Continuum thermodynamics of multicomponent fluids and implications for modeling electromigration of ionic species

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Workshop on
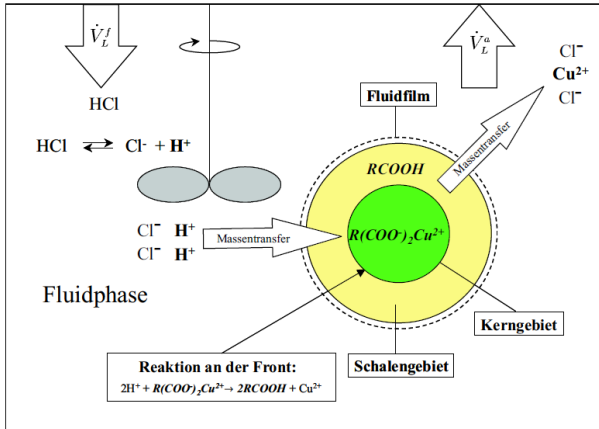
Transport of Ionic Particles in Biological Environments

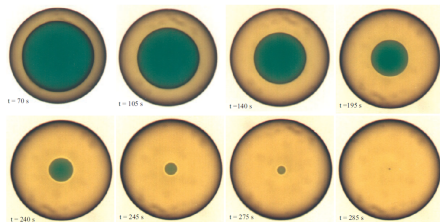Fields Institute, Toronto, July 28 - August 1, 2014

Contents

Motivation 1: Ion Exchange Processes

Regeneration of exhausted (Cu^{2+}-loaded) ion exchange pellets

Regeneration of Single Pellets

experiment: evolution of regeneration front
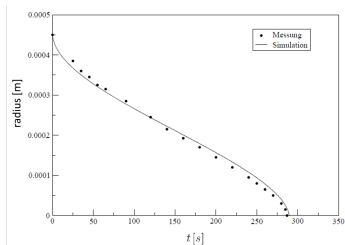
radius versus time

- hindered diffusion inside the pellet (resin)

- radius evolution of single pellet can be describe with/without electrical forces

- hindrance factors: 0.072 for Fick, 0.14 for Nernst-Planck fluxes corresponding H^+-diffusivities: 0.67×10^{-9} m^2 s^{-1} (Fick), 1.3×10^{-9} m^2 s^{-1} (Nernst-Planck)

Regeneration of Single Pellets

Simulated concentration profiles inside the pellet:
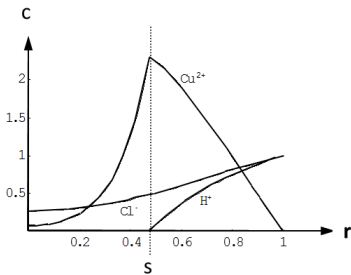
profiles: without electrical forces   with electrical forces
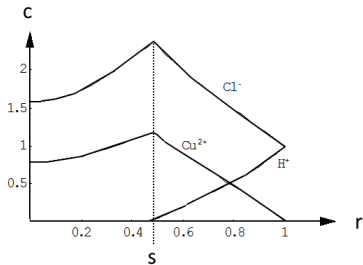
CSTR Bulk Concentration Dynamics

Bulk concentrations during regeneration process:
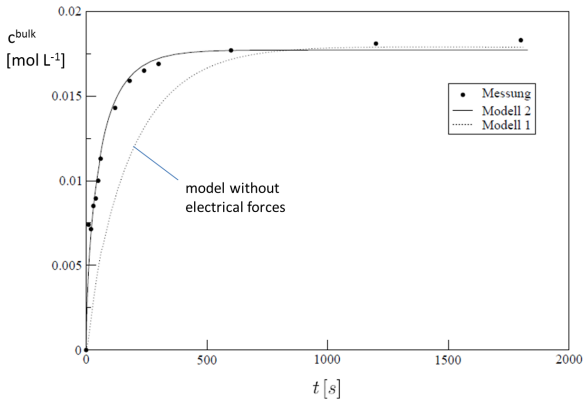
evolution of the bulk concentration in the CSTR

Motivation 2: Mass Transfer in G/L-Systems

Dissolution of CO_2 bubbles
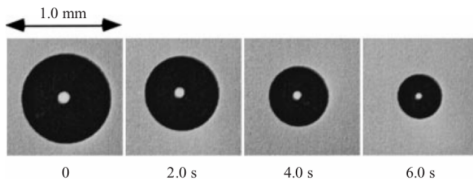
Dissolution of a freely rising carbon dioxide bubble in water. [1]
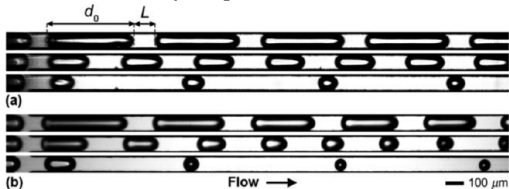
Dissolution of a CO_2 Taylor bubble in a micro-channel [2]

Chemisorption of CO_2 in NaOH solution

Simplified situation near interface:

ionic species:
$$Na^+, OH^-, CO_3^{2-}, H^+$$

mass transfer:
$$CO_2^g \to CO_2^{aq}$$

chemical reaction:
$$CO_2^{aq} + 2\,OH^- \to CO_3^{2-} + H_2O$$
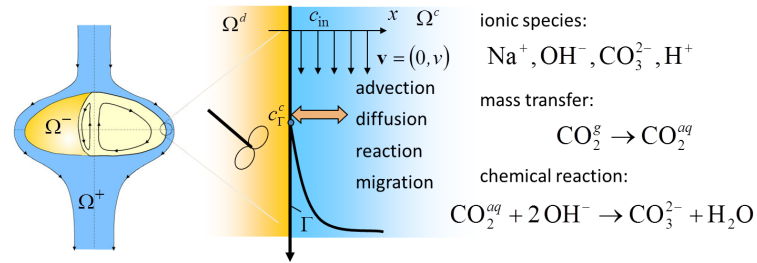
Preliminary computations: mass transfer results w/o electromigration for CO_2 in acidic solutions can be 10-20% off!

