On the Structure of Continuum Thermodynamical Diffusion Fluxes

Dieter Bothe

Fachbereich Mathematik

Technische Universität Darmstadt

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joint work with Pierre-Étienne Druet (WIAS Berlin)

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Continuum Thermodynamics (CT)

partial mass balances:

$$\partial_t \varrho_i + \operatorname{div}(\varrho_i \mathbf{v}_i) = \sum_{a=1}^{N_R} M_i \nu_i^a R_a =: r_i$$

total mass balance:

$$\partial_t \varrho + \operatorname{div}(\varrho \mathbf{v}) = 0; \qquad \varrho = \sum_i \varrho_i, \ \ \varrho \mathbf{v} = \sum_i \varrho_i \mathbf{v}_i$$

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:

$$\partial_t(\varrho e) + \operatorname{div}(\varrho e \mathbf{v} + \mathbf{q}) = \nabla \mathbf{v} : \mathbf{S} + \varrho \pi;$$

Class-I Model - Balance Equations

partial mass balances:

$$\partial_t \varrho_i + \mathrm{div}\,(\varrho_i \mathbf{v} + \mathbf{j}_i) = r_i; \qquad \mathbf{j}_i = \varrho_i(\mathbf{v}_i - \mathbf{v}),\ \sum_i \mathbf{j}_i = 0$$

total mass balance:

$$\partial_t \varrho + \mathrm{div}\,(\varrho \mathbf{v}) = 0; \qquad \varrho = \sum_i \varrho_i,\ \varrho \mathbf{v} = \sum_i \varrho_i \mathbf{v}_i$$

total momentum balance:

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

internal energy balance:

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

Class-I Model - Constitutive Modeling

Variables: $\varrho_1, \dots, \varrho_N$, $\mathbf{v}$, ϱe

class-I model requires constitutive equations for:

$$\mathbf{j}_i, \quad \mathbf{S}, \quad \mathbf{q}, \quad R_a$$

We consider **non-polar fluids**, hence the stress $\mathbf{S}$ is symmetric: $\mathbf{S} = \mathbf{S}^\mathsf{T}$.

Universal Principles:

1. material frame indifference
2. entropy principle (second law of thermodynamics)

The Entropy Principle

The entropy principle comprises the following postulates[1]:

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

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

Equilibria are characterized by $\zeta = 0$.

[1] Bothe, Dreyer: Acta Mech. 226, 1757-1805 (2015).

The Entropy Principle

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 objective quantities of negative, respectively positive parity[2].

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

Extended principle of detailed balance:

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

[2] parity +/- iff physical dimension s appears even/odd times

The Entropy Principle

For the considered fluid mixture class we also postulate:

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

6) The entropy density is given as

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

with a strictly concave material function, strictly increasing in ϱe.
The *absolute temperature* T and *chemical potentials* μ_i are defined via

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

Entropy Principle evaluated

Calculation of the entropy production:

Introduce the *mechanical pressure* as $P := -\frac{1}{3}\mathrm{tr}(\mathbf{S})$

$\Rightarrow \quad \mathbf{S} = -P\mathbf{I} + \mathbf{S}^\circ$ with $\mathbf{S}^\circ$ the traceless part of $\mathbf{S}$.

Entropy production:

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

$$\mathrm{div}\,\Big(\Phi - \frac{\mathbf{q}}{T} + \sum_{i=1}^{N} \frac{\mu_i \mathbf{j}_i}{T}\Big) - \frac{1}{T}\Big(P + \varrho e - \varrho s T - \sum_{i=1}^{N} \varrho_i \mu_i\Big)\mathrm{div}\,\mathbf{v}$$

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

Entropy Principle evaluated

Choice of entropy flux: $\Phi = \dfrac{\mathbf{q}}{T} - \sum_{i=1}^{N} \dfrac{\mu_i \, \mathbf{j}_i}{T}$

Reduced entropy production:

$$\zeta = \mathbf{q} \cdot \nabla \frac{1}{T} + \frac{1}{T} \mathbf{S}^\circ : \mathbf{D}^\circ - \frac{1}{T}\big(P + \varrho e - \varrho s T - \sum_{i=1}^{N} \varrho_i \mu_i\big) \operatorname{div} \mathbf{v}$$
$$- \sum_{i=1}^{N} \mathbf{j}_i \cdot \big(\nabla \frac{\mu_i}{T} - \frac{\mathbf{b}_i}{T}\big) - \frac{1}{T} \sum_{a=1}^{N_R} R_a \mathcal{A}_a$$

Dissipative Mechanisms:

heat flux, shear, compression/expansion, relative motion, chemical reactions

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Thermodynamics of Irreversible Processes (T.I.P.)

