Maxwell-Stefan models for fluid mixtures: derivation, analysis, stochastics

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Multi-species systems

- Most systems in nature are composed of multiple species
- Examples: tumor growth, lithium-ion batteries, pedestrian herding
- May be modeled on diffusive level by Maxwell-Stefan systems for partial densities ρ_i and given velocity V with $\sum_{i=1}^n \rho_i = \rho$:

$$\partial_t \rho_i + \operatorname{div}(\rho_i V + J_i) = r_i(\vec{\rho}), \quad \nabla \rho_i = -\sum_{j \neq i} C_{ij}(\rho_j J_i - \rho_i J_j)$$

- Total mass density solves $\partial_t \rho + \operatorname{div}(\rho V) = 0$
- First derivation by Maxwell (1866) and Stefan (1871)
- Extends Nernst-Planck eqs. (Duncan-Toor 1962, Dreyer et al. 2013)
- Aim of talk: derivation, existence analysis, stochastic PDE

Examples

$$\partial_t \rho_i + \operatorname{div} J_i = 0, \quad \nabla \rho_i = -\sum_{j \neq i} C_{ij}(\rho_j J_i - \rho_i J_j)$$

- Two-species systems: $\rho_1 + \rho_2 = 1$, $J_1 + J_2 = 0$

$$\partial_t \rho_1 + \operatorname{div} J_1 = 0, \quad \nabla \rho_1 = -c_{12}(\rho_2 J_1 - \rho_1 J_2) = -c_{12} J_1$$

  $\rightarrow$ linear diffusion equation

- Three-species systems: $\rho_1 + \rho_2 + \rho_3 = 1$

$$\partial_t \rho_i - \operatorname{div} \sum_{j=1}^{2} A_{ij}(\vec{\rho}) \nabla \rho_j = 0, \quad i = 1, 2$$

$$A(\vec{\rho}) = \frac{1}{a(\vec{\rho})} \begin{pmatrix} c_{22} + (c_{11} - c_{22})\rho_1 & (c_{11} - c_{12})\rho_1 \\ (c_{11} - c_{22})\rho_2 & c_{12} + (c_{11} - c_{12})\rho_2 \end{pmatrix}$$

  $\rightarrow$ cross-diffusion system with $A(\vec{\rho})$ generally not symm. pos. def.

Difficulties:

- Standard existence theory not applicable
- Maximum principles not available but $0 \le \rho_i \le 1$ expected
- Consistent thermodynamic modeling important for extensions

Derivation from Boltzmann equation

- Boltzmann transport equation for $f_i(x,v,t)$ in diffusive scaling

$$\varepsilon\partial_t f_i + v\cdot\nabla_x f_i = \frac{1}{\varepsilon}Q_i(f_i,f_i) + \frac{1}{\varepsilon}\sum_{j\neq i} Q_{ij}(f_i,f_j),\ \ i,j=1,\ldots,n$$

- Q_i mono-species, Q_{ij} bi-species collision operators
- Partial densities and fluxes:

$$\rho_i(x,t) = \int_{\mathbb{R}^3} f_i(x,v,t)dv, \quad \varepsilon(\rho_i v_i)(x,t) = \int_{\mathbb{R}^3} f_i(x,v,t)vdv$$

- Assume: collisions are elastic and conserve mass, $\sum_{i=1}^n \rho_i(x,0)=1$
- Ansatz: $f_i(x,v,t) = M_i := (2\pi)^{-3/2}\rho_i(x,t)\exp(-|v-\varepsilon v_i(x,t)|^2/2)$
- Insert into Boltzmann equation, compute moments, limit $\varepsilon\to 0$:

$$\partial_t\rho_i + \operatorname{div}(\rho_i v_i) = 0, \quad \nabla\rho_i = -\sum_{j\neq i} C_{ij}\rho_i\rho_j(v_i - v_j), \quad \sum_{i=1}^n \rho_i = 1$$