Chemisorption of CO_2 in NaOH solution

Simulated concentration profiles:
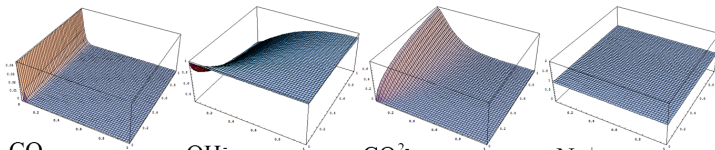
CO_2 OH^- CO_3^{2-} Na^+
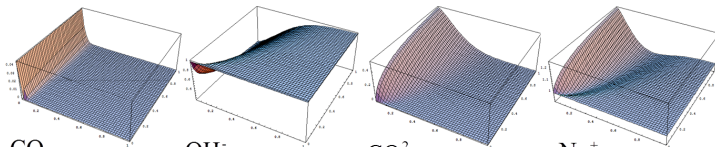
CO_2 OH^- CO_3^{2-} Na^+

DNS of Mass Transfer with Volume Effects

Simulated dissolution of a CO$_2$ Taylor bubble
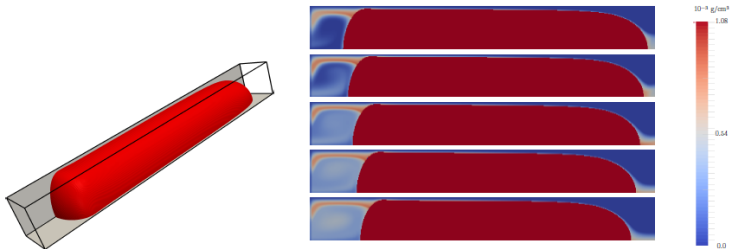
Shrinking of a Taylor bubble in a water/glycerol mixture. Left: Initial setup. Right: Concentration fields at $t = 0.01\,\text{s}, 0.03\,\text{s}, 0.05\,\text{s}, 0.07\,\text{s}, 0.09\,\text{s}$

DNS of Conjugated Mass Transfer

Simulated mass transfer at a free CO_2 bubble

	c_0^d	c_0^c	H
CO_2	4.464×10^{-2} mol/l	0	1.2
N_2	0	0.51×10^{-3} mol/l	67.0
O_2	0	$0.27 \times 10{-3}$ mol/l	31.5
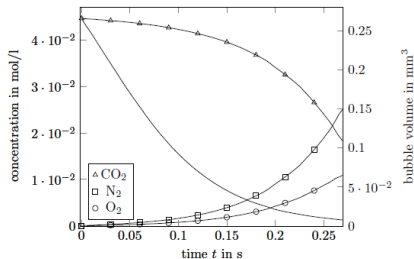
Dissolved air (N_2, O_2) from aqueous phase is transfers into the bubble

Motivation 3: Cross Diffusion Effects

Classical experiment by Duncan and Toor 1962 on ternary diffusion
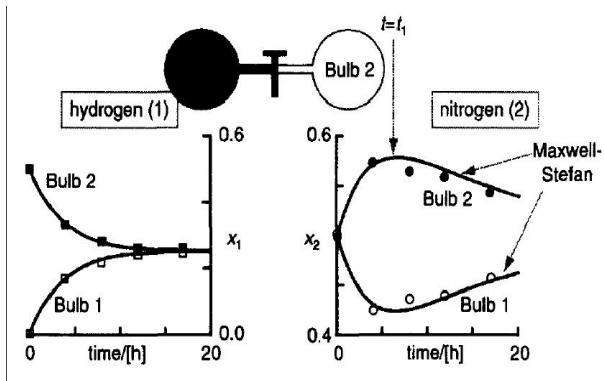
initial composition: left bulb $N_2 : CO_2$ (1:1), right bulb $N_2 : H_2$ (1:1)

Anomalous Diffusion

Typical phenomena in ternary systems

Chemically Reacting Fluid Mixture

Fluid composed of N chemically reacting components $A_1, \ldots, A_N$

N_R chemical reactions between the A_i:

$$\alpha_1^a A_1 + \ldots + \alpha_N^a A_N \rightleftharpoons \beta_1^a A_1 + \ldots + \beta_N^a A_N \quad \text{for } a = 1, \ldots, N_R$$

with stoichiometric coefficients $\alpha_i^a, \beta_i^a \in \mathbf{N}_0$

Let $R_a = R_a^f - R_a^b$ be the (molar) rate of reaction a and $\nu_i^a := \beta_i^a - \alpha_i^a$. Then

$$r_i = \sum_{a=1}^{N_R} M_i \nu_i^a R_a \quad \text{with } M_i \text{ the molar mass of species } A_i$$

is the total rate of change of mass of component A_i

Mass conservation in individual reactions: $\quad \sum_i M_i \nu_i^a = 0 \quad \forall a$

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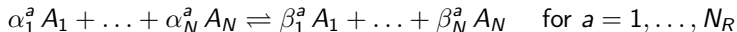
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Thermodynamics of Irreversible Processes (TIP)

Throughout this talk: $\mathbf{v}$ denotes the *barycentric* velocity of the mixture

Classical mixture balances in T.I.P. (cf. deGroot, Mazur):

partial mass balances:

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

total momentum balance:

$$\partial_t(\varrho\mathbf{v}) + \operatorname{div}\left(\varrho\mathbf{v} \otimes \mathbf{v} - \mathbf{S}\right) = \varrho\mathbf{b}; \qquad \varrho\mathbf{b} = \sum_i \varrho_i \mathbf{b}_i$$

internal energy balance:

$$\partial_t(\varrho e) + \operatorname{div}\left(\varrho e\mathbf{v} + \mathbf{q}\right) = \nabla\mathbf{v} : \mathbf{S} + \varrho\pi; \qquad \varrho\pi = \sum_i \mathbf{j}_i \cdot \mathbf{b}_i$$

Definition of internal energy: $\varrho e = \varrho e_{\text{tot}} - \frac{1}{2}\varrho\mathbf{v}^2$

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The 2nd Law: Entropy Inequality

