

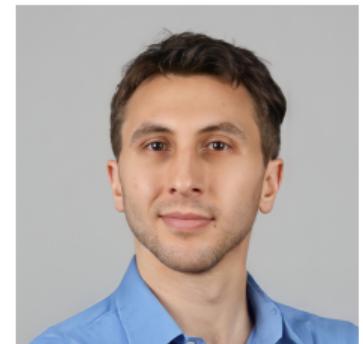
# Discretising the Navier–Stokes–Onsager–Stefan–Maxwell equations of multicomponent flow

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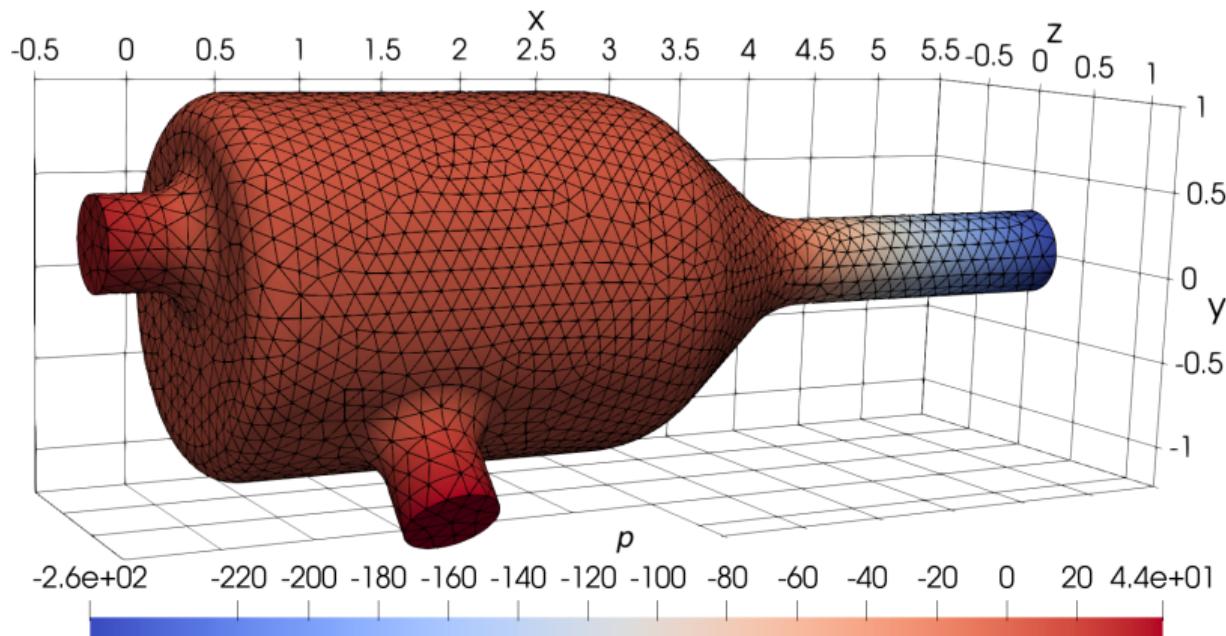
This talk

We describe a class-I model, the *Navier–Stokes–Onsager–Stefan–Maxwell* equations.