- Formal derivation: Takata-Aoki 1999, Boudin-Grec-Salvarani 2015
- Rigorous derivation: Bondesan-Briant 2019

Derivation from Euler equations

- Euler equations with energy E:

$$\partial_t\rho_i + \operatorname{div}(\rho_i v_i) = 0$$
$$\partial_t(\rho_i v_i) + \operatorname{div}(\rho_i v_i \otimes v_i) = -\rho_i\nabla\frac{\delta E}{\delta\rho_i}(\vec\rho) - \frac{1}{\varepsilon}\sum_{j=1}^n b_{ij}\rho_i\rho_j(v_i - v_j)$$

- Barycentric velocity: $V = \rho^{-1}\sum_{i=1}^n \rho_i v_i = V^\varepsilon + O(\varepsilon^2)$
- Chapman-Enskog expansion: $\rho_i = \rho_i^\varepsilon + O(\varepsilon^2)$, $v_i = v_i^\varepsilon + O(\varepsilon^2)$

$$\partial_t\rho_i^\varepsilon + \operatorname{div}(\rho_i^\varepsilon V^\varepsilon) = \varepsilon\operatorname{div}\sum_{j=1}^n D_{ij}(\vec\rho^\varepsilon)\nabla\frac{\delta E}{\delta\vec\rho} + O(\varepsilon^2)$$
$$\partial_t(\rho^\varepsilon V^\varepsilon) + \operatorname{div}(\rho^\varepsilon V^\varepsilon \otimes V^\varepsilon) = -\sum_{i=1}^n \rho_i^\varepsilon\nabla\frac{\delta E}{\delta\rho_i} + O(\varepsilon^2)$$

- $V^\varepsilon = 0$ gives Maxwell-Stefan system in gradient-flow formulation
- Rigorous limit (relative entropy method): Huo-A.J.-Tzavaras 2019

$$\|(\rho_i^\varepsilon)^{1/2}(v_i - v_i^\varepsilon)\|_{L^2} + \|\rho_i - \rho_i^\varepsilon\|_{L^2} \le C\varepsilon$$

- Rigorous limit (Chen-Levermore-Liu method): Boudin-Grec-Pavan 2019

Existence analysis of Maxwell-Stefan systems

$$\partial_t \rho_i + \operatorname{div} J_i = r_i(\vec{\rho}), \quad \nabla \rho_i = -\sum_{j \neq i} C_{ij}(\rho_j J_i - \rho_j J_i) =: (CJ)_i$$

$$\rho_i(0) = \rho_i^0 \quad \text{in } \Omega, \; i = 1, \ldots, n, \quad \text{no-flux b.c.}$$

- Aim: formulate as cross-diffusion system

$$\partial_t \rho_i - \operatorname{div} \sum_{j=1}^{n} A_{ij} \nabla \rho_j = r_i(\vec{\rho}), \quad i = 1, \ldots, n$$

- Problem 1: need to invert relation $\nabla \rho_i \leftrightarrow J_i$ but not invertible since $\sum_{i=1}^{n} \rho_i = 1 \Rightarrow \sum_{i=1}^{n} \nabla \rho_i = 0$
- Solution: invert $\nabla \vec{\rho} = CJ$ on $\ker(C)^{\perp} \Rightarrow J^* = (C^*)^{-1} \vec{\rho}^*$, where $\vec{\rho}^* = (\rho_1, \ldots, \rho_{n-1})$, $J^* = (J_1, \ldots, J_{n-1})$

$$\partial_t \rho_i - \operatorname{div} \sum_{j=1}^{n-1} (C^*)^{-1}_{ij} \nabla \rho_j = r_i(\rho^*), \; i = 1, \ldots, n-1, \; \rho_n = 1 - \sum_{i=1}^{n-1} \rho_i$$

- Problem 2: matrix $(C^*)^{-1}$ not positive semi-definite
- Solution: formulation in entropy variables (chemical potentials)

