



FACULTY  
OF MATHEMATICS  
AND PHYSICS  
Charles University

## LECTURE NOTES

Kamil Belán

# Theory of Mixtures

Based on the lecture by doc. Ondej Souek

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# 1 Introduction

Surprisingly, a *mixture* does not have a good universal definition. It can be *informally* said, that a mixture is a *more sophisticated* material.

- from geophysics: thermohaline circulation in oceans<sup>1</sup>, *porous media flows*<sup>2</sup>, avalanches, pollution spreading, phase transitions and changes (partial melting, glaciology), liquefaction of sediments
- from astrophysics: plasmas, gaseous mixtures, stellar mixtures
- from biophysics: flow of blood through tissue, membrane processes
- from chemistry: stoichiometry, chemical equilibrium, chemical kinetics
- from material science: composite materials

<sup>1</sup> Convection flows due to differences in densities and concentrations.

<sup>2</sup> This branch is having a renaissance period; a lot of money has been dumped into this.

There can be in fact more approaches to the theory of mixtures.

**Lemma 1.1** (Approach I: Molecular mixing). We imagine that the mixing of the constituents happens at a molecular level; we are thus discussing *multicomponent continuum theory*, or the so called *mixture theory*. At each point of the continuum, all the constituents are present

**Lemma 1.2** (Approach II: Multi-phase theory). The mixture is "less mixed": there exists an ensemble of simpler continua separated by interfaces. It is interesting that the multicomponent continuum theory can be obtained from multiphase theory through some kind of averaging.

# Kinematics of mixtures

As always, let us begin with the description of motion - *kinematics*.

**Lemma 2.1** (Postulate of co-occupancy, approach I). At each point of the mixture, *all components* are present at *all times*.

This postulate has serious consequences. At a chosen time  $t > 0$ , we suppose all  $N$  configurations are coexisting at a single point  $\mathbf{x}$ . On the other hand, each of the components can possess a *distinct reference configuration*. This means

$$\mathbf{x} \in \kappa_t(\mathcal{B}) : \mathbf{x} = \chi_1(t, \mathbf{X}_1) = \cdots = \chi_N(t, \mathbf{X}_N),$$

where  $\chi_\alpha(t, \mathbf{X}_\alpha)$ ,  $\alpha \in \{1, \dots, N\}$  are the motions of each component.

## 2.1 Basic quantities

**Definition 2.3** (Gradient). The referential gradient of a function  $\Phi$  is given as

$$(\text{Grad } \Phi)_K = \frac{\partial \Phi}{\partial X_\alpha^K}, \alpha = 1, \dots, N, K = 1, 2, 3.$$

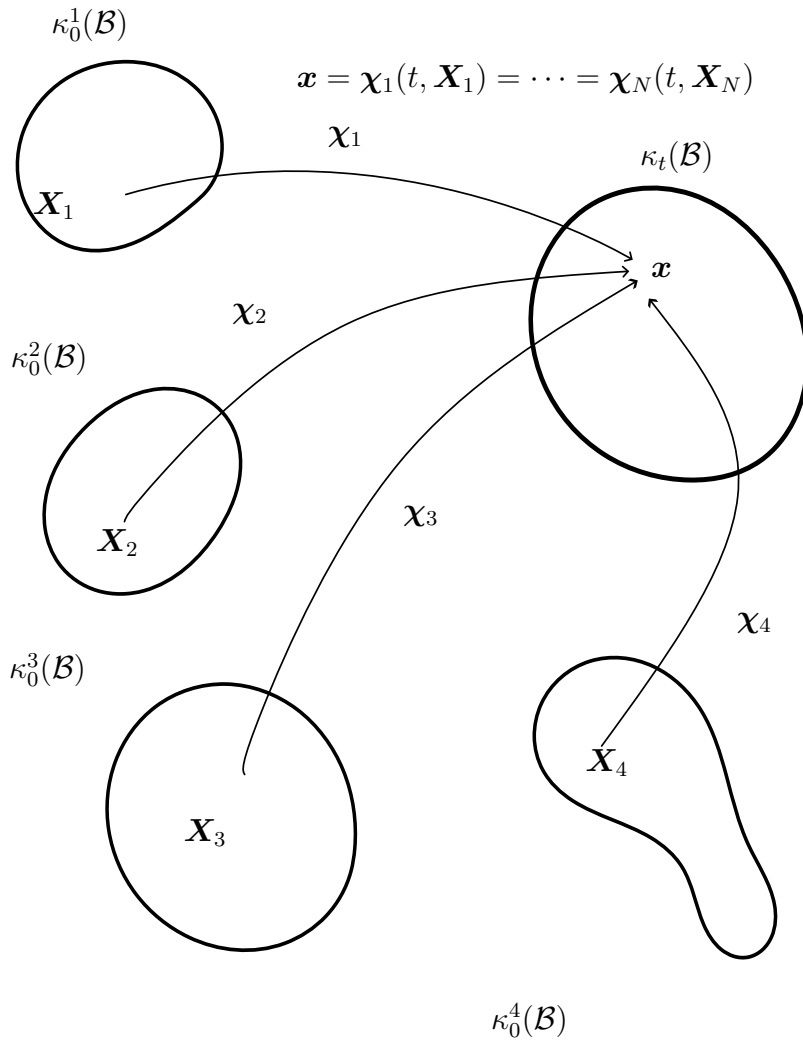
The case when  $\Phi = \chi_\alpha : \mathbb{R}^3 \times \mathbb{R} \rightarrow \mathbb{R}^3$ , leads to

$$(F_\alpha)_K^i = \frac{\partial \chi_\alpha^i}{\partial X_\alpha^K}, \alpha = 1, \dots, N. \quad (2.4)$$

**Definition 2.5** (Velocity). The lagrangian velocity of  $\alpha$ -component is given as

$$\mathbf{V}_\alpha(t, \mathbf{X}_\alpha) = \frac{\partial \chi(t, \mathbf{X}_\alpha)}{\partial t},$$

and the eulerian velocity is given as



**Figure 2.2** / The current configuration is the same for all species, but the referential may differ

$$\mathbf{v}_\alpha(t, \mathbf{x}) = \mathbf{V}_\alpha(t, \chi^{-1}(t, \mathbf{x})).$$

**Definition 2.6** (Material time derivative). For a lagrangian field:

$$\frac{d_\alpha \Phi(t, \mathbf{X}_\alpha)}{dt} = \frac{\partial \Phi(t, \mathbf{X}_\alpha)}{\partial t},$$

for an eulerian field:

$$\frac{d_\alpha \varphi(t, \mathbf{x})}{dt} = \frac{d_\alpha \varphi(t, \chi_\alpha(t, \mathbf{X}_\alpha))}{dt} = \frac{\partial \varphi}{\partial t}(t, \mathbf{x}) + \mathbf{v}_\alpha(t, \mathbf{x}) \cdot \nabla \varphi(t, \mathbf{x})$$

**Remark 2.7** (Pitfalls of the Lagrangian description of mixtures).

Suppose we know the density of some component  $\gamma$ :  $\rho_\gamma(t, \mathbf{x}_\gamma)$ .

It can happen that one has to compute something like

$$\frac{d\rho_\gamma(t, \mathbf{x}_\gamma)}{dt}$$

┘

## 2.2 Balance equations

Let us first realize what are some useful measures

- $m_\alpha(\Omega)$  is the mass of  $\alpha$ -component in  $\Omega$ ,
- $v_\alpha(\Omega)$  is the volume of  $\alpha$ -component in  $\Omega$ .
- $\rho$  is the mixture density,
- $\rho_\alpha$  is the density of  $\alpha$ -component,
- $c_\alpha$  is the concentration or the mass fraction of  $\alpha$ -component,
- $\Phi_\alpha$  is the volume fraction of  $\alpha$ -component,
- $\rho_\alpha^m$  is the *good old* material density.

We suppose the mass measure is absolutely continuous<sup>3</sup> w.r.t the volume measure, from which follows the existence of the (mass) density<sup>4</sup>.

<sup>3</sup> If the volume is zero, then the mass is zero. This means no mass can be concentrated on volume-less sets, *i.e.*, surfaces.

<sup>4</sup> Radon-Nikodym theorem...

$$m(\Omega) = \int_{\Omega} \rho \, dv .$$

We are also supposing  $m_{\alpha}(\Omega)$  is absolutely continuous w.r.t  $v(\Omega)$ , so

$$m_{\alpha}(\Omega) = \int_{\Omega} \rho_{\alpha} \, dv ,$$

and that  $m_{\alpha}(\Omega)$  is absolutely continuous w.r.t  $m(\Omega)$ , so

$$m_{\alpha}(\Omega) = \int_{\Omega} c_{\alpha} \, dm = \int_{\Omega} \gamma_{\alpha} \rho \, dv .$$

This also means  $\rho_{\alpha} = \rho \gamma_{\alpha}$ . Next, we suppose the volume-of-components measure is absolutely continuous w.r.t the total volume, so

$$v_{\alpha}(\Omega) = \int_{\Omega} \Phi_{\alpha} \, dv .$$

Finally, it makes sense to assume

$$m_{\alpha}(\Omega) = \int_{\Omega_{\alpha}} \rho_{\alpha}^m \, dv_{\alpha} = \int_{\Omega} \rho_{\alpha}^m \Phi_{\alpha} \, dv = \int_{\Omega} \rho_{\alpha} \, dv ,$$

so also  $\rho_{\alpha} = \rho_{\alpha}^m \varphi_{\alpha}$ .

## Constraints

It is also natural to assume some "additional" constraints:

$$m(\Omega) = \sum_{\alpha=1}^N m_{\alpha}(\Omega)$$

is the *mass additivity constraint*. This is directly equivalent to

$$\rho = \sum_{\alpha=1}^N \rho_{\alpha} \Leftrightarrow 1 = \sum_{\alpha=1}^N \underbrace{\frac{\rho_{\alpha}}{\rho}}_{=c_{\alpha}} .$$

This in particular means  $c_1, \dots, c_N$  are *not equivalent!*.



## 2.3 General form of a balance law in the bulk in the Eulerian config

How to compute

$$\frac{d}{dt} \int_{\Omega_\alpha(t)} \psi_\alpha \, dx$$

, for  $\Omega_\alpha(t)$  a  $\alpha$ -material volume?

Well, in general

$$\frac{d}{dt} \int_{\Omega_\alpha} \psi_\alpha \, dx = \int_{\partial\Omega_\alpha} \mathbf{\Phi}^{\psi_\alpha} \cdot \mathbf{n} \, ds + \int_{\Omega_\alpha(t)} \zeta^{\psi_\alpha} \, dx + \int_{\Omega_\alpha(t)} \Sigma^{\psi_\alpha} \, dx + \int_{\Omega_\alpha(t)} \Pi^{\psi_\alpha} \, dx, \quad (2.8)$$

where the first term is the non-convective flux of  $\psi_\alpha$ , the second term is the production of  $\psi_\alpha$  inside  $\Omega_\alpha$ , the third term is the external supply of  $\psi_\alpha$  and the last in is *the interaction (exchange) of  $\psi_\alpha$  with other components*. Since it is a exchange, there also is the constraint

$$\sum_{\alpha=1}^N \Pi^{\psi_\alpha} = 0. \quad (2.9)$$

The LHS can be easily manipulated using the Reynolds transport theorem, so upon localization

$$\partial_t \psi_\alpha + \nabla \cdot (\psi_\alpha \otimes \mathbf{v}_\alpha) = \nabla \cdot \varphi^{\psi_\alpha} + \zeta^{\psi_\alpha} + \Sigma^{\psi_\alpha} + \Pi^{\psi_\alpha}, \quad \sum_{\alpha=1}^N \Pi^{\psi_\alpha} = 0 \quad (2.10)$$

### Balance of mass

In the case of  $\psi_\alpha = \rho_\alpha$ , we have

- $\Phi^{\rho_\alpha} = 0$ ,
- $\zeta^{\rho_\alpha} = 0$ ,
- $\Sigma^{\rho_\alpha} = 0$ ,
- $\Pi^{\rho_\alpha} = m_\alpha$ .