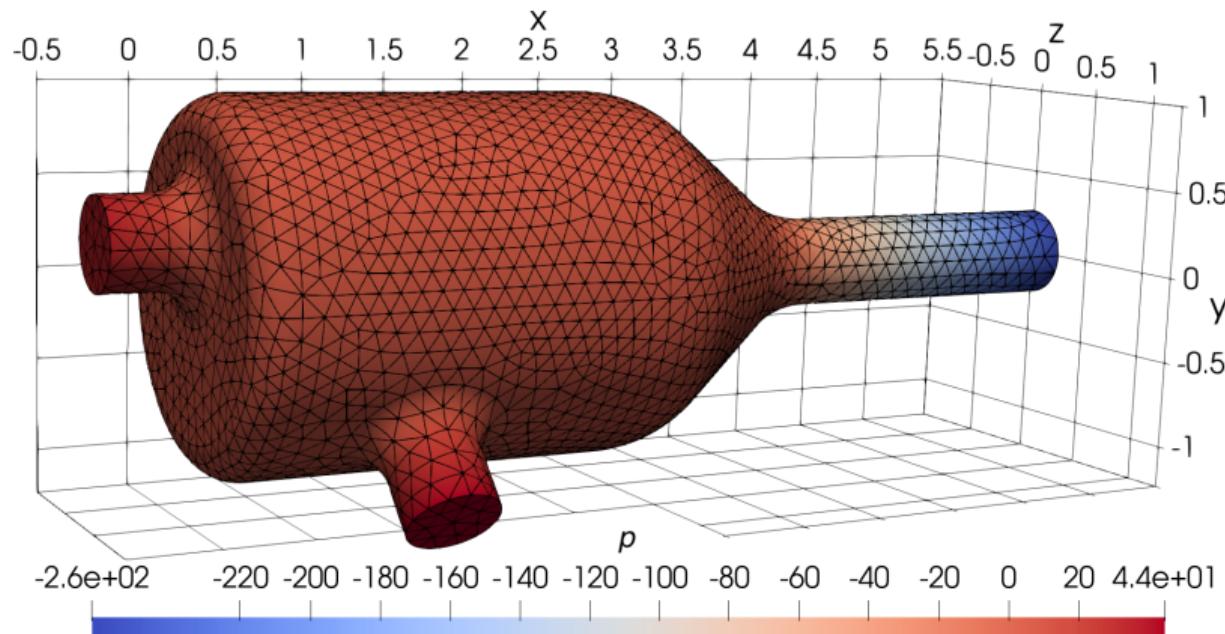
## Section 2

Examples

We consider the microfluidic mixing of benzene ( $C_6H_6$ ) and cyclohexane ( $C_6H_{12}$ ).