Entropy variables

$$\partial_t \rho_i - \operatorname{div} \sum_{j=1}^{n-1} (C^*)^{-1}_{ij} \nabla \rho_j = r_i(\rho^*) \quad \text{in } \Omega,\ t > 0,\ i = 1, \ldots, n-1$$

- Entropy density: $h(\vec{\rho}^*) = \sum_{i=1}^n \rho_i(\log \rho_i - 1)$, $\rho_n = 1 - \sum_{i=1}^{n-1} \rho_i$
- Entropy variables (chem. potentials): $w_i = \partial h / \partial \rho_i$, $i = 1, \ldots, n-1$

$$\partial_t \rho_i - \operatorname{div} \sum_{j=1}^{n-1} B_{ij}(\vec{w}) \nabla w_j = r_i(\vec{\rho}), \quad i = 1, \ldots, n-1$$

Benefits:

- Diffusion matrix $B(\vec{w}) = (C^*)^{-1} h''(\vec{\rho}^*)^{-1}$ positive definite
- Lower and upper bounds: $w_i = \log(\rho_i / \rho_n)$ can be inverted

$$\rho_i = \frac{e^{w_i}}{1 + \sum_{j=1}^{n-1} e^{w_j}} \in (0, 1)$$

- A priori estimates from entropy production:

$$\frac{d}{dt} \int_\Omega h(\vec{\rho}^*) dx + \kappa \int_\Omega \sum_{i=1}^{n-1} |\nabla \sqrt{\rho_i}|^2 dx \le \int_\Omega \sum_{i=1}^{n-1} r_i \cdot \frac{\partial h}{\partial \rho_i} dx \le 0$$

Global existence of weak solutions

$$\partial_t \rho_i - \operatorname{div} \sum_{j=1}^{n-1} (C^*)^{-1}_{ij} \nabla \rho_j = r_i(\rho^*) \quad \text{in } \Omega,\ t > 0,\ i = 1, \ldots, n-1$$

Theorem (A.J.-Stelzer 2013)

Let $\rho_i^0 \geq 0$, $\sum_{i=1}^n \rho_i^0 \leq 1$, $\sum_{i=1}^n r_i = 0$, $\sum_{i=1}^n r_i \log \rho_i \leq 0$. *Then* $\exists$ *weak solution* $\rho_i \in L^2(0,T;H^1(\Omega))$, $\partial_t \rho_i \in L^2(0,T;H^{-2}(\Omega))$, *and*

$$0 \leq \rho_i \leq 1 \quad \text{in } \Omega,\ t > 0,\ i = 1, \ldots, n-1, \quad \rho_n = 1 - \sum_{i=1}^{n-1} \rho_i \geq 0$$

Boundedness-by-entropy method: (A.J. 2015)

- Approximations: implicit Euler in time, higher-order regularization in space (important: preserves entropy structure)
- Fixed-point argument for approximated system: compactness comes from higher-order regularization term
- De-regularization limit: compactness comes from entropy estimate and nonlinear discrete Aubin-Lions lemma

Previous results: Giovangigli-Massot 1998, Bothe 2011

Extension: Maxwell-Stefan-Poisson systems

$$\partial_t \rho_i + \operatorname{div} J_i = r_i(\vec{\rho}), \quad D_i = -\sum_{j \neq i} C_{ij}(\rho_j J_i - \rho_i J_j), \quad \rho_i(0) = \rho_i^0 \quad \text{in } \Omega$$

$$J_i \cdot \nu = 0 \text{ on } \partial\Omega = \Gamma_D \cup \Gamma_N, \quad \Phi = \Phi_D \text{ on } \Gamma_D, \quad \nabla\Phi \cdot \nu = 0 \text{ on } \Gamma_N$$