Constitutive equations required for:

$$\mathbf{q}, \quad \mathbf{S}^\circ, \quad P, \quad \mathbf{j}_i, \quad R_a$$

under the constraint $\sum_{i=1}^{N} \mathbf{j}_i = 0$. Eliminate one flux, say $\mathbf{j}_N = -\sum_{i=1}^{N-1} \mathbf{j}_i$.

Entropy production:

$$\zeta = \mathbf{q} \cdot \nabla \frac{1}{T} + \frac{1}{T}\mathbf{S}^\circ : \mathbf{D}^\circ - \frac{1}{T}\Big(P + \varrho e - \varrho s T - \sum_{i=1}^{N} \varrho_i \mu_i\Big) \operatorname{div} \mathbf{v}$$
$$- \sum_{i=1}^{N-1} \mathbf{j}_i \cdot \Big(\nabla \frac{\mu_i - \mu_N}{T} - \frac{\mathbf{b}_i - \mathbf{b}_N}{T}\Big) - \frac{1}{T} \sum_{a=1}^{N_R} R_a \mathcal{A}_a$$

Closure within T.I.P.

Closure: Linear in the co-factors

1. heat flux: $\mathbf{q} = \alpha \nabla \frac{1}{T}, \quad \alpha \geq 0$
2. shear stress: $\mathbf{S}^\circ = 2\eta \mathbf{D}^\circ, \quad \eta \geq 0$
3. compression: $P + \varrho e - \varrho s T - \sum_{i=1}^{N} \varrho_i \mu_i = -\lambda \mathrm{div}\, \mathbf{v}, \quad \lambda \geq 0$
4. relative motion: $\mathbf{j}_i = -\sum_{j=1}^{N-1} L_{ij} \big(\nabla \frac{\mu_j - \mu_N}{T} - \frac{\mathbf{b}_j - \mathbf{b}_N}{T} \big), \quad [L_{ij}]$ s.p.d.
5. reactions: $R_a = -\sum_{b=1}^{N_R} l_{ab} \mathcal{A}_b, \quad [l_{ab}]$ s.p.d.

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Closure within T.I.P.

Multicomponent diffusion within T.I.P.:

$$\mathbf{j}_i = -\sum_{j=1}^{N-1} L_{ij}\left(\nabla\frac{\mu_j - \mu_N}{T} - \frac{\mathbf{b}_j - \mathbf{b}_N}{T}\right) \quad i = 1, \ldots, N-1$$

Extend $[L_{ij}]$ to $N \times N$ such that

$$\sum_{i=1}^{N} L_{ij} = 0 \quad \text{and} \quad \sum_{j=1}^{N} L_{ij} = 0.$$

Fick-Onsager diffusion:

$$\mathbf{j}_i = -\sum_{j=1}^{N} L_{ij}\left(\nabla\frac{\mu_j}{T} - \frac{\mathbf{b}_j}{T}\right) \quad i = 1, \ldots, N.$$

Closure within T.I.P.

Fick-Onsager diffusion within T.I.P. – Pros and Cons:

+ thermodynamically consistent closure
+ explicit expressions for the diffusion fluxes

− incorporation of flux-constraint requires dense matrix $[L_{ij}]$
− phenomenological coefficients L_{ij} show strong dependence on composition
− constant coefficients L_{ij} lead to possible loss of positivity
− no non-trivial diagonal closure possible

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The Maxwell-Stefan Equations

Alternative approach to multicomponent diffusion:

assume local balance between driving forces and friction forces:

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

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

$c = \sum_i c_i$ total concentration
$x_i = c_i/c$ molar fractions
$\mathbf{J}_i = \mathbf{j}_i/M_i$ molar mass fluxes
$Đ_{ij} = 1/f_{ij}$ the *Maxwell-Stefan diffusivities*

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).