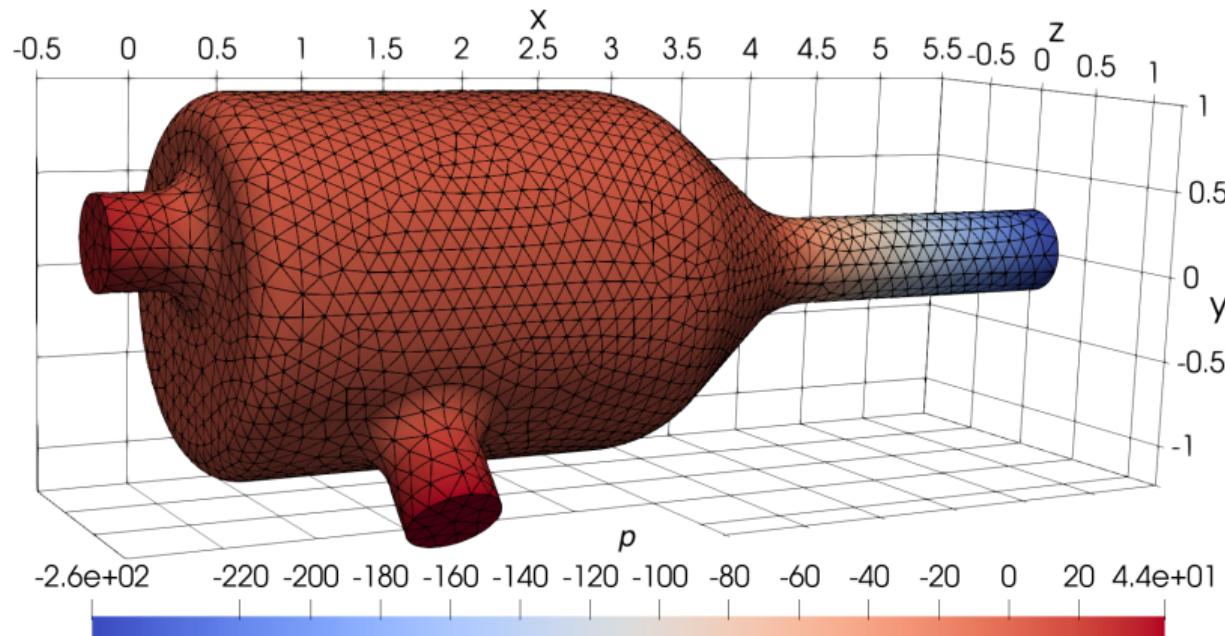


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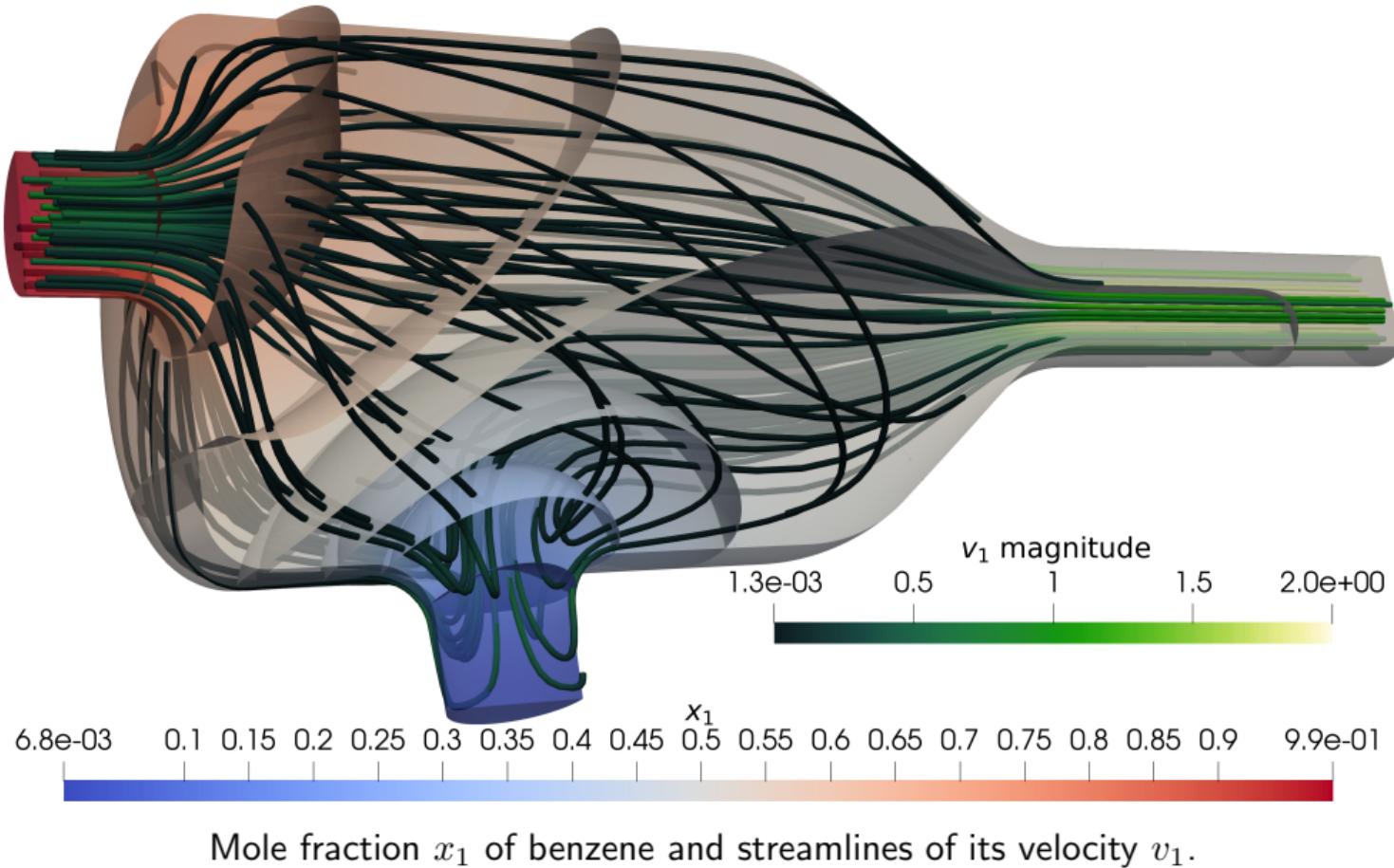
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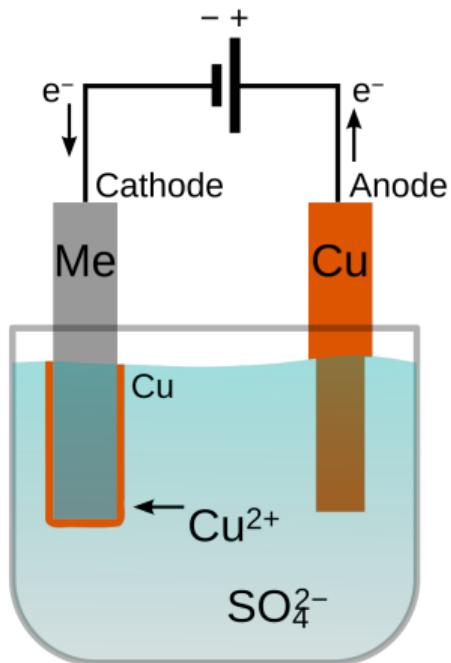


This forms a *non-ideal* mixture with nonlinear activity coefficients in the thermodynamic equation of state: interactions between B-C molecules different to B-B or C-C.

