Weierstrass Institute for
Applied Analysis and Stochastics

Leibniz Association

Sharp Limits of Diffuse Interface Models in the Context Energy Storage

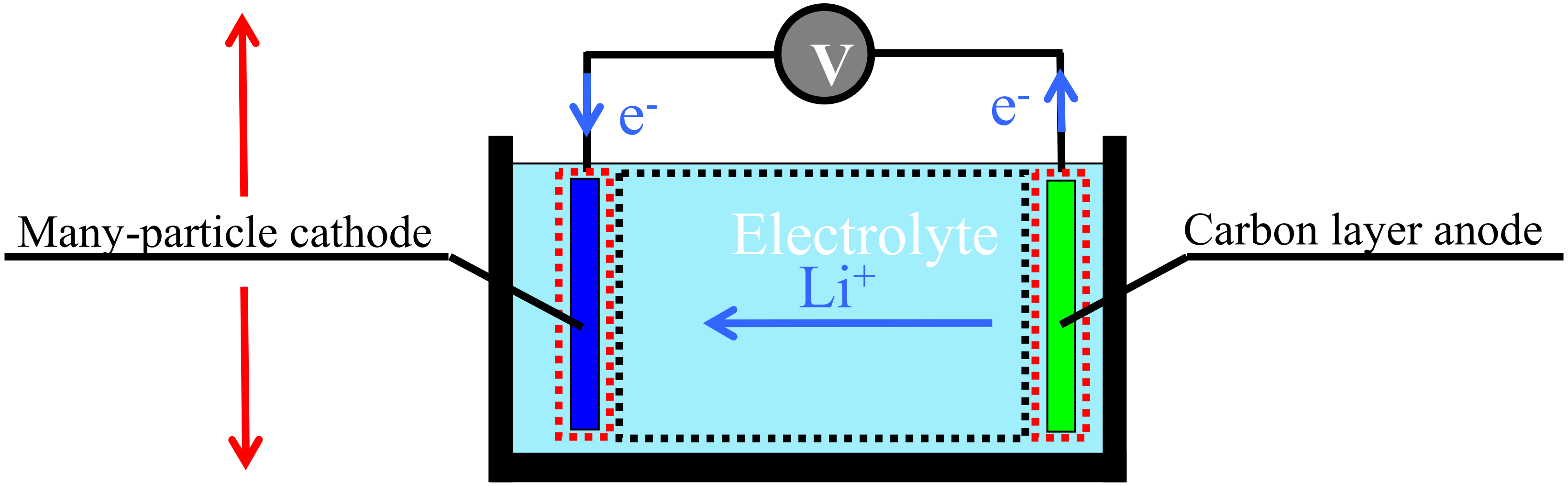
Wolfgang Dreyer Clemens Guhlke Rüdiger Müller

- Overcoming the shortcomings of the Nernst-Planck model
- Does the Cahn-Hilliard model approximate a sharp interface model ?

Mathematical modelling of Li-ion batteries at WIAS

Phase Transition
due to fast charging
Viscous Cahn-Hilliard-Lamé

Interfaces
Conditions across singular surfaces
improved Butler/Volmer rates



Phase Transition
due to slow charging
Nonlocal Fokker-Planck

Electrolyte
Reaction-Diffusion-Fourier-Poisson
improved Nernst-Planck fluxes

N constituents A_1, A_2, ….., A_N
with atomic masses m_1, m_2, ….., m_N
and electric charges z_1, z_2, ….., z_N

N_R chemical reactions

$$i \in \{1,2,\dots, N_R\}$$

$$a_1^i A_1 + a_2^i A_2 + \dots + a_N^i A_N \underset{R_{\mathrm{b}}^i}{\overset{R_{\mathrm{f}}^i}{\rightleftarrows}} b_1^i A_1 + b_2^i A_2 + \dots + b_2^i A_N$$

Def. $\nu_\alpha^i \equiv a_\alpha^i - b_\alpha^i$ stoichiometric coefficents $R^i \equiv R_{\mathrm{f}}^i - R_{\mathrm{b}}^i$ reaction rates

$$\alpha, \beta, \dots \in \{1,2,\dots., N\}$$

$$\sum_{\alpha=1}^{N} m_\alpha \nu_\alpha^i = 0 \qquad \sum_{\alpha=1}^{N} z_\alpha \nu_\alpha^i = 0$$

$$\Delta\varphi = -\frac{1}{\varepsilon_0} n^e \quad \text{with} \quad n^e = \sum_{\alpha=1}^{N} z_\alpha n_\alpha - \mathrm{div}(\mathbf{P})$$

$$\partial_t \rho \boldsymbol{\upsilon} + \mathrm{div}(\rho \boldsymbol{\upsilon} \otimes \boldsymbol{\upsilon} - \boldsymbol{\sigma}) = -n^e \nabla \varphi$$

$$\partial_t m_\alpha n_\alpha + \mathrm{div}(m_\alpha n_\alpha \boldsymbol{\upsilon} + \mathbf{J}_\alpha) = \sum_{i=1}^{N_\mathrm{R}} \mathrm{m}_\alpha \nu_\alpha^i (R_\mathrm{f}^i - R_\mathrm{b}^i) \qquad \alpha \in \{1,2,\dots,N\}$$

Variables

φ	electric potential
$(n_\alpha)_{\alpha\in\{1,2,\dots,N\}}$	particle densities
$\boldsymbol{\upsilon}$	barycentric velocity

$$\Delta\varphi = -\frac{1}{\varepsilon_0} n^e \quad \text{with} \quad n^e = \sum_{\alpha=1}^{N} z_\alpha n_\alpha - \mathrm{div}(\mathbf{P})$$

$$\partial_t \rho \boldsymbol{\upsilon} + \mathrm{div}(\rho \boldsymbol{\upsilon} \otimes \boldsymbol{\upsilon} - \boldsymbol{\sigma}) = -n^e \nabla \varphi$$

$$\partial_t m_\alpha n_\alpha + \mathrm{div}(m_\alpha n_\alpha \boldsymbol{\upsilon} + \mathbf{J}_\alpha) = \sum_{i=1}^{N_\mathrm{R}} \mathrm{m}_\alpha \nu_\alpha^i (R_\mathrm{f}^i - R_\mathrm{b}^i) \qquad \alpha \in \{1,2,\dots,N\}$$

Variables

- φ electric potential
- $(n_\alpha)_{\alpha\in\{1,2,\dots,N\}}$ particle densities
- $\boldsymbol{\upsilon}$ barycentric velocity

$$\partial_t \rho + \mathrm{div}(\rho \boldsymbol{\upsilon}) = 0$$

Definitions

$$\rho = \sum_{\alpha=1}^{N} m_\alpha n_\alpha \qquad \rho\boldsymbol{\upsilon} = \sum_{\alpha=1}^{N} m_\alpha n_\alpha \boldsymbol{\upsilon}_\alpha \qquad \mathbf{J}_\alpha = m_\alpha n_\alpha (\boldsymbol{\upsilon}_\alpha - \boldsymbol{\upsilon}) \quad \Longrightarrow \quad \sum_{\alpha=1}^{N} \mathbf{J}_\alpha = 0$$

$$\Delta\varphi = -\frac{1}{\varepsilon_0} n^e \quad \text{with} \quad n^e = \sum_{\alpha=1}^{N} z_\alpha n_\alpha - \operatorname{div}(\mathbf{P})$$

$$\partial_t \rho\boldsymbol{\upsilon} + \operatorname{div}(\rho\boldsymbol{\upsilon} \otimes \boldsymbol{\upsilon} - \boldsymbol{\sigma}) = -n^e \nabla\varphi$$

$$\partial_t m_\alpha n_\alpha + \operatorname{div}(m_\alpha n_\alpha \boldsymbol{\upsilon} + \mathbf{J}_\alpha) = \sum_{i=1}^{N_\mathrm{R}} \mathrm{m}_\alpha \nu_\alpha^i (R_\mathrm{f}^i - R_\mathrm{b}^i) \qquad \alpha \in \{1,2,\ldots,N\}$$

