Mathematical modeling of reactive multicomponent fluid systems

Dieter Bothe

Mathematical Modeling and Analysis
Center for Smart Interfaces
Technical University Darmstadt

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Work in Progress, jointly with Wolfgang Dreyer (WIAS Berlin)

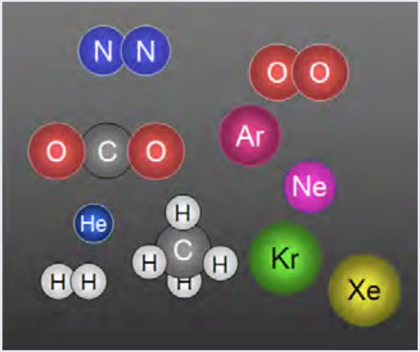
Part I : Single Phase Fluid Mixtures

Contents of Part I

Multicomponent Fluid Mixtures

atmospheric chemistry

average composition of dry atmosphere



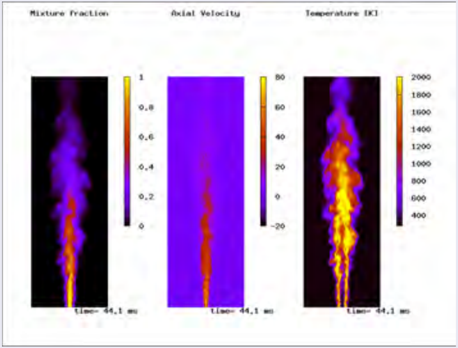
nitrogen N_2	78.084 %
oxygen O_2	20.946 %
argon Ar	0.934 %
carbon dioxide CO_2	383 ppm
neon Ne	18.18 ppm
helium He	5.24 ppm
methane CH_4	1.7 ppm
krypton Kr	1.14 ppm
hydrogen H_2	0.55ppm

real air contains water vapor, typically about 1 % or more

Example 1 - Spray Combustion

Spray combustion

Mixture fraction, velocity and temperature around a burning jet



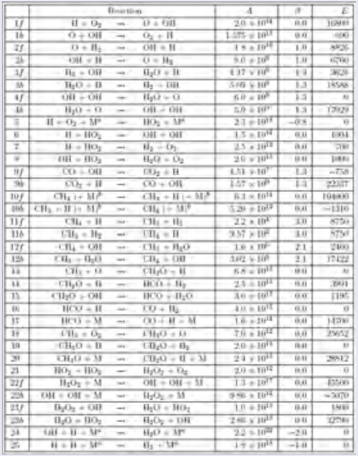
typical:

$\approx$ 100 reactions

CFD-simulations: Institute for Technical Combustion, K.I.T.

Example 1 - Chemical Reaction Mechanism

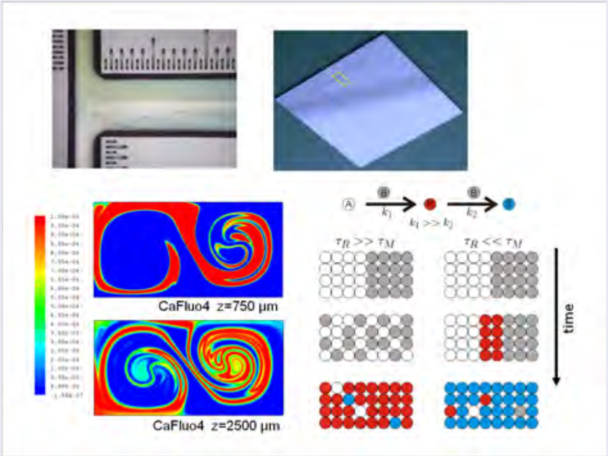
Reduced Methane-Air reaction mechanism



	Reaction			A	β	E
1f	$H + O_2$	→	$O + OH$	2.0×10^{14}	0.0	16800
1b	$O + OH$	→	$O_2 + H$	1.575×10^{13}	0.0	690
2f	$O + H_2$	→	$OH + H$	1.8×10^{10}	1.0	8826
2b	$OH + H$	→	$O + H_2$	8.0×10^{9}	1.0	6760
3f	$H_2 + OH$	→	$H_2O + H$	1.17×10^{9}	1.3	3626
3b	$H_2O + H$	→	$H_2 + OH$	5.09×10^{9}	1.3	18588
4f	$OH + OH$	→	$H_2O + O$	6.0×10^{8}	1.3	0
4b	$H_2O + O$	→	$OH + OH$	5.9×10^{9}	1.3	17029
5	$H + O_2 + M^*$	→	$HO_2 + M^*$	2.3×10^{18}	−0.8	0
6	$H + HO_2$	→	$OH + OH$	1.5×10^{14}	0.0	1004
7	$H + HO_2$	→	$H_2 + O_2$	2.5×10^{13}	0.0	700
8	$OH + HO_2$	→	$H_2O + O_2$	2.0×10^{13}	0.0	1000
9f	$CO + OH$	→	$CO_2 + H$	1.51×10^{7}	1.3	−758
9b	$CO_2 + H$	→	$CO + OH$	1.57×10^{9}	1.3	22337
10f	$CH_4 (+ M)^a$	→	$CH_3 + H (+ M)^a$	6.3×10^{14}	0.0	104000
10b	$CH_3 + H (+ M)^a$	→	$CH_4 (+ M)^a$	5.20×10^{12}	0.0	−1310
11f	$CH_4 + H$	→	$CH_3 + H_2$	2.2×10^{4}	3.0	8750
11b	$CH_3 + H_2$	→	$CH_4 + H$	9.57×10^{2}	3.0	8750
12f	$CH_4 + OH$	→	$CH_3 + H_2O$	1.6×10^{6}	2.1	2460
12b	$CH_3 + H_2O$	→	$CH_4 + OH$	3.02×10^{5}	2.1	17422
13	$CH_3 + O$	→	$CH_2O + H$	6.8×10^{13}	0.0	0
14	$CH_2O + H$	→	$HCO + H_2$	2.5×10^{13}	0.0	3991
15	$CH_2O + OH$	→	$HCO + H_2O$	3.0×10^{13}	0.0	1195
16	$HCO + H$	→	$CO + H_2$	4.0×10^{13}	0.0	0
17	$HCO + M$	→	$CO + H + M$	1.6×10^{14}	0.0	14700
18	$CH_3 + O_2$	→	$CH_3O + O$	7.0×10^{12}	0.0	25652
19	$CH_3O + H$	→	$CH_2O + H_2$	2.0×10^{13}	0.0	0
20	$CH_3O + M$	→	$CH_2O + H + M$	2.4×10^{13}	0.0	28812
21	$HO_2 + HO_2$	→	$H_2O_2 + O_2$	2.0×10^{12}	0.0	0
22f	$H_2O_2 + M$	→	$OH + OH + M$	1.3×10^{17}	0.0	45500
22b	$OH + OH + M$	→	$H_2O_2 + M$	9.86×10^{14}	0.0	−5070
23f	$H_2O_2 + OH$	→	$H_2O + HO_2$	1.0×10^{13}	0.0	1800
23b	$H_2O + HO_2$	→	$H_2O_2 + OH$	2.86×10^{13}	0.0	32790
24	$OH + H + M^*$	→	$H_2O + M^*$	2.2×10^{22}	−2.0	0
25	$H + H + M^*$	→	$H_2 + M^*$	1.8×10^{18}	−1.0	0

Example 2 - Microreactor

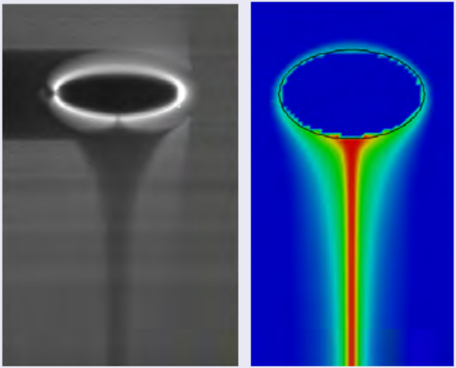
Reactive flow in a microchannel



Example 3 - Physical Mass Transfer

Mass transfer from rising bubbles

Oxygen concentration around a rising air bubble



gas bubble:
O_2, N_2, CO_2,
water vapor

ambient liquid:
water,
O_2, N_2, CO_2

Example 4 - Reactive Mass Transfer

Reactive mass transfer into a settling droplet

pH-value inside the settling droplet

(Loading bubble column)

droplet (initially):
NaOH, water,
phenolphthalein

ambient liquid:
toluol,
acetic acid

Experiments M. Kraume, TU Berlin

Origin of the Maxwell-Stefan Equations

The starting point:

- 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).

"It is a striking symptom of the common ignorance in this field that not one of the phenomenological schemes which are fit to describe the general case of diffusion is widely known" - L. Onsager (1945)

taken from *Multicomponent Mass Transfer*, R. Taylor, R. Krishna, Wiley 1993.