So our balance law reduces to

$$\partial_t \rho_\alpha + \nabla \cdot (\rho_\alpha \mathbf{v}_\alpha) = m_\alpha, \quad (2.11)$$

or equivalently

$$\frac{D_\alpha \rho_\alpha}{Dt} + \rho_\alpha \nabla \cdot \mathbf{v}_\alpha = m_\alpha. \quad (2.12)$$

Both times with the constraint

$$\sum_{\alpha=1}^N m_\alpha = 0.$$

But hold on - if i look away from the fact we are dealing with mixtures, i would like to have some compatibility with the single-component theory of continuum. So let us deal with the *balance of mass for the mixture as a whole*.

We know

$$\rho = \sum_{\alpha}^N \rho_\alpha,$$

so let us sum all the equations:

$$\partial_t \left( \sum_{\alpha} \rho_\alpha \right) + \nabla \cdot \left( \sum_{\alpha} \rho_\alpha \mathbf{v}_\alpha \right) = \sum_{\alpha} m_\alpha = 0.$$

This begs the definitions

$$\rho \mathbf{v} := \sum_{\alpha=1}^N \rho_\alpha \mathbf{v}_\alpha,$$

with the definition of the *barycentric velocity*<sup>5</sup>

Then the equation becomes

$$\partial_t \rho + \nabla \cdot (\rho \mathbf{v}) = 0.$$

## Balance of (linear) momentum

- $\psi_\alpha = \rho_\alpha \mathbf{v}_\alpha$ ,
- $\Phi^{\psi_\alpha} = \mathbb{T}_\alpha$  the partial Cauchy stres,

<sup>5</sup> This is some kind of a "velocity of the whole mixture". Note that there are more ways to define this concept, but only this one gives us *some* connection to the "single-component" treatment.

$$\mathbf{v} = \sum_{\alpha=1}^N c_\alpha \mathbf{v}_\alpha.$$

One could also set

$$v^\Phi = \sum_{\alpha=1}^N \Phi_\alpha \mathbf{v}_\alpha,$$

$$v^x = \sum_{\alpha=1}^N x_\alpha \mathbf{v}_\alpha,$$

as "volumetric" and "molar" velocities.

- $\xi^{\psi_\alpha} = 0$  (zero production,
- $\Sigma^{\psi_\alpha} = \rho_\alpha \mathbf{b}_\alpha$ ,
- $\Pi^{\psi_\alpha} = \mathbf{I}_\alpha + m_\alpha \mathbf{v}_\alpha$  *interaction force*.  $\mathbf{I}_\alpha$  is the "true interaction force" and  $m_\alpha \mathbf{v}_\alpha$  is the change of momentum due to the change of mass<sup>6</sup>

<sup>6</sup> Imagine a radioactive process - one part of the mixture is losing the momentum, just because it is losing the particles that are moving...

$$\partial_t(\rho_\alpha \mathbf{v}_\alpha) + \nabla \cdot (\rho_\alpha \mathbf{v}_\alpha \otimes \mathbf{v}_\alpha) = \nabla \cdot \mathbb{T}_\alpha + \rho_\alpha \mathbf{b}_\alpha + m_\alpha \mathbf{v}_\alpha + \mathbf{I}_\alpha, \quad (2.13)$$

$$\alpha = 1, \dots, N$$

$$\sum_{\alpha=1}^N (m_\alpha \mathbf{v}_\alpha + \mathbf{I}_\alpha) = 0. \quad (2.14)$$

Let us manipulate the previous a bit:

$$\begin{aligned} \partial_t(\rho_\alpha \mathbf{v}_\alpha) + \nabla \cdot (\rho_\alpha \mathbf{v}_\alpha \otimes \mathbf{v}_\alpha) &= \\ &= \mathbf{v}_\alpha (\partial_t \rho_\alpha + \nabla \cdot (\rho_\alpha \mathbf{v}_\alpha)) + \rho_\alpha (\partial_t \mathbf{v}_\alpha + \mathbf{v}_\alpha \cdot \nabla \mathbf{v}_\alpha) = \\ &= \mathbf{v}_\alpha m_\alpha + \rho_\alpha \frac{D_\alpha \mathbf{v}_\alpha}{Dt}, \end{aligned}$$

so this means

$$\rho_\alpha \frac{D_\alpha \mathbf{v}_\alpha}{Dt} = \nabla \cdot \mathbb{T}_\alpha + \rho_\alpha \mathbf{b}_\alpha + \mathbf{I}_\alpha, \quad \alpha = 1, \dots, N \quad (2.15)$$

$$\sum_{\alpha=1}^N (\mathbf{I}_\alpha + m_\alpha \mathbf{v}_\alpha) = 0. \quad (2.16)$$

Notice there are *many pitfalls*:

**Example 2.17** (Partial Cauchy stress). It should hold

$$\mathbb{T}_\alpha \mathbf{n} dS = \mathbf{t}_\alpha(\mathbf{n}) dS,$$

where  $\mathbf{t}_\alpha$  is the traction vector exerted on  $\alpha$  by the *outer world* - so in particular through all *other species*.

One could imagine a flow through a porous solid all processes relaxed and isotropic. Then

$$\mathbb{T}_\alpha = -p_\alpha \mathbb{I},$$

with  $p_\alpha$  being the partial pressure. But in fact

$$-p_f \mathbf{n} dS = -p_f^T \mathbf{n} dS_\alpha,$$

↯

↳ where  $p_f$  is the pressure of the fluid,  $p_f^T$  is the *true porous pressure*. The surface elements  $dS, dS_\alpha$  are different - and we are mixing jablka s hruskama. ┘

The total momentum would be

$$\sum_{\alpha=1}^N \rho_\alpha \mathbf{v}_\alpha = \rho \mathbf{v},$$

which is *surprisingly* the RHS. If we sum this up, we obtain

$$\partial_t \left( \sum_\alpha \rho_\alpha \mathbf{v}_\alpha \right) + \nabla \cdot \left( \sum_\alpha \rho_\alpha \mathbf{v}_\alpha \otimes \mathbf{v}_\alpha \right) = \nabla \cdot \left( \sum_\alpha \Pi_\alpha \right) + \sum_\alpha \rho_\alpha \mathbf{b}_\alpha,$$

let us now set

$$\mathbf{v}_\alpha = \mathbf{v} + \mathbf{u}_\alpha, \quad (2.18)$$

where  $\mathbf{u}_\alpha$  is the *diffusive* <sup>7</sup>*velocity of the component  $\alpha$* . This allows us to write

<sup>7</sup> Kind of a relative velocity of the component w.r.t the barycenter

$$\sum_\alpha \rho_\alpha \mathbf{v}_\alpha = \sum_\alpha \rho_\alpha \mathbf{v} + \sum_\alpha \rho_\alpha \mathbf{u}_\alpha,$$

so this means

$$\sum_{\alpha=1}^N \rho_\alpha \mathbf{u}_\alpha = 0. \quad (2.19)$$

Finally, this leads to

$$\sum_\alpha \rho_\alpha (\mathbf{v} + \mathbf{u}_\alpha) \otimes (\mathbf{v} + \mathbf{u}_\alpha) = \left( \sum_\alpha \rho_\alpha \right) \mathbf{v} \otimes \mathbf{v} + \underbrace{\mathbf{v} \otimes \sum_\alpha \rho_\alpha \mathbf{u}_\alpha}_{=0} + \underbrace{\sum_\alpha \rho_\alpha \mathbf{u}_\alpha \otimes \mathbf{v}}_{=0} + \sum_\alpha \rho_\alpha \mathbf{u}_\alpha \otimes \mathbf{u}_\alpha,$$

so finally

$$\partial_t(\rho \mathbf{v}) + \nabla \cdot (\rho \mathbf{v} \otimes \mathbf{v}) = \nabla \cdot \left( \sum_\alpha (\Pi_\alpha - \rho_\alpha \mathbf{u}_\alpha \otimes \mathbf{u}_\alpha) \right) + \sum_{\alpha=1}^N \rho_\alpha \mathbf{b}_\alpha. \quad (2.20)$$

So if one would again want to treat the whole continuum as having a single component, it should be set

$$\mathbb{T}^{(\text{mix})} = \sum_{\alpha=1}^N \mathbb{T}_{\alpha} - \rho_{\alpha} \mathbf{u}_{\alpha} \otimes \mathbf{u}_{\alpha}, \quad (2.21)$$

$$\rho \mathbf{b}^{(\text{mix})} = \sum_{\alpha=1}^N \rho_{\alpha} \mathbf{b}_{\alpha} \quad (2.22)$$

so in particular

$$\mathbb{T}^{(\text{mix})} \neq \sum_{\alpha=1}^N \mathbb{T}_{\alpha}.$$

## Balance of angular momentum (micropolar case)

In the single-component setting, the balance of angular momentum implied

$$\mathbb{T} = \mathbb{T}^T$$

Our setting is *much richer*. We will deal with the *micropolar case*: our continuum has another degree of freedom corresponding to *rotations*. The rotations will be described by an (*mesoscopic*) *internal angular momentum*  $\mathbf{s}_{\alpha}$  called *spin*.

- $\boldsymbol{\psi}_{\alpha} = (\mathbf{x} \times \rho_{\alpha} \mathbf{v}_{\alpha}) + \mathbf{s}_{\alpha}$ ,
- $\boldsymbol{\Phi}^{\psi_{\alpha}} = \mathbf{x} \times \mathbb{T}_{\alpha} + \mathbb{M}_{\alpha}$ <sup>8</sup>, where  $\mathbb{M}_{\alpha}$  is the *couple stress*,
- $\boldsymbol{\xi}^{\psi_{\alpha}} = 0$ ,
- $\boldsymbol{\Sigma}^{\psi_{\alpha}} = \mathbf{x} \times \rho_{\alpha} \mathbf{b}_{\alpha} + \rho_{\alpha} \mathbf{l}_{\alpha}$ , where  $\mathbf{l}_{\alpha}$  is the *spin supply*
- $\boldsymbol{\Pi}^{\psi_{\alpha}} = \mathbf{x} \times (m_{\alpha} \mathbf{v}_{\alpha} + \mathbf{I}_{\alpha}) + \mathbf{p}_{\alpha}$ , where  $\mathbf{p}_{\alpha}$  is the interaction couple.