We use order five finite elements in a curved geometry: discrete problem has 6m unknowns. 5 / 42



A Hull cell is a device used to test electroplating.

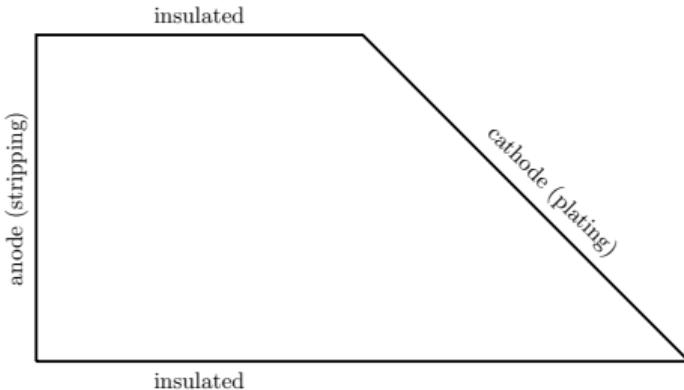


The electroplating of copper.



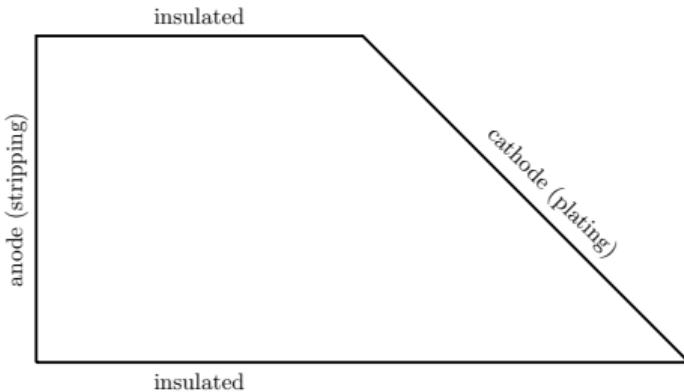
A Hull cell.

We consider  $\text{LiPF}_6$  in ethyl methyl carbonate (EMC), which dissolves into  $\text{Li}^+$  and  $\text{PF}_6^-$ .



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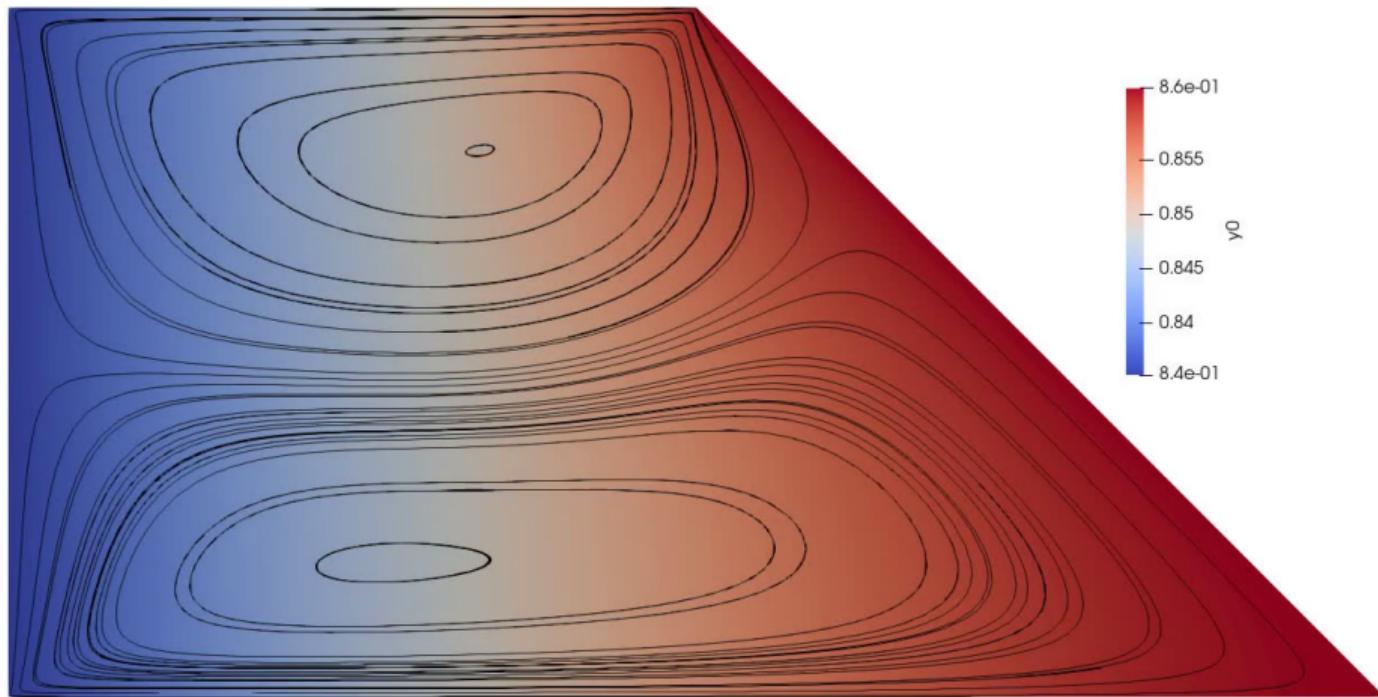
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We fit ionic conductivity, Stefan–Maxwell diffusivity, Darken factor, cation transference number, and density from experimental data reported by

