_{N-1}^{\Sigma}) = g_i^{\Sigma}(T, p^{\Sigma}) + RT \ln x_i^{\Sigma}$$

Resulting (ad-)sorption kinetics:

$$s_i^{\mathrm{de},\pm} = k_i^{\mathrm{de},\pm} x_i^{\Sigma}, \qquad s_i^{\mathrm{ad},\pm} = k_i^{\mathrm{de},\pm} \exp\left(\frac{g_i^{\pm} - g_i^{\Sigma}}{RT}\right) x_i^{\pm} =: k_i^{\mathrm{ad},\pm} x_i^{\pm}$$

approximation: $[\![\dot{m}_i]\!] = 0 \quad \Leftrightarrow \quad \dot{m}_i^{+,\Sigma} + \dot{m}_i^{-,\Sigma} = 0$

Resulting mass transfer rates:

$$\dot{m}_i = \frac{k_i^{\mathrm{de},+} k_i^{\mathrm{de},-}}{k_i^{\mathrm{de},+} + k_i^{\mathrm{de},-}} \exp\left(-\frac{g_i^{\Sigma}}{RT}\right) \left(\exp\left(\frac{g_i^{+}}{RT}\right) x_i^{+} - \exp\left(\frac{g_i^{-}}{RT}\right) x_i^{-}\right)$$

k_{trans}

influence of surface tension

Mass Transfer Hindrance Model

- **combination of several* interface free energy models**

$$\mu_k^{\Sigma,\mathrm{mol}} = a_k(T) + \alpha_k RT \ln\left(1 + \frac{\pi^\Sigma}{K^\Sigma}\right) + \beta_k \pi^\Sigma + \sum_{i=1}^{N} f_i(c_j^\Sigma) c_i^\Sigma + RT \ln \chi_k^\Sigma$$

χ_k^Σ is one of c_k^Σ / c_S^Σ, $c_k^\Sigma / c_k^{\Sigma,\infty}$ or $x_k^\Sigma = c_k^\Sigma / c^\Sigma$

final result:

$$\dot{m}_i^{\mathrm{contam}} = \alpha(\sigma)\, \dot{m}_i^{\mathrm{clean}}$$

matches experimental findings by A. Tomiyama

up to non-linear corrections for non-ideal interface mixtures

* lattice-based, area-based, gas-type, explicit solvent contribution, excluded area

Mass Transfer Hindrance Model

- **combination of several* interface free energy models**

$$\mu_k^{\Sigma,\mathrm{mol}} = a_k(T) + \alpha_k RT \ln\left(1 + \frac{\pi^\Sigma}{K^\Sigma}\right) + \beta_k \pi^\Sigma + \sum_{i=1}^{N} f_i(c_j^\Sigma) c_i^\Sigma + RT \ln \chi_k^\Sigma$$

main effect of surface pressure = - σ

final result:

$$\dot{m}_i^{\mathrm{contam}} = \alpha(\sigma)\, \dot{m}_i^{\mathrm{clean}}$$

Langmuir energy barrier

$$\alpha(\sigma) = \exp\left(-\frac{\sigma_0 - \sigma}{c_\Sigma^\infty RT}\right)$$

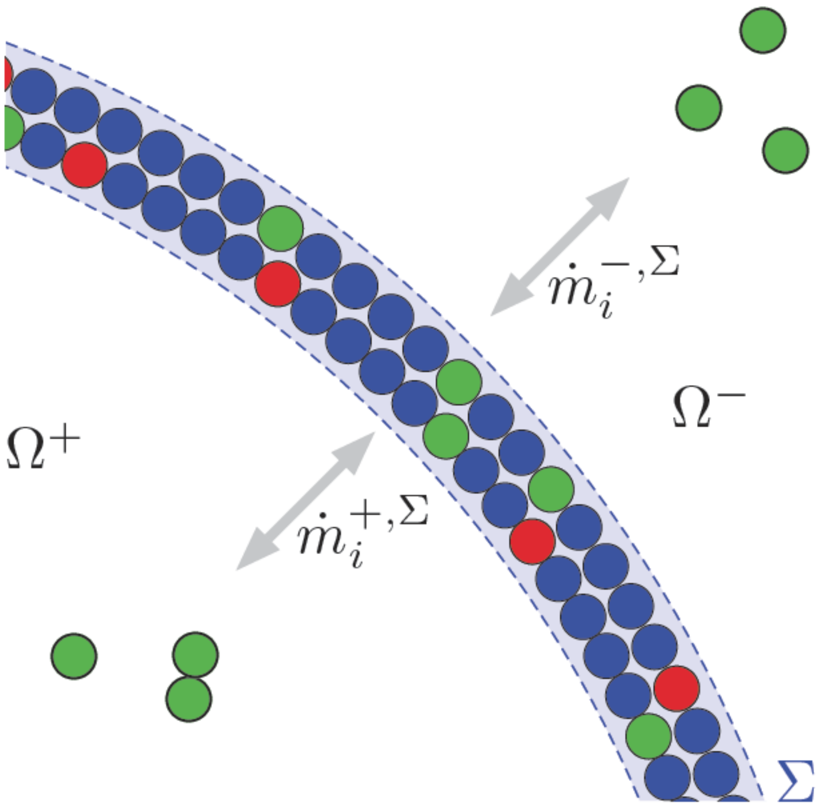
Boltzmann factor

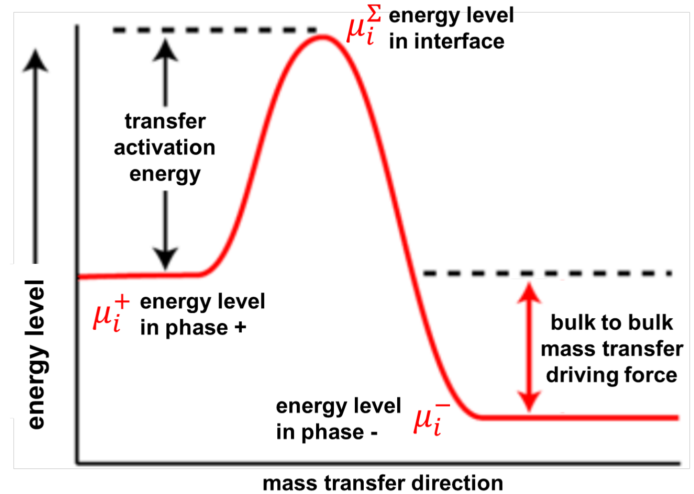
Since $\mu_i^\Sigma = \mu_i^\Sigma(T^\Sigma, \sigma, x_k^\Sigma)$ depends on surface tension:

surfactant $k \rightarrow$ changes $\sigma \rightarrow$ changes all $\mu_i^\Sigma \rightarrow$ changes $\dot{m}_i^\pm$

One-sided Mass Transfer Processes in Series

- mass transfer as a sequence of „ad- and desorption“ processes





- transfer species pass through the force field of the other (adsorbed) constituents

Thank You for Your kind attention !