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$$(\mathbf{x} \times \mathbb{T}_{\alpha})_{ij} = \epsilon_{ikl} x_k (\mathbb{T}_{\alpha})_{lj}$$

Our balance thus is

$$\begin{aligned} & \partial_t (\mathbf{x} \times \rho_{\alpha} \mathbf{v}_{\alpha} + \mathbf{s}_{\alpha}) + \nabla \cdot ((\mathbf{x} \times \rho_{\alpha} \mathbf{v}_{\alpha} + \mathbf{s}_{\alpha}) \otimes \mathbf{v}_{\alpha}) = \\ & = \nabla \cdot (\mathbf{x} \times \mathbb{T}_{\alpha} + \mathbb{M}_{\alpha}) + \mathbf{x} \times \rho_{\alpha} \mathbf{b}_{\alpha} + \rho_{\alpha} \mathbf{l}_{\alpha} + \mathbf{x} \times (m_{\alpha} \mathbf{v}_{\alpha} + \mathbf{I}_{\alpha}) + \mathbf{p}_{\alpha}, \\ & \quad \alpha = 1, \dots, N \end{aligned}$$

This can be further manipulated:

$$\begin{aligned} & \partial_t (\epsilon_{ijk} x_j \rho_{\alpha} v_{\alpha k} + s_{\alpha i}) + \partial_l (\epsilon_{ijk} x_j \rho_{\alpha} x_l v_{\alpha k} + s_{\alpha i} v_{\alpha l}) = \\ & = \partial_j (\epsilon_{ikl} x_k T_{\alpha lj} + M_{\alpha ij}) + (\epsilon_{ijk} x_j \rho_{\alpha} b_{\alpha k} + \rho_{\alpha} l_{\alpha i}) + \epsilon_{ijk} x_j (m_{\alpha} v_{\alpha k} + I_{\alpha k}) + p_{\alpha i}, \end{aligned}$$

Our goal is to obtain

$$\mathbf{x} \times \text{balance of linear momentum} + \text{something} = 0,$$

so

$$\begin{aligned} & \epsilon_{ijk} x_j (\partial_t (\rho_\alpha \mathbf{v}_\alpha)_k + \partial_l (\rho_\alpha v_{\alpha k} v_{\alpha l}) + 0^9 - \partial_j (T_{\alpha l j}) - \rho_\alpha b_k - m_\alpha v_{\alpha k} - I_{\alpha k}) + \\ & + \partial_t s_{\alpha i} \partial_k (s_{\alpha i} v_{\alpha l}) - \partial_j (M_{\alpha i j}) - \rho_\alpha l_{\alpha i} - p_{\alpha i} - \epsilon_{ijk} T_{\alpha k j} = 0. \end{aligned}$$

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Using 2.13 we see

$$\partial_t \mathbf{s}_\alpha + \nabla \cdot (\mathbf{s}_\alpha \otimes \mathbf{v}_\alpha) = \nabla \cdot \mathbb{M}_\alpha + \rho_\alpha \mathbf{l}_\alpha + \mathbf{p}_\alpha + \mathbf{A}_\alpha, \quad (2.23)$$

$$= \epsilon_{ijk} \partial_l x_j \rho_\alpha v_{\alpha k} v_{\alpha l}$$

and  $\epsilon_{ijk}$  is antisymmetric and  $\partial_l x_j = \delta_{lj}$  is symmetric

where

$$A_{\alpha i} = \epsilon_{ijk} T_{\alpha k j}, \quad (2.24)$$

realize that

$$\begin{aligned} A_{\alpha i} \epsilon_{imn} &= \epsilon_{ijk} \epsilon_{imn} T_{\alpha k j} = (\delta_{jm} \delta_{kn} - \delta_{jn} \delta_{km}) T_{\alpha k j} = \\ &= T_{\alpha k j} \delta_{jm} \delta_{kn} - T_{\alpha k j} \delta_{jn} \delta_{km} = T_{\alpha nm} - T_{\alpha mn} = 2 \text{asym}(\mathbb{T}_\alpha)_{nm} \end{aligned}$$

**Example 2.25** (Simple situation). Imagine the case

$$\mathbf{s}_\alpha = 0, \mathbb{M}_\alpha = 0, \mathbf{l}_\alpha = 0,$$

but

$$\mathbf{p}_\alpha = 0,$$

so

$$\mathbf{p}_\alpha + \mathbf{A}_\alpha = 0 \Rightarrow \mathbf{A}_\alpha \neq 0 \Rightarrow \mathbb{T}_\alpha \neq \mathbb{T}^\top.$$

This can be achieved in a *dipole dielectric* for example.  $\lrcorner$

Our constraint reads as

$$\sum \text{interaction terms} = 0.$$

So

$$\sum_\alpha \mathbf{x} \times (m_\alpha \mathbf{v}_\alpha + \mathbf{I}_\alpha) + \mathbf{p}_\alpha + m_\alpha \mathbf{s}_\alpha = 0$$

but since 2.13 we have

$$\sum_{\alpha} \mathbf{x} \times (m_{\alpha} \mathbf{v}_{\alpha} + \mathbf{I}_{\alpha}) = \mathbf{x} \times \sum_{\alpha} m_{\alpha} \mathbf{v}_{\alpha} + \mathbf{I}_{\alpha} = 0,$$

so in total the constraint reads as

$$\sum_{\alpha=1}^n (\mathbf{p}_{\alpha} + m_{\alpha} \mathbf{s}_{\alpha}) = 0. \quad (2.26)$$

Let

$$\mathbf{v}^{\Phi} = \sum_{\alpha=1}^N \Phi_{\alpha} \mathbf{v}_{\alpha}, \quad (2.27)$$

be the *volumetric velocity*. Assume now<sup>10</sup>

$$\rho_{\alpha}^m = K_{\alpha}, \quad 10$$

for some constants  $K_{\alpha}$ .

$$\rho_{\alpha} = \rho_{\alpha}^m \Phi_{\alpha}$$

## Balance of energy

- $\psi_{\alpha} = \rho_{\alpha} E_{\alpha} = \rho_{\alpha} \left( e_{\alpha} + \frac{1}{2} |\mathbf{v}_{\alpha}|^2 \right)$ , where  $e_{\alpha}$  is the *specific internal energy*,
- $\Phi^{\psi_{\alpha}} = \mathbf{v}_{\alpha} \mathbb{T}_{\alpha} - \mathbf{q}_{\alpha}$ , where the first term is the *power of the traction forces*, and the second one is the *(diffusive) energy flux*,
- $\xi^{\psi_{\alpha}} = 0$ ,
- $\Sigma^{\psi_{\alpha}} = \rho_{\alpha} \mathbf{b}_{\alpha} \cdot \mathbf{v}_{\alpha} + \rho_{\alpha} r_{\alpha}$ , where the first term is the *power of the external body forces* and the second one is the *external source* (of heat)
- $\Pi^{\psi_{\alpha}} = m_{\alpha} E_{\alpha} + \mathbf{I}_{\alpha} \cdot \mathbf{v}_{\alpha} + \epsilon_{\alpha}$ , where the last term is the *interaction power* and the penultimate one is the *power of internal forces*

Thus the balance takes the form

$$\begin{aligned} & \partial_t \left( \rho_{\alpha} \left( e_{\alpha} + \frac{1}{2} |\mathbf{v}_{\alpha}|^2 \right) \right) + \nabla \cdot \left( \rho_{\alpha} \left( e_{\alpha} + \frac{1}{2} |\mathbf{v}_{\alpha}|^2 \right) \mathbf{v}_{\alpha} \right) = (2.28) \\ & = \nabla \cdot (\mathbb{T}_{\alpha} \mathbf{v}_{\alpha} - \mathbf{q}_{\alpha}) + \rho_{\alpha} \mathbf{b}_{\alpha} \cdot \mathbf{v}_{\alpha} + \rho_{\alpha} r_{\alpha} + m_{\alpha} \left( e_{\alpha} + \frac{1}{2} |\mathbf{v}_{\alpha}|^2 \right) + \mathbf{I}_{\alpha} \cdot \mathbf{v}_{\alpha} + \epsilon_{\alpha}, \\ & \sum_{\alpha=1}^N \left( m_{\alpha} \left( e_{\alpha} + \frac{1}{2} |\mathbf{v}_{\alpha}|^2 \right) + \mathbf{I}_{\alpha} \cdot \mathbf{v}_{\alpha} + \epsilon_{\alpha} \right) = 0, \\ & \alpha = 1, \dots, N \end{aligned}$$

Our goal is to arrive at the *reduced* balance of internal energy:

balance of total energy - balance of kinetic energy

.

The balance of kinetic energy is <sup>11</sup>

$$\begin{aligned} & (\partial_t \rho_\alpha) \mathbf{v}_\alpha + \rho_\alpha (\partial_t \mathbf{v}_\alpha) + \partial_j (\rho_\alpha v_{\alpha i} v_{\alpha j}) = \\ & = (\partial_t \rho_\alpha) \mathbf{v}_\alpha + \rho_\alpha (\partial_t \mathbf{v}_\alpha) + \partial_j (\rho_\alpha v_{\alpha j}) v_{\alpha i} + (\partial_j v_{\alpha i}) \rho_\alpha v_{\alpha j}, \end{aligned}$$

using the balance of mass 2.11

$$\partial_t \rho_\alpha + \nabla \cdot (\rho_\alpha \mathbf{v}_\alpha) = m_\alpha,$$

we can write

$$m_\alpha \mathbf{v}_\alpha + \rho_\alpha (\partial_t \mathbf{v}_\alpha + (\mathbf{v}_\alpha \cdot \nabla) \mathbf{v}_\alpha) = \nabla \cdot \mathbb{T}_\alpha + \rho_\alpha \mathbf{b}_\alpha + m_\alpha \mathbf{v}_\alpha + \mathbf{I}_\alpha,$$

and so

$$\rho_\alpha (\partial_t \mathbf{v}_\alpha + (\mathbf{v}_\alpha \cdot \nabla) \mathbf{v}_\alpha) = \nabla \cdot \mathbb{T}_\alpha + \rho_\alpha \mathbf{b}_\alpha + \mathbf{I}_\alpha.$$

As ususally, we take the dot product with  $\mathbf{v}_\alpha$  and write

$$\frac{1}{2} \rho_\alpha \left( \partial_t |\mathbf{v}_\alpha|^2 + \underbrace{\mathbf{v}_\alpha \cdot \nabla |\mathbf{v}_\alpha|^2}_{=2(\nabla \mathbf{v}_\alpha \mathbf{v}_\alpha) \cdot \mathbf{v}_\alpha} \right) = \nabla \cdot (\mathbb{T}_\alpha \mathbf{v}_\alpha) - \mathbb{T}_\alpha : \nabla \mathbf{v}_\alpha + \rho_\alpha \mathbf{b}_\alpha \cdot \mathbf{v}_\alpha + \mathbf{I}_\alpha \cdot \mathbf{v}_\alpha.$$