Entropy production:

$$\zeta^{\text{TIP}} = \mathbf{q} \cdot \nabla \frac{1}{T} + \sum_{i=1}^{N} \mathbf{j}_i \cdot \left(\nabla \frac{\mu_i}{T} - \frac{\mathbf{b}_i}{T} \right) + \frac{1}{T} \mathbf{S}^{\text{irr}} : \mathbf{D} - \frac{1}{T} \sum_{a=1}^{N_R} R_a \mathcal{A}_a$$

$$\mathbf{S} = -p\mathbf{I} + \mathbf{S}^{\text{irr}}, \quad \mathbf{S}^{\text{irr}} : \mathbf{D} = \mathbf{S}^{\circ} : \mathbf{D}^{\circ} + \Pi \, \text{div} \, \mathbf{v}$$

Notation:

- T denotes the (absolute) temperature
- μ_i denotes the chemical potentials
- $\mathbf{S}^{\circ}$ denotes the traceless part of $\mathbf{S}$
- $\mathbf{D}^{\circ}$ denotes the symmetric, traceless part of $\nabla \mathbf{v}$
- Π denotes the dynamic pressure (or, irreversible pressure part)
- $\mathcal{A}_a := \sum_i \mu_i M_i \nu_i^a$ are the *chemical affinities*.

The Phenomenological Equations

Standard closure: fluxes linear in the (so-called) driving forces
$\Rightarrow$ **quadratic form**

heat flux and diffusive fluxes:

$$\mathbf{q} \;=\; L_{00}\nabla\tfrac{1}{T} \;-\; \sum_{i=1}^{N-1} L_{0i}\Big(\nabla\tfrac{\mu_i-\mu_N}{T} - \tfrac{1}{T}(\mathbf{b}_i - \mathbf{b}_N)\Big)$$

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viscous stress, dynamic pressure and chemical reaction rates:

$$\mathbf{S}^\circ = L\,\mathbf{D}^\circ, \quad \Pi = -l\operatorname{div}\mathbf{v} - \sum_a l_{0a}\mathcal{A}_a, \qquad R_a = -l_{a0}\operatorname{div}\mathbf{v} - \sum_b l_{ab}\mathcal{A}_b$$

Entropy inequality: $[L_{ij}]$ and $[l_{ab}]$ positive semi-definite and $L \geq 0$

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Entropy inequality: $[L_{ij}]$ and $[l_{ab}]$ positive semi-definite and $L \geq 0$

Onsager-Casimir reciprocal relations: $[L_{ij}]$, $[l_{ab}]$ symmetric, but $l_{0a} = -l_{a0}$

Remarks on Classical TIP

- Curie's principle: driving forces couple only to fluxes of the same tensorial rank

  is a rigorous consequence of material frame indifference for linear constitutive relations

- Onsager's reciprocal relations: $[L_{ij}]$ and $[l_{ab}]$ are symmetric

  relies on microscopic theory; only derived for rates (ODE case), not for transport coefficients

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- Some disadvantages of classical TIP / Fickean form:
  - the L_{ij} show complex nonlinear dependence on the composition
  - the linear closure for chemical reaction rates is not appropriate
  - in recent applications different species can experience different BCs

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The Maxwell-Stefan Equations

Alternative approach to multicomponent diffusion:

assume local balance between driving and friction forces:

$$\mathbf{d}_i = -\sum_{j \neq i} f_{ij}\, x_i\, x_j (\mathbf{v}_i - \mathbf{v}_j) = -\sum_{j \neq i} \frac{x_j \mathbf{J}_i - x_i \mathbf{J}_j}{c\, \mathrm{\DJ}_{ij}}$$

$\mathbf{d}_i$ the *thermodynamic driving forces*, $\mathbf{d}_i = \frac{x_i}{RT} \nabla_p \mu_i^{\mathrm{mol}} + \frac{\phi_i - y_i}{\varrho RT} \nabla p - \frac{y_i}{\varrho RT}(\mathbf{b}_i - \mathbf{b})$

$c = \sum_i c_i$ total concentration, $x_i = c_i/c$ molar fractions, $\mathbf{J}_i = \mathbf{j}_i/M_i$ molar mass fluxes; $\mathrm{\DJ}_{ij} = 1/f_{ij}$ the *Maxwell-Stefan diffusivities*; in many cases: $\mathrm{\DJ}_{ij}$ nearly constant or affine functions of the composition

Origin of the Maxwell-Stefan Equations:

- James Clerk Maxwell: On the dynamical theory of gases,
  Phil. Trans. R. Soc. **157**, 49-88 (1866).

- Josef Stefan: Über das Gleichgewicht und die Bewegung insbesondere die Diffusion von Gasgemengen,
  Sitzber. Akad. Wiss. Wien **63**, 63-124 (1871).

Maxwell-Stefan Equations - Criticism

Problems and open issues:

- rigorous derivation of the Maxwell-Stefan equations, including the thermodynamic driving forces

- proper coupling to the mass and momentum balance

- extension to non-simple fluid mixtures

- extension to chemically reacting fluid mixtures

Aim: thermodynamically consistent mathematical modeling of reacting fluid mixtures, guided by rational thermodynamics

joint work with Wolfgang Dreyer (WIAS, Berlin)
Preprint – arXiv:1401.5991v2 [physics.flu-dyn]

Maxwell-Stefan Equations - Derivation

Four different derivations of the Maxwell-Stefan equations:

I. Employing only the <u>barycentric momentum balance</u>:

- naive balance of forces

  ad hoc; mixes continuum balances with kinetic theory

- standard T.I.P. with "resistance form" of the closure

  consistency with kinetic theories only achievable via thermo-diffusive terms

II. Employing <u>partial momentum balances</u>:

- diffusive approximation using time-scale separation

  not applicable with chemical reactions

- entropy invariant model reduction

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Partial Balances of Mass, Momentum and Energy