Continuum Mechanical Reactive Flow Model

Simple continuum mechanical model for an *isothermal* fluid mixture:

Navier-Stokes equations

$$\partial_t \varrho + \mathrm{div}\,(\varrho \mathbf{v}) = 0$$

$$\varrho \partial_t \mathbf{v} + \varrho(\mathbf{v}\cdot\nabla)\mathbf{v} + \nabla p = \eta \Delta \mathbf{v} + \varrho \mathbf{b}$$

ϱ mixture mass density, $\mathbf{v}$ mixture velocity, p pressure, η mixture viscosity, $\mathbf{b}$ external force

Species equations

$$\partial_t c_i + \mathrm{div}\,(c_i \mathbf{v} + \mathbf{J}_i) = r_i^{\mathrm{tot}},$$

c_i molar concentrations, r_i^{tot} total reaction rates, $\mathbf{J}_i = c_i(\mathbf{v}_i - \mathbf{v})$ the relative mass flux with $\mathbf{v}_i$ the individual species velocity

- the model only applies for ideally dilute species
- the model is not closed

Constitutive flux models

Standard flux model

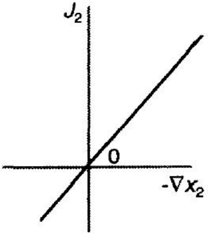
Fickian diffusion:

$$\mathbf{J}_i = -D_i \operatorname{grad} c_i$$

linear, decoupled relationship between individual fluxes and driving forces

$\hookrightarrow$ **Reaction-Diffusion System:**

$$\partial_t c_i - D_i \Delta c_i = r_i^{\mathrm{tot}}$$

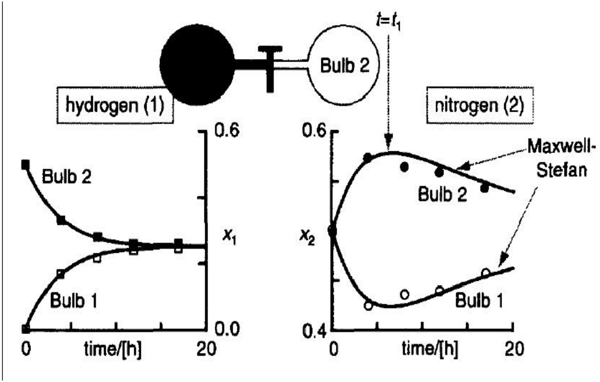


$x_i := c_i / c_{\mathrm{tot}}$ the molar fractions

- Neglects *cross diffusion* effects
- Neglects *non-ideal solution* effects

Cross Diffusion Effects

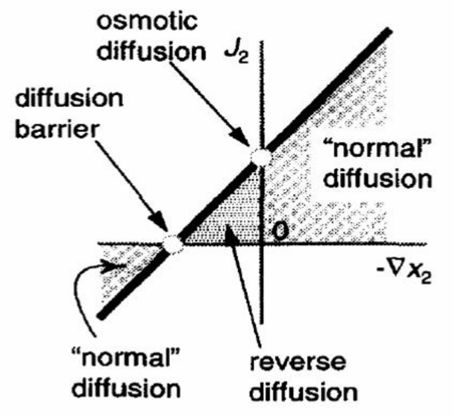
Classical experiment by Duncan and Toor 1962 on ternary diffusion



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



Thermodynamics of Irreversible Processes (TIP)

Constitutive law for isobaric isothermal multicomponent diffusion:

$$\mathbf{J}_i = -\sum_{j=1}^{n} D_{ij}\,\mathrm{grad}\,c_j$$

with binary diffusivities $D_{ij} = D_{ij}(\mathbf{c})$.

Properties of $[D_{ij}]$ from irreversible thermodynamics:

- $[D_{ij}]$ is *symmetric* (Onsager reciprocal relations)
- $[D_{ij}]$ is *positive semidefinite* (entropy inequality)

Quasilinear RD-system which - probably after reduction - satisfies parabolicity assumption sufficient for (local in time) well-posedness.

Thermodynamics of Irreversible Processes (TIP)

Difficulties:

- Individual $D_{ij}(\mathbf{c})$ can be *negative*
- Dependence of D_{ij} on $\mathbf{c}$ is *not given*
- Unclear whether solutions will stay *non-negative*

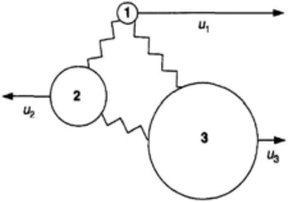
Maxwell-Stefan Approach to Multicomponent Diffusion

Force balance:

driving force = *frictional force*

Ansatz: frictional forces between species A_i and A_j are proportional to relative velocity and to the molar fractions $x_i = c_i / c_{\mathrm{tot}}$, i.e.

$$\textit{frictional force} = f_{ij}\, x_i\, x_j (\mathbf{v}_i - \mathbf{v}_j)$$



exchange of momentum

Let $\mathbf{d}_i$ denote the total driving force for species A_i. Then:

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

with the so-called *Maxwell-Stefan diffusivities* $\text{Đ}_{ij} = 1/f_{ij}$.

Thermodynamical Driving Forces

Driving force for isobaric isothermal diffusion:

$$\mathbf{d}_i = \frac{x_i}{RT}\,\mathrm{grad}\,\mu_i$$

with temperature T, universal gas constant R, chemical potential μ_i.

Chemical potential:

$$\mu_i = \frac{\partial g}{\partial c_i} = \mu_i^0 + RT\ln a_i$$

with the activity a_i. The activities are given by $a_i = \gamma_i c_i$, where the *activity coefficients* $\gamma_i = \gamma_i(\mathbf{c})$ model deviations from ideal solution.

Generalizations to pressure & temperature diffusion, electro-migration:

$$\mathbf{d}_i = \frac{x_i}{RT}\,\mathrm{grad}\,\mu_i + \dots$$

Maxwell-Stefan Equations

The simplest case of isobaric isothermal MS-diffusion:

$$\mathbf{v} = 0, \qquad \partial_t c_i + \operatorname{div} \mathbf{J}_i = r_i^{\mathrm{tot}},$$

$$(\mathbf{d}_i =) \quad \frac{x_i}{RT} \operatorname{grad} \mu_i = - \sum_{j \neq i} \frac{x_j \mathbf{J}_i - x_i \mathbf{J}_j}{c_{\mathrm{tot}} \,Đ_{ij}}, \tag{MS}$$

$$\textstyle\sum_i \mathbf{J}_i = 0.$$

Remark. The Maxwell-Stefan diffusivities $Đ_{ij}$ are (assumed to be) *nonnegative, constant & symmetric!*

In this case $\sum_i \mathbf{d}_i = 0$ necessarily holds due to $Đ_{ij} = Đ_{ji}$.

Maxwell-Stefan Equations - Criticism

Problems and open issues:

- rigorous derivation of the Maxwell-Stefan equations
- 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, based on rational thermodynamic mixture theories due to Truesdell, Gurtin, I. Müller and others

Chemically Reacting Fluid Mixture

Fluid composed of N chemically reacting components $A_1, \ldots, A_N$ with N_R chemical reactions between the A_i:

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

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

Let R_a be the (molar) rate of reaction a and set $\nu_i^a := \beta_i^a - \alpha_i^a$. 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: $\sum_i M_i \nu_i^a = 0 \quad \forall a$

Partial Balances of Mass, Momentum and Energy

Continuum mechanical balances of the fluid components A_i

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

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

$$\textbf{energy}: \partial_t(\varrho_i e_i + \frac{\varrho_i}{2}\mathbf{v}_i^2) + \mathrm{div}\,((\varrho_i e_i + \frac{\varrho_i}{2}\mathbf{v}_i^2)\mathbf{v}_i - \mathbf{v}_i \sigma_i + \tilde{\mathbf{q}}_i) = h_i + \varrho_i \mathbf{b}_i \cdot \mathbf{v}_i$$

mass conservation: $\sum_i r_i = 0$

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

energy conservation: $\sum_i h_i = 0$

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 heat flux

Notations: Individual Quantities

ϱ_i	individual mass density
$\mathbf{v}_i$	individual velocity field
r_i	mass production rate for A_i due to chemical reactions
σ_i	partial stresses
$\mathbf{f}_i$	rate of momentum exchange
$\mathbf{b}_i$	body force acting on A_i
e_i	internal energy density for species i
$\tilde{\mathbf{q}}_i$	individual heat fluxes
h_i	rate of energy exchange

Overall Strategy

Strategy for deriving consistent multicomponent diffusion fluxes:

1. class-III model as starting point (without closure)
2. derive mixture model, keeping structural information from the individual balances
3. evaluate the 2^{nd} law to obtain a framework for closure laws
4. fix corresponding closure laws for class-II model
5. reduce to class-I model, using separation of time-scales

Non-Conservative Form of Momentum Balance

partial momentum balances: (nonconservative form)

$$\varrho_i\big(\partial_t \mathbf{v}_i + \mathbf{v}_i \cdot \nabla \mathbf{v}_i\big) - \operatorname{div}\sigma_i = \mathbf{f}_i - r_i \mathbf{v}_i + \varrho_i \mathbf{b}_i$$

The acceleration along a path of the i-component fluid particles, i.e. $\partial_t \mathbf{v}_i + \mathbf{v}_i \cdot \nabla \mathbf{v}_i$ is an objective vector [see below].