The Maxwell-Stefan Equations

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$c = \sum_i c_i$ total concentration
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$Đ_{ij} = 1/f_{ij}$ the *Maxwell-Stefan diffusivities*

Maxwell-Stefan Equations embedded into T.I.P. ?

Resistance Form for Diffusion Fluxes

Entropy production due to relative motion:

$$\zeta_{\mathrm{DIFF}} = -\sum_{i=1}^{N} \varrho_i \mathbf{u}_i \cdot \left(\nabla \frac{\mu_i}{T} - \frac{\mathbf{b}_i}{T}\right)$$

with diffusion velocities $\mathbf{u}_i = \mathbf{v}_i - \mathbf{v}$.

Shuffle ϱ_i and exploit $\sum_{i=1}^{N} \mathbf{j}_i = 0$:

$$\zeta_{\mathrm{DIFF}} = -\sum_{i=1}^{N} \mathbf{u}_i \cdot \varrho_i \left(\nabla \frac{\mu_i}{T} - \frac{\mathbf{b}_i}{T} + \frac{\Lambda}{T}\right)$$

holds for any Λ.

Resistance Form for Diffusion Fluxes

Special choice of Lagrange parameter Λ :

$$\Lambda = -\frac{\nabla p}{\varrho} + \mathbf{b} + \left(e + \frac{p}{\varrho}\right)\nabla \ln T$$

in order to have $\sum_{i=1}^{N} \mathbf{d}_i = 0$. This yields

$$\zeta_{\mathrm{DIFF}} = -\sum_{i=1}^{N} \mathbf{u}_i \cdot \mathbf{d}_i$$

with the so-called *(generalized) thermodynamic driving forces*

$$\mathbf{d}_i = \varrho_i \nabla \frac{\mu_i}{T} - \frac{y_i}{T}\nabla p - \varrho_i \frac{\mathbf{b}_i - \mathbf{b}}{T} - y_i(\varrho e + p)\nabla \frac{1}{T}$$

Resistance Form for Diffusion Fluxes

Linear closure using resistance form:

$$\zeta_{\mathrm{DIFF}} = -\sum_{i=1}^{N-1} (\mathbf{u}_i - \mathbf{u}_N) \cdot \mathbf{d}_i \quad \Rightarrow \quad \mathbf{d}_i = -\sum_{j=1}^{N-1} \tau_{ij} (\mathbf{u}_j - \mathbf{u}_N)$$

with a symmetric, positive definite matrix $[\tau_{ij}]$.

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

$$\sum_{i=1}^{N} \tau_{ij} = 0 \qquad \text{and} \qquad \sum_{j=1}^{N} \tau_{ij} = 0$$

yields

$$\mathbf{d}_i = \sum_{j=1}^{N} \tau_{ij} \, (\mathbf{u}_i - \mathbf{u}_j) \quad \text{for } i = 1, \ldots, N.$$

Maxwell-Stefan Equations

Assumption of binary type interactions:

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

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

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

Note: $f_{ij} = f_{ji} > 0$ is often assumed. Then $[\tau_{ij}]$ has the requested props.

Yields the Maxwell-Stefan equations:

$$-\sum_{i=1}^{N} \varrho f_{ij}(y_j \mathbf{j}_i - y_i \mathbf{j}_j) = \varrho_i \nabla \frac{\mu_i}{T} - \frac{y_i}{T} \nabla p - \varrho_i \frac{\mathbf{b}_i - \mathbf{b}}{T} - h_i \nabla \frac{1}{T}$$

with $h_i = y_i(e + p/\varrho)$.