Continuum mechanical balances of the fluid components A_i

mass : $\partial_t \varrho_i + \operatorname{div}(\varrho_i \mathbf{v}_i) = r_i$

mom. : $\partial_t(\varrho_i \mathbf{v}_i) + \operatorname{div}(\varrho_i \mathbf{v}_i \otimes \mathbf{v}_i - \mathbf{S}_i) = \mathbf{f}_i + \varrho_i \mathbf{b}_i$

energy : $\partial_t(\varrho_i e_i + \dfrac{\varrho_i}{2}\mathbf{v}_i^2) + \operatorname{div}((\varrho_i e_i + \dfrac{\varrho_i}{2}\mathbf{v}_i^2)\mathbf{v}_i - \mathbf{v}_i \mathbf{S}_i + \mathbf{q}_i) = l_i + \varrho_i \mathbf{b}_i \cdot \mathbf{v}_i$

mass conservation: $\qquad \sum_i r_i = 0$

momentum conservation: $\quad \sum_i \mathbf{f}_i = 0$

energy conservation: $\qquad \sum_i l_i = 0$

Note: power due to external forces is $\varrho_i \mathbf{b}_i \cdot \mathbf{v}_i$, while internal forces
(mechanical and chemical interactions) contribute to the l_i

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Balance of internal energy

Partial balance of internal energy:

$$\partial_t(\varrho_i e_i) + \operatorname{div}(\varrho_i e_i \mathbf{v}_i + \mathbf{q}_i) = \nabla \mathbf{v}_i : \mathbf{S}_i + l_i - \mathbf{v}_i \cdot \left(\mathbf{f}_i - \tfrac{1}{2}r_i\mathbf{v}_i\right)$$

Alternative definition of internal energy:

$$\varrho e := \sum_i \varrho_i e_i \text{ total internal energy } = \varrho(e_{\text{tot}} - \tfrac{1}{2}\mathbf{v}^2) - \sum_i \tfrac{1}{2}\varrho_i \mathbf{u}_i^2$$

$$P_i := -\tfrac{1}{3}\operatorname{tr}(\mathbf{S}_i) \text{ partial pressures, } P_i = p_i + \Pi_i \text{ with } \Pi_{i|E} = 0$$

$$\mathbf{q} := \sum_i (\mathbf{q}_i + (\varrho_i e_i + p_i)\mathbf{u}_i) \text{ mixture heat flux, } p := \sum_i p_i$$

mixture internal energy balance:

$$\partial_t(\varrho e) + \operatorname{div}(\varrho e \mathbf{v} + \mathbf{q}) = -p \operatorname{div} \mathbf{v} + \sum_i \nabla \mathbf{v}_i : \mathbf{S}_i^\circ$$

$$- \sum_i \mathbf{u}_i \cdot \left(\mathbf{f}_i - r_i\mathbf{v}_i + \tfrac{1}{2}r_i\mathbf{u}_i - \nabla p_i\right)$$

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Constitutive Modeling

Variables: $\varrho_1, \ldots, \varrho_N$, $\mathbf{v}_1, \ldots, \mathbf{v}_N$, ϱe

class-II model requires constitutive equations for:

$$R_a, \quad \mathbf{S}_i, \quad \mathbf{f}_i - r_i\mathbf{v}_i, \quad \mathbf{q}$$

Decompose the partial stresses as $\mathbf{S}_i = -P_i\mathbf{I} + \mathbf{S}_i^{\circ} = -p_i\mathbf{I} + \mathbf{S}_i^{\mathrm{irr}}$

We consider **non-polar fluids**, hence the stresses $\mathbf{S}_i$ are **symmetric**.

Universal Principles:

1. material frame indifference

2. entropy principle (second law of thermodynamics)

Notation: any (local) solution of the PDE-system is called
           thermodynamic process

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The Entropy Principle

The entropy principle comprises the following postulates:

1) There is an entropy/entropy-flux pair $(\varrho s, \Phi)$ as a material dependent quantity, satisfying the principle of material frame indifference (ϱs is an objective scalar, Φ is an objective vector).

2) The pair $(\varrho s, \Phi)$ satisfies the balance equation

$$\partial_t(\varrho s) + \operatorname{div}(\varrho s \mathbf{v} + \Phi) = \zeta,$$

where the entropy production ζ satisfies

$$\zeta \geq 0 \quad \text{for every thermodynamic process.}$$

Equilibria are characterized by $\zeta = 0$.

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3) Every admissible entropy flux is such that the entropy production becomes a sum of binary products according to

$$\zeta = \sum_m \mathcal{N}_m \mathcal{P}_m,$$

where $\mathcal{N}_m$, $\mathcal{P}_m$ denote factors of negative, resp. positive parity.

The parity of a time-dependent quantity characterizes its behavior under time reversal in the *unclosed* balance equations. Resulting rule:

$[\,\cdot\,]$ contains the time units s^k with k even $\;\Rightarrow\;$ *positive parity*

$[\,\cdot\,]$ contains the time units s^k with k odd $\;\Rightarrow\;$ *negative parity*

Note: parity replaces the classical concept of "flux $\times$ driving force", since the latter is misleading!

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4) Each binary product in the entropy production describes a
   dissipative mechanism which has to be introduced *in advance*.

   Extended principle of detailed balance:

   $$\mathcal{N}_m \mathcal{P}_m \geq 0 \quad \text{for every } m \text{ and any thermodynamic process.}$$

   Note: the specific form of the decomposition into binary products is not
   unique and has to be chosen as part of the modeling. Even the number
   of dissipative mechanisms is not fixed, but can be changed.

   This non-uniqueness is the basis for:

   - introduction of cross-effects via entropy-neutral mixing
   - improvement of classical TIP-models

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Consequences of the extended principle of detailed balance

- the closure between the co-factors in the entropy production,

$$\zeta = \sum_m \mathcal{N}_m \mathcal{P}_m =: \langle \mathbf{N}, \mathbf{P} \rangle,$$

decouples. In a linear (in $\mathcal{N}_m$, $\mathcal{P}_m$) constitutive theory, this enforces a block-diagonal closure.

Note: $\mathcal{N}_m \mathcal{P}_m$ refers to a single mechanism, but may itself be a sum.