In particular, $\mathbf{f}_i - r_i \mathbf{v}_i$ is also objective, hence $\mathbf{f}_i$ is split according to

$$\mathbf{f}_i = \mathbf{F}_i + r_i \mathbf{v}_i^*$$

$\mathbf{F}_i$ are objective vectors denoting thermo-mechanical interactions, whereas $r_i \mathbf{v}_i^*$ is due to mass production. Note that in reactive collisions, momentum is transferred between different species.
Hence

$$\varrho_i\big(\partial_t \mathbf{v}_i + \mathbf{v}_i \cdot \nabla \mathbf{v}_i\big) - \operatorname{div}\sigma_i = \mathbf{F}_i + r_i(\mathbf{v}_i^* - \mathbf{v}_i) + \varrho_i \mathbf{b}_i$$

Partial Balances of Internal Energy

auxiliary computation:

$$\partial_t(\varrho_i \frac{\mathbf{v}_i^2}{2}) + \operatorname{div}(\varrho_i \frac{\mathbf{v}_i^2}{2}\mathbf{v}_i) = \frac{\mathbf{v}_i^2}{2} r_i + \varrho_i \mathbf{v}_i \cdot (\partial_t \mathbf{v}_i + \mathbf{v}_i \cdot \nabla \mathbf{v}_i)$$

$$\textit{energy} : \partial_t(\varrho_i e_i + \frac{\varrho_i}{2}\mathbf{v}_i^2) + \operatorname{div}((\varrho_i e_i + \frac{\varrho_i}{2}\mathbf{v}_i^2)\mathbf{v}_i - \mathbf{v}_i \sigma_i + \tilde{\mathbf{q}}_i) = \varrho_i \mathbf{b}_i \cdot \mathbf{v}_i + h_i$$

$$\textit{mom.} : \varrho_i \big(\partial_t \mathbf{v}_i + \mathbf{v}_i \cdot \nabla \mathbf{v}_i\big) - \operatorname{div} \sigma_i = \mathbf{F}_i + r_i(\mathbf{v}_i^* - \mathbf{v}_i) + \varrho_i \mathbf{b}_i$$

partial balance of internal energy:

$$\partial_t(\varrho_i e_i) + \operatorname{div}(\varrho_i e_i \mathbf{v}_i - \mathbf{v}_i \sigma_i + \tilde{\mathbf{q}}_i) = h_i - \mathbf{v}_i \cdot \big(\operatorname{div} \sigma_i + \mathbf{F}_i + r_i(\mathbf{v}_i^* - \frac{\mathbf{v}_i}{2})\big)$$

$$\Rightarrow \partial_t(\varrho_i e_i) + \operatorname{div}(\varrho_i e_i \mathbf{v}_i + \tilde{\mathbf{q}}_i) = \nabla \mathbf{v}_i : \sigma_i + h_i - \mathbf{v}_i \cdot \big(\mathbf{F}_i + r_i(\mathbf{v}_i^* - \frac{\mathbf{v}_i}{2})\big)$$

Balance of total mass, momentum and internal energy

definition of mixture quantities

$$\varrho := \sum_i \varrho_i, \quad \varrho \mathbf{v} := \sum_i \varrho_i \mathbf{v}_i \quad \Rightarrow \quad \text{barycentric velocitiy } \mathbf{v}$$

$$\mathbf{u}_i := \mathbf{v}_i - \mathbf{v} \;\; \text{diffusion velocities}, \quad \mathbf{j}_i := \varrho_i \mathbf{u}_i \;\; \text{diffusive mass fluxes}$$

$$\sigma := \sum_i \big(\sigma_i - \varrho_i \mathbf{u}_i \otimes \mathbf{u}_i \big) \;\; \text{mixture stress tensor}$$

$$\varrho \mathbf{b} := \sum_i \varrho_i \mathbf{b}_i \;\; \text{total external force}$$

$$\varrho e := \sum_i \varrho_i e_i \;\; \text{total internal energy}$$

$$\mathbf{q} := \sum_i \mathbf{q}_i \;\; \text{with} \;\; \mathbf{q}_i = \tilde{\mathbf{q}}_i + \varrho_i e_i \mathbf{u}_i - \mathbf{u}_i \sigma_i$$

mixture modeling meta principle: the mixture equations resemble partial balances, but for mixture quantities instead of individual ones.

Balance of total mass, momentum and internal energy

continuity equation:

$$\partial_t \varrho + \operatorname{div}(\varrho \mathbf{v}) = 0 \qquad \text{(recall } \textstyle\sum_i r_i = 0\text{)}$$

mixture momentum balance:

$$\partial_t \varrho \mathbf{v} + \operatorname{div}(\varrho \mathbf{v} \otimes \mathbf{v} - \sigma) = \varrho \mathbf{b} \qquad \text{(recall } \textstyle\sum_i \mathbf{f}_i = 0\text{)}$$

mixture energy balance:

$$\begin{aligned}\partial_t(\varrho e) + \operatorname{div}(\varrho e \mathbf{v} + \mathbf{q}) &= \nabla \mathbf{v} : \textstyle\sum_i \sigma_i \\ &\quad - \textstyle\sum_i \mathbf{u}_i \cdot \Big(\mathbf{F}_i + r_i(\mathbf{v}_i^* - \mathbf{v}_i) + \operatorname{div} \sigma_i + \frac{r_i}{2}\mathbf{u}_i\Big)\end{aligned}$$

$$\text{(recall } \textstyle\sum_i h_i = 0,\ \sum_i \mathbf{F}_i + r_i \mathbf{v}_i^* = 0\text{)}$$

1. Introduction
2. The Maxwell-Stefan Equations - Modeling
3. Partial and Mixture Balances
4. **Constitutive Modeling**
5. The Maxwell-Stefan Equations - Analysis

Constitutive Modeling

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

required are constitutive equations (models) for

$$R_a, \quad \mathbf{u}_i \text{ (or } \mathbf{j}_i), \quad \sigma_i, \quad \mathbf{F}_i, \quad \mathbf{q}, \quad r_i(\mathbf{v}_i^* - \mathbf{v}_i)$$

Below we always assume **non-polar fluids**, i.e. the partial moments of momentum are conserved. Hence the stresses σ_i are symmetric.

Define the partial pressures by $p_i := -\frac{1}{3} trace(\sigma_i) \Rightarrow \sigma_i = -p_i \mathbf{I} + \sigma_i^o$

Preliminary information on equilibria: necessary conditions are

$$R_a = 0, \quad \mathbf{u}_i = 0, \quad \sigma_i^o = 0, \quad p_i = \tilde{p}_i(\varrho e, \varrho_1, \dots, \varrho_N), \quad \mathbf{q} = 0$$

Note: the condition on p_i means that pressure contributions due to compressibility (bulk viscosity) vanish at equilibria

Constitutive Modeling

Universal Principles:

1. material frame indifference
2. entropy principle

ad 1. objectivity, frame indifference & form invariance

ad 2. The second law of thermodynamics

Notation: a solution of the PDE-system is called a *thermodynamic process*

Objectivity

Assume 3+1 dimensional Euclidean space-time

Euclidean transformation: $(\mathbf{x}, t) \rightarrow (\mathbf{x}^*, t^*)$, where

$$\mathbf{x}^* = \mathbf{c}(t) + \mathbf{Q}(t)\mathbf{x} \text{ with } \mathbf{Q}(\mathbf{t})\mathbf{Q}(t)^{\mathsf{T}} = \mathbf{I}, \qquad t^* = t + \alpha$$

idea: an Euclidean observer can measure distances and time intervals

objectivity: specific behavior under a Euclidean transformation as

- objective scalar: $a^* = a$
- objective vector: $\mathbf{a}^* = \mathbf{Q}(t)\mathbf{a}$
- objective tensor: $\mathbf{A}^* = \mathbf{Q}(t)\mathbf{A}\mathbf{Q}(t)^{\mathsf{T}}$

Below we always let $\alpha = 0$.

Objectivity

Examples. (a) the position $\mathbf{x}$ is **not** objective, but displacement is:

$$\mathbf{x}^* - \mathbf{y}^* = \mathbf{c}(t) + \mathbf{Q}(t)\mathbf{x} - (\mathbf{c}(t) + \mathbf{Q}(t)\mathbf{y}) = \mathbf{Q}(t)(\mathbf{x} - \mathbf{y})$$

(b) the velocity $\mathbf{v}$ is **not** objective:

$$\mathbf{v}^*(\mathbf{x}^*, t^*) = \mathbf{Q}(t)\mathbf{v}(\mathbf{x}, t) + \dot{\mathbf{c}}(t) + \mathbf{\Omega}(t)(\mathbf{x}^* - \mathbf{c}(t))$$

with the *spin tensor* $\mathbf{\Omega}(t) := \dot{\mathbf{Q}}(t)\mathbf{Q}(t)^{\mathsf{T}}$.

(c) relative velocities are objective:

$$\mathbf{v}^*(\mathbf{x}^*, t^*) - \mathbf{w}^*(\mathbf{x}^*, t^*) = \mathbf{Q}(t)(\mathbf{v}(\mathbf{x}, t) - \mathbf{w}(\mathbf{x}, t))$$

(d) acceleration is **not** objective:

$$\mathbf{a}^* = \mathbf{Q}\mathbf{a} + \ddot{\mathbf{c}} + (\dot{\mathbf{\Omega}} - \mathbf{\Omega}^2)(\mathbf{x}^* - \mathbf{c}) + 2\mathbf{\Omega}(\mathbf{v} - \dot{\mathbf{c}})$$

unless $\ddot{\mathbf{c}} = 0$ and $\dot{\mathbf{Q}} = 0$, i.e. unless the transformation is a Galilean transformation

Material Frame Indifference

The principle of material frame indifference consists of two parts:

1. **frame indifference**

   The constitutive mappings are observer-invariant, but they may depend on the motion of the material w.r. to an arbitrary chosen frame of reference

2. **form invariance**

   Different uniform motions of the material (rigid body motions) do not influence the material properties

Example: stress in a fluid. Constitutive mapping (for instance):

$$\sigma = \mathbf{S}(\operatorname{grad}\mathbf{v}), \qquad \sigma^* = \mathbf{S}^*(\operatorname{grad}^*\mathbf{v}^*)$$

Since stress is an objective tensor, the relation $\sigma^* = \mathbf{Q}\sigma\mathbf{Q}^\mathsf{T}$ always holds. Given $\mathbf{S}$, this determines $\mathbf{S}^*$ for any Euclidean transformation. If also $\mathbf{S} = \mathbf{S}^*$ holds, then $\mathbf{S}$ satisfies the principle of material frame indifference.