One can also write 2.28 in the form

$$\rho_\alpha \frac{D_\alpha \left( e_\alpha + \frac{1}{2} |\mathbf{v}_\alpha|^2 \right)}{Dt} = \nabla \cdot (\mathbb{T}_\alpha \mathbf{v}_\alpha) - \mathbf{q}_\alpha + \rho_\alpha \mathbf{b}_\alpha \cdot \mathbf{v}_\alpha + \rho_\alpha r_\alpha + \mathbf{I}_\alpha \cdot \mathbf{v}_\alpha + \epsilon_\alpha, \quad (2.29)$$

so subtracting the equations yields

$$\rho_\alpha \frac{D_\alpha e_\alpha}{Dt} = -\nabla \cdot \mathbf{q}_\alpha + \mathbb{T}_\alpha : \mathbb{D}_\alpha + \rho_\alpha r_\alpha + \epsilon_\alpha, \quad (2.30)$$

or equivalently

<sup>11</sup> Realize

$$\partial_t (\rho_\alpha \mathbf{v}_\alpha) + \nabla \cdot (\rho_\alpha \mathbf{v}_\alpha \otimes \mathbf{v}_\alpha) = \rho_\alpha \frac{D_\alpha \mathbf{v}_\alpha}{Dt}$$

is not straightforward! I have multiple terms from the alance of mass also.



$$\partial_t(\rho_\alpha e_\alpha) + \nabla \cdot (\rho_\alpha e_\alpha \mathbf{v}_\alpha) = -\nabla \cdot \mathbf{q}_\alpha + \mathbb{T}_\alpha : \mathbb{D}_\alpha + \rho_\alpha r_\alpha + \epsilon_\alpha + m_\alpha e_\alpha. \quad (2.31)$$

Now we would again like to obtain the balance of energy *of the whole mixture*: take the component energies and sum them up

$$\partial_t \left( \sum_{\alpha=1}^N \rho_\alpha E_\alpha \right) + \nabla \cdot \left( \sum_{\alpha=1}^N \rho_\alpha E_\alpha \mathbf{v}_\alpha \right) = \nabla \cdot \left( \sum_{\alpha=1}^N \mathbb{T}_\alpha \mathbf{v}_\alpha - \mathbf{q}_\alpha \right) + \sum_{\alpha=1}^N (\rho_\alpha \mathbf{b}_\alpha \cdot \mathbf{v}_\alpha + \rho_\alpha r_\alpha),$$

further manipulate

$$\rho E := \sum_{\alpha=1}^N \rho_\alpha E_\alpha = \sum_{\alpha} \rho_\alpha \left( e_\alpha + \frac{1}{2} |\mathbf{v}_\alpha|^2 \right),$$

where

$$\sum_{\alpha=1}^N \frac{1}{2} \rho_\alpha |\mathbf{v}_\alpha|^2 = \sum_{\alpha=1}^N \frac{1}{2} \rho_\alpha (\mathbf{v} + \mathbf{u}_\alpha) \cdot (\mathbf{v} + \mathbf{u}_\alpha) = \left( \sum_{\alpha=1}^N \rho_\alpha \right) \frac{1}{2} |\mathbf{v}|^2 + \underbrace{\left( \sum_{\alpha=1}^N \rho_\alpha \mathbf{u}_\alpha \right) \cdot \mathbf{v}}_{=0} + \sum_{\alpha=1}^N \frac{1}{2} \rho_\alpha |\mathbf{u}_\alpha|^2,$$

so the previous equation becomes

$$\rho E = \sum_{\alpha=1}^N \rho_\alpha \left( e_\alpha + \frac{1}{2} |\mathbf{u}_\alpha|^2 \right) + \frac{1}{2} \rho |\mathbf{v}|^2.$$

The right hand side can be manipulated as

$$\nabla \cdot \left( \sum_{\alpha=1}^N \rho_\alpha E_\alpha (\mathbf{v} + \mathbf{u}_\alpha) \right) = \nabla \cdot (\rho E \mathbf{v}) + \nabla \cdot \left( \sum_{\alpha=1}^N \rho_\alpha E_\alpha \mathbf{u}_\alpha \right),$$

where the last term is

$$\begin{aligned} & \nabla \cdot \left( \sum_{\alpha=1}^N \rho_\alpha \left( e_\alpha + \frac{1}{2} (\mathbf{v} + \mathbf{u}_\alpha) \cdot (\mathbf{v} + \mathbf{u}_\alpha) \right) \mathbf{u}_\alpha \right) = \\ &= \nabla \cdot \left( \sum_{\alpha=1}^N \rho_\alpha e_\alpha \mathbf{u}_\alpha \right) + \nabla \cdot \left( \sum_{\alpha=1}^N \frac{1}{2} \rho_\alpha (|\mathbf{v}|^2 + 2(\mathbf{v} \cdot \mathbf{u}_\alpha) + |\mathbf{u}_\alpha|^2) \mathbf{u}_\alpha \right) = \\ &= \nabla \cdot \left( \sum_{\alpha=1}^N \rho_\alpha e_\alpha \mathbf{u}_\alpha \right) + \nabla \cdot \left( \sum_{\alpha=1}^N \frac{1}{2} \rho_\alpha |\mathbf{u}_\alpha|^2 \mathbf{u}_\alpha \right) + \nabla \cdot \left( \sum_{\alpha=1}^N \underbrace{\rho_\alpha (\mathbf{u}_\alpha \otimes \mathbf{u}_\alpha)}_{=\rho_\alpha \mathbf{u}_\alpha (\mathbf{u}_\alpha \cdot \mathbf{v})} \mathbf{v} \right) \end{aligned}$$

and so the LHS of our balance is

$$\partial_t(\rho E) + \nabla \cdot (\rho E \mathbf{v}) + \nabla \cdot \left( \sum_{\alpha=1}^N \rho_\alpha e_\alpha \mathbf{u}_\alpha \right) + \nabla \cdot \left( \sum_{\alpha=1}^N \frac{1}{2} \rho_\alpha |\mathbf{u}_\alpha|^2 \mathbf{u}_\alpha \right) + \nabla \cdot \left( \sum_{\alpha=1}^N \rho_\alpha (\mathbf{u}_\alpha \otimes \mathbf{u}_\alpha) \mathbf{v} \right),$$

whereas the RHS can be manipulated as

$$\nabla \cdot \left( \sum_{\alpha=1}^N \mathbb{T}_\alpha \mathbf{v}_\alpha \right) = \nabla \cdot \left( \sum_{\alpha=1}^N \mathbb{T}_\alpha (\mathbf{v} + \mathbf{u}_\alpha) \right) = \nabla \cdot \left( \underbrace{\sum_{\alpha=1}^N \mathbb{T}_\alpha}_{=\mathbb{T} + \nabla \cdot \left( \sum_{\alpha=1}^N \rho_\alpha \mathbf{u}_\alpha \otimes \mathbf{u}_\alpha \right) \mathbf{v}} \right) + \nabla \cdot \left( \sum_{\alpha=1}^N \mathbb{T}_\alpha \mathbf{u}_\alpha \right).$$

In total, the balance takes the form

$$\partial_t(\rho E) + \nabla \cdot (\rho E \mathbf{v}) = \nabla \cdot \mathbb{T} \mathbf{v} - \nabla \cdot \left( \sum_{\alpha=1}^N \mathbf{q}_\alpha - \mathbb{T}_\alpha \mathbf{u}_\alpha + \rho_\alpha \left( e_\alpha + \frac{1}{2} |\mathbf{u}_\alpha|^2 \right) \mathbf{u}_\alpha \right) + \rho \mathbf{b} \cdot \mathbf{v} + \sum_{\alpha=1}^N (\rho_\alpha r_\alpha + \rho_\alpha \mathbf{b}_\alpha \cdot \mathbf{u}_\alpha).$$

Which motivates the definitions of the *energy flux of the whole mixture* and the *total external sources*

$$\mathbf{q}^{\text{mix}} := \sum_{\alpha=1}^N \left( \mathbf{q}_\alpha - \mathbb{T}_\alpha \mathbf{u}_\alpha + \rho_\alpha \left( e_\alpha + \frac{1}{2} |\mathbf{u}_\alpha|^2 \right) \mathbf{u}_\alpha \right), \quad (2.32)$$

$$\rho r := \sum_{\alpha=1}^N r_\alpha \quad (2.33)$$

This is the balance of energy of the whole mixture, so subtracting the balance of kinetic energy of the whole mixture leads to the *balance of internal energy of the whole mixture*

$$\rho \frac{De}{Dt} = -\nabla \cdot \mathbf{q}^{\text{mix}} + \mathbb{T} : \mathbb{D} + \rho r, \quad (2.34)$$

where

## Balance of entropy

- $\psi_\alpha = \rho_\alpha \eta_\alpha$ , where  $\eta_\alpha$  is the *specific entropy*
- $\Phi^{\psi_\alpha} = \mathbf{q}_{\epsilon\alpha}$ , is the *entropy flux*,
- $\Sigma^{\psi_\alpha} = \rho_\alpha r_{\eta\alpha}$ , is the *entropy supply*,
- $\xi^{\psi_\alpha} = \zeta_\alpha$ , is the *entropy production*,

- $\Pi^{\psi_\alpha} = \tilde{\zeta}_\alpha + m_\alpha \eta_\alpha$  is the *entropy exchange*.

The balance has the general form

$$\begin{aligned} \partial_t(\rho_\alpha \eta_\alpha) + \nabla \cdot (\rho_\alpha \eta_\alpha \mathbf{v}_\alpha) &= -\nabla \cdot \mathbf{q}_\eta + \rho_\alpha r_{\eta_\alpha} + \zeta_\alpha + m_\alpha \eta_\alpha + \tilde{\zeta}_\alpha, \quad (2.35) \\ \sum_{\alpha=1}^N (m_\alpha \eta_\alpha + \tilde{\zeta}_\alpha) &= 0, \\ \alpha &= 1, \dots, N. \end{aligned}$$

**Theorem 2.36** (Second law of thermodynamics). We postulate

$$\zeta_\alpha \geq 0. \quad (2.37)$$

Notice that however the above theory is just *formal*. In particular we are not able to find the relations for the functions - in particular it is almost impossible to assure the second law holds.

A formal manipulation is nevertheless possible: if we sum all the equations we obtain

$$\partial_t \left( \sum_{\alpha=1}^N \rho_\alpha \eta_\alpha \right) + \nabla \cdot \left( \left( \sum_{\alpha=1}^N \rho_\alpha \eta_\alpha \right) \mathbf{v} \right) = -\nabla \cdot \left( \sum_{\alpha=1}^N \mathbf{q}_{\eta_\alpha} + \rho_\alpha \eta_\alpha \mathbf{u}_\alpha \right) + \sum_{\alpha=1}^N \rho_\alpha r_{\eta_\alpha} + \sum_{\alpha=1}^N \zeta_\alpha,$$

where it is natural to define

$$\rho \eta := \sum_{\alpha=1}^N \rho_\alpha \eta_\alpha, \quad (2.38)$$

$$\zeta := \sum_{\alpha=1}^N \zeta_\alpha \geq 0. \quad (2.39)$$

**Remark 2.40.** In practice one postulates the second law for the mixture as a whole:

$$\zeta \geq 0,$$

not for each of the components

$$\zeta_\alpha \geq 0.$$

As we mentioned, it is in practice almost *impossible* to differentiate between  $\zeta_\alpha$  and  $\tilde{\zeta}_\alpha$ , *i.e.*, between entropy production and entropy exchange.  $\lrcorner$

## 2.4 Classification of mixture theories

We are ready to provide a nice classification of mixture theories.