Maxwell-Stefan Equations

Isothermal Maxwell-Stefan equations in molar-based form:

$$-\sum_{k=1}^{N} \frac{x_k \mathbf{j}_i^{\mathrm{mol}} - x_i \mathbf{j}_k^{\mathrm{mol}}}{Đ_{ik}} = c_i \nabla \frac{\mu_i^{\mathrm{mol}}}{RT} - \frac{y_i}{RT} \nabla p - \varrho_i \frac{\mathbf{b}_i - \mathbf{b}}{RT},$$

where $c_i = \varrho_i / M_i$, $x_i = c_i / c$ with $c = \sum_k c_k$, $\mathbf{j}_i^{\mathrm{mol}} = \mathbf{j}_i / M_i$, $\mu_i^{\mathrm{mol}} = M_i \mu_i$ and Maxwell-Stefan diffusivities $Đ_{ik}$.

Maxwell-Stefan Equations

Multicomponent diffusion via M-S Equations – Pros and Cons:

+ thermodynamically consistent closure
+ $Đ_{ik}$ regular with moderate dependence on composition
+ local-in-time strong wellposedness with positivity

– (numerical) flux computation requires inversion of Maxwell-Stefan matrix (in every time step and every mesh cell).

– equivalent MS-form of a diagonal closure not clear

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Novel Closure Scheme

Aim: new closure for thermodynamically consistent diffusion fluxes

- which is direct, avoiding the inversion of the Maxwell-Stefan equations
- which allows for a diagonal closure in which only minimal cross-effects are present
- which displays the structure which is necessary to guarantee consistency with total mass conservation

Question:[3] how to incorporate the constraint $\sum_{i=1}^{N} \varrho_i \mathbf{u}_i = 0$ into

$$\zeta_{\mathrm{DIFF}} = -\sum_{i=1}^{N} \mathbf{u}_i \cdot \varrho_i \nabla \frac{\mu_i}{T} = -\langle \mathbf{U}\,,\, \mathbf{R}\,\nabla \frac{\boldsymbol{\mu}}{T} \rangle \;?$$

[3] From here on $\mathbf{b}_i = \mathbf{b}$ for simplicity

Novel Closure Scheme

Consider diffusion velocities against an *undetermined reference velocity* $\mathbf{v}^*$:

$$\mathbf{u}_i^* = \mathbf{v}_i - \mathbf{v}^*.$$

Then

$$\mathbf{u}_i = \mathbf{u}_i^* - \sum_{k=1}^{N} y_k \mathbf{u}_k^*.$$

In short hand notation with $\mathbf{e} = (1, ..., 1)^\mathsf{T}$:

$$\mathbf{U} = \mathbf{P}\,\mathbf{U}^* \quad \text{with the projection } \mathbf{P} = \mathbf{I} - \mathbf{e} \otimes \mathbf{y}.$$

Then

$$\frac{1}{R}\zeta_{\mathrm{DIFF}} = -\langle \mathbf{P}\,\mathbf{U}^*, \mathbf{R}\,\nabla\frac{\boldsymbol{\mu}}{RT}\rangle = -\langle \mathbf{U}^*, \mathbf{P}^\mathsf{T}\,\mathbf{R}\,\nabla\frac{\boldsymbol{\mu}}{RT}\rangle$$

and there is <u>no constraint</u> on $\mathbf{U}^*$!

A First Closure

A first closure in this scheme:

$$\mathbf{U}^* = -\mathbf{A}\,\mathbf{P}^\mathsf{T}\,\mathbf{R}\,\nabla\frac{\boldsymbol{\mu}}{RT} \quad\Rightarrow\quad \mathbf{U} = -\mathbf{P}\,\mathbf{A}\,\mathbf{P}^\mathsf{T}\,\mathbf{R}\,\nabla\frac{\boldsymbol{\mu}}{RT}$$

with positive definite and symmetric **A**. This yields the mass diffusion fluxes

$$\mathbf{J} = -\mathbf{R}\,\mathbf{P}\,\mathbf{A}\,\mathbf{P}^\mathsf{T}\,\mathbf{R}\,\nabla\frac{\boldsymbol{\mu}}{RT}$$

Physical dimensions: $[\mathbf{A}] \neq \mathrm{m}^2\,\mathrm{s}^{-1} \;\Rightarrow\;$ **A** is not a diffusion matrix!

but note: A *diagonal* closure would be consistent!