-  A. A. Wang et al. "Shifting-reference concentration cells to refine composition-dependent transport characterization of binary lithium-ion electrolytes". In: *Electrochimica Acta* 358 (2020), p. 136688. DOI: 10.1016/j.electacta.2020.136688.



Solvent streamlines and mole fraction.

## Section 3

The model

We present the model in isothermal, nonreactive conditions.

There is a beautiful, thermodynamically rigorous derivation of a thermal class-II model with chemical reactions and its associated class-I reduction in



D. Bothe and W. Dreyer. “Continuum thermodynamics of chemically reacting fluid mixtures”. In: *Acta Mechanica* 226.6 (2014), pp. 1757–1805. DOI: 10.1007/s00707-014-1275-1.



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... but our numerics haven't gotten that far yet.



Wolfgang Dreyer

## Subsection 1

### Continuity equations

Let  $\rho_i$  and  $v_i$  denote the mass density and velocity of species  $i$ ,  $i = 1 : N$ .

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The relation

$$\rho v = \sum_i \rho_i v_i$$

is the *mass-average constraint on the fluxes*.

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This is reasonable when

$$\frac{UV}{C^2} \ll 1$$

where  $U$  is the reference diffusive speed,  $V$  is the reference speed, and  $C = \sqrt{p_0/\rho_0}$  is on the order of the speed of sound. Here  $p_0$  is the reference pressure and  $\rho_0$  the reference density.

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## Onsager relations

We employ Onsager's linear framework for constitutive relations (more later).

## Subsection 2

### Momentum equation

The balance equation we solve for  $v$  is the usual Cauchy momentum equation with pressure  $p$ , deviatoric stress  $\mathbb{S}$  and body force  $f$ :

$$\partial_t(\rho v) + \nabla \cdot (\rho v \otimes v) + \nabla p - \nabla \cdot \mathbb{S} = \rho f.$$



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We again require a constitutive equation relating  $\mathbb{D}v$  to  $\mathbb{S}$ . We employ the usual Newtonian relation:

$$\mathbb{S} = 2\mu\mathbb{D}v + \lambda(\nabla \cdot v)\mathbb{I}.$$

### Subsection 3

Constitutive relations for transport

The entropy production  $\xi$  in the isothermal, nonreactive case is given by

$$T\xi = \sum_i d_i \cdot (v_i - v) + \mathbb{S} : \mathbb{D}v$$

where  $d_i$  are the *diffusion driving forces*

$$d_i := -c_i \nabla \mu_i + (\rho_i / \rho) \nabla p,$$



Lars Onsager

with  $\mu_i$  the *(electro)chemical potential* of species  $i$ ,  $c_i := \rho_i / M_i$  its molar concentration, and  $M_i$  is its molar mass.

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Employing the constitutive framework of Onsager yields

$$d_i = \sum_{j=1}^N \mathcal{M}_{ij}(v_j - v), \quad \mathbb{D}v = \mathcal{A}\mathbb{S},$$

where  $\mathcal{M}$  and  $\mathcal{A}$  are symmetric positive semi-definite operators (at least).