- Molar masses M_i, molar concentrations $c_i = \rho_i / M_i$, molar fractions $x_i = c_i / c$ with $c = \sum_{j=1}^n c_j$
- Electric potential Φ computed from $-\lambda\Delta\Phi = \sum_{i=1}^n z_i c_i + f$, electric charge z_i, background charge f
- Driving forces: $D_i = \nabla x_i + (z_i x_i - (\vec{z} \cdot \vec{x})\rho_i)\nabla\Phi$

Boundedness-by-entropy method:

- Entropy density:

$$h(\vec{\rho}) = c \sum_{i=1}^n x_i \log x_i + \frac{\lambda}{2} |\nabla(\Phi - \Phi_D)|^2$$

- Entropy variables:

$$w_i = \frac{\partial h}{\partial \rho_i} = \frac{\log x_i}{M_i} - \frac{\log x_n}{M_n} + \left(\frac{z_i}{M_i} - \frac{z_n}{M_n} \right) \Phi$$

Extension: Maxwell-Stefan-Poisson systems

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$$J_i\cdot\nu = 0 \text{ on } \partial\Omega = \Gamma_D\cup\Gamma_N, \quad \Phi = \Phi_D \text{ on } \Gamma_D, \quad \nabla\Phi\cdot\nu = 0 \text{ on } \Gamma_N$$

- Formulation in entropy variables:

$$\partial_t\rho_i - \operatorname{div}\sum_{j=1}^{n-1} B_{ij}\nabla w_i = r_i(\vec x), \quad i = 1,\ldots,n-1$$

- Entropy production inequality:

$$\frac{d}{dt}\int_\Omega h(\vec\rho)dx + \int_\Omega\sum_{i,j=1}^{n-1}\underbrace{B_{ij}\nabla w_i\cdot\nabla w_j}_{\geq\kappa\sum_{i=1}^{n-1}|\nabla\sqrt{x_i}|^2} \leq C(\Phi_D) + \int_\Omega\sum_{i=1}^{n-1} r_i(\vec x)\frac{\partial h}{\partial\rho_i}dx$$

Theorem (A.J.-Leingang 2019)

Let $\rho_i^0\geq 0$, $\sum_{i=1}^n\rho_i^0 = 1$, $\sum_{i=1}^n r_i\log x_i/M_i\leq C$.
Then $\exists$ *weak solution* $(\rho_1,\ldots,\rho_{n-1},\Phi)$ *such that* $0\leq\rho_i\leq 1$,

$$x_i = \frac{\rho_i}{cM_i}, \ \Phi\in L^2(0,T;H^1), \quad \partial_t\rho_i\in L^2(0,T;(H^1)')$$

Stochastic Maxwell-Stefan systems

$$d\rho_i - \operatorname{div}\Big(\sum_{j=1}^n A_{ij}(\vec{\rho})\nabla\rho_j\Big)dt = \sum_{j=1}^n \sigma_{ij}(\vec{\rho})\circ dW_j(t) \quad \text{in } \mathcal{O},\ t>0$$

- Partial concentrations $\rho_i = \rho_i(x,\omega,t)$, $x\in\mathcal{O}$, $\omega\in\Omega$, $t>0$
- Matrix A_{ij} corresponds to $(C^*)^{-1}$ in Maxwell-Stefan system
- Finite-dimensional Wiener process $(W_1,\ldots,W_n)$, models external perturbations or lack of knowledge of source terms
- Weak formulation: For all $\phi\in H^1(\mathcal{O})$

$$\int_{\mathcal{O}}\rho_i(t)\phi dx - \int_{\mathcal{O}}\rho_i(0)\phi dx = \sum_{j=1}^n\int_0^t\int_{\mathcal{O}} A_{ij}\nabla\rho_j\cdot\nabla\phi dxds + \sum_{j=1}^n\int_{\mathcal{O}}\Big(\int_0^t\sigma_{ij}\circ dW_j(s)\Big)\phi dx$$