The Second Law of Thermodynamics

The second law 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
$$\partial_t(\varrho s) + \mathrm{div}\,(\varrho s \mathbf{v} + \Phi) = \zeta,$$
where the entropy production ζ satisfies $\zeta \geq 0$ for every thermodynamic process. Equilibria are characterized by $\zeta = 0$.
3. The entropy production has the form $\zeta = \sum_m \mathbf{F}_m \mathbf{D}_m$, where the so-called fluxes $\mathbf{F}_m$ and driving forces $\mathbf{D}_m$ vanish at equilibria.

Definition. We define the absolute temperature T and chemical potentials μ_i by
$$\frac{1}{T} := \frac{\partial h}{\partial \varrho e}, \qquad \frac{\mu_i}{T} := -\frac{\partial h}{\partial \varrho_i}$$
where h is the material function for the entropy ϱs

Entropy Production

Assumption. We here restrict the dependence of the entropy in the way that $\varrho s = h(\varrho e, \varrho_1, \ldots, \varrho_N)$.

Note: If further dependencies on all $\mathbf{u}_i$ are included, these would drop out as a consequence of the 2^{nd} law.

Starting point for evaluation of the 2^{nd} law: entropy balance in the form

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

Using $\varrho s = h(\varrho e, \varrho_1, \ldots, \varrho_N)$, a straight forward computation yields

$$\boxed{\begin{aligned}&\zeta = \tfrac{1}{T}\Big(\partial_t(\varrho e) + \mathrm{div}\,(\varrho e \mathbf{v})\Big) - \textstyle\sum_i \tfrac{\mu_i}{T}\Big(\partial_t \varrho_i + \mathrm{div}\,(\varrho_i \mathbf{v}_i)\Big)\\ &+\tfrac{1}{T}\big(\varrho s T - \varrho e + \textstyle\sum_i \varrho_i \mu_i\big)\,\mathrm{div}\, \mathbf{v} + \textstyle\sum_i \tfrac{\mu_i}{T}\mathrm{div}\,(\varrho_i \mathbf{u}_i) + \mathrm{div}\, \Phi\end{aligned}}$$

The Free Energy (or Helmholtz potential)

It is common to change for T to become an independent variable. By definition of T, μ_i, the total differential of $\varrho s = h(\varrho e, \varrho_1, \ldots, \varrho_N)$ is:

$$d(\varrho s) = \frac{1}{T} d(\varrho e) - \sum_i \frac{\mu_i}{T} d\varrho_i \Rightarrow \quad d(\varrho e) = T d(\varrho s) + \sum_i \mu_i d\varrho_i$$

T becomes an independent variable by Legendre transformation:

$$\varrho e - \varrho s T =: \varrho\psi \qquad \text{(the free energy)}$$

$$\Rightarrow \quad d(\varrho\psi) = d(\varrho e) - d(\varrho s T) = -\varrho s \, dT + \sum_i \mu_i d\varrho_i$$

Hence: $\varrho\psi = \varrho\psi(T, \varrho_1, \ldots, \varrho_N)$, $\partial_T(\varrho\psi) = -\varrho s$, $\partial_{\varrho_i}(\varrho\psi) = \mu_i$

Note for later use:

$$\nabla(\varrho\psi) = \partial_T(\varrho\psi)\nabla T + \sum_i \partial_{\varrho_i}(\varrho\psi)\nabla\varrho_i = -\varrho s \nabla T + \sum_i \mu_i \nabla\varrho_i$$

Entropy Production with viscosity and chemistry

Entropy production in terms of the free energy $\varrho\psi = \varrho e - \varrho s T$:

$$\zeta = \operatorname{div}\Big(\boldsymbol{\Phi} - \frac{\mathbf{q}}{T} + \sum_i \frac{\varrho_i \mathbf{u}_i \mu_i}{T}\Big) - \frac{1}{T}\Big(p + \varrho\psi - \sum_i \varrho_i \mu_i\Big) \operatorname{div} \mathbf{v}$$

$$- \sum_i \mathbf{u}_i \cdot \Big(\varrho_i \nabla \frac{\mu_i}{T} + \frac{1}{T}(\mathbf{F}_i + r_i(\mathbf{v}_i^* - \mathbf{v}_i) - \nabla p_i + \operatorname{div} \sigma_i^o)\Big)$$

$$- \frac{1}{T} \sum_{a=1}^{N_R} R_a \sum_{i=1}^{N} \big(\mu_i + \tfrac{1}{2}\mathbf{u}_i^2\big) M_i \nu_i^a + \sum_i \sigma_i^o : \mathbf{D}^o + \mathbf{q} \cdot \nabla \frac{1}{T},$$

where $\mathbf{D}^o$ denotes the symmetric, traceless part of $\nabla \mathbf{v}$

Employ the second law to obtain

1. the entropy flux
2. the Gibbs-Duhem equation (in the form of an Euler relation)
3. restrictions for constitutive equations for all dissipative mechanisms

Case 1: no viscosity, no chemistry

Now $\zeta \geq 0$ for any thermodynamic process necessarily requires:

ad 1. the entropy flux is given by

$$\Phi = \frac{\mathbf{q}}{T} - \sum_i \frac{\varrho_i \mathbf{u}_i \mu_i}{T}$$

ad 2. the Gibbs-Duhem equation holds, i.e.

$$p + \varrho\psi - \sum_i \varrho_i \mu_i = 0$$

Note: the latter implication requires some knowledge on the variables which are allowed for the constitutive equations. One needs that ζ is linear in $\operatorname{div} \mathbf{v}$. This also holds in the general case, but requires more arguments.

$$\Rightarrow \qquad \zeta = -\sum_i \mathbf{u}_i \cdot \Big(\varrho_i \nabla \tfrac{\mu_i}{T} + \tfrac{1}{T}(\mathbf{F}_i - \nabla p_i)\Big) + \mathbf{q} \cdot \nabla \tfrac{1}{T}$$

Case 1: no viscosity, no chemistry

Note: the heat flux **q** contains two terms with diffusion velocities, which leads to some ambiguity in the decomposition into a sum of products

$$\Rightarrow \quad \zeta = -\sum_i \mathbf{u}_i \cdot \Big(\varrho_i \nabla \tfrac{\mu_i}{T} - \tfrac{1}{T} \nabla p_i - h_i \nabla \tfrac{1}{T} + \tfrac{1}{T} \mathbf{F}_i \Big) + \tilde{\mathbf{q}} \cdot \nabla \tfrac{1}{T}$$

with the partial enthalpies $h_i := \varrho_i e_i + p_i$ and $\tilde{\mathbf{q}} := \sum_i \tilde{\mathbf{q}}_i$.

Hence

$$\zeta = -\sum_i \mathbf{u}_i \cdot \Big(\mathbf{B}_i + \tfrac{1}{T} \mathbf{F}_i \Big) + \tilde{\mathbf{q}} \cdot \nabla \tfrac{1}{T}$$

with

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

Aim: employ the entropy inequality to obtain constitutive laws for the thermo-mechanical interactions, i.e. for the structure of the $\mathbf{F}_i$

Case 1: no viscosity, no chemistry

Since the $\mathbf{B}_i$ are part of the driving forces, we compute $\sum_i \mathbf{B}_i$

$$\begin{aligned}\sum_i \mathbf{B}_i &= \sum_i \varrho_i \nabla \tfrac{\mu_i}{T} - \tfrac{1}{T}\nabla p - (\varrho e + p)\nabla \tfrac{1}{T} \\ &= \tfrac{1}{T}\Big(\sum_i \varrho_i \nabla \mu_i - \nabla p\Big) + \Big(\sum_i \varrho_i \mu_i - (\varrho e + p)\Big)\nabla \tfrac{1}{T}\end{aligned}$$

The Gibbs-Duhem equation ($p + \varrho\psi - \sum_i \varrho_i \mu_i = 0$) implies

$$T \sum_i \mathbf{B}_i = \sum_i \varrho_i \nabla \mu_i - \nabla p - \varrho s T^2 \nabla \tfrac{1}{T}$$

Now recall that $\nabla(\varrho\psi) = -\varrho s \nabla T + \sum_i \mu_i \nabla \varrho_i$. Hence

$$T \sum_i \mathbf{B}_i = \sum_i \varrho_i \nabla \mu_i - \nabla p + \sum_i \mu_i \nabla \varrho_i - \nabla(\varrho\psi) = 0$$

Note: $\sum_i \mathbf{B}_i = 0$ only results for this decomposition of ζ !

Exploiting the second law

The interaction term necessarily satisfies

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

Hence

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

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

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

with a positive definite matrix $[\tau_{ij}]$. Extension to $N \times N$ format:

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

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

Exploiting the second law

Prop. The extended $N \times N$-matrix $[\tau_{ij}]_1^N$ is positive semi-definite if the $(N-1) \times (N-1)$-matrix $[\tau_{ij}]_1^{N-1}$ is positive (semi-)definite.

Proof. by the criterion of Sylvester, a quadratic matrix M is positive semi-definite iff the determinant of every upper left sub-matrix is non-negative.

Here: show that $\det([\tau_{ij}]_1^N) \geq 0$. Laplace formula:

$$\det([\tau_{ij}]_1^N) = \sum_{j=1}^N (-1)^{N+j} \tau_{Nj} \det([\tau]_{Nj}),$$

where $[\tau]_{Nj}$ results from deletion of the j^{th} column and N^{th} row.

