Continuum thermodynamics of chemically reacting multicomponent fluid systems

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Contents

Reaction-Diffusion-Advection Model

Standard Reaction-Diffusion-Advection system:

$$\begin{aligned} \partial_t c_1 + \mathbf{v} \cdot \nabla c_1 - D_1 \Delta c_1 &= r_1(c_1, \dots, c_N) \\ \vdots \qquad & \qquad \vdots \\ \partial_t c_N + \mathbf{v} \cdot \nabla c_N - D_N \Delta c_N &= r_N(c_1, \dots, c_N) \end{aligned}$$

with molar concentrations c_i, velocity $\mathbf{v}$, diffusivities D_i, reaction rates r_i

- cross-effects not included
- non-idealities not included; chemical potentials & activities
- consistency with continuity equations requires equal D_i's
- assumption of constant total density (i.e. $\operatorname{div} \mathbf{v} = 0$) inconsistent
- not applicable to reactions which change the particle numbers

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Chemically Reacting Fluid Mixture

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

N_R chemical reactions between the A_i:

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

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

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: $\sum_i M_i \nu_i^a = 0 \quad \forall a$

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Thermodynamics of Irreversible Processes (TIP)

Throughout this talk: **v** denotes the *barycentric* velocity of the mixture

Classical mixture balances in T.I.P:

partial mass balances:

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

total momentum balance:

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

internal energy balance:

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

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

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The 2$^{\mathrm{nd}}$ Law: Entropy Inequality

Entropy production:

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

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

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:

$$\begin{aligned}
\mathbf{q} &= L_{00}\nabla\frac{1}{T} - \sum_{i=1}^{N-1} L_{0i}\left(\nabla\frac{\mu_i-\mu_N}{T} - \frac{1}{T}(\mathbf{b_i}-\mathbf{b_N})\right)\\
\mathbf{j}_i &= L_{i0}\nabla\frac{1}{T} - \sum_{j=1}^{N-1} L_{ij}\left(\nabla\frac{\mu_j-\mu_N}{T} - \frac{1}{T}(\mathbf{b_j}-\mathbf{b_N})\right) \quad i=1,..,N-1
\end{aligned}$$

viscous stress, dynamic pressure and chemical reaction rates:

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

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:

  - the L_{ij} show complex nonlinear dependence on the composition
  - the linear closure for chemical reactions 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:

local balance between driving and friction forces:

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

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

$\mathbf{J}_i = \mathbf{j}_i / M_i$ molar mass fluxes; $\text{Đ}_{ij} = 1/f_{ij}$ the *Maxwell-Stefan diffusivities*

in many cases: Đ_{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,
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Implicitly constituted multicomponent diffusion fluxes

Maxwell-Stefan Equations - Criticism

Problems and open issues:

- rigorous derivation of the Maxwell-Stefan equations, including the thermodynamical driving forces
- proper coupling to the mass and momentum balance
- extension to non-isobaric, non-isothermal situation
- extension to chemically reacting fluid mixtures

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

1. Introduction
2. Partial Balances and Modeling Framework
3. Case 1: Non-Reactive Systems
4. Case 2: Reactive Systems
5. Class-II → Class-I model reduction

Partial Balances of Mass, Momentum and Energy

Continuum mechanical balances of the fluid components A_i

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

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

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

mass conservation: $\sum_i r_i = 0$

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

energy conservation: $\sum_i l_i = 0$

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

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Alternative definition of internal energy:

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

$p_i := -\frac{1}{3}\operatorname{tr}(\mathbf{S}_i)$ partial pressures, $p := \sum_i p_i$

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

mixture energy balance:

$$\begin{aligned}\partial_t(\varrho e) + \operatorname{div}\left(\varrho e \mathbf{v} + \mathbf{q}\right) &= -p \operatorname{div} \mathbf{v} + \textstyle\sum_i \nabla \mathbf{v}_i : \mathbf{S}_i^\circ \\ &\quad - \textstyle\sum_i \mathbf{u}_i \cdot \left(\mathbf{f}_i - r_i \mathbf{v}_i + \frac{1}{2} r_i \mathbf{u}_i - \nabla p_i\right)\end{aligned}$$

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Constitutive Modeling

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

class-II model requires constitutive equations for:

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

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)

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Universal Principles:

1. material frame indifference
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Assumption: $\varrho s = h(\varrho e, \varrho_1, \ldots, \varrho_N)$ with a concave function h.