## Warning

Linear does not mean simple!

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The Onsager transport matrix  $\mathcal{M}_{ij}$  models the drag exerted between species, and encodes Stefan–Maxwell coefficients:

$$\mathcal{M}_{ij} := \begin{cases} -\frac{RTc_i c_j}{\mathcal{D}_{ij} c_T} & \text{if } i \neq j, \\ \sum_{k=1, k \neq i}^n \frac{RTc_i c_k}{\mathcal{D}_{ik} c_T} & \text{if } i = j, \end{cases}$$

where  $c_T := \sum_i c_i$ .  $\mathcal{M}$  thus depends nonlinearly on our state variables. The Stefan–Maxwell diffusivities  $\mathcal{D}_{ij}$  can also depend on concentrations and pressure.

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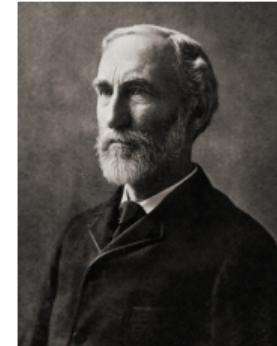
More significantly, the matrix  $\mathcal{M}_{ij}$  is singular with nullspace of constants (if all species are present in nonzero amounts). The Onsager–Stefan–Maxwell equations

$$d_i = \sum_{j=1}^N \mathcal{M}_{ij}(v_j - v)$$

therefore appear ill-posed?

The remedy is to realise that the diffusion driving forces must satisfy the *Gibbs–Duhem* relation

$$\sum_i d_i = 0.$$



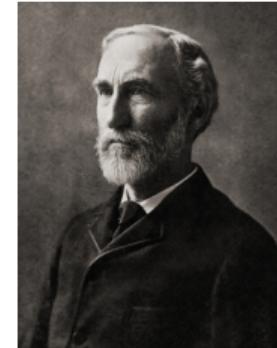
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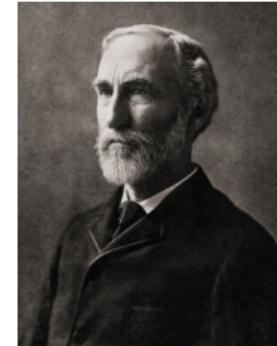
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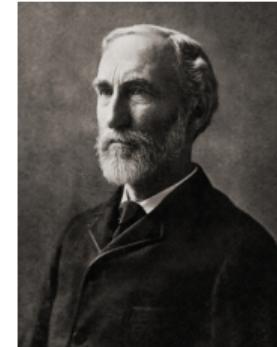
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Imposing the mass-average constraint

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finally yields a unique solution for  $\{v_i\}$ .



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Pierre Duhem

## Subsection 4

Constitutive relations for thermodynamics

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$$\partial_t \rho_i + \nabla \cdot (\rho_i v_i) = 0 \quad \forall i \in 1 : N,$$

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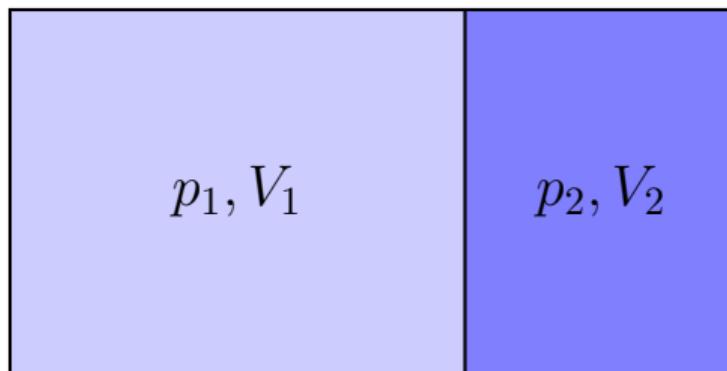
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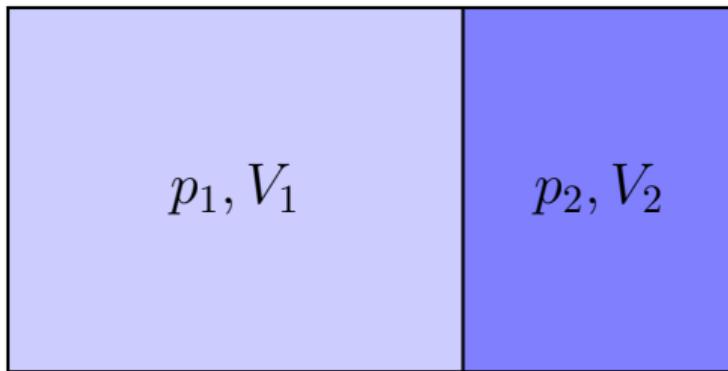
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This still is not closed: the diffusion driving forces depend on chemical potentials  $\{\mu_i\}$ , but do not yet have equations for them.