Variables

- φ electric potential
- $(n_\alpha)_{\alpha\in\{1,2,\ldots,N\}}$ particle densities
- $\boldsymbol{\upsilon}$ barycentric velocity

$$\partial_t \rho + \operatorname{div}(\rho\boldsymbol{\upsilon}) = 0$$

Definitions

$$\rho = \sum_{\alpha=1}^{N} m_\alpha n_\alpha \qquad \rho\boldsymbol{\upsilon} = \sum_{\alpha=1}^{N} m_\alpha n_\alpha \boldsymbol{\upsilon}_\alpha \qquad \mathbf{J}_\alpha = m_\alpha n_\alpha(\boldsymbol{\upsilon}_\alpha - \boldsymbol{\upsilon}) \Longrightarrow \sum_{\alpha=1}^{N} \mathbf{J}_\alpha = 0$$

$$\partial_t \rho\boldsymbol{\upsilon} + \operatorname{div}(\rho\boldsymbol{\upsilon} \otimes \boldsymbol{\upsilon} - \boldsymbol{\Sigma}) = 0$$

$$\boldsymbol{\Sigma} = \boldsymbol{\sigma} + \varepsilon_0 \left(\nabla\varphi \otimes \nabla\varphi - \frac{1}{2}|\nabla\varphi|^2 \mathbf{1}\right)$$

$$\Delta\varphi = -\frac{1}{\varepsilon_0}\left(\sum_{\alpha=1}^{N} z_\alpha n_\alpha - \operatorname{div}(\mathbf{P})\right)$$

$$\partial_t \rho\boldsymbol{\upsilon} + \operatorname{div}(\rho\boldsymbol{\upsilon}\otimes\boldsymbol{\upsilon} - \boldsymbol{\sigma}) = \left(\sum_{\alpha=1}^{N} z_\alpha n_\alpha - \operatorname{div}(\mathbf{P})\right)\nabla\varphi$$

$$\partial_t m_\alpha n_\alpha + \operatorname{div}(m_\alpha n_\alpha \boldsymbol{\upsilon} + \mathbf{J}_\alpha) = \sum_{i=1}^{N_\mathrm{R}} \mathrm{m}_\alpha \nu_\alpha^i (R_\mathrm{f}^i - R_\mathrm{b}^i) \qquad \alpha \in \{1,2,\ldots,N\}$$

Variables

- φ electric potential
- $(n_\alpha)_{\alpha\in\{1,2,\ldots,N\}}$ particle densities
- $\boldsymbol{\upsilon}$ barycentric velocity

$$\mathbf{P} = \frac{\partial\rho\psi}{\partial\nabla\varphi} \qquad \mu_\alpha = -\frac{\partial\rho\psi}{\partial\rho_\alpha}$$

$$\boldsymbol{\sigma} = -p\,\mathbf{1} - \nabla\varphi\otimes\mathbf{P} + \frac{1}{3}\nabla\varphi\cdot\mathbf{P}\,\mathbf{1} \qquad p = -\rho\psi + \sum_{\beta=1}^{N}\rho_\beta\mu_\beta + \frac{1}{3}\nabla\varphi\cdot\mathbf{P}$$

$$\mathbf{J}_\alpha = -\sum_{\beta=1}^{N-1} M_{\alpha\beta}\left(\nabla\left(\frac{\mu_\beta}{T} - \frac{\mu_N}{T}\right) + \frac{1}{T}\left(\frac{z_\beta}{m_\beta} - \frac{z_N}{m_N}\right)\nabla\varphi\right) \qquad \alpha \in \{1,2,\ldots,N-1\}$$

$$R_\mathrm{b}^i = R_\mathrm{f}^i \exp\left(\frac{1}{kT}\sum_{\beta=1}^{N}\mathrm{m}_\beta \nu_\beta^i \mu_\beta\right)$$

The diffusion flux of the Nernst-Planck model

Variables

φ	electric potential
$(n_\alpha)_{\alpha\in\{1,2,\ldots,N\}}$	particle densities
~~$\boldsymbol{v}$~~	barycentric velocity

The diffusion flux of the Nernst-Planck model

ZEITSCHRIFT

FÜR

PHYSIKALISCHE CHEMIE

STÖCHIOMETRIE UND VE

UNTER MIT

VON

M. BERTHELOT IN PARIS, J. W. BRÜHL IN
H. LE CHATELIER IN PARIS, C. M. GULI
A. HORSTMANN IN HEIDELBERG, H. LANDOL
D. MENDELEJEW UND N. MENSCHUTKIN IN ST
VICTOR MEYER IN HEIDELBERG L. F. NILSO
L. PFAUNDLER IN INNSBRUCK, W. RAMSAY
R. SCHIFF IN MODENA, W. SPRING IN
J. THOMSEN IN KOPENHAGEN,

SOWIE ANDERER

HERAUSGEGEBEN VON

WILH. OSTWALD, PROFESSOR A. D. UNIVERS. ZU LEIPZIG UND J. H. VAN'T HOFF, PROFESSOR A. D. UNIVERS. ZU AMSTERDAM.

Die elektromotorische Wirksamkeit der Ionen.

Von

Walther Nernst.

(Mit 3 Holzschnitten.)

Übersicht: 1. Die Fundamentalhypothesen. 2. Über ein allgemeines Prinzip für die in Elektrolyten wirksamen Kräfte. 3. Potentialdifferenz zwischen zwei verschieden konzentrierten Lösungen desselben Elektrolyten. 4. Flüssigkeitsketten. 5. Über die an der Grenzfläche umkehrbarer Elektroden auftretenden elektromotorischen Kräfte. 6. Über den Vorgang der Auflösung fester Körper. 7. Theorie der Konzentrationsketten. 8. Messungen. 9. Vergleich mit der v. Helmholtzschen Theorie der Konzentrationsketten. 10. Potentialdifferenz an der Grenzfläche zweier Elektrolyte. 11. Elektrolytische Thermoketten; Theorie und Messungen. 12. Über galvanische Elemente. [Kapitel 3, 5, 6, 7 im Auszuge bereits mitgeteilt: Berl. Sitzungsber. S. 83—95. 1889.]

Variables

φ electric potential

$(n_\alpha)_{\alpha\in\{1,2,\ldots,N\}}$ particle densities

~~υ~~ barycentric velocity

1890. ANNALEN DER PHYSIK UND CHEMIE. № 2.

NEUE FOLGE. BAND XXXIX.

I. *Ueber die Erregung von Electricität und Wärme in Electrolyten; von Max Planck.*

The diffusion flux of the Nernst-Planck model

Nernst-Planck, 1890

$$\mathbf{J}_\alpha = -M_\alpha^{\mathrm{NP}}(\nabla n_\alpha + n_\alpha z_\alpha \nabla \varphi) \qquad \text{for} \qquad \alpha \in \{1,2,\ldots,N\}$$

Dreyer, Guhlke, Müller, 2012

$$\mathbf{J}_\alpha = -\sum_{\beta=1}^{N-1} M_{\alpha\beta}\left(\nabla\left(\frac{\mu_\beta}{T} - \frac{\mu_N}{T}\right) + \frac{1}{T}\left(\frac{z_\beta}{m_\beta} - \frac{z_N}{m_N}\right)\nabla\varphi\right) \qquad \text{for} \qquad \alpha \in \{1,2,\ldots,N-1\}$$

$$\mathbf{J}_N = -\sum_{\alpha=1}^{N-1} \mathbf{J}_\alpha$$

The diffusion flux of the Nernst-Planck model

Nernst-Planck, 1890

$$\mathbf{J}_\alpha = -M_\alpha^{\mathrm{NP}}(\nabla n_\alpha + n_\alpha z_\alpha \nabla\varphi) \qquad \text{for} \qquad \alpha \in \{1,2,\ldots,N\}$$

Navier-Stokes community, e.g. T. Roubíček, 2006

$$\mathbf{J}_\alpha = -M_1 \nabla \frac{n_\alpha}{n} - M_2 (n_\alpha z_\alpha - n^{\mathrm{F}})\nabla\varphi) \qquad \text{for} \qquad \alpha \in \{1,2,\ldots,N\}$$

$$\Longrightarrow \quad \sum_{\alpha=1}^{N} \mathbf{J}_\alpha = 0$$

Dreyer, Guhlke, Müller, 2012

$$\mathbf{J}_\alpha = -\sum_{\beta=1}^{N-1} M_{\alpha\beta}\left(\nabla(\frac{\mu_\beta}{T} - \frac{\mu_N}{T}) + \frac{1}{T}(\frac{z_\beta}{m_\beta} - \frac{z_N}{m_N})\nabla\varphi\right) \qquad \text{for} \qquad \alpha \in \{1,2,\ldots,N-1\}$$

$$\mathbf{J}_N = -\sum_{\alpha=1}^{N-1} \mathbf{J}_\alpha$$

$$\Delta\varphi = -\frac{1}{\varepsilon_0}\left(\sum_{\alpha=1}^{N} z_\alpha n_\alpha - \operatorname{div}(\mathbf{P})\right)$$

$$\operatorname{div}(-\boldsymbol{\sigma}) = -\left(\sum_{\alpha=1}^{N} z_\alpha n_\alpha - \operatorname{div}(\mathbf{P})\right)\nabla\varphi$$

$$\operatorname{div}(\mathbf{J}_\alpha) = 0 \qquad \alpha \in \{1,2,\ldots,N-1\} \qquad \sum_{\alpha=1}^{N} \mathbf{J}_\alpha = 0$$