Show by elementary properties of the determinant:

$$\det([\tau]_{Nj}) = (-1)^{N-j} \det([\tau]_{NN})$$

Hence

$$\det([\tau_{ij}]_1^N) = \det([\tau]_{NN}) \sum_{j=1}^N \tau_{Nj} = \ldots = 0$$

Symmetry of Interactions

Straight forward computation yields

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

Assumption of binary type interactions: (Truesdell)

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

This implies symmetry of $[\tau]$: Evaluate $\sum_{i,j} \tau_{ij}\,(\mathbf{u}_i - \mathbf{u}_j) = 0$.

$N = 2$: $(\tau_{12} - \tau_{21})\,(\mathbf{u}_1 - \mathbf{u}_2) = 0$ for any TD process $\Rightarrow \tau_{12} = \tau_{21}$

$N = 3$:
$(\tau_{12} - \tau_{21})\,(\mathbf{u}_1 - \mathbf{u}_2) + (\tau_{13} - \tau_{31})\,(\mathbf{u}_1 - \mathbf{u}_3) + (\tau_{23} - \tau_{32})\,(\mathbf{u}_2 - \mathbf{u}_3) = 0$
$\varrho_3 \to 0+ \ \Rightarrow\ \tau_{12} = \tau_{21}$; $\varrho_2 \to 0+ \ \Rightarrow\ \tau_{13} = \tau_{31}$; $\varrho_1 \to 0+ \ \Rightarrow\ \tau_{23} = \tau_{32}$

$N > 3$: induction over N.

Exploiting the second law

Ansatz to incorporate both symmetry and binary interactions:

$$\tau_{ij} = -\, f_{ij}\varrho_i\varrho_j \quad \text{with } f_{ij} = f_{ij}(\varrho_i, \varrho_j, T)$$

$$\Rightarrow \quad \mathbf{B}_i + \tfrac{1}{T}\mathbf{F}_i = -\, \textstyle\sum_{j=1}^N f_{ij}\varrho_i\varrho_j(\mathbf{u}_i - \mathbf{u}_j) \quad = -\, \textstyle\sum_{j=1}^N f_{ij}\varrho_i\varrho_j(\mathbf{v}_i - \mathbf{v}_j)$$

dissipation due to interactions:

$$\begin{aligned} -\textstyle\sum_{i=1}^N \mathbf{u}_i \cdot \left(\mathbf{B}_i + \tfrac{1}{T}\mathbf{F}_i\right) &= \textstyle\sum_{i,j=1}^N f_{ij}\varrho_i\varrho_j(\mathbf{u}_i - \mathbf{u}_j)\cdot\mathbf{u}_i \\ &= \tfrac{1}{2}\textstyle\sum_{i,j=1}^N f_{ij}\varrho_i\varrho_j(\mathbf{u}_i - \mathbf{u}_j)^2 \quad \geq 0\ ! \end{aligned}$$

Hence the f_{ij} are symmetric and non-negative "friction factors"

Momentum Balance with Thermo-mechanical Interactions

partial momentum balances: (nonconservative form)

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

Employ

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

This yields the final form of the partial momentum balance in the case without viscosity and chemical reactions as

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

isothermal case:

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

Class - II Model

Resulting model (non reactive, non viscous, symmetric interactions)

$$\textbf{mass} : \partial_t \varrho_i + \operatorname{div}(\varrho_i \mathbf{v}_i) = 0$$

$$\textbf{momentum} : \partial_t(\varrho_i \mathbf{v}_i) + \operatorname{div}(\varrho_i \mathbf{v}_i \otimes \mathbf{v}_i) = -\varrho_i T \nabla \frac{\mu_i}{T} + T h_i \nabla \frac{1}{T} - T \sum_j f_{ij} \varrho_i \varrho_j (\mathbf{v}_i - \mathbf{v}_j) + \varrho_i \mathbf{b}_i$$

$$\textbf{energy} : \partial_t(\varrho e) + \operatorname{div}(\varrho e \mathbf{v} + \mathbf{q}) = \nabla \mathbf{v} : \sum_i \sigma_i - \sum_i \mathbf{u}_i \cdot \mathbf{F}_i$$

constitutive equation for the heat flux:

$$\tilde{\mathbf{q}} = \alpha \nabla \frac{1}{T} \ \text{ with } \alpha \geq 0 \quad \Rightarrow \quad \tilde{\mathbf{q}} \cdot \nabla \frac{1}{T} \geq 0$$

Hence

$$\mathbf{q} = \tilde{\mathbf{q}} + \sum_i h_i \mathbf{u}_i = \alpha \nabla \tfrac{1}{T} + \sum_i h_i \mathbf{u}_i$$

Comparison with Existing Models

Partial momentum balances due to P. Kerkhof (TU/e):

$$\begin{aligned}\partial_t(\varrho_i \mathbf{v}_i) + \nabla \cdot (\varrho_i \mathbf{v}_i \otimes \mathbf{v}_i) = & - c_i \nabla_T \hat{\mu}_i + \varrho_i \mathbf{b}_i \\ & - c^{\mathrm{tot}} R T \sum_{j \neq i} \tfrac{x_i x_j}{Đ_{ij}} (\mathbf{v}_i - \mathbf{v}_j) \\ & - c^{\mathrm{tot}} R T \sum_{j \neq i} \tfrac{x_i x_j}{Đ_{ij}} \Big(\frac{D_i^T}{\varrho_i} - \frac{D_j^T}{\varrho_j} \Big) \nabla \ln T\end{aligned}$$

Result from above (rational thermodynamics):

$$\begin{aligned}\partial_t(\varrho_i \mathbf{v}_i) + \mathrm{div}\,(\varrho_i \mathbf{v}_i \otimes \mathbf{v}_i) = & - \varrho_i \nabla \mu_i + \varrho_i \mathbf{b}_i \\ & - T \sum_j f_{ij} \varrho_i \varrho_j (\mathbf{v}_i - \mathbf{v}_j) \\ & - (h_i - \varrho_i \mu_i) \nabla \ln T\end{aligned}$$

Note: ∇_T denotes "the gradient taken at constant T", $c_i = \varrho_i / M_i$, $\hat{\mu}_i = M_i \mu_i$. Hence agreement is achieved in the isothermal case

Scale-Reduced Class - I Model

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

$y_i \times$ **total mom.** : $\quad y_i \varrho(\partial_t \mathbf{v} + \mathbf{v} \cdot \nabla \mathbf{v}) = -y_i \nabla p + y_i \varrho \mathbf{b}$

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

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

Assume quasi-stationarity w.r. to changes in diffusion velocities along mixture trajectories and obey objectivity; set $D_{ij} := R/f_{ij}$ and $\mathbf{j}_i := \varrho_i \mathbf{u}_i$

$$\Rightarrow \; -\textstyle\sum_{j \neq i} \frac{y_j \mathbf{j}_i - y_i \mathbf{j}_j}{D_{ij}} = \frac{y_i}{RT} \nabla \mu_i - \frac{y_i}{\varrho RT} \nabla p + \frac{\varrho_i \mu_i - h_i}{\varrho R} \nabla \frac{1}{T} - \frac{y_i}{\varrho RT}(\mathbf{b}_i - \mathbf{b})$$

Notation from Eng. literature: $\nabla \mu_i = \nabla_{p,T} \mu_i + \partial_p \mu_i \nabla p + \partial_T \mu_i \nabla T$.

$$\Rightarrow \; \mathbf{d}_i = \tfrac{y_i}{RT} \nabla_{p,T} \mu_i + \tfrac{\phi_i - y_i}{\varrho RT} \nabla p + \tfrac{h_i - \varrho_i s_i T - \varrho_i \mu_i}{\varrho RT} \nabla \ln T - \tfrac{y_i}{RT}(\mathbf{b}_i - \mathbf{b})$$

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

Euler-Maxwell-Stefan Equations

Resulting model (non reactive, non viscous, symmetric interactions)

species : $\partial_t \varrho_i + \operatorname{div}(\varrho_i \mathbf{v} + \mathbf{j}_i) = 0$

momentum : $\partial_t(\varrho \mathbf{v}) + \operatorname{div}(\varrho \mathbf{v} \otimes \mathbf{v}) = -\nabla p + \varrho \mathbf{b}$

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

diff fluxes : $\mathbf{d}_i = -\sum_{j \neq i} \dfrac{y_j \mathbf{j}_i - y_i \mathbf{j}_j}{D_{ij}}, \qquad \sum_i \mathbf{j}_i = 0$

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

driving f. : $\mathbf{d}_i = \frac{y_i}{RT} \nabla_{p,T} \mu_i + \frac{\phi_i - y_i}{\varrho RT} \nabla p + \frac{h_i - \varrho_i s_i T - \varrho_i \mu_i}{\varrho RT} \nabla \ln T - \frac{y_i}{RT}(\mathbf{b}_i - \mathbf{b})$

Note: p obeys an EOS $p = p(\varrho_i, T)$; an incompressible version is possible

Case 2: no viscosity, with chemical reactions

With chemical reactions, the entropy production is:

$$\zeta = -\tfrac{1}{T}\sum_{a=1}^{N_R} R_a \sum_{i=1}^{N} \left(\mu_i + \tfrac{1}{2}\mathbf{u}_i^2\right) M_i \nu_i^a + \tilde{\mathbf{q}} \cdot \nabla \tfrac{1}{T}$$
$$- \sum_i \mathbf{u}_i \cdot \Big(\mathbf{B}_i + \tfrac{1}{T}(\mathbf{F}_i + r_i(\mathbf{v}_i^* - \mathbf{v}_i))\Big)$$

with the partial enthalpies $h_i := \varrho_i e_i + p_i$, heat flux $\tilde{\mathbf{q}} := \sum_i \tilde{\mathbf{q}}_i$ and