Definition: *absolute temperature* T and *chemical potentials* μ_i:

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

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Entropy Principle evaluated

Evaluation of the entropy principle:

1. entropy flux: $\Phi = \frac{\mathbf{q}}{T} - \sum_i \frac{\varrho_i \mathbf{u}_i \mu_i}{T}$
2. Gibbs-Duhem equation $p + \varrho\psi - \sum_i \varrho_i \mu_i = 0$
3. restrictions for constitutive equations for dissipative mechanisms: **entropy inequality, i.e.** $\zeta \geq 0$

Entropy production rate:

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

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

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Case 1: no viscosity, no chemistry

entropy production without viscosity, no chemical reactions:

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

with partial enthalpies $h_i := \varrho_i e_i + p_i$.

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with partial enthalpies $h_i := \varrho_i e_i + p_i$.

Shuffle diffusive part from **q** to the left term:

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

with

$$\mathbf{B}_i := \varrho_i \nabla \frac{\mu_i}{T} - \frac{1}{T} \nabla p_i - h_i \nabla \frac{1}{T}$$

Note: The Gibbs-Duhem equation implies: $\sum_i \mathbf{B}_i = 0$

Exploiting the second law

The interaction term necessarily satisfies

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

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 $\mathbf{B}_i+\frac{1}{T}\mathbf{f}_i$ is

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

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

Exploiting the second law

The interaction term necessarily satisfies

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

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

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

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

Closure for thermo-mechanical Interactions

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

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

Straight forward computation:

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

Assumption of binary type interactions: (Truesdell)

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

implies symmetry of $[\tau_{ij}]$ & $\tau_{ij} \leq 0 \;\; \forall i \neq j$

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

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Momentum Balance with Thermo-mechanical Interactions

partial momentum balances: (non-conservative form)

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

with

$$\mathbf{f}_i = -\varrho_i T \nabla \tfrac{\mu_i}{T} + \nabla p_i + h_i T \nabla \tfrac{1}{T} - T \textstyle\sum_j f_{ij} \varrho_i \varrho_j (\mathbf{v}_i - \mathbf{v}_j)$$

class-II momentum balances (no viscosity, no chemical reactions):

$$\varrho_i\big(\partial_t \mathbf{v}_i + \mathbf{v}_i \cdot \nabla \mathbf{v}_i\big) = -\varrho_i T \nabla \tfrac{\mu_i}{T} + T h_i \nabla \tfrac{1}{T} - T \textstyle\sum_j f_{ij} \varrho_i \varrho_j (\mathbf{v}_i - \mathbf{v}_j) + \varrho_i \mathbf{b}_i$$

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special case of a *simple mixture*:

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1. Introduction

2. Partial Balances and Modeling Framework

3. Case 1: Non-Reactive Systems

4. Case 2: Reactive Systems

5. Class-II → Class-I model reduction

Case 2: Chemical Reactions, no Viscosity

With chemical reactions, the entropy production is:

$$\zeta = \sum_i \mathbf{q}_i \cdot \nabla \frac{1}{T} - \sum_i \mathbf{u}_i \cdot \left(\mathbf{B}_i + \frac{1}{T}\left(\mathbf{f}_i - r_i \mathbf{v}_i + \frac{1}{2} r_i \mathbf{u}_i\right)\right) - \frac{1}{T} \sum_a R_a \mathcal{A}_a$$

- decompose $\mathbf{f}_i - r_i \mathbf{v}_i$ as $\quad \mathbf{f}_i^M + \mathbf{f}_i^C - r_i \mathbf{v}_i$
- structure of $\mathbf{f}_i^C$ from partial momentum balance