- structure of entropy production as $\zeta = \sum_m \mathcal{N}_m \mathcal{P}_m$ is **not unique**
In particular: mixing of different fluxes or forces is possible!

$$\zeta = \langle A\,\mathbf{N}, B\,\mathbf{P} \rangle = \langle \mathbf{N}, A^\mathsf{T} B\,\mathbf{P} \rangle = \langle \mathbf{N}, \mathbf{P} \rangle \quad \forall \mathbf{N}, \mathbf{P} \;\Rightarrow\; A^{-1} = B^\mathsf{T}$$

the diagonal closure implies cross-effects with Onsager symmetry:

$$A\,\mathbf{N} := \Lambda B\,\mathbf{P} \text{ with } \Lambda = \mathrm{diag}(\lambda_i) \geq 0 \;\Rightarrow\; \mathbf{N} := B^\mathsf{T} \Lambda B\,\mathbf{P}$$

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Example: Entropy Inequality of T.I.P.

the strengthened entropy principle can be used in T.I.P. !

$\zeta^{\mathrm{TIP}} = \mathbf{q}\cdot\nabla\frac{1}{T} + \sum_{i=1}^{N}\mathbf{j}_i\cdot\left(\nabla\frac{\mu_i}{T} - \frac{\mathbf{b}_i}{T}\right) + \frac{1}{T}\mathbf{S}^\circ : \mathbf{D}^\circ - \frac{1}{T}\Pi\operatorname{div}\mathbf{v} - \frac{1}{T}\sum_{a=1}^{N_R} R_a\mathcal{A}_a$

Consider a coupling between volume variations and chemical reactions

Parity of the factors Π, $\operatorname{div}\mathbf{v}$, R_a, $\mathcal{A}_a$: $+1$, -1, -1, $+1$

Cross-effects via entropy neutral mixing:

$\operatorname{div}\mathbf{v}\,\Pi + \sum_{a=1}^{N_R} R_a\mathcal{A}_a = \operatorname{div}\mathbf{v}\left(\Pi + \sum_{a=1}^{N_R} l_a\mathcal{A}_a\right) + \sum_{a=1}^{N_R}\left(R_a - l_a\operatorname{div}\mathbf{v}\right)\mathcal{A}_a$

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Hence the apparent anti-symmetry (Onsager-Casimir relations):

$$\Pi = \lambda^{-1}\operatorname{div}\mathbf{v} - \sum_{a=1}^{N_R} l_a\mathcal{A}_a, \quad R_a = l_a\operatorname{div}\mathbf{v} + \sum_{b=1}^{N_R} L_{ab}\mathcal{A}_b$$

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For the considered fluid mixture class we also postulate:

5) The dissipative mechanisms are: *multi-component diffusion*, *heat conduction*, *chemical reaction*, *viscous flow*.

6) The entropy density is given as

$$\varrho s = h(\varrho e, \varrho_1, \ldots, \varrho_N)$$

with a strictly concave material function h.

The *absolute temperature* T and *chemical potentials* μ_i are defined as

$$\frac{1}{T} := \frac{\partial \varrho s}{\partial \varrho e}, \qquad -\frac{\mu_i}{T} := \frac{\partial \varrho s}{\partial \varrho_i}$$

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Entropy Principle evaluated

Evaluation of the entropy principle:

1. entropy flux: $\qquad\qquad\qquad \Phi = \frac{\mathbf{q}}{T} - \sum_i \frac{\varrho_i \mathbf{u}_i \mu_i}{T}$

2. Gibbs-Duhem equation: $\quad p + \varrho\psi - \sum_i \varrho_i \mu_i = 0$

3. restrictions to constitutive equations for dissipative mechanisms:

Entropy inequality, i.e. $\zeta \geq 0$ with the entropy production rate

$$\zeta = -\frac{1}{T}\sum_{a=1}^{N_R} R_a \mathcal{A}_a + \frac{1}{T}\sum_i \mathbf{S}_i^{\mathrm{irr}} : \mathbf{D}_i + \sum_i \mathbf{q}_i \cdot \nabla \frac{1}{T}$$

$$-\sum_i \mathbf{u}_i \cdot \left(\varrho_i \nabla \frac{\mu_i}{T} + \frac{1}{T}(\mathbf{f}_i - r_i \mathbf{v}_i + \frac{1}{2} r_i \mathbf{u}_i - \nabla p_i) - (\varrho_i e_i + p_i)\nabla \frac{1}{T} \right)$$

$$\mathbf{S}_i^{\mathrm{irr}} = -\Pi_i \mathbf{I} + \mathbf{S}_i^\circ, \ \text{ i.e. } \ \mathbf{S}_i = -p_i \mathbf{I} + \mathbf{S}_i^{\mathrm{irr}}$$

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Nonreactive fluids without viscosity

entropy production without viscosity, no chemical reactions:

$$\zeta = - \sum_i \mathbf{u}_i \cdot \left(\varrho_i \nabla \frac{\mu_i}{T} + \frac{1}{T}(\mathbf{f}_i - \nabla p_i) - h_i \nabla \frac{1}{T} \right) + \sum_i \mathbf{q}_i \cdot \frac{1}{T}$$

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With short-hand notation:

$$\zeta = - \sum_i \mathbf{u}_i \cdot \left(\mathbf{B}_i + \frac{1}{T}\mathbf{f}_i \right) + \sum_i \mathbf{q}_i \cdot \nabla \frac{1}{T}$$

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Exploiting the second law

The interaction terms $\mathbf{f}_i$ necessarily satisfy

$$-\sum_{i=1}^{N} \mathbf{u}_i \cdot \left(\mathbf{B}_i + \tfrac{1}{T}\mathbf{f}_i \right) \geq 0 \quad \text{and} \quad \sum_{i=1}^{N} \mathbf{B}_i = 0, \quad \sum_{i=1}^{N} \mathbf{f}_i = 0$$

Hence

$$-\sum_{i=1}^{N-1} (\mathbf{u}_i - \mathbf{u}_N) \cdot \left(\mathbf{B}_i + \tfrac{1}{T}\mathbf{f}_i \right) \geq 0,$$

with build-in constraints.

The standard linear Ansatz for $\mathbf{B}_i + \tfrac{1}{T}\mathbf{f}_i$ is

$$\mathbf{B}_i + \tfrac{1}{T}\mathbf{f}_i = -\sum_{j=1}^{N-1} \tau_{ij} \left(\mathbf{u}_j - \mathbf{u}_N \right) \qquad \text{(for } i = 1, \ldots, N-1)$$

with a positive (semi-)definite matrix $[\tau_{ij}]$.