<sup>12</sup> The level of description can be very detailed, or fairly simple. In the table 2.41 below, the indexed quantity represents the assumption the quantity is *different* for each component; if the quantity is not with an index, it is considered as *the same* for each components.

<sup>12</sup> This goes back to *Hutter*.

class IV	class III	class II	class I	quantity
$\rho_\alpha$	$\rho_\alpha$	$\rho_\alpha$	$\rho_\alpha$	mass
$\mathbf{v}_\alpha$	$\mathbf{v}_\alpha$	$\mathbf{v}_\alpha$	$\mathbf{v}$	momentum
$e_\alpha$	$e_\alpha$	$e$	$e$	energy
$\eta_\alpha$	$\eta$	$\eta$	$\eta$	entropy

**Table 2.41** / Classification of mixtures

**Example 2.42** (Applications). • class I: advection - reaction  
- diffusion systems, Fick:  $\mathbf{j}_\alpha \propto \nabla c_\alpha$ ,

- class II: porous media flow, bubbly flows.
- class III: plasma stellar physics.

The theory for class IV is extremely complicated and is not developed at all; we won't be dealing with it. ┘

# 3 Thermodynamics reminder

## 3.1 Fundamental relations

Let us begin with the<sup>13</sup> *fundamental thermodynamical relation*

<sup>13</sup> Mistrovska funkce!

$$S = \hat{S}(E, X^1, \dots, X^n),$$

where  $X^k$  are some *extensive* parameters of the system - volumes, masses, molar masses etc. The function  $\hat{S}$  has some properties:

- it is differentiable and  $\frac{\partial \hat{S}}{\partial E} > 0$ ,
- it is 1-homogenous:  $\hat{S}(\lambda E, \lambda X^k) = \lambda \hat{S}(E, X^k), \forall \lambda > 0$ .

Let us choose  $S = \hat{S}(E, V, m_1, \dots, m_n)$ . Then the differential of the entropy has the form

$$dS = \left( \frac{\partial \hat{S}}{\partial E} \right) dE + \left( \frac{\partial \hat{S}}{\partial V} \right) dV + \sum_{\alpha} \left( \frac{\partial \hat{S}}{\partial m_{\alpha}} \right) dm_{\alpha}.$$

It is customary to set

$$\frac{\partial \hat{S}}{\partial E} = \frac{1}{\theta}, \quad \frac{\partial \hat{S}}{\partial V} = \frac{p}{\theta}, \quad \frac{\partial \hat{S}}{\partial m_{\alpha}} = -\frac{\mu_{\alpha}}{\theta},$$

as the temperature, pressure, chemical potential.

## 3.2 Local equilibrium thermodynamics

The material point in the continuum is *not a point* - it is in fact a bulk. Our assumption is

**Lemma 3.1.** Every material point is an isolated thermodynamical system in equilibrium.

This allows one to define intensive<sup>14</sup> qualities! At least locally...

We have

$$\theta dS = dE + p dv - \sum_{\alpha} \mu_{\alpha} dm_{\alpha},$$

and from 1-homogeneity follows the Euler relation<sup>15</sup>

<sup>14</sup> Realize that the temperature, pressure, etc. are defined only in equilibria!

<sup>15</sup> Differentiate w.r.t  $\lambda$  and set  $\lambda = 1$ .

$$\theta S = E + pV - \sum_{\alpha} \mu_{\alpha} m_{\alpha},$$

so taking the differential of the fundamental relation yields

$$d\theta S + \theta dS = dE + p dV + V dp - \sum_{\alpha} \mu_{\alpha} dm_{\alpha} - \sum_{\alpha} m_{\alpha} d\mu_{\alpha},$$

and substituting from the fundamental relation yields the *Gibbs-Duhem relation*

**Theorem 3.2** (Gibbs-Duhem relation).

$$S d\theta = V dp - \sum_{\alpha} m_{\alpha} d\mu_{\alpha}$$

If one takes  $\lambda = \frac{1}{m}$  and uses the 1-homogeneity, we obtain

$$\hat{S}\left(\frac{E}{m}, \frac{V}{m}, \frac{m_{\alpha}}{m}\right) = \frac{S}{m} := \eta = \hat{\eta}\left(e, \frac{1}{\rho}, c_{\alpha}\right).$$

This allows one to define

$$\frac{\partial \hat{\eta}}{\partial e} = \frac{1}{\theta}, \quad \frac{\partial \hat{\eta}}{\partial \left(\frac{1}{\rho}\right)} = \frac{p}{\rho}, \quad \frac{\partial \hat{\eta}}{\partial c_{\alpha}} = -\frac{\mu_{\alpha}}{\theta}.$$

**v, v, v, v**

# 4

## Classes of mixtures

### 4.1 Class I mixtures

The evolution equations are

$$\begin{aligned}\partial_t \rho_\alpha + \nabla \cdot \rho_\alpha \mathbf{v}_\alpha &= m_\alpha, \\ \partial_t (\rho \mathbf{v}_\alpha) + \nabla \cdot \rho \mathbf{v} \otimes \mathbf{v} &= \nabla \cdot \mathbb{T} + \rho \mathbf{b}, \\ \partial_t \left( \rho \left( e + \frac{1}{2} |\mathbf{v}|^2 \right) \right) + \nabla \cdot \left( \rho \left( e + \frac{1}{2} |\mathbf{v}|^2 \right) \mathbf{v} \right) &= \nabla \cdot (\mathbb{T} \mathbf{v} - \mathbf{q}) + \rho \mathbf{b} \cdot \mathbf{v} + \rho r.\end{aligned}$$

But the problem is that the balance of mass still *contains the velocities*  $\mathbf{v}_\alpha$ . Let us deal with it by using the *diffusive velocity* and then use some constitutive relations:

$$\partial_t \rho_\alpha + \nabla \cdot \left( \rho_\alpha \overbrace{(\mathbf{v}_\alpha - \mathbf{v})}^{=\mathbf{u}_\alpha} \right) + \nabla \cdot (\rho_\alpha \mathbf{v}) = m_\alpha,$$

where we set

$$\mathbf{j}_\alpha := \rho_\alpha \mathbf{u}_\alpha, \quad (4.1)$$

and so our equation reads as

$$\partial_t \rho_\alpha + \nabla \cdot (\rho_\alpha \mathbf{v}) = m_\alpha - \nabla \cdot \mathbf{j}_\alpha, \quad \sum_{\alpha=1}^N m_\alpha = 0, \quad \sum_{\alpha=1}^N \mathbf{j}_\alpha = \mathbf{0}.$$

Let us sum the equations up, so then we obtain: (recall  $\rho = \sum_{\alpha=1}^N \rho_\alpha$ )

$$\partial_t \rho + \nabla \cdot (\rho \mathbf{v}) = 0,$$

because of the constraints.

It is convenient to rewrite the equations in a single form, with the constraints involved.

Recall:

$$c_\alpha = \frac{\rho_\alpha}{\rho},$$

and the quality

$$\frac{D\rho c_\alpha}{Dt} = \frac{D\rho}{Dt} c_\alpha + \rho \frac{Dc_\alpha}{Dt} = (\partial_t \rho + (\mathbf{v} \cdot \nabla) \rho) c_\alpha + \rho (\partial_t c_\alpha + (\mathbf{v} \cdot \nabla) c_\alpha),$$

using

$$0 = \partial_t \rho + \nabla \cdot (\rho \mathbf{v}) = \partial_t \rho + \nabla \rho \cdot \mathbf{v} + \rho (\nabla \cdot \mathbf{v}),$$

we obtain

$$-\rho (\nabla \cdot \mathbf{v}) c_\alpha + \rho \frac{Dc_\alpha}{Dt},$$

on the other hand

$$\frac{D(\rho c_\alpha)}{Dt} = \frac{D\rho_\alpha}{Dt} = \partial_t \rho_\alpha + \mathbf{v} \cdot \nabla \rho_\alpha = -\rho_\alpha (\nabla \cdot \mathbf{v}) + m_\alpha - \nabla \cdot \mathbf{j}_\alpha,$$

so in fact

$$\rho \frac{Dc_\alpha}{Dt} = (\nabla \cdot \mathbf{v}) (c_\alpha \rho - \rho_\alpha) + m_\alpha - \nabla \cdot \mathbf{j}_\alpha = m_\alpha - \nabla \cdot \mathbf{j}_\alpha.$$

Our final equations reads as

$$\rho \frac{Dc_\alpha}{Dt} = m_\alpha - \nabla \cdot \mathbf{j}_\alpha, \sum_{\alpha=1}^N m_\alpha = 0, \sum_{\alpha=1}^N \mathbf{j}_\alpha = 0, \sum_{\alpha=1}^N c_\alpha = 1, \quad (4.2)$$

which is the typical advection-reaction-diffusion system. In total

$$\partial_t \rho + \nabla \cdot (\rho \mathbf{v}) = 0, \quad (4.3)$$

$$\rho \frac{Dc_\alpha}{Dt} = m_\alpha - \nabla \cdot \mathbf{j}_\alpha, \quad (4.4)$$

$$\sum_{\alpha=1}^N m_\alpha = 0, \sum_{\alpha=1}^N \mathbf{j}_\alpha = 0, \sum_{\alpha=1}^N c_\alpha = 1 \quad (4.5)$$

$$\partial_t (\rho \mathbf{v}_\alpha) + \nabla \cdot (\rho \mathbf{v} \otimes \mathbf{v}) = \nabla \cdot \mathbb{T} + \rho \mathbf{b}, \quad (4.6)$$

$$\partial_t \left( \rho \left( e + \frac{1}{2} |\mathbf{v}|^2 \right) \right) + \nabla \cdot \left( \rho \left( e + \frac{1}{2} |\mathbf{v}|^2 \right) \mathbf{v} \right) = \nabla \cdot (\mathbb{T} \mathbf{v} - \mathbf{q}) + \rho \mathbf{b} \cdot \mathbf{v} + \rho r. \quad (4.7)$$

Our goal is to complete the system with *thermodynamic closures*, *i.e.*, to provide a *constitutive theory*.