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

Furthermore:

$\sum_i \mathbf{B}_i = 0$ as before , $\sum_i (\mathbf{F}_i + r_i \mathbf{v}_i^*) = 0$ momentum conservation

But

$$\sum_i (\mathbf{F}_i + r_i(\mathbf{v}_i^* - \mathbf{v}_i)) \neq 0 \,!$$

Case 2: no viscosity, with chemical reactions

Way out: another regrouping of the entropy production terms as

$$\zeta = -\tfrac{1}{T}\sum_{a=1}^{N_R} R_a \sum_{i=1}^{N} \left(\mu_i - \tfrac{1}{2}\mathbf{u}_i^2\right) M_i \nu_i^a + \tilde{\mathbf{q}} \cdot \nabla \tfrac{1}{T}$$

$$- \sum_i \mathbf{u}_i \cdot \Big(\mathbf{B}_i + \tfrac{1}{T}(\mathbf{F}_i + r_i(\mathbf{v}_i^* - \mathbf{v}))\Big)$$

Because of $\sum_i r_i = 0$ we now have:

$$\sum_i \mathbf{B}_i = 0 \ \text{ and } \qquad \sum_i (\mathbf{F}_i + r_i(\mathbf{v}_i^* - \mathbf{v})) = 0$$

Hence, as before:

$$\tfrac{1}{T}\Big(\mathbf{F}_i + r_i(\mathbf{v}_i^* - \mathbf{v})\Big) + \mathbf{B}_i = -\sum_j f_{ij} \varrho_i \varrho_j (\mathbf{v}_i - \mathbf{v}_j) \ \text{ with } f_{ij} = f_{ji} > 0$$

$$\Rightarrow \quad \mathbf{F}_i + r_i(\mathbf{v}_i^* - \mathbf{v}_i) = -r_i \mathbf{u}_i - T\mathbf{B}_i - T\sum_j f_{ij} \varrho_i \varrho_j (\mathbf{v}_i - \mathbf{v}_j)$$

Class - II Model with Chemical Reactions

Resulting model (reactive, non viscous, symmetric interactions)

$$\textbf{mass}: \partial_t \varrho_i + \operatorname{div}(\varrho_i \mathbf{v}_i) = 0$$

$$\begin{aligned}\textbf{mom.}: \partial_t(\varrho_i \mathbf{v}_i) + \operatorname{div}(\varrho_i \mathbf{v}_i \otimes \mathbf{v}_i) &= -\varrho_i T \nabla \frac{\mu_i}{T} + T h_i \nabla \frac{1}{T} + \varrho_i \mathbf{b}_i \\ &\quad - T \textstyle\sum_j f_{ij} \varrho_i \varrho_j (\mathbf{v}_i - \mathbf{v}_j) - r_i(\mathbf{v}_i - \mathbf{v})\end{aligned}$$

$$\textbf{energy}: \partial_t(\varrho e) + \operatorname{div}(\varrho e \mathbf{v} + \mathbf{q}) = \nabla \mathbf{v} : \textstyle\sum_i \sigma_i - \sum_i \mathbf{u}_i \cdot (\mathbf{F}_i + r_i(\mathbf{v}_i^* - \mathbf{v}_i))$$

constitutive equation for the heat flux (as before):

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

Result: chemical reactions change the partial momentum balance, hence also the relative velocities!

Scale-Reduced Class - I Model with Chemical Reactions

Assuming again quasi-stationarity w.r. to changes in diffusion velocities along mixture trajectories and using objectivity yields:

$$-\sum_{j\neq i}\frac{y_j\mathbf{j}_i-y_i\mathbf{j}_j}{D_{ij}}=\frac{y_i}{RT}\nabla\mu_i-\frac{y_i}{\varrho RT}\nabla p+\frac{\varrho_i\mu_i-h_i}{\varrho R}\nabla\frac{1}{T}-\frac{y_i}{RT}(\mathbf{b}_i-\mathbf{b})+\frac{r_i}{\varrho RT}\mathbf{u}_i$$

Eng. literature notation: $\nabla\mu_i=\nabla_{p,T}\mu_i+\partial_p\mu_i\nabla p+\partial_T\mu_i\nabla T$.

$$\mathbf{d}_i=\frac{y_i}{RT}\nabla_{p,T}\mu_i+\frac{\phi_i-y_i}{\varrho RT}\nabla p+\frac{h_i-\varrho_i s_i T-\varrho_i\mu_i}{\varrho RT}\nabla\ln T-\frac{y_i}{RT}(\mathbf{b}_i-\mathbf{b})+\frac{r_i}{\varrho RT}\mathbf{u}_i$$

molecular, pressure, thermo- (Sorét effect), forced & reactive diffusion

Reactive Euler-Maxwell-Stefan Equations

Resulting model (reactive, non viscous, symmetric interactions)

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

mom. : $\partial_t(\varrho \mathbf{v}) + \operatorname{div}(\varrho \mathbf{v} \otimes \mathbf{v}) = -\nabla p + \varrho \mathbf{b}$ (plus an EOS for p)

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

diff fluxes : $\mathbf{d}_i = -\sum_{j \neq i} \frac{y_j \mathbf{j}_i - y_i \mathbf{j}_j}{D_{ij}}, \qquad \sum_i \mathbf{j}_i = 0$

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

driving f. : $\mathbf{d}_i = \frac{y_i}{RT} \nabla_{p,T} \mu_i + \frac{\phi_i - y_i}{\varrho RT} \nabla p + \frac{h_i - \varrho_i s_i T - \varrho_i \mu_i}{\varrho RT} \nabla \ln T$

$$- \frac{y_i}{RT}(\mathbf{b}_i - \mathbf{b}) + \frac{r_i}{\varrho RT} \mathbf{u}_i$$

Case 3: shear viscosity and chemical reactions

With chemical reactions and shear viscosity, the entropy production is:

$$\zeta = -\tfrac{1}{T}\sum_{a=1}^{N_R} R_a \sum_{i=1}^{N} \left(\mu_i - \tfrac{1}{2}\mathbf{u}_i^2\right) M_i \nu_i^a + \tilde{\mathbf{q}} \cdot \nabla \tfrac{1}{T}$$

$$+\tfrac{1}{T}\sum_i \sigma_i^o : \mathbf{D}^o - \sum_i \mathbf{u}_i \cdot \Big(\mathbf{B}_i + \tfrac{1}{T}(\mathbf{F}_i + r_i(\mathbf{v}_i^* - \mathbf{v}))\Big)$$

with the partial enthalpies $h_i := \varrho_i e_i + p_i$, heat flux $\tilde{\mathbf{q}} := \sum_i \tilde{\mathbf{q}}_i$ and

$$\mathbf{B}_i := \varrho_i \nabla \frac{\mu_i}{T} - \frac{1}{T}\nabla p_i - h_i \nabla \frac{1}{T} + \operatorname{div} \frac{\sigma_i^o}{T} - \lambda \varrho_i,$$

where $\lambda := \frac{1}{\varrho}\sum_i \operatorname{div} \frac{\sigma_i^o}{T}$ acts like a Lagrange multiplier

Note: $\sum_i \mathbf{u}_i \cdot \lambda \varrho_i = \lambda \sum_i \mathbf{j}_i = 0$ for every $\lambda \in \mathbb{R}$

Furthermore, as before:

$$\sum_i \mathbf{B}_i = 0 \text{ and } \sum_i (\mathbf{F}_i + r_i(\mathbf{v}_i^* - \mathbf{v})) = 0$$

Case 3: no viscosity, with chemical reactions

Consequently, as before:

$$\mathbf{F}_i + r_i(\mathbf{v}_i^* - \mathbf{v}_i) = -r_i\mathbf{u}_i - T\mathbf{B}_i - T\sum_j f_{ij}\varrho_i\varrho_j(\mathbf{v}_i - \mathbf{v}_j)$$

with

$$\mathbf{B}_i := \varrho_i\nabla\frac{\mu_i}{T} - \frac{1}{T}\nabla p_i - h_i\nabla\frac{1}{T} + \mathrm{div}\,\frac{\sigma_i^o}{T} - y_i\sum_k \mathrm{div}\,\frac{\sigma_k^o}{T}$$

Assuming again quasi-stationarity and using objectivity yields:

$$-\sum_{j\neq i}\frac{y_j\mathbf{j}_i - y_i\mathbf{j}_j}{D_{ij}} = \frac{y_i}{RT}\nabla\mu_i - \frac{y_i}{\varrho RT}\nabla p + \frac{\varrho_i\mu_i - h_i}{\varrho R}\nabla\frac{1}{T} - \frac{y_i}{RT}(\mathbf{b}_i - \mathbf{b}) + \frac{r_i}{\varrho RT}\mathbf{u}_i$$

$$-\frac{1}{\varrho RT}\Big(\sigma_i^o - y_i\sum_k\sigma_k^o\Big) : \nabla\ln T + \frac{y_i}{\varrho RT}\mathrm{div}\,\Big(\sigma^0 - \sum_k\sigma_k^o\Big)$$

Note: $\mathrm{div}\,(\sigma^0 - \sum_k\sigma_k^o) = \mathrm{div}\,\big((\varrho_i\mathbf{u}_i\otimes\mathbf{u}_i)^o\big)$ is of second order in $\mathbf{u}_i$