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Closure for thermo-mechanical Interactions

Extension to $N \times N$ format (positive semi-definite):

$$\tau_{Nj} = -\sum_{i=1}^{N-1} \tau_{ij} \ (i = 1, \ldots, N-1), \quad \tau_{iN} = -\sum_{j=1}^{N-1} \tau_{ij} \ (j = 1, \ldots, N)$$

Straight forward computation:

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Assumption of binary type interactions: (C. Truesdell)

$$\tau_{ij} = \tau_{ij}(T, \varrho_i, \varrho_j) \to 0 \quad \text{if } \varrho_i \to 0+ \text{ or } \varrho_j \to 0+$$

This implies symmetry of $[\tau_{ij}]$! (evaluate $\sum_{i,j} \tau_{ij} \left(\mathbf{u}_i - \mathbf{u}_j\right) = 0$)

$$\Rightarrow \quad \tau_{ij} = -f_{ij}\varrho_i\varrho_j \quad \text{for } i \neq j \text{ with } f_{ij} = f_{ji} \geq 0, \ f_{ij} = f_{ij}(\varrho_i, \varrho_j, T).$$

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Momentum Balance with Thermo-mechanical Interactions

partial momentum balances:

with
$$\varrho_i\big(\partial_t\mathbf{v}_i + \mathbf{v}_i\cdot\nabla\mathbf{v}_i\big) + \nabla p_i = \mathbf{f}_i + \varrho_i\mathbf{b}_i$$

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Partial Momentum Balances due to Stefan

Scale-Reduced Model: Maxwell-Stefan Eqs

Consider the difference: momentum of species i $-$ $y_i \times$ total momentum

$\varrho_i(\partial_t + \mathbf{v} \cdot \nabla)\mathbf{u}_i + \varrho_i \mathbf{u}_i \cdot \nabla \mathbf{v}_i =$

$y_i \nabla p - \varrho_i \nabla \mu_i + T(h_i - \varrho_i \mu_i)\nabla \frac{1}{T} + \varrho_i(\mathbf{b}_i - \mathbf{b}) - T \sum_j f_{ij}\varrho_i\varrho_j(\mathbf{u}_i - \mathbf{u}_j)$

nondimensionalized form:

$\frac{U}{C}\frac{V}{C} y_i(\partial_t^* \mathbf{u}_i^* + \mathbf{v}^* \cdot \nabla^* \mathbf{u}_i^* + \mathbf{u}_i^* \cdot \nabla^* \mathbf{v}_i^*) =$

$y_i \frac{\nabla^* p^*}{\varrho^*} - \frac{c_0 R T_0}{p_0} y_i \nabla^* \mu_i^* - (\frac{h_0}{p_0}\frac{h_i^*}{\varrho^*} - \frac{c_0 R T_0}{p_0} y_i \mu_i^*)\nabla^* \ln T^*$

$+ \frac{\varrho_0 B L}{p_0} y_i(\mathbf{b}_i^* - \mathbf{b}^*) - \frac{c_0 R T_0}{p_0}\frac{UL}{D} \varrho^* T^* \sum_j \frac{y_i y_j}{M_i^* M_j^* \mathcal{D}_{ij}^*}(\mathbf{u}_i^* - \mathbf{u}_j^*)$

some characteristic reference quantities:

U diffusion velocity, V mixture velocity, $\tau = L/V$ convective time scale, $C = \sqrt{p_0/\varrho_0}$ about the speed of sound in gas mixture

Scale-Reduced Model: Maxwell-Stefan Eqs

Consider the difference: momentum of species $i - y_i \times$ total momentum

$$\varrho_i(\partial_t + \mathbf{v} \cdot \nabla)\mathbf{u}_i + \varrho_i\mathbf{u}_i \cdot \nabla\mathbf{v}_i =$$

$$y_i\nabla p - \varrho_i\nabla\mu_i + T(h_i - \varrho_i\mu_i)\nabla\tfrac{1}{T} + \varrho_i(\mathbf{b}_i - \mathbf{b}) - T\sum_j f_{ij}\varrho_i\varrho_j(\mathbf{u}_i - \mathbf{u}_j)$$

nondimensionalized form:

$$\frac{U}{C}\frac{V}{C}y_i(\partial_t^*\mathbf{u}_i^* + \mathbf{v}^* \cdot \nabla^*\mathbf{u}_i^* + \mathbf{u}_i^* \cdot \nabla^*\mathbf{v}_i^*) =$$

$$y_i\frac{\nabla^*p^*}{\varrho^*} - \frac{c_0RT_0}{p_0}y_i\nabla^*\mu_i^* - \left(\frac{h_0}{p_0}\frac{h_i^*}{\varrho^*} - \frac{c_0RT_0}{p_0}y_i\mu_i^*\right)\nabla^*\ln T^*$$

$$+ \frac{\varrho_0BL}{p_0}y_i(\mathbf{b}_i^* - \mathbf{b}^*) - \frac{c_0RT_0}{p_0}\frac{UL}{D}\varrho^*T^*\sum_j\frac{y_iy_j}{M_i^*M_j^*\mathsf{D}_{ij}^*}(\mathbf{u}_i^* - \mathbf{u}_j^*)$$

some characteristic reference quantities:

U diffusion velocity, V mixture velocity, $\tau = L/V$ convective time scale,
$C = \sqrt{p_0/\varrho_0}$ about the speed of sound in gas mixture

Scale-Reduced Model: Maxwell-Stefan Eqs

Approximation for $\frac{U}{c}\frac{V}{c} \ll 1$: **generalized Maxwell-Stefan equations**

$$-\sum_{j \neq i} \frac{y_j \mathbf{j}_i - y_i \mathbf{j}_j}{c M_i M_j \, \DH_{ij}} = \frac{y_i}{RT}\nabla \mu_i - \frac{y_i}{\varrho RT}\nabla p + \frac{\varrho_i \mu_i - h_i}{\varrho R}\nabla \frac{1}{T} - \frac{y_i}{\varrho RT}(\mathbf{b}_i - \mathbf{b})$$