For single reaction; forward path with rate R^f:

$$\alpha_1 A_1 + \ldots + \alpha_N A_N \rightarrow \beta_1 A_1 + \ldots + \beta_N A_N$$

rate of change of i-momentum from reaction: $-R^f \alpha_i M_i \mathbf{v}_i + R^f \beta_i M_i \mathbf{v}_i^f$

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chemical momentum exchange:

$$\mathbf{f}_i^C - r_i \mathbf{v}_i = - \sum_{i=1}^{N} C_{ij} (\mathbf{v}_i - \mathbf{v}_j)$$

with the chemical matrix

$$C_{ij} = \sum_{a=1}^{N_a} \frac{M_i M_j}{\sum_k \alpha_k^a M_k} \left(R_a^f \beta_i^a \alpha_j^a + R_a^b \alpha_i^a \beta_j^a \right)$$

Recall: $\sum_k \alpha_k^a M_k = \sum_k \beta_k^a M_k$ due to mass conservation

Note: $[C_{ij}]$ is, in general, **not symmetric** – it is symmetric in equilibrium

Check thermodynamic consistency: chemical momentum exchange part for a single reaction, forward path:

$$\zeta_{\mathrm{exchange}} = R^f \left(\sum_i M_i \frac{\alpha_i + \beta_i}{2} \mathbf{u}_i^2 - \sum_{i,j} \frac{M_i M_j \beta_i \alpha_j}{\sum_k \alpha_k M_k} \mathbf{u}_i \cdot \mathbf{u}_j \right) \geq 0$$

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Case 2: Chemical Interaction - Reaction

Closure for reaction rate functions:

$$\zeta = \ldots - \frac{1}{T}\sum_{a=1}^{N_R}(R_a^f - R_a^b)\sum_{i=1}^{N}\mu_i M_i \nu_i^a$$

nonlinear closure since chemical processes often far away from equilibrium:

$$\log(\frac{R_a^f}{R_a^b}) = -\frac{\alpha}{RT}\sum_{i=1}^{N}\mu_i M_i \nu_i^a, \quad \alpha > 0$$

- one reaction path is to be modeled, the reverse path is determined
- this closure implies detailed balance, i.e. $R_a^f = R_a^b$ for all a in equilibrium:

$$\zeta_{\mathrm{chem}} = \alpha R \sum_{a=1}^{N_R}(R_a^f - R_a^b)(\log R_a^f - \log R_a^b)$$

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Reactive Class-II Model

Resulting model (reactive, non viscous)

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

$$\textbf{mom.} : \partial_t(\varrho_i \mathbf{v}_i) + \operatorname{div}(\varrho_i \mathbf{v}_i \otimes \mathbf{v}_i) = -\varrho_i T \nabla \frac{\mu_i}{T} + T h_i \nabla \frac{1}{T} + \varrho_i \mathbf{b}_i$$

$$- T \textstyle\sum_j f_{ij} \varrho_i \varrho_j (\mathbf{v}_i - \mathbf{v}_j) - T \sum_j C_{ij} (\mathbf{v}_i - \mathbf{v}_j)$$

$$\textbf{energy} : \partial_t(\varrho e) + \operatorname{div}(\varrho e \mathbf{v} + \mathbf{q}) = -p \operatorname{div} \mathbf{v} - \textstyle\sum_i \mathbf{u}_i \cdot (\mathbf{f}_i - r_i \mathbf{v}_i)$$

$$\textit{reaction rates} : r_i = \textstyle\sum_a R_a^f M_i \nu_i^a (1 - \exp\left(\frac{1}{RT} \sum_{k=1}^N \mu_k M_k \nu_k^a\right))$$

$$\textit{chemical matrix} : C_{ij} = \textstyle\sum_{a=1}^{N_a} \frac{M_i M_j}{\sum_k \alpha_k^a M_k} \left(R_a^f \beta_i^a \alpha_j^a + R_a^b \alpha_i^a \beta_j^a\right)$$

$$\textit{heat flux} : \mathbf{q} = \alpha \nabla \tfrac{1}{T} + \textstyle\sum_i h_i \mathbf{u}_i$$