Symmetric Form of Binary Product

Diffusive entropy production in molar-based form: $(\mu_i^{\text{mol}} := M_i\, \mu_i)$

$$\frac{1}{R}\zeta_{\text{DIFF}} \;=\; -\langle \mathbf{U}^*, \mathbf{R}\,\mathbf{P}\,\nabla \frac{\boldsymbol{\mu}}{RT}\rangle \;=\; -\langle \mathbf{U}^*, \mathbf{C}\,\mathbf{P}_{\text{mol}}\,\nabla \frac{\boldsymbol{\mu}^{\text{mol}}}{RT}\rangle$$

with $\mathbf{C} = \text{diag}(c_1, \ldots, c_N)$, $\mathbf{P}_{\text{mol}} = \mathbf{M}\mathbf{P}\mathbf{M}^{-1}$, $\mathbf{M} = \text{diag}(M_1, \ldots, M_N)$.

Diffusive entropy production with symmetrized binary product:

$$\frac{1}{Rc}\zeta_{\text{DIFF}} \;=\; -\langle \mathbf{X}^{1/2}\,\mathbf{U}^*, \mathbf{X}^{1/2}\,\mathbf{P}_{\text{mol}}\,\nabla \frac{\boldsymbol{\mu}^{\text{mol}}}{RT}\rangle$$

with $\mathbf{X} = \text{diag}(x_1, \ldots, x_N)$, $x_i = c_i/c$.

The Novel Closure

Final closure in the novel scheme:

$$\mathbf{X}^{1/2}\,\mathbf{U}^{*} \;=\; -\mathbf{D}\,\mathbf{X}^{1/2}\,\mathbf{P}_{\mathrm{mol}}\,\nabla\frac{\boldsymbol{\mu}^{\mathrm{mol}}}{RT}$$

with symmetric $\mathbf{D}$ being positive definite on $\{\sqrt{\mathbf{x}}\}^{\perp}$.

This yields the diffusion velocities

$$\mathbf{U} \;=\; -\mathbf{P}\,\mathbf{X}^{-1/2}\,\mathbf{D}\,\mathbf{X}^{1/2}\,\mathbf{P}_{\mathrm{mol}}\,\nabla\frac{\boldsymbol{\mu}^{\mathrm{mol}}}{RT}$$

Physical dimensions: $[\mathbf{D}] = \mathrm{m}^2\,\mathrm{s}^{-1} \;\Rightarrow\;$ $\mathbf{D}$ is a diffusion matrix!

The Novel Closure

Splitting into (diagonal) main and (binary) cross-diffusion:

$$\mathbf{D} = \mathcal{D} + \mathbf{X}^{1/2}\,\mathbf{K}\,\mathbf{X}^{1/2}$$

with diagonal $\mathcal{D}$ and symmetric, off-diagonal $\mathbf{K}$.

This yields the mass diffusion fluxes

$$\mathbf{J} = -\mathbf{P}^{\mathsf{T}}\,\mathbf{R}\,\big(\mathcal{D} + \mathbf{K}\,\mathbf{X}\big)\,\mathbf{M}\,\mathbf{P}\,\nabla\frac{\boldsymbol{\mu}}{RT}$$

Remaining degrees of freedom concerning $\mathbf{D}$, resp. $\mathbf{K}$!

The additional condition $\mathbf{K}\mathbf{e} = 0$ determines $\mathbf{K}$ uniquely.

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Positivity Requirements

MS-closure yields positive solutions due to structure of fluxes:

$$\mathbf{j}_i = -d_i(T, \varrho, \mathbf{y})\nabla \varrho_i + \varrho_i \, \mathbf{f}_i(T, \varrho, \nabla \varrho, \mathbf{y}, \nabla \mathbf{y}),$$

where $d_i(T, \varrho, \mathbf{y}) \to d_i^0(T, \varrho, y_1, .., y_{i-1}, y_{i+1}, .., y_N) > 0$ as $y_i \to 0+$, the $\mathbf{f}_i$ are non-singular.