This (just) leads to a shear induced correction of the Sorét effect:

$$\mathbf{d}_i = \frac{y_i}{RT}\nabla_{p,T}\mu_i + \frac{\phi_i - y_i}{\varrho RT}\nabla p - \frac{y_i}{RT}(\mathbf{b}_i - \mathbf{b}) + \frac{r_i}{\varrho RT}\mathbf{u}_i$$

$$+\frac{1}{\varrho RT}\Big(h_i - \varrho_i s_i T - \varrho_i\mu_i - \big(\sigma_i^o - y_i\sum_k\sigma_k^o\big)\Big)\nabla\ln T$$

Reactive Navier-Stokes-Maxwell-Stefan Equations

Resulting model (reactive, shear viscosity, symmetric interactions)

species : $\partial_t \varrho_i + \mathrm{div}\,(\varrho_i \mathbf{v} + \mathbf{j}_i) = r_i$

mom. : $\partial_t(\varrho \mathbf{v}) + \mathrm{div}\,(\varrho \mathbf{v} \otimes \mathbf{v}) + \nabla p = \eta \Delta \mathbf{v} + \varrho \mathbf{b}$ (+ an EOS for p)

energy : $\partial_t(\varrho e) + \mathrm{div}\,(\varrho e \mathbf{v} + \mathbf{q}) = -p\,\mathrm{div}\,\mathbf{v} - \sum_i \mathbf{u}_i \cdot (\mathbf{F}_i + r_i(\mathbf{v}_i^* - \mathbf{v}_i))$

diff fluxes : $\mathbf{d}_i = -\sum_{j \neq i} \frac{y_j \mathbf{j}_i - y_i \mathbf{j}_j}{D_{ij}}, \qquad \sum_i \mathbf{j}_i = 0$

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

driving f. : $\mathbf{d}_i = \frac{y_i}{RT} \nabla_{p,T} \mu_i + \frac{\phi_i - y_i}{\varrho RT} \nabla p - \frac{y_i}{RT}(\mathbf{b}_i - \mathbf{b}) + \frac{r_i}{\varrho RT} \mathbf{u}_i$

$+ \frac{1}{\varrho RT}(h_i - \varrho_i s_i T - \varrho_i \mu_i - (\sigma_i^o - y_i \sum_k \sigma_k^o)) \nabla \ln T$

Reactive Navier-Stokes-Maxwell-Stefan Equations

An isothermal and incompressible variant:

$$\begin{aligned}
&\operatorname{div} \mathbf{v} = 0\\
&\partial_t(\varrho \mathbf{v}) + \operatorname{div}(\varrho \mathbf{v} \otimes \mathbf{v}) + \nabla p = \eta \Delta \mathbf{v} + \varrho \mathbf{b}\\
&\varrho(\partial_t y_i + \mathbf{v} \cdot y_i) + \operatorname{div} \mathbf{j}_i = r_i
\end{aligned}$$

$$\mathbf{d}_i = -\sum_{j \neq i} \frac{y_j \mathbf{j}_i - y_i \mathbf{j}_j}{D_{ij}}, \qquad \textstyle\sum_i \mathbf{j}_i = 0$$

$$\mathbf{d}_i = \tfrac{y_i}{RT} \nabla_{p,T} \mu_i + \tfrac{\phi_i - y_i}{\varrho RT} \nabla p - \tfrac{y_i}{RT}(\mathbf{b}_i - \mathbf{b}) + \tfrac{r_i}{\varrho RT} \mathbf{u}_i$$

Chemical Reaction Kinetics

Since TD developed from an equilibrium theory, reactions are assumed to be reversible:

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

The (molar) rate R_a of reaction a can be shown to only depend as

$$R_a = R_a(T, \varrho_1, \ldots, \varrho_N) \;\text{ resp. }\; R_a(T, c_1, \ldots, c_N) \;\text{ resp. }\; R_a(p, T, c_1, \ldots, c_{N-1})$$

For systems not far from equilibrium: closure is linear in the driving forces

$$\Rightarrow \quad R_a = -\sum_{b=1}^{N_R} L_{ab} \sum_{i=1}^{N} (\mu_i - \frac{\mathbf{u}_i^2}{2}) M_i \nu_i^b \;\text{ with } [L_{ab}] \text{ positive (semi-)definite}$$

Chemical Reaction Kinetics

Example: $A_1 + A_2 \rightleftharpoons A_3$. For diluted case:

$$\mu_i = \mu_i^0 + RT \ln c_i \quad \text{with } \mu_i^0 = \mu_i^0(p, T), \quad i = 1, 2, 3$$

Hence (ignoring the diffusive velocity influence for simplicity)

$$R = -k\Big(- \mu_1^0 - \mu_1^0 + \mu_1^0 - RT \ln \frac{c_1 c_2}{c_3}\Big)$$

equi: $c_1^{eq} c_2^{eq} = K c_3^{eq}$ with some equilibrium "constant" K and $R = 0$

$$R = -kRT\Big(\ln K - \ln \frac{c_1 c_2}{c_3}\Big) \doteq kRT\big(\frac{c_1 c_2}{K\, c_3} - 1\big)$$

Resulting form of kinetic equation is of **mass action type**:

$$R = k^f c_1 c_2 - k^b c_3 \quad \text{with } k^f, k^b \text{ depending on } p, T, c_i$$

Maxwell-Stefan Equations

The simplest case of isobaric isothermal MS-diffusion:

$$\mathbf{v} = 0, \qquad \partial_t c_i + \operatorname{div} \mathbf{J}_i = r_i^{\mathrm{tot}},$$

$$(\mathbf{d}_i =) \quad \frac{x_i}{RT} \operatorname{grad} \mu_i = -\sum_{j \neq i} \frac{x_j \mathbf{J}_i - x_i \mathbf{J}_j}{c_{\mathrm{tot}}\, Đ_{ij}}, \qquad \text{(MS)}$$

$$\textstyle\sum_i \mathbf{J}_i = 0.$$

Remark. The Maxwell-Stefan diffusivities $Đ_{ij}$ are usually assumed to be *nonnegative, constant & symmetric*. But they may depend on **c** below!

In this case $\sum_i \mathbf{d}_i = 0$ necessarily holds due to $Đ_{ij} = Đ_{ji}$.

Maxwell-Stefan Equations for Binary Systems

Example (binary system).

$$\mathbf{J}_1 = -\mathbf{J}_2 = -\frac{Đ_{12}}{RT} c_1 \operatorname{grad} \mu_1 .$$

$$\boxed{\partial_t c - \Delta \phi(c) = r(c)}$$

with

$$\phi'(s) = \frac{Đ_{12}}{RT}(1 + s\gamma'(s)/\gamma(s)), \quad \phi(0) = 0.$$

Sufficient for parabolicity:

$$s \to s\gamma(s) \text{ increasing } \Leftrightarrow \mu(\cdot) \text{ increasing } \Leftrightarrow \text{ convex energy}$$

Inversion of the Flux-Force Relations - I

Direct approach: eliminate $\mathbf{J}_n (= \sum_{i=1}^{n-1} \mathbf{J}_i)$ and $x_n (= 1 - \sum_{i=1}^{n-1} x_i)$

$$c_{\text{tot}} \begin{bmatrix} \mathbf{d}_1 \\ \vdots \\ \mathbf{d}_{n-1} \end{bmatrix} = \mathbf{B} \begin{bmatrix} \mathbf{J}_1 \\ \vdots \\ \mathbf{J}_{n-1} \end{bmatrix}$$

with

$$B_{ij} = x_i \left(\frac{1}{D_{1n}} - \frac{1}{D_{ij}} \right) \text{ for } i \neq j, \quad B_{ii} = \frac{x_i}{D_{in}} + \sum_{k \neq i} \frac{x_k}{D_{ik}}.$$

Formally,

$$\begin{bmatrix} \mathbf{J}_1 \\ \vdots \\ \mathbf{J}_{n-1} \end{bmatrix} = c_{\text{tot}} \mathbf{B}^{-1} \mathbf{\Gamma} \begin{bmatrix} \nabla x_1 \\ \vdots \\ \nabla x_{n-1} \end{bmatrix},$$

where

$$\mathbf{\Gamma} = (\Gamma_{ij}) \quad \text{with} \quad \Gamma_{ij} = \delta_{ij} + x_i \frac{\partial \ln \gamma_i}{\partial c_j}.$$

Maxwell-Stefan Equations for Ternary Systems

Example (ternary system).

$$\mathbf{B} = \begin{bmatrix} \frac{1}{D_{13}} + x_2\left(\frac{1}{D_{12}} - \frac{1}{D_{13}}\right) & -x_1\left(\frac{1}{D_{12}} - \frac{1}{D_{13}}\right) \\ -x_2\left(\frac{1}{D_{12}} - \frac{1}{D_{23}}\right) & \frac{1}{D_{23}} + x_1\left(\frac{1}{D_{12}} - \frac{1}{D_{23}}\right) \end{bmatrix}$$

$\det(\mathbf{B} - \lambda\mathbf{I}) = \lambda^2 - \mathrm{tr}\,\mathbf{B}\,\lambda + \det\mathbf{B}$ with

$$\det\mathbf{B} = \frac{x_1}{D_{12}\,D_{13}} + \frac{x_2}{D_{12}\,D_{23}} + \frac{x_3}{D_{13}\,D_{23}} \geq \min\{\frac{1}{D_{12}\,D_{13}}, \frac{1}{D_{12}\,D_{23}}, \frac{1}{D_{13}\,D_{23}}\} > 0$$

and

$$\mathrm{tr}\,\mathbf{B} = \frac{x_1 + x_2}{D_{12}} + \frac{x_1 + x_3}{D_{13}} + \frac{x_2 + x_3}{D_{23}} \geq 2\min\{\frac{1}{D_{12}}, \frac{1}{D_{13}}, \frac{1}{D_{23}}\} > 0.$$