## Constitutive theory

Our thermodynamical potential of choice is the *Helmholtz free energy*

$$\psi = e - \theta\eta, \psi = \hat{\psi}\left(\theta, \frac{1}{\rho}, c_1, \dots, c_N\right).$$

And our goal is to obtain

$$\rho \frac{D\eta}{Dt} = (\text{something}) \geq 0.$$

For simplicity, let us first do this in a binary setting:  $N = 2, c_1 = c, c_2 = 1 - c$ . Let us begin <sup>16</sup>

<sup>16</sup> Recall that from the relation

$$e = \hat{e}\left(\eta, \frac{1}{\rho}, c_1, \dots, c_N\right)$$

one can define

$$\psi = \inf_{\eta > 0} \left( \hat{e}\left(\eta, \frac{1}{\rho}, c_1, \dots, c_N\right) - \theta\eta \right),$$

and then the infimum is at the point where the derivative vanishes, so

$$0 = \frac{\partial \hat{e}}{\partial \eta} \left( \eta, \frac{1}{\rho}, c_1, \dots, c_N \right) - \theta$$

. The rest of the relation is just chain rule...

$$\begin{aligned} \frac{D\psi}{Dt} &= \frac{De}{Dt} - \frac{D\theta}{Dt}\eta - \theta \frac{D\eta}{Dt} = \frac{\partial \hat{\psi}}{\partial \theta} \frac{D\theta}{Dt} + \frac{\partial \hat{\psi}}{\partial \left(\frac{1}{\rho}\right)} \frac{D\left(\frac{1}{\rho}\right)}{Dt} + \frac{\partial \hat{\psi}}{\partial c} \frac{Dc}{Dt} = \\ &= -\eta \frac{D\theta}{Dt} + p \frac{1}{\rho^2} \frac{D\rho}{Dt} + \mu \frac{Dc}{Dt}, \end{aligned}$$

so in fact

$$\begin{aligned} \theta \rho \frac{D\eta}{Dt} &= \rho \frac{De}{Dt} - \frac{p}{\rho} \underbrace{\frac{D\rho}{Dt}}_{=-\rho(\nabla \cdot \mathbf{v})} - \mu \rho \frac{Dc}{Dt} = \\ &= \mathbb{T} : \mathbb{D} - \nabla \cdot \mathbf{q} = \rho r + p(\nabla \cdot \mathbf{v}) - \mu(m - \nabla \cdot \mathbf{j}), \end{aligned}$$

using the decomposition

$$\mathbb{T} = \frac{1}{3} \text{tr } \mathbb{T} \mathbb{I} + \mathbb{T}^d = M \mathbb{I} + \mathbb{T}^d,$$

one obtains

$$\theta \rho \frac{D\eta}{Dt} = (M + p)(\nabla \cdot \mathbf{v}) + \mathbb{T}^d : \mathbb{D} - \nabla \cdot \mathbf{q} - \mu m + \underbrace{\mu \nabla \cdot \mathbf{j}}_{=\nabla \cdot (\mu \mathbf{j}) - \mathbf{j} \cdot \nabla \mu}.$$

Recall the general balance of entropy:

$$\rho \frac{D\eta}{Dt} = -\nabla \cdot \mathbf{q}_\eta + r_\eta + \zeta.$$

So if we divide our equation by entropy, we obtain

$$\begin{aligned}\rho \frac{D\eta}{Dt} &= \frac{1}{\theta} \left( (M + P)(\nabla \cdot \mathbf{v}) + \mathbb{T}^d : \mathbb{D}^d - \mu m \right) - \frac{1}{\theta} \nabla \cdot (\mathbf{q} - \mu \mathbf{j}) - \frac{1}{\theta} \mathbf{j} \cdot \nabla \mu = \frac{\rho r}{\theta} = \\ &= \frac{1}{\theta} \left( (M + p)(\nabla \cdot \mathbf{v}) + \mathbb{T}^d : \mathbb{D}^d - \mu m \right) + \frac{\rho r}{\theta} - \nabla \cdot \left( \frac{\mathbf{q} - \mu \mathbf{j}}{\theta} \right) + (\mathbf{q} - \mu \mathbf{j}) \cdot \nabla \left( \frac{1}{\theta} \right) - \frac{1}{\theta} \mathbf{j} \cdot \nabla \mu.\end{aligned}$$

So one can *interpret*

$$\mathbf{q}_\eta := \frac{\mathbf{q} - \mu \mathbf{j}}{\theta}, \quad (4.8)$$

$$\rho r_\eta := \frac{\rho r}{\rho}, \quad (4.9)$$

$$\zeta := \frac{1}{\theta} \left( (M + p)(\nabla \cdot \mathbf{v}) + \mathbb{T}^d : \mathbb{D}^d - \mu m \right) - \frac{1}{\theta} \mathbf{j} \cdot \nabla \mu + (\mathbf{q} - \mu \mathbf{j}) \cdot \nabla \left( \frac{1}{\theta} \right). \quad (4.10)$$

How to make the entropy production positive? inspired by Navier-Stokes-Fourier one can take

$$\begin{aligned}M + P &= \frac{3\lambda + 2\nu}{3} (\nabla \cdot \mathbf{v}), 3\lambda + 2\nu \geq 0, \\ \mathbb{T}^d &= 2\nu \mathbb{D}^d, \nu \geq 0 \\ m &= -b\mu, \beta \geq 0 \\ \mathbf{j} &= -\alpha \nabla \mu, \mathbf{q} - \mu \mathbf{j} = \kappa \nabla \left( \frac{1}{\theta} \right) \\ \mathbf{j} &= -\alpha \nabla \left( \frac{\mu}{\theta} \right), \mathbf{q} = \kappa \nabla \left( \frac{1}{\theta} \right) \text{ (this one is in fact preferred by statistical physics).}\end{aligned}$$

This implies

$$\mathbb{T} = -p \left( \theta, \frac{1}{\rho}, c \right) \mathbb{I} + \lambda (\nabla \cdot \mathbf{v}) \mathbb{I} + 2\nu \mathbb{D}, 3\lambda + 2\nu > 0, \nu > 0, \quad (4.11)$$

$$\mathbf{q} = \kappa \nabla \left( \frac{1}{\theta} \right) = -\frac{\kappa}{\theta^2} \nabla \theta, \quad (4.12)$$

$$m = -\beta \mu, \beta > 0 \quad (4.13)$$

$$\mathbf{j} = -\alpha \nabla \left( \frac{\mu}{\theta} \right), \alpha > 0 \quad (4.14)$$

One can see the last relation is very similliar to the Fourier law.

Suppose for a second now that

$$\hat{\psi}\left(\theta, \frac{1}{\rho}, c\right) = \hat{\psi}_0\left(\theta, \frac{1}{\rho}\right) + \hat{\psi}_1(c),$$

than

$$\mu = \frac{\partial \hat{\psi}}{\partial c} = \psi'_1(c), \nabla \mu = \psi''_1(c) \nabla c.$$

In the isothermal case, our constitutive relation reads

$$\mathbf{j} = -\alpha \nabla \left( \frac{\mu}{\theta} \right) = -\frac{\alpha}{\theta} \nabla \mu = -\frac{\alpha}{\theta} \psi''_1(c) \nabla c = -\tilde{k} \nabla c, \tilde{k} > 0.$$

Which is a law in the form

$$\mathbf{j} = -\tilde{k} \nabla c, k > 0,$$

exactly similar to  $\mathbf{q} = -\tilde{\kappa} \nabla \theta$ . This law is known as the *Fick law*.

The governing equations are

$$\rho \frac{Dc}{Dt} = -\nabla \cdot \mathbf{j} + m = \nabla \cdot (k(c) \nabla c) - 3\psi'_1(c)$$

$$\rho(\partial_t c + \mathbf{v} \cdot \nabla c) - \nabla \cdot (k(c) \nabla c) + 3\psi'_1(c) = 0,$$

which is again an advection-diffusion-reaction system.

## Multi-component diffusion

The previous result have been done in a binary setting - let us repeat it in more generality: we again have

$$\psi = \hat{\psi}\left(\theta, \frac{1}{\rho}, c_1, \dots, c_N\right),$$

so we obtain

$$\psi \rho \frac{D\eta}{Dt} = (M + p)(\nabla \cdot \mathbf{v}) + \mathbb{T}^d : \mathbb{D}^d - \nabla \cdot \mathbf{q} + \rho r - \sum_{\alpha=1}^N \mu_\alpha m_\alpha + \sum_{\alpha=1}^N \mu_\alpha (\nabla \cdot \mathbf{j}_\alpha),$$

where the last term can in fact be written

$$\sum_{\alpha=1}^{N-1} (\mu_{\alpha} - \mu_N) m_{\alpha} + \sum_{\alpha=1}^{N-1} (\mu_{\alpha} - \mu_N) (\nabla \cdot \mathbf{j}_{\alpha}).$$

Dividing by temperature yields

$$\begin{aligned} \rho \frac{D\eta}{Dt} = & -\nabla \cdot \left( \frac{\mathbf{q} - \sum_{\alpha=1}^N \mu_{\alpha} \mathbf{j}_{\alpha}}{\theta} \right) + \frac{\rho r}{\theta} + \frac{1}{\theta} \left( (M+p) \nabla \cdot \mathbf{v} + \right. \\ & \left. + \mathbb{T}^d : \mathbb{D}^d - \sum_{\alpha=1}^{N-1} (\mu_{\alpha} - \mu_N) m_{\alpha} + \mathbf{q} \cdot \nabla \left( \frac{1}{\theta} \right) - \sum_{\alpha=1}^{N-1} \mathbf{j}_{\alpha} \cdot \nabla \left( \frac{\mu_{\alpha} - \mu_N}{\theta} \right) \right). \end{aligned}$$

Linear irreversible thermodynamics proposes to define

$$\begin{bmatrix} -\mathbf{j}_1 \\ \vdots \\ -\mathbf{j}_{N-1} \\ \mathbf{q} \end{bmatrix} = \mathbb{L} \begin{bmatrix} \nabla \left( \frac{\mu_1 - \mu_N}{\theta} \right) \\ \vdots \\ \nabla \left( \frac{\mu_{N-1} - \mu_N}{\theta} \right) \\ \nabla \left( \frac{1}{\theta} \right) \end{bmatrix},$$

where in general  $\mathbb{L}$  is a *full matrix*. If  $\mathbb{L}$  is diagonal, we call the closures *diagonal*. We see that if  $\mathbb{L}$  is positive semi-definite, the entropy production is nonnegative.

The matrix  $\mathbb{L}$  has some other qualities, called the *Onsager-Casimir relations*:<sup>17</sup>

- $\mathbb{L} = \mathbb{L}^{\top}$ .

The problem is that the matrix  $\mathbb{L}$  is in general *not known*; for example, *the choice of a constant matrix is **totally wrong***.

Let us show a different approach: the *Maxwell-Stefan* closure.

### Maxwell-Stefan closure

$$\begin{aligned} \rho \frac{D\eta}{Dt} + \nabla \cdot \left( \frac{\mathbf{q} - \sum_{\alpha=1}^N \mu_{\alpha} \mathbf{j}_{\alpha}}{\theta} \right) = & \frac{\rho r}{\theta} + \mathbf{q} \cdot \nabla \left( \frac{1}{\theta} \right) - \sum_{\alpha=1}^N \mathbf{j}_{\alpha} \cdot \nabla \left( \frac{\mu_{\alpha}}{\theta} \right) + \\ & + \frac{1}{\theta} \left( (M+p) (\nabla \cdot \mathbf{v}) + \mathbb{T}^d : \mathbb{D}^d - \sum_{\alpha=1}^N \mu_{\alpha} m_{\alpha} \right) \end{aligned}$$

recall that

<sup>17</sup> For  $N = 2$  we have

$$\begin{bmatrix} -\mathbf{j} \\ \mathbf{q} \end{bmatrix} = \begin{bmatrix} L_{11} & L_{12} \\ L_{12} & L_{22} \end{bmatrix} \begin{bmatrix} \nabla \left( \frac{\mu}{\theta} \right) \\ \nabla \left( \frac{1}{\theta} \right) \end{bmatrix},$$

and so we see

$$\mathbf{j} = -L_{11} \nabla \left( \frac{\mu}{\theta} \right) - L_{12} \nabla \left( \frac{1}{\theta} \right)$$

. The diffusive flux  $\mathbf{j}$  is thus proportional to  $\nabla \left( \frac{1}{\theta} \right)$ ; this effect is called the *Soret effect*.