Variables

φ electric potential

$(n_\alpha)_{\alpha\in\{1,2,\ldots,N\}}$ particle densities

$$\lambda^2 \partial_{zz}\varphi = -n_{\mathrm{F}}$$

$$a^2 \partial_z p = -n_{\mathrm{F}} \partial_z \varphi$$

$$\partial_z(\mu_C - \frac{m_C}{m_S}\mu_S + z_C\varphi) = 0$$

$$\partial_z(\mu_A - \frac{m_A}{m_S}\mu_S + z_A\varphi) = 0$$

$$\varphi(z=0) = \varphi_{\mathrm{L}} \qquad \varphi(z=1) = \varphi_{\mathrm{R}} \qquad \Sigma_{11}(z=1) = -p_0$$

$$m_\alpha \int_0^1 n_\alpha \, dz = M_\alpha \qquad \int_0^1 n_{\mathrm{F}} \, dz = 0$$

$$n = n_C + n_A + n_S$$

$$n_{\mathrm{F}} = z_C n_C + z_A n_A$$

$$\Sigma_{11} = -p + \varepsilon_0(1+\chi)(\nabla\varphi \otimes \nabla\varphi - \frac{1}{2}|\nabla\varphi|^2 \mathbf{1})$$

$$p = 1 + K(n-1)$$

$$\mu_\alpha = g_\alpha(T,p) + \ln(y_\alpha)$$

$$g_\alpha(T,p) = g_\alpha^{\mathrm{R}} + a^2 K \ln(1 + \frac{1}{K}(p-1))$$

$$\lambda^2 \partial_{zz}\varphi = -n_{\mathrm{F}}$$

$$a^2 \partial_z p = -n_{\mathrm{F}} \partial_z \varphi$$

$$\partial_z (\mu_C - \frac{m_C}{m_S}\mu_S + z_C \varphi) = 0$$

$$\partial_z (\mu_A - \frac{m_A}{m_S}\mu_S + z_A \varphi) = 0$$

$$\varphi(z=0) = \varphi_{\mathrm{L}} \qquad \varphi(z=1) = \varphi_{\mathrm{R}} \qquad \Sigma_{11}(z=1) = -p_0$$

$$m_\alpha \int_0^1 n_\alpha \, dz = M_\alpha \qquad \int_0^1 n_{\mathrm{F}} \, dz = 0$$

Incompressibility $K \to \infty$

$$n = n_C + n_A + n_S$$

$$n_{\mathrm{F}} = z_C n_C + z_A n_A$$

$$\Sigma_{11} = -p + \varepsilon_0 (1+\chi)(\nabla\varphi \otimes \nabla\varphi - \frac{1}{2}|\nabla\varphi|^2 \mathbf{1})$$

$$p = 1 + K(n-1)$$

$$\mu_\alpha = g_\alpha(T,p) + \ln(y_\alpha)$$

$$g_\alpha(T,p) = g_\alpha^{\mathrm{R}} + a^2 K \ln(1 + \frac{1}{K}(p-1))$$

$$\lambda^2 \partial_{zz}\varphi = -n_\mathrm{F}$$

$$a^2 \partial_z p = -n_\mathrm{F}\partial_z \varphi$$

$$\partial_z(\mu_C - \frac{m_C}{m_S}\mu_S + z_C\varphi) = 0$$

$$\partial_z(\mu_A - \frac{m_A}{m_S}\mu_S + z_A\varphi) = 0$$

$$\varphi(z=0) = \varphi_\mathrm{L} \qquad \varphi(z=1) = \varphi_\mathrm{R} \qquad \Sigma_{11}(z=1) = -p_0$$

$$m_\alpha \int_0^1 n_\alpha \, dz = M_\alpha \qquad \int_0^1 n_\mathrm{F} \, dz = 0$$

$$n = n_C + n_A + n_S$$

$$n_\mathrm{F} = z_C n_C + z_A n_A$$

$$\Sigma_{11} = -p + \varepsilon_0(1+\chi)(\nabla\varphi \otimes \nabla\varphi - \frac{1}{2}|\nabla\varphi|^2 \mathbf{1})$$

$$p = 1 + K(n-1)$$

$$\mu_\alpha = g_\alpha(T,p) + \ln(y_\alpha)$$

$$g_\alpha(T,p) = g_\alpha^\mathrm{R} + a^2 K \ln(1 + \frac{1}{K}(p-1))$$

Incompressibility $K \to \infty$

$$n - 1 \to 0$$

Incompressible limit

$$\lambda^2 \partial_{zz}\varphi = -n_{\mathrm{F}}$$

$$a^2 \partial_z p = -n_{\mathrm{F}} \partial_z \varphi$$

$$\partial_z(\mu_C - \frac{m_C}{m_S}\mu_S + z_C\varphi) = 0$$

$$\partial_z(\mu_A - \frac{m_A}{m_S}\mu_S + z_A\varphi) = 0$$

$$\varphi(z=0) = \varphi_{\mathrm{L}} \qquad \varphi(z=1) = \varphi_{\mathrm{R}} \qquad \Sigma_{11}(z=1) = -p_0$$

$$m_\alpha \int_0^1 n_\alpha \, dz = M_\alpha \qquad \int_0^1 n_{\mathrm{F}} \, dz = 0$$

$$n = n_C + n_A + n_S$$

$$n_{\mathrm{F}} = z_C n_C + z_A n_A$$

$$\Sigma_{11} = -p + \varepsilon_0(1+\chi)(\nabla\varphi \otimes \nabla\varphi - \frac{1}{2}|\nabla\varphi|^2 \mathbf{1})$$

$$p = 1 + K(n-1)$$

$$\mu_\alpha = g_\alpha(T,p) + \ln(y_\alpha)$$

$$g_\alpha(T,p) = g_\alpha^{\mathrm{R}} + a^2 K \ln(1 + \frac{1}{K}(p-1))$$

Incompressibility $K \to \infty$

$$n - 1 \to 0$$

p not determined by constitutive law

$\Longrightarrow$ p becomes a variable **!!!**

$$g_\alpha(T,p) = g_\alpha^{\mathrm{R}} + a^2(p-1)$$

$$\varphi(z=0)=\varphi_{\mathrm{L}} \qquad \varphi(z=1)=\varphi_{\mathrm{R}} \qquad \Sigma_{11}(z=1)=-p_0$$

$$m_\alpha \int_0^1 n_\alpha \, dz = M_\alpha \qquad \int_0^1 n_{\mathrm{F}} \, dz = 0$$

$$\lambda^2 \partial_{zz}\varphi = -(z_C y_C + z_A y_A)$$

$$\partial_z\left(\frac{1}{2}\lambda^2(\partial_z\varphi)^2 + \ln(y_C) + z_C\varphi\right) = 0$$

$$\partial_z\left(\frac{1}{2}\lambda^2(\partial_z\varphi)^2 + \ln(y_A) + z_A\varphi\right) = 0$$

$$y_S = 1 - y_C - y_A$$

Representation of the mole fractions

$$\alpha \in \{\mathrm{C}, \mathrm{A}, \mathrm{S}\}$$

$$y_\alpha = c_\alpha \exp(-z_\alpha \varphi - \lambda^2 (\partial_z \varphi)^2) \quad \text{with} \quad c_\alpha = \bar{y}_\alpha \left(\int_0^1 \exp(-z_\alpha \varphi - \lambda^2 (\partial_z \varphi)^2) dz \right)^{-1}$$

Representation of the mole fractions

$$\alpha \in \{\mathrm{C}, \mathrm{A}, \mathrm{S}\}$$

$$y_\alpha = c_\alpha \exp(-z_\alpha \varphi - \lambda^2 (\partial_z \varphi)^2) \quad \text{with} \quad c_\alpha = \bar{y}_\alpha \left(\int_0^1 \exp(-z_\alpha \varphi - \lambda^2 (\partial_z \varphi)^2) dz \right)^{-1}$$

First integral of Poisson equation

$$y_\mathrm{C} + y_\mathrm{A} + y_\mathrm{S} = 1 \quad \Rightarrow \quad \frac{1}{2} \lambda^2 (\partial_z \varphi)^2 = \log(c_\mathrm{S} + c_\mathrm{C} \exp(-z_\mathrm{C} \varphi) + c_\mathrm{A} \exp(-z_\mathrm{A} \varphi))$$

General properties of the solution

Representation of the mole fractions

$$\alpha \in \{\mathrm{C}, \mathrm{A}, \mathrm{S}\}$$

$$y_\alpha = c_\alpha \exp(-z_\alpha \varphi - \lambda^2 (\partial_z \varphi)^2) \quad \text{with} \quad c_\alpha = \bar{y}_\alpha \left(\int_0^1 \exp(-z_\alpha \varphi - \lambda^2 (\partial_z \varphi)^2) dz \right)^{-1}$$

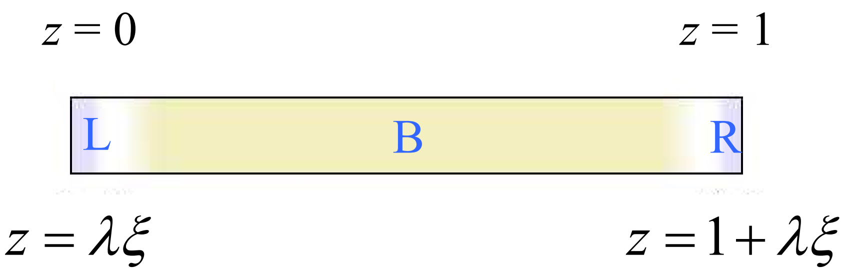
First integral of Poisson equation

$$y_\mathrm{C} + y_\mathrm{A} + y_\mathrm{S} = 1 \quad \Rightarrow \quad \frac{1}{2} \lambda^2 (\partial_z \varphi)^2 = \log(c_\mathrm{S} + c_\mathrm{C} \exp(-z_\mathrm{C} \varphi) + c_\mathrm{A} \exp(-z_\mathrm{A} \varphi))$$