$(\mathrm{tr}\,\mathbf{B})^2 \geq 3\det\mathbf{B} \quad \Rightarrow$

$$\sigma(\mathbf{B}^{-1}(\mathbf{x})) \subset \Sigma_\theta := \{\lambda \in \mathbb{C} \setminus \{0\} : |\arg\lambda| < \theta\} \quad \text{for } \theta = \frac{\pi}{6}.$$

Inversion of the Flux-Force Relations - II

Invariant Formulation: solve $A\,\mathbf{J} = \mathbf{d}$ on $E = \{u \in \mathbb{R}^n : \sum_i u_i = 0\}$,

$$A = \begin{bmatrix} -s_1 & & & d_{ij} \\ & \cdot & & \\ & & \cdot & \\ d_{ij} & & & -s_n \end{bmatrix}, \quad s_i = \sum_{k \neq i} \frac{x_k}{\text{Đ}_{ik}}, \quad d_{ij} = \frac{x_i}{\text{Đ}_{ij}}$$

Properties of A:

- $N(A) = \mathrm{span}\{\mathbf{x}\}$ for $\mathbf{x} = (x_1, \ldots, x_n)$
- $R(A) = \{\mathbf{e}\}^{\perp}$ for $\mathbf{e} = (1, \ldots, 1)$
- $A = [a_{ij}]$ is quasi-positive, i.e. $a_{ij} \geq 0$ for $i \neq j$
- If $\mathbf{x} \gg 0$ then A is irreducible, i.e. $a_{ij} \neq 0$ for some $(i, j) \in I \times J$ for all disjoint decompositions $\{1, \ldots, n\} = I \cup J$

Apply Perron-Frobenius theorem (for quasi-positive matrices)!

Spectrum of A

The Perron-Frobenius theorem yields the following properties of $\sigma(A)$:

- the spectral bound $\lambda_0 := s(A) = \max\{\mathrm{Re}\,\lambda : \lambda \in \sigma(A)\}$ is an eigenvalue of A
- λ_0 is a simple eigenvalue with a strictly positive eigenvector
- eigenvalues different from λ_0 have no positive eigenvector or positive generalized eigenvector
- $\mathrm{Re}\,\lambda < s(A)$ for all $\lambda \in \sigma(A)$, $\lambda \neq s(A)$.

Here: $\mathbf{x}$ is an eigenvector to the eigenvalue 0, hence for $\mathbf{x} \gg 0$:

$$\sigma(A) \subset \{0\} \cup \{z \in \mathbb{C} : \mathrm{Re}\, z < 0\}$$

Symmetrized version of A

Let $\mathbf{x} \gg 0$ and $X := \operatorname{diag}(x_1, \dots x_n)$. Then $A_S := X^{-\frac{1}{2}}\, A\, X^{\frac{1}{2}}$ satisfies

$$A_S = \begin{bmatrix} -s_1 & & \hat{d}_{ij} \\ & \ddots & \\ \hat{d}_{ij} & & -s_n \end{bmatrix}, \quad s_i = \sum_{k \neq i} \frac{x_k}{\text{Đ}_{ik}}, \quad \hat{d}_{ij} = \frac{\sqrt{x_i x_j}}{\text{Đ}_{ij}},$$

i.e. A_S is symmetric with $N(A_S) = \operatorname{span}\{\sqrt{\mathbf{x}}\}$.

Moreover,

$$A_S(\alpha) = A_S - \alpha\sqrt{\mathbf{x}} \otimes \sqrt{\mathbf{x}}$$

has the same properties as A_S for small $\alpha > 0$. In particular, A_S is quasi-positive, irreducible and $\sqrt{\mathbf{x}} \gg 0$ is an eigenvector for the eigenvalue $-\alpha$. This holds for all $\alpha < \delta := \min\{1/\text{Đ}_{ij} : i \neq j\}$. Hence

$$\sigma(A) \setminus \{0\} = \sigma(A_S(\alpha)) \setminus \{-\alpha\} \subset (-\infty, -\delta]$$

Inversion of the MS-Equations

$A_{|E} : E = \{u \in \mathbb{R}^n : \sum_i u_i = 0\} \to E$ is invertible and

$$[\mathbf{J}_i] = X^{\frac{1}{2}} (A_{S|E})^{-1} X^{-\frac{1}{2}} [\mathbf{d}_i] = \frac{1}{RT} X^{\frac{1}{2}} (A_{S|E})^{-1} X^{\frac{1}{2}} [\nabla \mu_i] .$$

Hence

$$[\mathbf{J}_i] : [\nabla \mu_i] = \frac{1}{RT} \Big((A_{S|E})^{-1} X^{\frac{1}{2}} [\nabla \mu_i] \Big) : \Big(X^{\frac{1}{2}} [\nabla \mu_i] \Big) \leq 0,$$

i.e. the entropy inequality is satisfied.

If $G := \varrho\psi$ is strongly convex:

$$\operatorname{div}(-\mathbf{D}(\mathbf{c})\nabla \mathbf{c}) := \operatorname{div}([\mathbf{J}_i]) \ \text{ has elliptic principal part}$$

This will be shown below

Isothermal isobaric single-phase case

Theorem (Local-in-time Wellposedness, B. 2010)

Let $\Omega \subset \mathbb{R}^N$ *be open bounded with smooth* $\partial\Omega$. *Let* $p > \frac{N+2}{2}$ *and* $\mathbf{c}_0 \in W_p^{2-\frac{2}{p}}(\Omega)$ *such that* $c_i^0 > 0$ *in* $\bar{\Omega}$ *and* c_0^{tot} *is constant in* Ω. *Let the diffusion matrix* $\mathbf{D}(\mathbf{c})$ *be given by*

$$\mathbf{D}(\mathbf{c}) = X^{\frac{1}{2}}(A_{S|E})^{-1}X^{\frac{1}{2}}G''(\mathbf{x}) \quad \textit{with } \mathbf{x} = \mathbf{c}/c^{\mathrm{tot}}, X = \mathrm{diag}(\mathbf{x}),$$

where $G := \varrho\psi$ *is smooth and strongly convex on* $\{c^{\mathrm{tot}} = c_0^{\mathrm{tot}}\}$. *Then there exists - locally in time - a unique strong solution (in the* L^p*-sense) of*

$$\partial_t \mathbf{c} + \mathrm{div}\,(-\mathbf{D}(\mathbf{c})\nabla\mathbf{c}) = 0, \qquad \partial_\nu \mathbf{c}_{|\partial\Omega} = 0, \quad \mathbf{c}_{|t=0} = \mathbf{c}_0$$

This solution is in fact classical.

Isothermal isobaric single-phase case

Idea of proof: Let u be given by $c_{\mathrm{tot}} x_i = u_i + c^0_{\mathrm{tot}}/n$.

- evolution for u lives in $E = \{u \in \mathbb{R}^n : \sum_i u_i = 0\}$
- $\mathrm{div}\,(-\mathbf{D}(u)\nabla u) = \mathbf{D}(u)\,(-\Delta u) \; + \;$ lower order terms
- $\lambda \in \mathbb{C}$ and $v \in E$ with $\mathbf{D}(u)\,v = \lambda v$ means

$$-X^{\frac{1}{2}}(A_{S|E})^{-1} X^{\frac{1}{2}} G''(\mathbf{x})\,v = \lambda v$$

$$\Rightarrow \; \langle -(A_{S|E})^{-1} X^{\frac{1}{2}} G''(\mathbf{x})\,v, X^{\frac{1}{2}} G''(\mathbf{x})\,v\rangle = \lambda \langle v, G''(\mathbf{x})\,v\rangle$$

- left-hand side > 0 and $\langle v, G''(\mathbf{x})\,v\rangle > 0$ by assumption on G, hence $\lambda > 0 \;\Rightarrow\; \sigma(\mathbf{D}(u)) \subset (0,\infty)$ in $\mathcal{L}(E;E)$
- apply well-known existence results for quasilinear parabolic systems, e.g. the theory of L_p-maximal regularity as to be found in "Denk, Hieber, Prüss: AMS Memoirs 166, 2003"

Some Additions

- **Extension to reaction-diffusion systems**

  $$\partial_t u + \operatorname{div}\left(-\mathbf{D}(u)\nabla u\right) = f(t,u), \qquad \partial_\nu u_{|\partial\Omega} = 0, \quad u_{|t=0} = u_0$$

  admits a unique local strong solution if f is locally Lipschitz with $\sum_i f_i = 0$.

- **Non-Negativity**

  Solutions stay non-negative because of the structure of diffusive fluxes:

  $$\boxed{\mathbf{J}_i(\mathbf{c}) = -D_i(\mathbf{c})\,\mathrm{grad}\,c_i + c_i\,\mathbf{F}_i(\mathbf{c},\nabla\mathbf{c}).}$$

Outlook

- next steps:
  - strict positivity of solutions
  - global existence (without reaction)
  - asymptotic behavior
  - non-ideal mixtures
- extension to the reactive case:
  - local-in-time existence
    (work in progress, jointly with J. Prüss)
  - implication for blow-up in Reaction-Diffusion-systems
- extension to the non-isobaric case:
  - MS-equations coupled with Navier-Stokes-equation
    (work in progress, jointly with H. Amann)