Also

$$\mathbf{q} = L_{12} \nabla \left( \frac{\mu}{\theta} \right) + L_{22} \nabla \left( \frac{1}{\theta} \right),$$

called the *Dufour effect*.

$$\rho r = \sum_{\alpha=1}^N (\rho_{\alpha} r_{\alpha} + \mathbf{j}_{\alpha} \cdot \mathbf{b}_{\alpha}),$$

so if we borrow this we obtain

$$\begin{aligned} & \rho \frac{D\eta}{Dt} + \nabla \cdot \left( \frac{\mathbf{q} - \sum_{\alpha=1}^N \mu_{\alpha} \mathbf{j}_{\alpha}}{\theta} \right) = \\ & = \frac{1}{\theta} \left( (M + p)(\nabla \cdot \mathbf{v}) + \mathbb{T}^d : \mathbb{D}^d - \sum_{\alpha=1}^N \mu_{\alpha} m_{\alpha} \right) + \frac{\rho r}{\theta} + \mathbf{q} \cdot \nabla \left( \frac{1}{\theta} \right) - \sum_{\alpha=1}^N \mathbf{j}_{\alpha} \cdot \left( \nabla \left( \frac{\mu_{\alpha}}{\theta} - \frac{\mathbf{b}_{\alpha}}{\theta} \right) \right). \end{aligned}$$

Let us now work only with the "diffusive component of the entropy production"

$$- \sum_{\alpha=1}^N \mathbf{j}_{\alpha} \cdot \left( \nabla \left( \frac{\mu_{\alpha}}{\theta} \right) - \frac{\mathbf{b}_{\alpha}}{\theta} \right) = - \sum_{\alpha=1}^N \mathbf{u}_{\alpha} \cdot \left( \rho_{\alpha} \nabla \left( \frac{\mu_{\alpha}}{\theta} \right) - \frac{\mathbf{b}_{\alpha}}{\theta} \rho_{\alpha} - \rho_{\alpha} \Lambda \right),$$

which is legit, since  $\sum_{\alpha=1}^N \mathbf{u}_{\alpha} = 0$ . Denote

$$\mathbf{d}_{\alpha} = \rho_{\alpha} \left( \nabla \left( \frac{\mu_{\alpha}}{\theta} \right) - \frac{\mathbf{b}_{\alpha}}{\theta} \rho_{\alpha} - \Lambda \right),$$

and thus we can write

$$- \sum_{\alpha=1}^N \mathbf{j}_{\alpha} \cdot \left( \nabla \left( \frac{\mu_{\alpha}}{\theta} \right) - \frac{\mathbf{b}_{\alpha}}{\theta} \right) = - \sum_{\alpha=1}^N \mathbf{u}_{\alpha} \cdot \mathbf{d}_{\alpha}.$$

We require  $\Lambda$  to be such that

$$\sum_{\alpha=1}^N \mathbf{d}_{\alpha} = 0,$$

*i.e.*,

$$\rho \Lambda = \sum_{\alpha=1}^N \rho_{\alpha} \left( \nabla \left( \frac{\mu_{\alpha}}{\theta} \right) - \frac{\mathbf{b}_{\alpha}}{\theta} \right),$$

from which it follows

$$\Lambda = \sum_{\alpha=1}^N c_{\alpha} \left( \nabla \left( \frac{\mu_{\alpha}}{\theta} \right) - \frac{\mathbf{b}_{\alpha}}{\theta} \right),$$

and so  $\mathbf{d}_\alpha$  have the form

$$\begin{aligned}\mathbf{d}_\alpha &= \rho_\alpha \left( \nabla \left( \frac{\mu_\alpha}{\theta} \right) \right) = \frac{\mathbf{b}_\alpha}{\theta} - \rho_\alpha \sum_{\beta=1}^N c_\beta \left( \nabla \left( \frac{\mu_\beta}{\theta} \right) - \frac{\mathbf{b}_\beta}{\theta} \right) = \\ &= \rho_\alpha \left( \nabla \left( \frac{\mu_\alpha}{\theta} \right) - \frac{\mathbf{b}_\alpha}{\theta} - \frac{\rho_\alpha}{\rho} \sum_{\beta=1}^N \rho_\beta \nabla \left( \frac{\mu_\beta}{\theta} \right) + \frac{\rho_\alpha}{\rho} \sum_{\beta=1}^N \frac{\rho_\beta \mathbf{b}_\beta}{\rho} \right) = \\ &= \rho_\alpha \left( \nabla \left( \frac{\mu_\alpha}{\theta} \right) - \sum_{\beta=1}^N c_\beta \nabla \left( \frac{\mu_\beta}{\theta} \right) - \frac{\mathbf{b}_\alpha - \mathbf{b}}{\theta} \right),\end{aligned}$$

where we have used the definition of the body forces

$$\rho \mathbf{b} = \sum_{\alpha=1}^N \rho_\alpha \mathbf{b}_\alpha.$$

This means that the "diffusive entropy production is"

$$\Pi_\eta^{\text{diff}} = \sum_{\alpha=1}^N \mathbf{u}_\alpha \cdot \mathbf{d}_\alpha,$$

with

$$\mathbf{d}_\alpha = \rho_\alpha \left( \nabla \left( \frac{\mu_\alpha}{\theta} \right) - \sum_{\beta=1}^N c_\beta \nabla \left( \frac{\mu_\beta}{\theta} \right) = \frac{\mathbf{b}_\alpha - \mathbf{b}}{\theta} \right).$$

To proceed, we need some thermodynamical relations

- the *Gibbs relation*

$$\theta \, d\eta = de + p \, d\left(\frac{1}{\rho}\right) - \sum_{\alpha=1}^N \mu_\alpha \, dc_\alpha,$$

- the *Euler relation*

$$\rho \eta = e + p \frac{1}{\rho} - \sum_{\alpha=1}^N \mu_\alpha c_\alpha$$

,

- the *Gibbs-Duhem relation*

$$\eta \, d\theta = \frac{1}{\rho} \, dp - \sum_{\alpha=1}^N c_\alpha \, d\mu_\alpha.$$

<sup>18</sup> Gibbs-Duhem works for  $\nabla$  also, since that is almost the same like  $dd$ .

So we can in fact write (using Gibbs-Duhem<sup>18</sup> in the first step and Euler in the second)

$$\sum_{\beta=1}^N c_{\beta} \nabla \left( \frac{\mu_{\beta}}{\theta} \right) = \underbrace{\frac{1}{\theta} \sum_{\beta=1}^N c_{\beta} \nabla \mu_{\beta}}_{=\frac{\nabla p}{\rho} - \eta \nabla \theta} + \underbrace{\sum_{\beta=1}^N c_{\beta} \mu_{\beta} \nabla \left( \frac{1}{\theta} \right)}_{=e - \theta \eta + \frac{p}{\rho}} = \frac{1}{\theta} \frac{\nabla p}{\rho} - \eta \frac{1}{\theta} \nabla \theta + \left( e - \theta \eta + \frac{p}{\rho} \right) \left( \frac{-\nabla \theta}{\theta^2} \right) = h \nabla \left( \frac{1}{\theta} \right) + \frac{\nabla p}{\rho \theta},$$

where we have denoted

$$h = e + \frac{p}{\rho}, \quad (4.15)$$

as the (*specific*) *enthalpy*. We can thus write

$$\mathbf{d}_{\alpha} = \rho_{\alpha} \nabla \left( \frac{\mu_{\alpha}}{\theta} \right) - \rho_{\alpha} h \nabla \left( \frac{1}{\theta} \right) - \frac{c_{\alpha}}{\theta} \nabla p - \rho_{\alpha} \frac{\mathbf{b}_{\alpha} - \mathbf{b}}{\theta}, \quad (4.16)$$

and the diffusive entropy production is

$$\Pi_{\eta}^{\text{diff}} = - \sum_{\alpha=1}^N \mathbf{u}_{\alpha} \cdot \mathbf{d}_{\alpha} = - \sum_{\alpha=1}^N (\mathbf{u}_{\alpha} - \mathbf{u}_N) \cdot \mathbf{d}_{\alpha}.$$

We now *postulate*

$$\mathbf{d}_{\alpha} := - \sum_{\beta=1}^{N-1} \tau_{\alpha\beta} (\mathbf{u}_{\beta} - \mathbf{u}_N), \quad (4.17)$$

where the matrix  $\tau = \tau^{\text{T}} \in \mathbb{R}^{N-1 \times N-1}$  is some symmetric positive semi-definite matrix to make sure  $\Pi_{\eta}^{\text{diff}} \geq 0$ .

But the true beauty of the *Maxwell-Stefan closure* lies in the construction of a *different matrix*  $\tilde{\tau} \in \mathbb{R}^{N \times N}$ , such that we require

$$\begin{aligned} \sum_{\alpha=1}^N \tilde{\tau}_{\alpha\beta} = 0 &\Leftrightarrow \tilde{\tau}_{N\beta} = - \sum_{\alpha=1}^{N-1} \tau_{\alpha\beta}, \\ \sum_{\beta=1}^N \tilde{\tau}_{\alpha\beta} = 0 &\Leftrightarrow \tilde{\tau}_{\alpha N} = - \sum_{\beta=1}^N \tau_{\alpha\beta}, \\ \tilde{\tau}_{NN} &= - \sum_{\alpha=1}^{N-1} \tilde{\tau}_{\alpha N} = - \sum_{\beta=1}^{N-1} \tilde{\tau}_{N\beta}, \\ \alpha, \beta &= 1, \dots, N-1. \end{aligned}$$

This is in particular handy, because we omit the *privileged* position of  $\mathbf{u}_N$  and obtain

$$\mathbf{d}_\alpha = - \sum_{\beta=1}^N \tilde{\tau}_{\alpha\beta} (\mathbf{u}_\beta - \mathbf{u}_\alpha), \quad (4.18)$$

which is in fact very *nice*, because  $\mathbf{u}_\beta - \mathbf{u}_\alpha = \mathbf{v}_\beta - \mathbf{v}_\alpha$ . Some popular choices are

$$\tilde{\tau}_{\alpha\beta} = \rho_\alpha \rho_\beta f_{\alpha\beta}, \quad (4.19)$$

for some<sup>19</sup>  $\mathbb{f} = \mathbb{f}^\top \in \mathbb{R}^{N \times N}$  *symmetric positive semi-definite matrix*. This ansatz gives

$$\mathbf{d}_\alpha = - \sum_{\beta=1}^N f_{\alpha\beta} (\rho_\beta \mathbf{j}_\alpha - \rho_\alpha \mathbf{j}_\beta),$$

<sup>19</sup> The structure of  $\mathbb{f}$  can be obtained from statistical physics, whereas the structure of  $\mathbb{L}$  not. In fact, one can obtain a different matrix  $\mathbb{d}$  related to  $\mathbb{f}$  which *can be taken as constant*.

and so the full *Maxwell-Stefan* closure reads as

$$- \sum_{\beta=1}^N f_{\alpha\beta} (\rho_\beta \mathbf{j}_\alpha - \rho_\alpha \mathbf{j}_\beta) = \rho_\alpha \nabla \left( \frac{\mu_\alpha}{\theta} \right) - \frac{c_\alpha}{\theta} \nabla p - \rho_\alpha h \nabla \left( \frac{1}{\theta} \right) - \rho_\alpha \frac{\mathbf{b}_\alpha - \mathbf{b}}{\theta}, \quad (4.20)$$