Reduction: Class-II → Class-I

Class-I model does not consider internal structures of momentum and energy

Strategy: all quantities shall be determined from identification of balances for partial mass, internal energy and entropy

partial mass balances:

$$\partial_t \varrho_i + \operatorname{div}\left(\varrho_i \mathbf{v} + \mathbf{j}_i^{\mathrm{I}}\right) = \sum_a M_i \nu_i^a R_a^{\mathrm{I}}$$

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Identification yields:

$$\mathbf{j}_i^{\mathrm{I}} = \varrho_i \mathbf{u}_i, \qquad R_a^{\mathrm{I}} = R_a$$

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$$\partial_t(\varrho e^{\mathrm{I}}) + \operatorname{div}(\varrho e^{\mathrm{I}}\mathbf{v} + \mathbf{q}^{\mathrm{I}}) = \mathbf{S}^{\mathrm{I}} : \nabla\mathbf{v} + \textstyle\sum_i \mathbf{j}_i^{\mathrm{I}} \cdot \mathbf{b}_i$$

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

$$- \textstyle\sum_i \mathbf{u}_i \cdot \big(\mathbf{f}_i - r_i\mathbf{v}_i + \frac{1}{2} r_i\mathbf{u}_i - \nabla p_i\big)$$

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$$\varrho e^{\mathrm{I}} = \textstyle\sum_i \varrho_i e_i, \quad \mathbf{q}^{\mathrm{I}} = \sum_i \big(\mathbf{q}_i + (\varrho_i e_i + p_i - \mathbf{S}_i)\mathbf{u}_i\big), \quad \mathbf{S}^{\mathrm{I}} = \sum_i \mathbf{S}_i$$

$$\mathbf{f}_i - r_i\mathbf{v}_i = \nabla p_i - y_i\nabla p - \tfrac{1}{2}\big(r_i\mathbf{u}_i + y_i \textstyle\sum_k r_k\mathbf{u}_k\big)$$

$$-\operatorname{div}\mathbf{S}_i^{\mathrm{irr}} + y_i\operatorname{div}\mathbf{S}^{\mathrm{irr}} - \varrho_i(\mathbf{b}_i - \mathbf{b})$$

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Metaprinciple of Truesdell does not apply

Reduction: Class-II $\rightarrow$ Class-I

entropy balance:

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

with

$$\Phi^{\mathrm{I}} = \tfrac{1}{T}\big(\mathbf{q}^{\mathrm{I}} - \textstyle\sum_i \mu_i \mathbf{j}_i^{\mathrm{I}}\big),$$

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Identifying $\varrho s^{\mathrm{I}} = \varrho s$ and inserting all above identifications yields:

$$\Phi^{\mathrm{I}} = \Phi, \qquad \zeta^{\mathrm{I}} = \zeta$$

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Chemical Reacting Class-I model

Maxwell-Stefan equations for chemically reactive flows

Diffusion approximation in the reactive case follows similarly by *entropy invariant model reduction*

$$\begin{aligned}-T\sum_j f_{ij}\varrho_i\varrho_j(\mathbf{u}_i-\mathbf{u}_j)-T\sum_j C_{ij}(\mathbf{u}_i-\mathbf{u}_j)+\tfrac{1}{2}r_i\mathbf{u}_i+\tfrac{1}{2}y_i\sum_k r_k\mathbf{u}_k\\ =\varrho_i T\nabla\tfrac{\mu_i}{T}-y_i\nabla p-h_i T\nabla\tfrac{1}{T}-\mathrm{div}\,\mathbf{S}_i^{\mathrm{irr}}+y_i\mathrm{div}\,\mathbf{S}^{\mathrm{irr}}-\varrho_i(\mathbf{b}_i-\mathbf{b})\end{aligned}$$

with the chemical matrix

$$C_{ij}=\sum_{a=1}^{N_a}\frac{M_iM_j}{\sum_k\alpha_k^aM_k}\left(R_a^f\beta_i^a\alpha_j^a+R_a^b\alpha_i^a\beta_j^a\right)$$