To understand chemical potentials, it's useful to first think about two homogeneous gases initially separated by a partition.

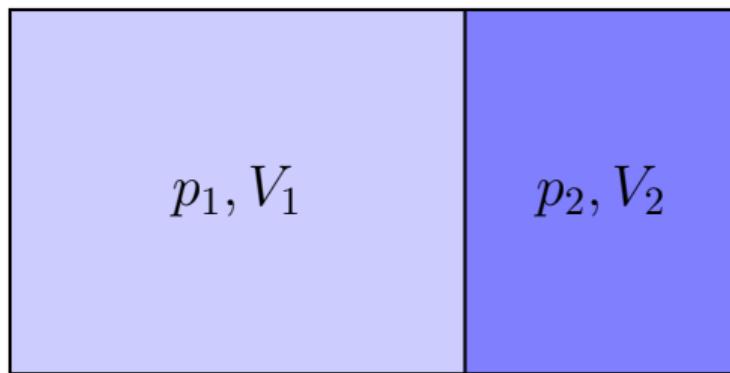


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What happens when the partition is removed?

The two gases *exchange volume until the pressures equalise*. Why?

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For any thermodynamic potential, these variables can be paired, with units of energy:

$$dG = -TdS + VdP + \sum_i \mu_i dn_i,$$

where  $G$  is the Gibbs free energy.



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Formally, the chemical potentials are the partial derivatives of the Gibbs free energy, holding everything else constant:

$$\mu_i = \left( \frac{\partial G}{\partial n_i} \right)_{T,p,\{n_j, j \neq i\}} .$$

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Particles tend to move from higher to lower chemical potentials because this reduces the free energy.

For the thermodynamics it is convenient to reformulate the equations in terms of mole fractions

$$x_i := \frac{c_i}{c_T}$$

instead of partial densities  $\rho_i$ . These satisfy  $\sum_i x_i = 1$ , so one is redundant.

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With this, we close the system with given thermodynamic relations of the form

$$\mu_i = g_i(T, p, \{x_j\})$$

$$1/c_T = \sum_i x_i V_i(T, p, \{x_j\})$$

where  $\{g_i\}$  are *partial molar Gibbs functions* and  $\{V_i\}$  are *partial molar volume functions*.

It might be useful to see concrete examples of these. For the benzene and cyclohexane mixture, we employ a Margules model

$$\mu_1 = g_1(T, p, x_1, x_2) = p/c_1^{\text{ref}} + RT \ln x_1 + RT x_2^2 (A_{12} + 2(A_{21} - A_{12})x_1),$$
$$\mu_2 = g_2(T, p, x_1, x_2) = p/c_2^{\text{ref}} + RT \ln x_2 + RT x_1^2 (A_{21} + 2(A_{12} - A_{21})x_2).$$



Max Margules

The reference values and coefficients are drawn from *Perry's Chemical Engineers' Handbook*:



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The partial molar volumes are then computed from

$$V_i := \left( \frac{\partial \mu_i}{\partial p} \right)_{T, \{x_j\}} .$$

## Subsection 5

Problem statement

We are now in a position to state the PDE system to solve:

$$\partial_t \rho_i + \nabla \cdot (\rho_i v_i) = 0 \quad \forall i \in 1 : N,$$

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$$\rho_i = x_i M_{iCT} \quad \forall i \in 1 : N,$$

$$\sum_j x_j = 1,$$

$$\mu_i = g_i(T, p, \{x_j\}) \quad \forall i \in 1 : N,$$

$$c_T^{-1} = \sum_j x_j V_j(T, p, \{x_j\}).$$

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$$\partial_t \rho_i + \nabla \cdot (\rho_i v_i) = 0 \quad \forall i \in 1 : N,$$

$$\partial_t(\rho v) + \nabla \cdot (\rho v \otimes v) + \nabla p - \nabla \cdot (\mathcal{A}^{-1} \mathbb{D}v) = \rho f,$$

$$\rho = \sum_j \rho_j,$$

$$\rho v = \sum_j \rho_j v_j,$$

$$d_i(T, p, \{\rho_j\}, \{\mu_j\}) = \sum_j \mathcal{M}_{ij}(T, p, \{\rho_l\})(v_j - v) \quad \forall i \in 1 : N,$$

$$\rho_i = x_i M_{iCT} \quad \forall i \in 1 : N,$$

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## Section 4

Simplifications

We should relate our PDE system to more familiar ones.