Behavior of $\partial_z \varphi$ at the boundaries

$$0 = \int_0^1 (z_\mathrm{C} y_\mathrm{C} + z_\mathrm{A} y_\mathrm{A}) dz = -\lambda^2 \int_0^1 \partial_{zz} \varphi dz = \lambda^2 (\partial_z \varphi(0) - \partial_z \varphi(1))$$

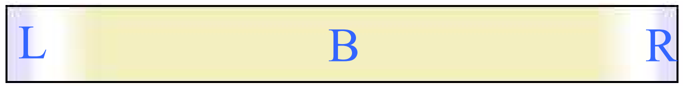
$$\Rightarrow \quad c_\mathrm{C} \exp(-z_\mathrm{C} \varphi_\mathrm{L}) + c_\mathrm{A} \exp(-z_\mathrm{A} \varphi_\mathrm{L}) = c_\mathrm{C} \exp(-z_\mathrm{C} \varphi_\mathrm{R}) + c_\mathrm{A} \exp(-z_\mathrm{A} \varphi_\mathrm{R})$$


$z = 0$
$z = 1$
L
B
R
$z = \lambda\xi$
$z = 1 + \lambda\xi$

B: $\varphi^{\lambda}(z) = \varphi^{0}(z) + \lambda \varphi^{1}(z) + \ldots$

$$y_{\alpha}^{\lambda}(z) = y_{\alpha}^{0}(z) + \lambda y_{\alpha}^{1}(z) + \ldots$$

$z = 0$ $\qquad$ $z = 1$



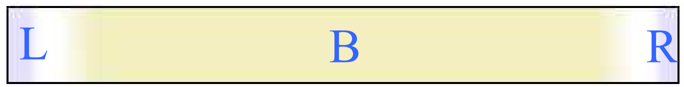
$z = \lambda \xi$ $\qquad$ $z = 1 + \lambda \xi$

Asymptotic analysis of boundary layers

B: $\varphi^{\lambda}(z) = \varphi^{0}(z) + \lambda\varphi^{1}(z) + \dots$

$$y_{\alpha}^{\lambda}(z) = y_{\alpha}^{0}(z) + \lambda y_{\alpha}^{1}(z) + \dots$$

$z = 0$ $\qquad$ $z = 1$



$z = \lambda\xi$ $\qquad$ $z = 1 + \lambda\xi$

L: $\tilde{\varphi}_{L}^{\lambda}(\xi) = \varphi^{\lambda}(\lambda\xi)$

$$\tilde{y}_{\alpha,L}^{\lambda}(\xi) = y_{\alpha}^{\lambda}(\lambda\xi)$$

R: $\tilde{\varphi}_{R}^{\lambda}(\xi) = \varphi^{\lambda}(1 + \lambda\xi)$

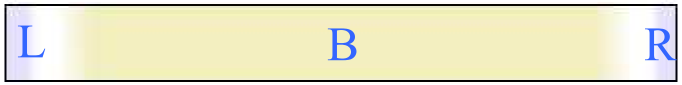
$$\tilde{y}_{\alpha,R}^{\lambda}(\xi) = y_{\alpha}^{\lambda}(1 + \lambda\xi)$$

Asymptotic analysis of boundary layers

B: $\varphi^{\lambda}(z) = \varphi^{0}(z) + \lambda\varphi^{1}(z) + \ldots$

$$y_{\alpha}^{\lambda}(z) = y_{\alpha}^{0}(z) + \lambda y_{\alpha}^{1}(z) + \ldots$$

$z = 0$ $\qquad$ $z = 1$



$z = \lambda\xi$ $\qquad$ $z = 1 + \lambda\xi$

L:

$$\tilde{y}_{\alpha,L}^{\lambda}(\xi) = \tilde{y}_{\alpha,L}^{0}(\xi) + \lambda\tilde{y}_{\alpha,L}^{1}(\xi) + \ldots$$

$$\tilde{\varphi}_{L}^{\lambda}(\xi) = \tilde{\varphi}_{L}^{0}(\xi) + \lambda\tilde{\varphi}_{L}^{1}(\xi) + \ldots$$

R:

$$\tilde{y}_{\alpha,R}^{\lambda}(\xi) = \tilde{y}_{\alpha,R}^{0}(\xi) + \lambda\tilde{y}_{\alpha,R}^{1}(\xi) + \ldots$$

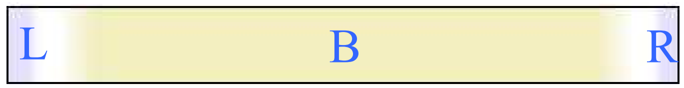
$$\tilde{\varphi}_{R}^{\lambda}(\xi) = \tilde{\varphi}_{R}^{0}(\xi) + \lambda\tilde{\varphi}_{R}^{1}(\xi) + \ldots$$

Asymptotic analysis of boundary layers

$$\widetilde{\varphi}^0_{\rm L}(0) = \frac{e_0}{kT}\varphi_{\rm L}$$

$$\widetilde{\varphi}^0_{\rm R}(0) = \frac{e_0}{kT}\varphi_{\rm R}$$

$z = 0$ $\qquad$ $z = 1$



$z = \lambda\xi$ $\qquad$ $z = 1 + \lambda\xi$

Matching conditions

$$\lim_{\xi\to\infty}\widetilde{\varphi}^0_{\rm L}(\xi) = \varphi^0(z=0)$$

$$\lim_{\xi\to\infty}\partial_\xi\widetilde{\varphi}^0_{\rm L}(\xi) = 0$$

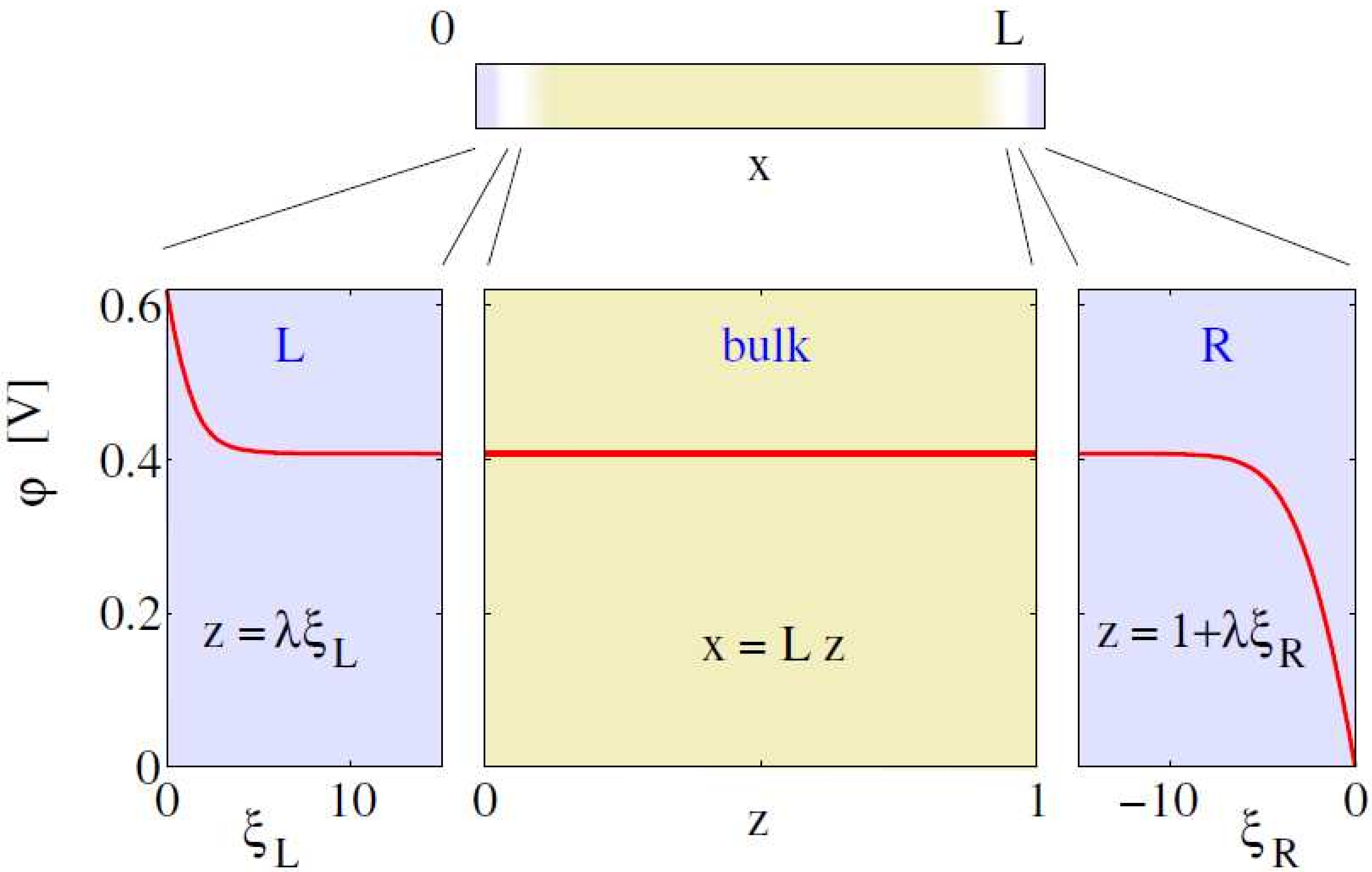
$$\lim_{\xi\to\infty}\widetilde{y}^0_{\alpha,\rm L}(\xi) = y^0(z=0)$$