To obtain the final PDE-system:

- invert the system to obtain $\mathbf{j}_i$; algebraical relation if $\mathbf{S}_i^{\mathrm{irr}}=y_i\mathbf{S}^{\mathrm{irr}}$
- model the free energy, i.e. pressure and chemical potentials

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$$\begin{aligned}&-T\sum_j f_{ij}\varrho_i\varrho_j(\mathbf{u}_i-\mathbf{u}_j)-T\sum_j C_{ij}(\mathbf{u}_i-\mathbf{u}_j)+\tfrac{1}{2}r_i\mathbf{u}_i+\tfrac{1}{2}y_i\sum_k r_k\mathbf{u}_k\\ &\quad=\varrho_i T\nabla\tfrac{\mu_i}{T}-y_i\nabla p-h_i T\nabla\tfrac{1}{T}-\mathrm{div}\,\mathbf{S}_i^{\mathrm{irr}}+y_i\mathrm{div}\,\mathbf{S}^{\mathrm{irr}}-\varrho_i(\mathbf{b}_i-\mathbf{b})\end{aligned}$$

with the chemical matrix

$$C_{ij}=\sum_{a=1}^{N_a}\frac{M_iM_j}{\sum_k\alpha_k^aM_k}\left(R_a^f\beta_i^a\alpha_j^a+R_a^b\alpha_i^a\beta_j^a\right)$$

To obtain the final PDE-system:

- invert the system to obtain $\mathbf{j}_i$; algebraical relation if $\mathbf{S}_i^{\mathrm{irr}}=y_i\mathbf{S}^{\mathrm{irr}}$
- model the free energy, i.e. pressure and chemical potentials

Final Remarks

- cross-effects, like *thermo-diffusion* can be incorporated via **entropy invariant mixing** between different flux-driving force products:

$$\sum_i \mathbf{q}_i \cdot \nabla \tfrac{1}{T} + \sum_i \mathbf{u}_i \cdot \big(- \mathbf{B}_i - \tfrac{1}{T}\mathbf{f}_i \big)$$

$$= \sum_i \big(\mathbf{q}_i - D_i^T \mathbf{u}_i\big) \cdot \nabla \tfrac{1}{T} + \sum_i \mathbf{u}_i \cdot \big(- \mathbf{B}_i - \tfrac{1}{T}\mathbf{f}_i + D_i^T \nabla \tfrac{1}{T} \big)$$

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

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

diagonal closure implies cross-effects with Onsager relations:

$$A\,\vec{\mathbf{F}} := \Lambda B\,\vec{\mathbf{D}} \text{ with } \Lambda = \mathrm{diag}(\lambda_i) \;\Rightarrow\; \vec{\mathbf{F}} := B^{\mathsf{T}} \Lambda B\,\vec{\mathbf{D}}$$

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- cross-effects, like *thermo-diffusion* can be incorporated via **entropy invariant mixing** between different flux-driving force products:

$$\begin{aligned} &\textstyle\sum_i \mathbf{q}_i \cdot \nabla \frac{1}{T} + \sum_i \mathbf{u}_i \cdot \big(-\mathbf{B}_i - \frac{1}{T}\mathbf{f}_i \big) \\ = &\textstyle\sum_i \big(\mathbf{q}_i - D_i^T \mathbf{u}_i\big) \cdot \nabla \frac{1}{T} + \sum_i \mathbf{u}_i \cdot \big(-\mathbf{B}_i - \frac{1}{T}\mathbf{f}_i + D_i^T \nabla \frac{1}{T} \big) \end{aligned}$$

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Thank You for Your Attention !