Same structure for Onsager coefficients requires:

$$L_{ik} = l_{ik} \, y_k \quad \forall i \neq k \qquad \text{with regular } l_{ik}$$

Structure of Onsager coefficients:

$$L_{ik} = \varrho_i \big(a_i \, \delta_{ik} + y_k \, Q_{ik} \big),$$

where a_i, Q_{ik} are regular, $\mathbf{Q} = [Q_{ik}]$ is symmetric and off-diagonal.

The Different Closures

Fick-Onsager diffusion fluxes:

$$\mathbf{J}^{\mathrm{FO}} = -\mathbf{L}\,\nabla\frac{\boldsymbol{\mu}}{RT} \quad \text{with } \mathbf{L} = \mathbf{R}(\mathbf{A}+\mathbf{Q}\mathbf{Y})$$

$\mathbf{L} = \mathbf{L}^{\mathsf{T}}$ p.d. on $\{\mathbf{e}\}^{\perp}$, $\mathbf{L}\,\mathbf{e} = 0$, $\mathbf{A}$ diagonal, $\mathbf{Q}^{\mathsf{T}} = \mathbf{Q}$ off-diagonal.

Maxwell-Stefan diffusion fluxes:

$$\mathbf{J}^{\mathrm{MS}} = -\mathbf{L}\,\nabla\frac{\boldsymbol{\mu}}{RT} \quad \text{with } \mathbf{L} = \mathbf{B}^{-}\mathbf{R}$$

$\mathbf{B}^{-}$ group-inverse of $\mathbf{B}$, $B_{ik} = -y_i f_{ik}$, $B_{ii} = \sum_{j\neq i} y_j f_{ij}$, $\mathbf{B}\mathbf{Y}$ p.d. on $\{\mathbf{e}\}^{\perp}$.

Novel form of diffusion fluxes:

$$\mathbf{J} = -\mathbf{L}\,\nabla\frac{\boldsymbol{\mu}}{RT} \quad \text{with } \mathbf{L} = \mathbf{P}^{\mathsf{T}}\mathbf{R}(\mathcal{D}+\mathbf{K}\mathbf{X})\mathbf{M}\mathbf{P}$$

$\mathcal{D} = \mathrm{diag}(d_i)$, $\mathbf{K} = \mathbf{K}^{\mathsf{T}}$, $\mathbf{K}\mathbf{e} = 0$, $K_{ii} = 0$, $\mathcal{D} + \mathbf{X}^{1/2}\mathbf{K}\mathbf{X}^{1/2}$ p.d. on $\{\sqrt{\mathbf{x}}\}^{\perp}$.

Equivalence of the Different Closures

Theorem. (B./Druet. Theorem 7.1 and 7.2 in arXiv:2008.05327)

1. The Fick-Onsager, the Maxwell-Stefan and the new closure are (algebraically) equivalent.

2. The following are equivalent:

   1. Fick-Onsager closure such that $\mathbf{L} \geq d_0 \, \mathbf{P}^\mathsf{T} \, \mathbf{M} \, \mathbf{R} \, \mathbf{P}$,
   2. Maxwell-Stefan closure such that $\mathbf{B} \, \mathbf{Y} \geq d_0 \, \mathbf{P}^\mathsf{T} \, \mathbf{M}^{-1} \, \mathbf{Y} \, \mathbf{P}$,
   3. Novel closure such that

$$\inf_{\mathbf{b} \in \{\sqrt{\mathbf{x}}\}^\perp} \langle (\mathcal{D} + \mathbf{X}^{\frac{1}{2}} \, \mathbf{K} \, \mathbf{X}^{\frac{1}{2}}) \, \frac{\mathbf{b}}{|\mathbf{b}|}, \, \frac{\mathbf{b}}{|\mathbf{b}|} \rangle \geq d_0,$$

   where d_0 denotes a strictly positive, regular function depending only on (T, ϱ).

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Core-Diagonal Closure

The novel closure allows for a (core-)diagonal special case:

$$\mathbf{J} = -\mathbf{P}^\mathsf{T}\,\mathbf{R}\,\mathcal{D}\,\mathbf{M}\,\mathbf{P}\,\nabla\frac{\boldsymbol{\mu}}{RT}$$

with $\mathcal{D} = \mathrm{diag}(d_i)$, $\mathbf{R} = \mathrm{diag}(\varrho_i)$, $\mathbf{M} = \mathrm{diag}(M_i)$, $\mathbf{P} = \mathbf{I} - \mathbf{e}\otimes\mathbf{y}$.