Phenomena: molecular, pressure, thermo- (partially) & forced diffusion

Chemical Eng. version of the generalized MS-eqs (isothermal case)*:

$$-\sum_{j \neq i} \frac{x_j \mathbf{J}_i - x_i \mathbf{J}_j}{c \, \DH_{ij}} = \frac{x_i}{RT}\nabla_p \mu_i^{\mathrm{mol}} + \frac{\phi_i - y_i}{\varrho RT}\nabla p - \frac{y_i}{\varrho RT}(\mathbf{b}_i - \mathbf{b})$$

x_i molar fractions, $\mathbf{J}_i$ molar mass fluxes, $\mu_i^{\mathrm{mol}} = M_i \mu_i$ molar based chemical potential

*R. Taylor, R. Krishna: Multicomponent Mass Transfer, 1993

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Scale-Reduced Model: Maxwell-Stefan Eqs

Thermodynamic consistency?

The mass fluxes $\mathbf{j}_i$ determined by the gen. Maxwell-Stefan equations (and $\sum_i \mathbf{j}_i = 0$) need to satisfy:

$$\zeta^{\mathrm{TIP}} = \left(\alpha\nabla\tfrac{1}{T} + \sum_i h_i\mathbf{u}_i\right)\cdot\nabla\tfrac{1}{T} - \tfrac{1}{T}\sum_i\mathbf{j}_i\cdot\left(T\nabla\tfrac{\mu_i}{T} - \mathbf{b}_i\right) \geq 0 \ !$$

Instead of inverting the MS-system, we use

$$-T\sum_j f_{ij}\varrho_i\varrho_j(\mathbf{u}_i - \mathbf{u}_j) = \varrho_i T\nabla\tfrac{\mu_i}{T} - y_i\nabla p - h_i T\nabla\tfrac{1}{T} - \varrho_i(\mathbf{b}_i - \mathbf{b})$$

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From Maxwell-Stefan to Nernst-Planck

Assume dilute solution: $x_0 \approx 1$, $x_i \ll 1$ for $i = 1, \ldots, N$. Then

$$-\frac{1}{D_{i0}}\mathbf{j}_i = \frac{c_i}{RT}\nabla_{p,T}\mu_i + \frac{\phi_i - y_i}{\varrho RT}\nabla p - \frac{\varrho_i}{RT}(\mathbf{b}_i - \mathbf{b}) \quad i = 1, \ldots, N$$

chemical potentials: $\mu_i(T, p, x) = g_i(T, p) + RT \log x_i, \qquad i = 1, \ldots, N$

forces on ions: $\mathbf{b}_i = -\frac{F}{M_i} z_i \nabla \phi$ (z_i charge numbers)

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Remarks on the Nernst-Planck fluxes

Shortcomings of the specialization to Nernst-Planck:

- If used for all constituents, Nernst-Planck (like Fickean) fluxes are inconsistent with the continuity equation

- If only used for the dilute components, Nernst-Planck (like Fickean) fluxes do not yield pointwise upper bounds

- Even for globally dilute mixtures, the diluteness assumption breaks down near interfaces (walls). The solvent concentration can actually approach zero when transversing the double layer at a wall!

- Pressure effects are usually <u>not</u> negligible (especially near walls).

Implications

Implication for modeling transport of ions in solution:

Use the full set of balance equations together with
thermodynamically consistent fluxes from Maxwell-Stefan theory
instead of only mass balances with Nernst-Planck fluxes!

For first results from a complete and thermodynamically consistent model
see the recent paper by Dreyer, Guhlke and Müller: "Overcoming the
shortcomings of the Nernst-Planck model", Phys. Chem. Chem. Phys.
15, 7075-86 (2013).

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simultaneously inside the bulk and in the boundary layer.

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Final Remark: Extension to chemically reacting fluid mixtures exists.

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Final Remark: Extension to chemically reacting fluid mixtures exists.

Joint work with A. Fischer, M. Pierre, G. Rolland

Navier-Stokes-Nernst-Planck-Poisson system (NSNPP)

$$(NS)\begin{cases} \partial_t v + (v \cdot \nabla)v - \Delta v + \nabla p + \sum_{i=1}^{N} z_i c_i \nabla \Phi &=& 0 &\text{in } \Omega, \\ \text{div } v &=& 0 &\text{in } \Omega, \\ u &=& 0 &\text{on } \partial\Omega, \\ v(0) &=& v^0 &\text{in } \Omega. \end{cases}$$

$$(NP)\begin{cases} \partial_t c_i + \text{div}\,(c_i v - d_i \nabla c_i - d_i z_i c_i \nabla \Phi) &=& 0 &\text{in } \Omega, \\ \partial_\nu c_i + z_i c_i \partial_\nu \Phi &=& 0 &\text{on } \partial\Omega, \\ c(0) &=& c^0 &\text{in } \Omega. \end{cases}$$

$$(P)\begin{cases} -\Delta \Phi - \sum_{i=1}^{N} z_i c_i &=& \sigma &\text{in } \Omega, \\ \partial_\nu \Phi + \tau \Phi &=& \xi &\text{on } \partial\Omega. \end{cases}$$

Unknowns: v velocity field, p pressure,
               c_i concentration of species i, Φ electrical potential.
Data: $d_i(t,x)$ diffusivity, $\sigma(x)$ fixed charges, $\xi(x)$ boundary datum.
Constants: $z_i \in \mathbf{Z}$ charge number, $\tau > 0$ boundary capacity.