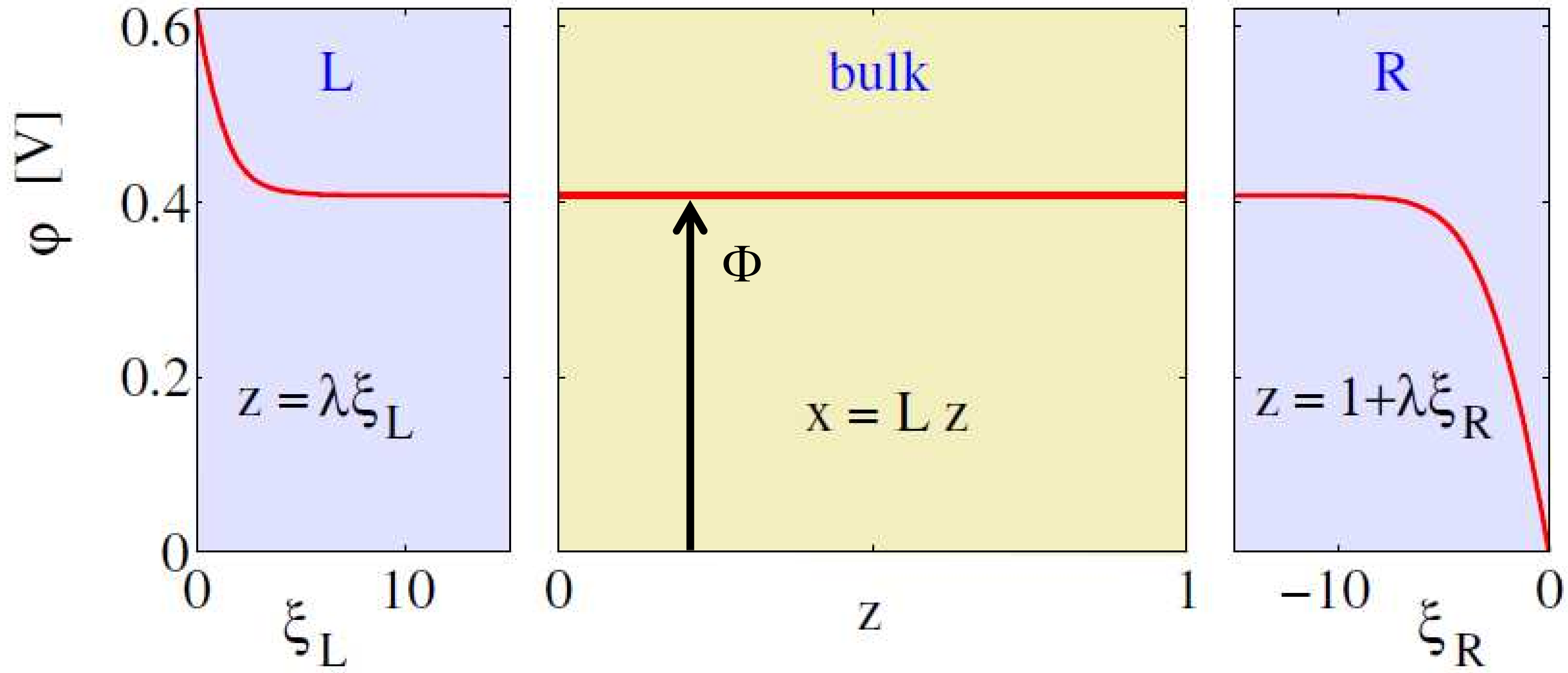
$$\partial_\xi\widetilde{\varphi}^0_{\rm L}(0) = \partial_\xi\widetilde{\varphi}^0_{\rm R}(0)$$

$$\lim_{\xi\to-\infty}\widetilde{\varphi}^0_{\rm R}(\xi) = \varphi^0(z=1)$$

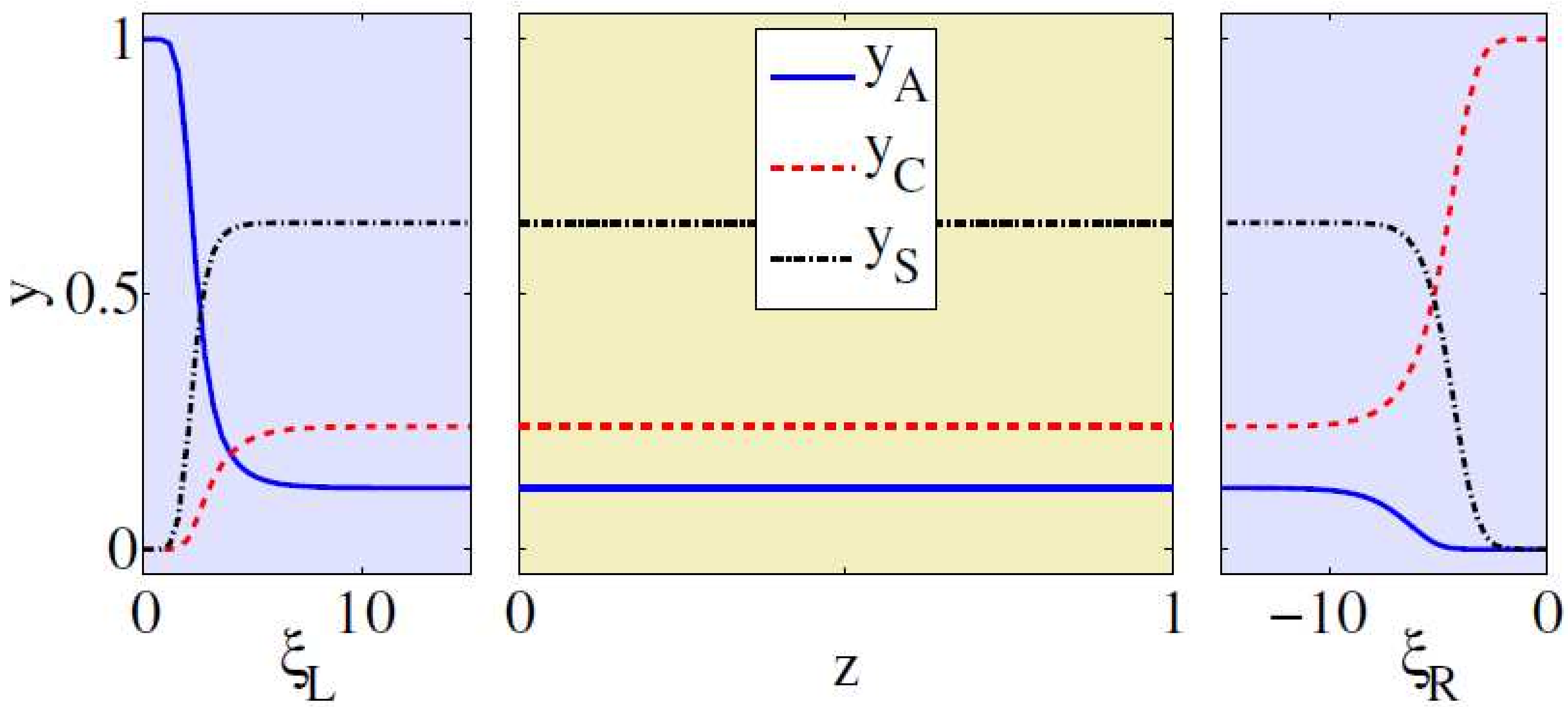
$$\lim_{\xi\to-\infty}\partial_\xi\widetilde{\varphi}^0_{\rm R}(\xi) = 0$$