- Stratonovich integral: needed for approximation argument

$$\int_0^t\sigma\circ dW(s) = L^2\text{-}\lim_{s\to 0}\sum_{i=0}^{k-1}\frac{\sigma(t_i+s)+\sigma(t_i)}{2}(W(t_i+s)-W(t_i))$$

Stochastic Maxwell-Stefan systems

$$d\rho_i - \operatorname{div}\left(\sum_{j=1}^n A_{ij}(\vec\rho)\nabla\rho_j\right)dt = \sum_{j=1}^n \sigma_{ij}(\vec\rho)\circ dW_j(t) \quad \text{in } \mathcal{O},\ t>0$$

- Martingale solution = weak solution in probabilistic sense: $\exists\ \widetilde{U}$ stochastic basis, $\widetilde{W_j}$ Wiener processes, $\widetilde{\rho}_i$ stochastic processes such that $\widetilde{\rho}_i \in L^2(\widetilde{\Omega}; L^2(0,T;H^1(\mathcal{O})))$, and for all $\phi \in H^1(\mathcal{O})$,

$$\int_{\mathcal{O}} \widetilde{\rho}_i(t)\phi dx - \int_{\mathcal{O}} \widetilde{\rho}_i(0)\phi dx = \sum_{j=1}^n \int_0^t \int_{\mathcal{O}} A_{ij}(\widetilde{\rho})\nabla\widetilde{\rho}_j \cdot \nabla\phi dx ds + \sum_{j=1}^n \int_{\mathcal{O}} \left(\int_0^t \sigma_{ij}(\widetilde{\rho})\circ d\widetilde{W_j}(s)\right)\phi dx$$

- Stochastic processes $\widetilde{\rho}_i(0)$ and ρ_i^0 have the same laws

Theorem (Dhariwal-Huber-A.J.-Kuehn-Neamtu 2019)

Under certain assumptions on ρ_i^0 and $\sigma_{ij}(\vec\rho)$, there exists a global martingale solution such that $0 \le \widetilde{\rho}_i \le 1$, $\sum_{i=1}^n \widetilde{\rho}_i \le 1$.

Stochastic Maxwell-Stefan systems

$$d\rho_i - \operatorname{div}\left(\sum_{j=1}^n A_{ij}(\vec\rho)\nabla\rho_j\right)dt = \sum_{j=1}^n \sigma_{ij}(\vec\rho)\circ dW_j(t) \quad \text{in } \mathcal{O},\ t>0$$

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Ideas of proof: N: Galerkin dimension, η: time step in Wang-Zakai approx.

- Stochastic Galerkin method: strong solution $\rho_i^{(N)}$ up to stopping time
- Stochastic Galerkin method & Wang-Zakai approximation of $W_j(t)$: global-in-time ODE solution $\rho_i^{(N,\eta)}$
- Wang-Zakai limit $\eta\to 0$: $\lim_{\eta\to 0}\rho_i^{(N,\eta)} = \rho_i^{(N)}$ up to stopping time
- Boundedness-by-entropy estimate and Itô lemma for $\rho_i^{(N)}$
- Various deregularization limits and $N\to\infty$ gives martingale solution

Summary and perspectives

Summary:

- Derivation of Maxwell-Stefan systems from Boltzmann or Euler eqs.
- Existence analysis using boundedness-by-entropy method
- Extensions with electrical or stochastic effects

Perspectives:

- Partial regularity of weak solutions to Maxwell-Stefan systems (Braukhoff-Raithel-Zamponi, in progress)
- Strong solutions for stochastic Maxwell-Stefan systems (Dhariwal-Huber-A.J.-Kuehn, in progress)
- Maxwell-Stefan systems for heat-conducting mixtures (Helmer-A.J., in progress)
- Stationary Maxwell-Stefan systems coupled to fluid models: Maxwell-Stefan & compressible Navier-Stokes-Fourier equations (Buliček-A.J.-Pokorný-Zamponi, in progress)