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### Dilute regime

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### Consequence

The system reduces to usual Navier–Stokes + decoupled convection-diffusion equations.

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An added benefit: Stefan–Maxwell diffusivities are much better approximated by constants.

## Section 5

Discretisation

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Our current preferred variational formulation solves

### Primary variables

$$\begin{aligned}\{x_i\} &\in [L^2]^N, \\ \{\mu_i\} &\in [L^2]^N, \\ v &\in H^1 \otimes \mathbb{R}^d, \\ p &\in L^2, \\ \rho^{-1} &\in H^1, \\ \{J_i\} &\in [H(\text{div})]^N\end{aligned}$$

where the species mass fluxes relate to the species velocities by

$$J_i = \rho_i v_i.$$

The other variables are eliminated algebraically.

We have a “chain” of constraints:

1. For mass continuity  $\partial_t \rho + \nabla \cdot (\rho v) = 0$  to hold, we must satisfy the mass-average constraint

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The interplay between these constraints, and to what extent they imply one another, is very subtle, especially upon discretisation.

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One strategy is to neglect pressure diffusion, eliminate one of the species velocities (say  $v_N$ ), and invert the Onsager transport matrix to get the *Onsager–Fick* formulation:

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However, this has several disadvantages:

- ▶ only works for simple expressions for  $\mu_i$ ;
- ▶ it neglects pressure diffusion (and other effects);
- ▶ it breaks the symmetry among the species;
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This approach is not going to be structure-preserving.

Instead, we adopt the *augmentation strategy* proposed by Helfand in 1960.

Define  $\omega_i := \rho_i / \rho$ , the mass fraction of species  $i$ . For an augmentation parameter  $\gamma > 0$ , we replace the Onsager–Stefan–Maxwell equations by

$$d_i + \underline{\gamma\omega_i v} = \sum_j \mathcal{M}_{ij}(v_j - v) + \underline{\gamma\omega_i\omega_j(v_j - v)}$$



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It turns out to be advantageous to add a dual augmentation to the momentum balance:

$$\partial_t(\rho v) + \nabla \cdot (\rho v \otimes v) + \nabla p - \nabla \cdot \mathbb{S} + \underline{\gamma v} - \underline{\gamma \sum \omega_j v_j} = \rho f.$$

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These are for incompressible flow, but they arise here, because instead of

$$\operatorname{div} v = 0$$

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We discretise  $(\{J_i\}, \{\mu_i\}, \{x_i\})$  using mixed-Poisson elements, e.g.

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With this we can prove convergence and quasi-optimality of the discretisation for a Picard linearisation.

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Solving the Newton iteration threw up many unanticipated subtleties.

First, the pressure diffusion term  $\nabla p$  in  $d_i$  appears to lead to suboptimal convergence by one power of  $h$ . It's not clear how to circumvent this.

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Second, we need to add 'density consistency terms'. For the true solution, we have

$$v \cdot \nu = \sum_i \rho^{-1} J_i \cdot \nu,$$

where  $\nu$  is the outward normal on  $\partial\Omega$ , but discretely we only satisfy the mass-average constraint approximately

$$v_h \cdot \nu \approx \sum_i \rho_h^{-1} J_{h,i} \cdot \nu,$$

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However, we have solved these problems and now appear to have robust solvers in place!

## Section 6

Conclusions

## Good news

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## Good news

I still think there are many important applications to be tackled.

Our immediate next steps are to use the thermal, electroneutral equations to simulate puzzling experiments for LiPF<sub>6</sub> in EMC.

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A key numerical question is efficient solvers. We now have excellent preconditioners for the non-ideal, thermal Onsager–Stefan–Maxwell equations with specified mass-average velocity, and we are starting on the full equations.

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## Future work

Numerical analysis, applications in electrochemistry and physiology, porous media, non-Newtonian mixtures, phase change, chemical reactions, ....