Energy dissipation for (NSNPP)

Exploit the following Lyapunov structure:

- Define the functionals E and D by

$$E(v, c, \Phi) := \frac{1}{2} \int_\Omega |v|^2 + \sum_{i=1}^N \int_\Omega c_i \log c_i + \frac{1}{2} \int_\Omega |\nabla\Phi|^2 + \frac{\tau}{2} \int_{\partial\Omega} |\Phi|^2,$$

$$D(v, c, \Phi) := \int_\Omega |\nabla v|^2 + \sum_{i=1}^N \int_\Omega \frac{1}{d_i c_i} \left| d_i \nabla c_i + d_i z_i c_i \nabla\Phi \right|^2 \geq 0.$$

- Given a regular solution (v, c, Φ) to (NSNPP), the functional

$$V(t) = E(v(t), c(t), \Phi(t))$$

is non-increasing in time with derivative

$$\dot{V}(t) = -D(v(t), c(t), \Phi(t)) \leq 0.$$

- Analogous situation for pure (NPP) without kinetic energy term.

Global existence for NPP in three or higher dimensions

Theorem (B., Fischer, Pierre, Rolland, Nonl. Anal. TMA '14)

Let $n \in \mathbb{N}$, $\Omega \subset \mathbb{R}^n$ bounded and sufficiently smooth and

- $d_i \in L^{\infty}_{loc}(\mathbb{R}_+; L^{\infty}(\Omega))$, $0 < \underline{d}(T) \le d_i(t,x) \le \overline{d}(T) < \infty$ a.e. on Q_T.
- $c^0 \in L^2(\Omega)^+$, $\sigma = 0$, $\xi \in L^2(\partial\Omega)$.

Then there exist $c \in L^{\infty}(\mathbb{R}_+; L^1(\Omega))$ and $\Phi \in L^{\infty}(\mathbb{R}_+; H^1(\Omega))$ such that (NPP) is satisfied in the following sense:

For all $T > 0$, $c_i \in L^1(0, T; W^{1,1}_{loc}(\Omega))$, $d_i \nabla c_i + d_i z_i c_i \nabla \Phi \in L^1(Q_T)$ s.t., for all $\psi \in C^{\infty}(\overline{Q_T})$ with $\psi(T) = 0$, $\varphi \in C^{\infty}(\overline{\Omega})$,

$$\int_{Q_T} -c_i \partial_t \psi + (d_i \nabla c_i + d_i z_i c_i \nabla \Phi) \nabla \psi = \int_{\Omega} c_i^0 \psi(0),$$

$$\int_{\Omega} \nabla \Phi(t) \cdot \nabla \varphi + \int_{\partial\Omega} \tau \Phi(t) \varphi = \int_{\Omega} \sum_{i=1}^{N} z_i c_i(t) \varphi \quad \text{a.e. } t \in \mathbb{R}_+.$$

Nernst-Planck-Poisson in nD

Global weak solutions in nD - Sketch of proof:

- A priori estimate for (NPP)

- Approximate (NPP) by (NPP^ε) while conserving the Lyapunov structure

- Global existence and uniqueness for (NPP^ε)

- Compactness for sequence of approximate solutions

- Limit as $\varepsilon \to 0$

Global weak solutions in nD - Sketch of proof

Recall from above (without v): $\dot{V} = -\sum_{i=1}^{N} \int_{\Omega} |d_i \nabla c_i + d_i z_i c_i \nabla \Phi|^2 / d_i c_i$
Integration in time yields

$$C \geq \int_{Q_T} \sum_{i=1}^{N} \frac{|\nabla c_i + z_i c_i \nabla \Phi|^2}{c_i} = \int_{Q_T} \sum_{i=1}^{N} \Big(\underbrace{\frac{|\nabla c_i|^2}{c_i} + z_i^2 c_i |\nabla \Phi|^2}_{\geq 0} + \boxed{2 z_i \nabla c_i \nabla \Phi} \Big)$$

Integration by parts and Poisson equation give

$$\int_{Q_T} \sum_{i=1}^{N} z_i \nabla c_i \nabla \Phi = -\int_{Q_T} \sum_{i=1}^{N} z_i c_i \Delta \Phi + \int_{\Gamma_T} \ldots = \int_{Q_T} \underbrace{|\Delta \Phi|^2}_{\geq 0!!} + \int_{\Gamma_T} \ldots .$$

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- Boundary terms difficult to estimate $\Rightarrow$ only local $W^{1,1}$-regularity, except in case $n = 3$, $\xi \in L^q(\partial\Omega)$ for $q > 2$.

- Appr. problem with global solution and similar Lyapunov structure?

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Approximate problem (based on an idea of Gajewski/Gröger):

$$\left.\begin{array}{rcll} \partial_t c_i + \operatorname{div}(-d_i \nabla h(c_i) - d_i z_i c_i \nabla \Phi) &=& 0 & \text{in } \Omega, \\ \partial_\nu h(c_i) + z_i c_i \partial_\nu \Phi &=& 0 & \text{on } \partial\Omega, \\ c_i(0) &=& c_i^0 & \text{in } \Omega, \end{array}\right\} \quad (\text{NP}^\eta)$$

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where $h(r) = r + \eta r^p$ for fixed, large $p > 1$.

The solutions satisfy the same dissipation inequality, if the free energy $\sum_i c_i \log c_i$ is replaced by $\sum_i (c_i \log c_i + \eta c_i^p/(p-1))$.

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$\Rightarrow$ appr. c_i^η *a priori* bounded in $L^\infty(0, T; L^p(\Omega))$.

$\Rightarrow$ appr. Φ^η *a priori* bounded in $L^\infty(0, T; W^{2,p}(\Omega))$.

$\Rightarrow$ appr. solution (c_i^η, Φ^η) via fixed point argument for Φ in $L^\infty(0, T; W^{1,\infty}(\Omega))$, using $p > n$.

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where $h(r) = r + \eta r^p$ for fixed, large $p > 1$.

The solutions satisfy the same dissipation inequality, if the free energy $\sum_i c_i \log c_i$ is replaced by $\sum_i (c_i \log c_i + \eta c_i^p/(p-1))$.

$\Rightarrow$ appr. c_i^η *a priori* bounded in $L^\infty(0, T; L^p(\Omega))$.

$\Rightarrow$ appr. Φ^η *a priori* bounded in $L^\infty(0, T; W^{2,p}(\Omega))$.

$\Rightarrow$ appr. solution (c_i^η, Φ^η) via fixed point argument for Φ in $L^\infty(0, T; W^{1,\infty}(\Omega))$, using $p > n$.

Thank You for Your Attention !