$$\lim_{\xi\to-\infty}\widetilde{y}^0_{\alpha,\rm R}(\xi) = y^0(z=1)$$

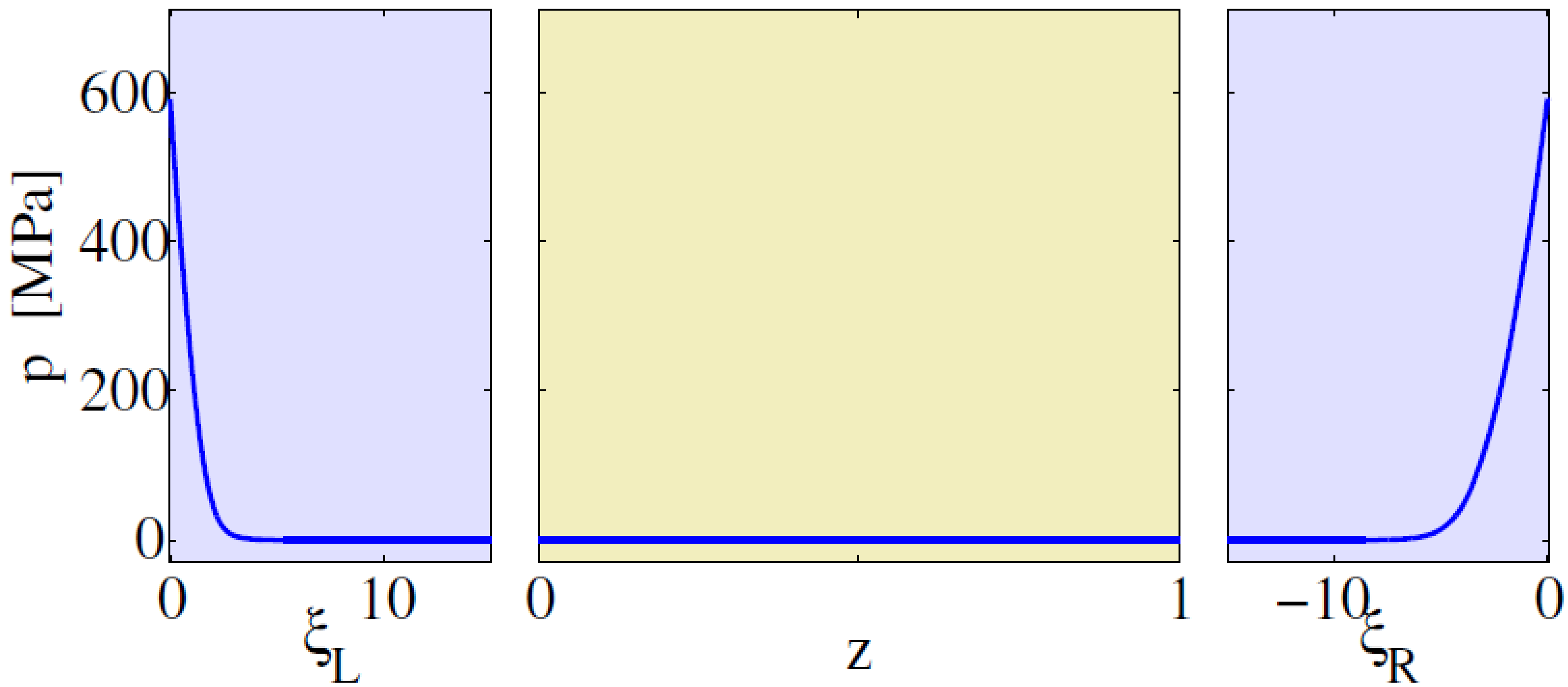

0
L
x
0.6
0.4
0.2
0
φ [V]
L
bulk
R
$z = \lambda \xi_L$
$x = L\,z$
$z = 1 + \lambda \xi_R$
0
10
ξ_L
0
z
1
−10
0
ξ_R

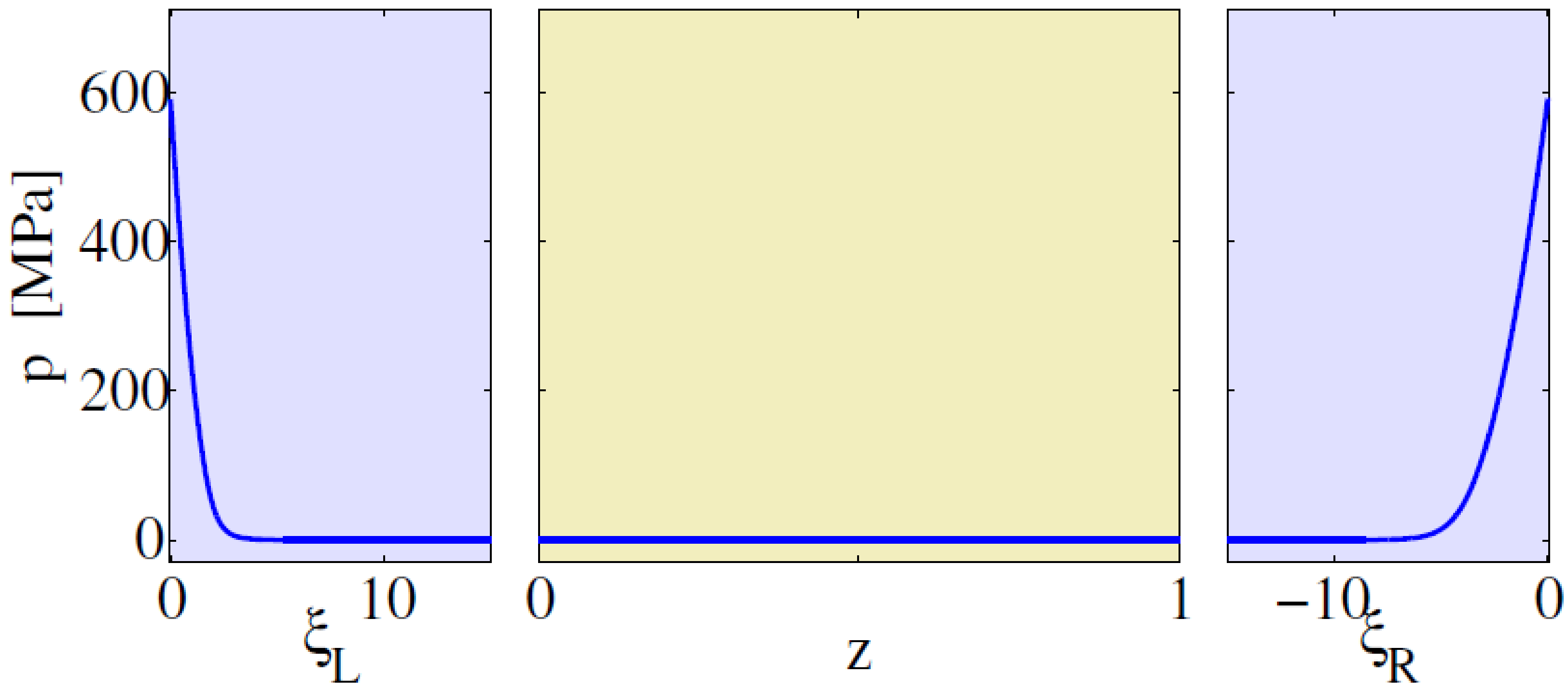


$$\Phi = \frac{e_0}{kT}\varphi_R + \frac{1}{z_A - z_C}\ln\left(\frac{z_A}{z_C}\frac{1-\exp(\frac{e_0}{kT}z_C(\varphi_R-\varphi_L))}{1-\exp(\frac{e_0}{kT}z_A(\varphi_R-\varphi_L))}\right)$$