In molar-based form:

$$\mathbf{J}^{\mathrm{mol}} = -\left[\mathbf{I} - \frac{c}{\varrho}\mathbf{x}\otimes\mathbf{m}\right]\mathcal{D}\,\mathbf{P}^\mathsf{T}\,\mathbf{C}\,\nabla\frac{\boldsymbol{\mu}^{\mathrm{mol}}}{RT}$$

How does the **Maxwell-Stefan form** of this case look like?

Core-Diagonal Closure

Maxwell-Stefan equations in molar form:

$$-\mathbf{B}^{\mathrm{mol}}\mathbf{J}^{\mathrm{mol}} = \mathbf{P}^{\mathsf{T}}\mathbf{C}\,\nabla\frac{\boldsymbol{\mu}^{\mathrm{mol}}}{RT},$$

with

$$B_{ij}^{\mathrm{mol}} = -\frac{x_i}{\text{Đ}_{ij}} \text{ for } i \neq j, \quad B_{ii}^{\mathrm{mol}} = \sum_{k\neq i}\frac{x_k}{\text{Đ}_{ik}}.$$

Insertion into core-diagonal closure yields:

$$\mathbf{J}^{\mathrm{mol}} = [\mathbf{I} - \frac{c}{\varrho}\mathbf{x}\otimes\mathbf{m}]\,\mathcal{D}\,\mathbf{B}^{\mathrm{mol}}\mathbf{J}^{\mathrm{mol}}.$$

Inversion yields

$$\mathbf{B}^{\mathrm{mol}}\mathbf{J}^{\mathrm{mol}} = \mathcal{D}^{-1}\left(\mathbf{I} - \frac{\mathbf{x}\otimes\mathcal{D}^{-1}\mathbf{e}}{\langle\mathbf{x},\mathcal{D}^{-1}\mathbf{e}\rangle}\right)\mathbf{J}^{\mathrm{mol}}.$$

Multicomponent Darken Equation

Maxwell-Stefan form of core-diagonal closure:

$$\frac{1}{\text{Đ}_{ik}} = \frac{d_i^{-1}\, d_k^{-1}}{\sum_{l=1}^{N} x_l d_l^{-1}} \qquad (i \neq k)$$

i.e.

$$\text{Đ}_{ik}(T, c, \mathbf{x}) = \sum_{l=1}^{N} \frac{x_l}{d_l(T, c, \mathbf{x})}\, d_i(T, c, \mathbf{x})\, d_k(T, c, \mathbf{x}) \qquad (i \neq k).$$

Multicomponent Darken equations[4]**:**

$$\text{Đ}_{ik} = \frac{D_{i,\mathrm{self}}\, D_{k,\mathrm{self}}}{D_{\mathrm{mix}}}, \quad \frac{1}{D_{\mathrm{mix}}} = \sum_{l=1}^{N} \frac{x_l}{D_{l,\mathrm{self}}}, \quad \frac{1}{D_{i,\mathrm{self}}} = \sum_{j=1}^{N} \frac{x_j}{D_{i,\mathrm{self}}^{x_j \to 1}}$$

with $D_{i,\mathrm{self}}^{x_j \to 1}$ the diffusivity of (dilute) species i in solvent species j.

[4] Liu, Vlugt, Bardow: Ind. End. Chem. Res. **50**, 10350-10358 (2011).

Final Conclusions

Remarks and Outlook:

- Novel closure yields explicit fluxes together with several advantages of the Maxwell-Stefan closure
- Positivity requirements lead to structural information which yields equivalence of the different closures
- Novel approach allows for (core-)diagonal closure which provides a rigorous fundament for the multicomponent Darken equation
- The structural information from the new closure can help to model the compositional dependence of the $Đ_{ik}$.
- The core-diagonal special case might stimulate the mathematical analysis.

Final Conclusions

Thank You for Your Attention !