1
y 0.5
0
0
10
ξ_L
0
1
z
y_A
y_C
y_S
−10
0
ξ_R

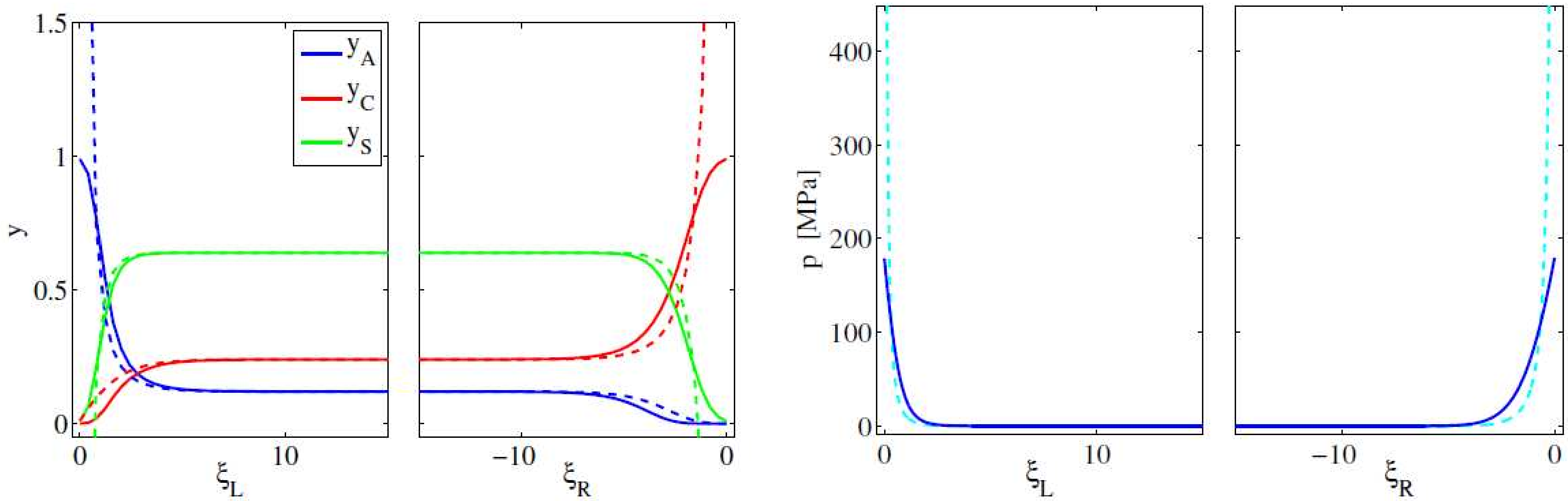
Simulation: Material pressure





Recall

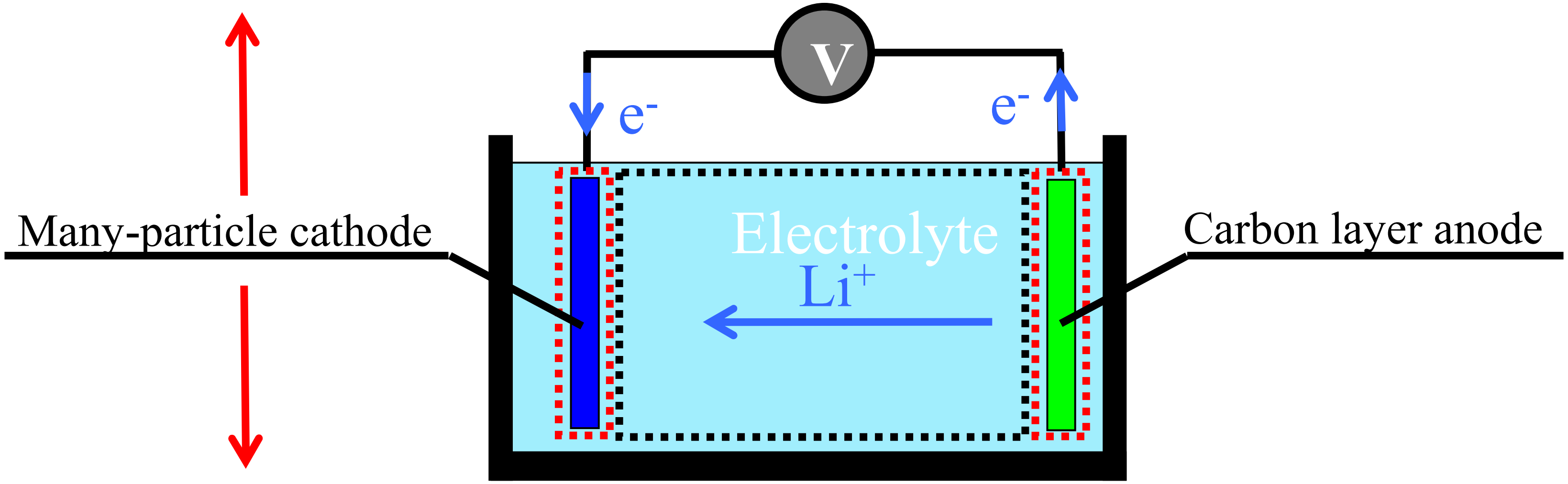
$$\mathbf{\Sigma} = -p + \varepsilon_0(1+\chi)(\nabla\varphi \otimes \nabla\varphi - \frac{1}{2}|\nabla\varphi|^2\mathbf{1}) = \text{constant} = 0.1\,\text{MPa}$$


1.5
1
0.5
0
y
y_A
y_C
y_S
0
10
ξ_L
−10
0
ξ_R
400
300
200
100
0
p [MPa]
0
10
ξ_L
−10
0
ξ_R

Mathematical modelling of Li-ion batteries at WIAS

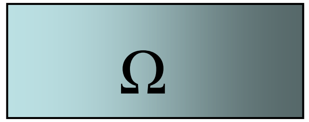
Phase Transition
due to fast charging
Viscous Cahn-Hilliard-Lamé

Interfaces
Conditions across singular surfaces
improved Butler/Volmer rates



Phase Transition
due to slow charging
Nonlocal Fokker-Planck

Electrolyte
Reaction-Diffusion-Fourier-Poisson
improved Nernst-Planck fluxes



Binary mixture with constant total mass

$$\partial_t u + \partial_x f = 0 \qquad f = -M\partial_x(\mu + \gamma\partial_t u) \qquad \mu = F'(u) - \beta\partial_{xx} u$$

$$M, \gamma, \beta > 0$$

Binary mixture with constant total mass

$$\partial_t u + \partial_x f = 0 \qquad f = -M\partial_x(\mu + \gamma\partial_t u) \qquad \mu = F'(u) - \beta\partial_{xx} u$$

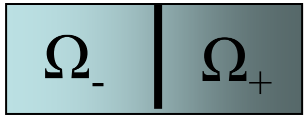
$$M, \gamma, \beta > 0$$

Free energy balance

$$\partial_t \psi + \partial_x (f(\mu + \gamma\partial_t u) - \beta\partial_x u \partial_t u) = -\xi \qquad \psi = F(u) + \frac{\beta}{2}(\partial_x u)^2$$

Entropy production

$$\xi = \frac{1}{M} f^2 + \gamma(\partial_t u)^2 \geq 0$$



$I^{\varepsilon}(t)$

Bulk

Binary mixture with constant total mass

$$\partial_t u + \partial_x f = 0 \qquad f = -M\partial_x \mu \qquad \mu = F'(u)$$

Free energy balance

Entropy production

$$\partial_t \psi + \partial_x (f\,\mu) = -\xi \qquad \psi = F(u) \qquad \xi = \frac{1}{M} f^2 \geq 0$$

Sharp Interface model

Ω_- | Ω_+

$I^{\varepsilon}(t)$

Bulk

Binary mixture with constant total mass

$$\partial_t u + \partial_x f = 0 \qquad f = -M\partial_x \mu \qquad \mu = F'(u)$$

Free energy balance

$$\partial_t \psi + \partial_x (f\mu) = -\xi \qquad \psi = F(u)$$

Entropy production

$$\xi = \frac{1}{M} f^2 \geq 0$$

Interface

Binary mixture with constant total mass

$$\partial_t u_{\mathrm{I}} + [[\dot{m}_1]] = 0 \quad \text{with} \quad \dot{m}_1^{\pm} = f^{\pm} - u^{\pm}\dot{x}_{\mathrm{I}}$$

Kinetic relations

$$\begin{pmatrix} \mu_{\mathrm{I}} - \mu^{\pm} \\ -\frac{1}{2}[[\mu_2]] \end{pmatrix} = \begin{pmatrix} L_{11} & L_{12} \\ L_{21} & L_{22} \end{pmatrix} \begin{pmatrix} \dot{m}_1^{\pm} \\ \dot{m} \end{pmatrix} \quad \text{with} \quad L \quad \text{pos.def.}$$

Free energy balance

$$\partial_t \psi_{\mathrm{I}} + [[\psi\dot{m} + f\mu]] = -\xi_{\mathrm{I}} \quad \text{with} \quad \psi_{\mathrm{I}} = F_{\mathrm{I}}(u_{\mathrm{I}})$$

Entropy production

$$\xi_{\mathrm{I}} = -[[\dot{m}_1(\mu_1 - \mu_{\mathrm{I},1}) + \dot{m}_2(\mu_2 - \mu_{\mathrm{I},2})]] \geq 0$$

$$[[\chi]] = \chi^+ - \chi^-$$

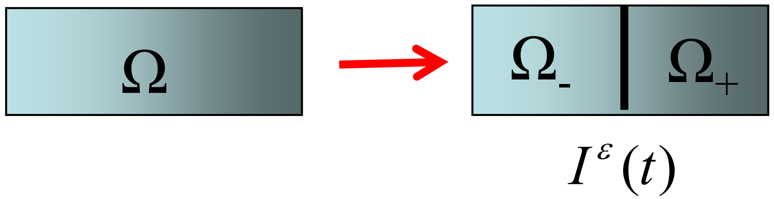
$$\dot{m} = -\dot{x}_{\mathrm{I}}$$
$$\dot{m}_2^{\pm} = \dot{m} - \dot{m}_1^{\pm}$$

$$\mu_1 = F + (1-u)\mu$$
$$\mu_2 = F - u\mu$$

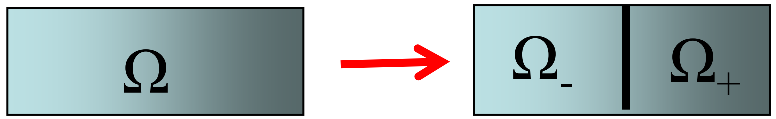
$$\mu_{\mathrm{I}} = F_{\mathrm{I}}'(u_{\mathrm{I}})$$
$$\mu_{\mathrm{I},1} = F_{\mathrm{I}} + (1-u_{\mathrm{I}})\mu_{\mathrm{I}}$$
$$\mu_{\mathrm{I},2} = F_{\mathrm{I}} - u_{\mathrm{I}}\mu_{\mathrm{I}}$$

Sharp limit of the viscous Cahn-Hilliard equation

$$\partial_t u + \partial_x \left(F'(u) - \beta\varepsilon^2 \partial_{xx} u + \gamma\varepsilon^2 \partial_t u \right) = 0$$



$$\partial_t u + \partial_x (F'(u) - \beta\varepsilon^2 \partial_{xx} u + \gamma\varepsilon^2 \partial_t u) = 0$$



$I^\varepsilon(t)$

Assumptions of formal asymptotic analysis

VCH has a solution $u^\varepsilon(t,x)$ with transition layer

Existence of an interface $I^\varepsilon(t) = \{x \in (0,1) : u^\varepsilon(t,x) = u_*\}$

Interface $I^\varepsilon(t)$ at $x_I^\varepsilon(t)$ separates Ω into $\Omega^- = [0, x_I^\varepsilon)$ and $\Omega^+ = (x_I^\varepsilon, 1]$

Outer expansion $u^\varepsilon(t,x) = u(t,x)^{(0)} + \varepsilon u(t,x)^{(1)} + O(\varepsilon^2)$

Inner coordinate $z = \dfrac{1}{\varepsilon}(x - x_I^{(\varepsilon)}(t))$ and inner variable $\tilde{u}(t,z)^\varepsilon = u^\varepsilon(t, x_I^\varepsilon + \varepsilon z)$

Inner expansion $\tilde{u}^\varepsilon(t,z) = \tilde{u}(t,z)^{(0)} + \varepsilon\tilde{u}(t,z)^{(1)} + O(\varepsilon^2)$

Expansion of $x_I^\varepsilon(t) = x_I(t)^{(0)} + \varepsilon x_I^\varepsilon(t)^{(1)} + O(\varepsilon^2)$

Matching conditions between inner and outer quantities

$$\tilde{u}^{(0)}(t,z) \to u^{(0),\pm}(t, x_I^{(0)}(t)) \quad \text{for} \quad z \to \pm\infty \qquad \ldots\ldots$$

Sharp limit and interfacial entropy production

Cahn-Hilliard entropy production

$$\xi_{\mathrm{CH}}^{\varepsilon} = \frac{1}{M}(f^{\varepsilon})^2 + \gamma\varepsilon^2(\partial_t u^{\varepsilon})^2$$

In inner coordinates

$$\tilde{\xi}_{\mathrm{CH}}^{\varepsilon}(z) = \xi_{\mathrm{CH}}^{\varepsilon}(x_{\mathrm{I}}^{\varepsilon} + \varepsilon z)$$

Without viscosity

$$\tilde{\xi}_{\mathrm{CH}}^{(0)}(z) = \frac{1}{M}(f^{(0)}(z))^2 = (\dot{x}_{\mathrm{I}}^{(0)})^2(\tilde{u}^{(0)}(z) - u_0)^2 \quad \mathbf{\geq 0} \quad \text{with} \quad u_0 = u^{(0),\pm} - \frac{1}{\dot{x}_{\mathrm{I}}^{(0)}} f^{(0),\pm}$$

With viscosity

$$\tilde{\xi}_{\mathrm{CH}}^{(0)}(z) = (\dot{x}_{\mathrm{I}}^{(0)})^2((\tilde{u}^{(0)}(z) - u_0)^2 + \gamma(\partial_z \tilde{u}^{(0)}(z))^2) \; \mathbf{\geq 0}$$

Sharp limit and interfacial entropy production

Cahn-Hilliard entropy

$$\xi_{\mathrm{CH}}^{\varepsilon} = \frac{1}{M}(f^{\varepsilon})^2 +$$

$$F(u) = \frac{1}{2}u^2(u-1)^2 \quad M = 1 \quad \beta = 1$$

$$\Longrightarrow \quad \tilde{u}^{(0)}(z) = \frac{1}{2} + \frac{1}{2}\tanh\left(\frac{z+\alpha}{2}\right) \qquad u^{(0),-} = 0 \quad u^{(0),+} = 1$$

In inner coordinates

$$\tilde{\xi}_{\mathrm{CH}}^{\varepsilon}(z) = \xi_{\mathrm{CH}}^{\varepsilon}(x_{\mathrm{I}}^{\varepsilon} + \varepsilon z)$$

Without viscosity

$$\tilde{\xi}_{\mathrm{CH}}^{(0)}(z) = \frac{1}{M}(f^{(0)}(z))^2 = (\dot{x}_{\mathrm{I}}^{(0)})^2(\tilde{u}^{(0)}(z) - u_0)^2 \quad \mathbf{\geq 0} \quad \text{with} \quad u_0 = u^{(0),\pm} - \frac{1}{\dot{x}_{\mathrm{I}}^{(0)}} f^{(0),\pm}$$

Sharp limit and interfacial entropy production

Cahn-Hilliard entropy

$$\xi^{\varepsilon}_{\mathrm{CH}} = \frac{1}{M}(f^{\varepsilon})^2 + \gamma$$

$$F(u) = \frac{1}{2}u^2(u-1)^2 \quad M = 1 \quad \beta = 1$$

$$\Longrightarrow \quad \tilde{u}^{(0)}(z) = \frac{1}{2} + \frac{1}{2}\tanh\left(\frac{z+\alpha}{2}\right) \qquad u^{(0),-} = 0 \quad u^{(0),+} = 1$$

In inner coordinates

$$\tilde{\xi}^{\varepsilon}_{\mathrm{CH}}(z) = \xi^{\varepsilon}_{\mathrm{CH}}(x^{\varepsilon}_{\mathrm{I}} + \varepsilon z)$$

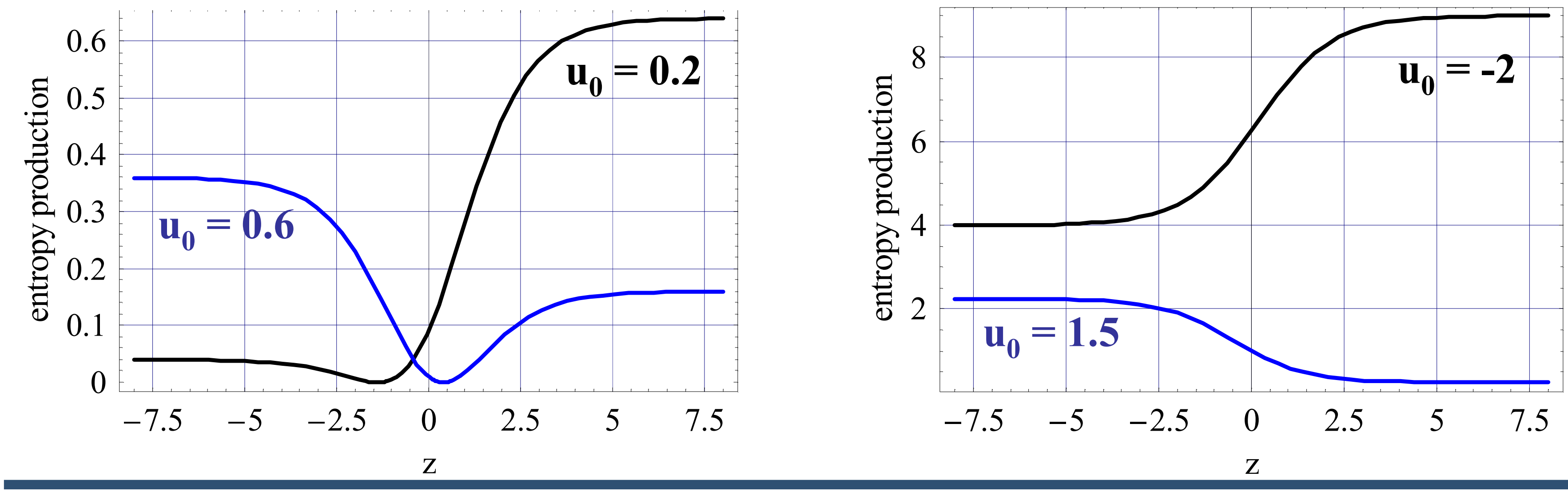
Without viscosity

$$\tilde{\xi}^{(0)}_{\mathrm{CH}}(z) = \frac{1}{M}(f^{(0)}(z))^2 = (\dot{x}^{(0)}_{\mathrm{I}})^2(\tilde{u}^{(0)}(z) - u_0)^2 \quad \mathbf{\geq 0} \quad \text{with} \quad u_0 = u^{(0),\pm} - \frac{1}{\dot{x}^{(0)}_{\mathrm{I}}} f^{(0),\pm}$$

Properties of the Cahn-Hilliard entropy production

$$\tilde{u}^{(0)} \in [0,1] \quad \Longrightarrow \quad \tilde{\xi}^{(0)}_{\mathrm{CH}}(z) = \begin{cases} \text{non-monotone } (!) & \text{for} \quad u_0 \in [0,1] \\ \text{monotone with } \partial_z \tilde{\xi}^{(0)}_{\mathrm{CH}}(z) < 0 & \text{for} \quad u_0 > 1 \\ \text{monotone with } \partial_z \tilde{\xi}^{(0)}_{\mathrm{CH}}(z) > 0 & \text{for} \quad u_0 < 0 \end{cases}$$

Diffuse entropy production versus interfacial entropy production



Diffuse entropy production versus interfacial entropy production

Proposition (Dreyer, Guhlke 2012)

- $u_0 \in [0,1]$
- $\xi_{\mathrm{I}}^{(0)} = 0$
- $\xi_{\mathrm{I}}^{(1)} = \int_{-\infty}^{0} (\widetilde{\xi}_{\mathrm{CH}}^{(0)}(z) - \xi^{(0),-})\,dz + \int_{0}^{+\infty} (\widetilde{\xi}_{\mathrm{CH}}^{(0)}(z) - \xi^{(0),+})\,dz$
- $\xi_{\mathrm{I}}^{(1)}$ **< 0** for $\gamma = 0$ $u_0 \in [0,1]$
- $\xi_{\mathrm{I}}^{(1)}$ **≥ 0** for $\gamma \geq 6$ (viscous Cahn-Hilliard)