## Constraints

How to add some constraints to the theory? For example, we would like to model the fluids in the mixture as *incompressible*. We will discuss two constraints

- incompressibility,
- quasi-compressibility

## Compressibility

The constraint reads as

$$\nabla \cdot \mathbf{v} = 0. \quad (4.21)$$

The entropy balance is



$$\rho\psi \frac{D\eta}{Dt} = \mathbb{T}^d : \mathbb{D}^d + (M + p)(\nabla \cdot \mathbf{v}) - \nabla \cdot \mathbf{q} - \mu m + \mu \nabla \cdot \mathbf{j} = \mathbb{T}^d : \mathbb{D}^d - \nabla \cdot \mathbf{q} - \mu m + \mu \nabla \cdot \mathbf{j},$$

and so

$$\mathbb{T}^d = 2\nu \mathbb{D}^d = {}^{20}2\nu \mathbb{D}, \quad (4.22)$$

$$\mathbf{q} = \kappa \nabla \left( \frac{1}{\theta} \right), \quad (4.23)$$

$$m = -\beta \mu, \quad (4.24)$$

$$\mathbf{j} = -\alpha \nabla \left( \frac{\mu}{\theta} \right) \quad (4.25)$$

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### Quasi-compressibility

$$\text{tr } \mathbb{D} = \nabla \cdot \mathbf{v} = 0.$$

Our assumption is

$$\rho = \hat{\rho}(c),$$

in general  $\rho = \hat{\rho}(c_1, \dots, c_N)$ . Compute the material time derivative:

$$\frac{D\rho}{Dt} = \frac{\partial \hat{\rho}}{\partial c} \frac{Dc}{Dt},$$

multiply by  $\rho$  and realize  $\frac{D\rho}{Dt} = -\rho(\nabla \cdot \mathbf{v})$ , and  $\rho \frac{Dc}{Dt} = m - \nabla \cdot \mathbf{j}$ , so

$$\rho \frac{D\rho}{Dt} = -\rho^2(\nabla \cdot \mathbf{v}) = \frac{\partial \hat{\rho}}{\partial c} \rho \frac{Dc}{Dt} = \frac{\partial \hat{\rho}}{\partial c} (m - \nabla \cdot \mathbf{j}),$$

and so

$$\nabla \cdot \mathbf{v} = -\frac{1}{\rho^2} \frac{\partial \hat{\rho}}{\partial c} (m - \nabla \cdot \mathbf{j}) = \left( \frac{d}{dc} \left( \frac{1}{\hat{\rho}(c)} \right) \right) (m - \nabla \cdot \mathbf{j})$$

**Example 4.26** (Porous media setting). Is the above setting even sensible? Suppose we have  $N = 2$  and are in the *volume-additivity* setting

$$\sum_{\alpha=1} \varphi_{\alpha} = 1, \varphi_{\alpha} = \frac{\rho_{\alpha}}{\rho_{\alpha}^m},$$

and each of the components are incompressible

$$\rho_{\alpha}^m = \text{const.}$$

↯

↳ Let us compute

$$1 = \sum_{\alpha=1}^N \varphi_{\alpha} = \sum_{\alpha=1}^N \frac{\rho_{\alpha}}{\rho_{\alpha}^m} = \sum_{\alpha=1}^N \frac{\rho c_{\alpha}}{\rho_{\alpha}^m},$$

and so

$$\frac{1}{\rho} = \sum_{\alpha=1}^N \frac{c_{\alpha}}{\rho_{\alpha}^m},$$

and in a binary mixture  $N = 2$  we have

$$\frac{1}{\rho} = \frac{c}{\rho_1^m} + \frac{1-c}{\rho_2^m},$$

and so

$$\frac{d}{dc} \left( \frac{1}{\hat{\rho}(c)} \right) = \frac{1}{\rho_1^m} - \frac{1}{\rho_2^m} = \frac{\rho_2^m - \rho_1^m}{\rho_1^m \rho_2^m},$$

so if we set

$$r_* := \frac{\rho_2^m - \rho_1^m}{\rho_1^m \rho_2^m},$$

we obtain

$$\nabla \cdot \mathbf{v} = r_*(m - \nabla \cdot \mathbf{j}).$$

Recall now the balance of entropy

$$\rho \theta \frac{D\eta}{Dt} = \mathbb{T}^d : \mathbb{D}^d + (M + p)(\nabla \cdot \mathbf{v}) - \mu(m - \nabla \cdot \mathbf{j}),$$

we see we have two options:

- (1) substitute for  $\nabla \cdot \mathbf{v}$  and suppose the chemical reactions are the *main ones*,
- (2) substitute for  $m - \nabla \cdot \mathbf{j}$  and suppose the mechanical interactions are the *main ones*.

First approach:

$$\rho \theta \frac{D\eta}{Dt} = \mathbb{T}^d : \mathbb{D}^d + (M + p)(r_*(m - \nabla \cdot \mathbf{j})) - \mu(m - \nabla \cdot \mathbf{j}) - \nabla \cdot \mathbf{q} \underset{\downarrow}{=} \mathbb{T}^d : \mathbb{D}^d - (m - \nabla \cdot \mathbf{j})(\mu - r_*(M + p)) - \nabla \cdot \mathbf{q}$$

↳ so if we set

$$\mu_* := \mu - r_*(M + P),$$

we are exactly in the "incompressible" Fick-Navier-Stokes-Fourier setting.

$$\rho\theta \frac{D\eta}{Dt} = \mathbb{T}^d : \mathbb{D}^d - (m - \nabla \cdot \mathbf{j})\mu_*,$$

and so

$$\begin{aligned} \mathbb{T} &= M\mathbb{I} + 2\nu\mathbb{D}^d, \\ \mathbf{q} &= \kappa \nabla \left( \frac{1}{\theta} \right), \\ \mathbf{j} &= -\alpha \nabla m_\alpha, m &= -\beta \mu_*. \end{aligned}$$

Plugging this into the balance equations we have

$$\begin{aligned} \rho \frac{D\mathbf{v}}{Dt} &= \nabla M + \nabla \cdot (2\nu\mathbb{D}^d) + \rho\mathbf{b}, \\ \nabla \cdot \mathbf{v} &= r_*(-\beta\mu_* + \nabla \cdot (\alpha \nabla \mu_\alpha)) = r_*(-\beta + \alpha \Delta (\mu_0 r_*(M + p))) = \\ &= r_*(-\beta + \alpha \Delta)(\mu(c, \theta) - r_*p(\theta, c)) + r_*^2(\beta - \alpha \Delta)M = \\ &= \gamma(\theta, c) + r_*^2(\beta - \alpha \Delta)M, \lambda > 0, \beta > 0, \\ &\text{concentration equation.} \end{aligned}$$

This is quite interesting - we see that the divergence of the velocity is proportional to some elliptical operator on  $M$ . This provides some mathematical rooting of the quasi-incompressibility concept; suppose the system

$$\begin{aligned} \nabla \cdot \mathbf{v}_\epsilon &= -\epsilon \Delta M, \\ \partial_t \mathbf{v}_\epsilon + \mathbf{v}_\epsilon \cdot \nabla \mathbf{v}_\epsilon &= \nabla M_\epsilon + \nu \Delta \mathbf{v}_\epsilon - \frac{1}{2} (\nabla \cdot \mathbf{v}_\epsilon) \mathbf{v}_\epsilon, \end{aligned}$$

the apriori estimates are

┘

## Cahn-Hilliard

Let us begin with a more general *ansatz* for the free energy

$$\psi = \hat{\psi} \left( \theta, \frac{1}{\rho}, c, |\nabla c| \right). \quad (4.27)$$

One can then derive

where

$$\boldsymbol{\mu}_c = \rho \frac{\partial \hat{\psi}}{\partial \nabla c}, \quad (4.28)$$

is the *vector chemical potential*,

$$\mu_c = \mu - \frac{\nabla \cdot \boldsymbol{\mu}_c}{\rho}, \mu = \frac{\partial \hat{\psi}}{\partial c}, \quad (4.29)$$

is the *concentration chemical potential* and

$$\mathbb{K} = \mathbf{m}_c \otimes \nabla c, \quad (4.30)$$

is the *Korteweg stress tensor*.

### Allen-Cahn-Fourier

This is the case  $\mathbf{j} = \mathbf{0}, m \neq 0$ . With the following ansatz for the free energy

$$\psi = \psi_0\left(\theta, \frac{1}{\rho}\right) + \psi_1(\theta, c) + \frac{s}{2\rho} |\nabla c|^2. \quad (4.31)$$

Let us also, for simplicity,  $\mathbf{v} = \mathbf{0}, \rho = \text{konst.}$  The evolution equations then are

$$\rho \frac{Dc}{Dt} = m - \nabla \cdot \mathbf{j} = m,$$

and so

$$\rho \partial_t c - \frac{\beta}{\rho} (\nabla \cdot (s \nabla c)) + \frac{\beta}{\rho} \frac{\partial \psi_1}{\partial c} = 0.$$

If one chooses the energetic representation

$$e = \bar{e}\left(\psi, \frac{1}{\rho}, c, \nabla c\right) = \hat{\psi} - \theta \frac{\partial \hat{\psi}}{\partial \theta},$$

and so it holds

$$\begin{aligned} \rho \left( \frac{\partial \bar{e}}{\partial \theta} \frac{\partial \theta}{\partial t} + \frac{\partial \bar{e}}{\partial c} \frac{\partial c}{\partial t} + \frac{\partial \bar{e}}{\partial \nabla c} \frac{\partial c}{\partial t} + \frac{\partial \bar{e}}{\partial \nabla c} \frac{\partial (\nabla c)}{\partial t} \right) = \\ = \nabla \cdot \left( \kappa \frac{\nabla \theta}{\theta} - \left( \frac{\beta s}{\rho^2} \right) \left( \frac{\partial \psi_1}{\partial c} - \nabla \cdot (s \nabla c) \right) \nabla c \right), \end{aligned}$$

realize now

$$\frac{\partial (\gamma \psi + \lambda c)}{\partial t} = \nabla \cdot (\kappa \nabla \psi),$$

and one also has

$$\frac{\partial c}{\partial t} = \frac{b}{\rho^2} \left( \nabla \cdot (s \nabla c) - \frac{\partial \hat{\psi}_1}{\partial c} \right),$$

where

$$\nabla \cdot \left( s \nabla c \frac{\partial c}{\partial t} \right) = \frac{\partial c}{\partial t} (\nabla \cdot (s \nabla c)) + s \nabla c \frac{\partial \nabla c}{\partial t},$$

and so

$$\rho \left( \frac{\partial \bar{e}}{\partial \theta} \frac{\partial \theta}{\partial t} + \left( \frac{\partial \bar{e}}{\partial c} - \frac{(\nabla \cdot (s \nabla c))}{\rho} + \left( \frac{\partial \bar{e}}{\partial \nabla c} \right) - \frac{s \nabla c}{\rho} \right) \cdot \nabla \right) \frac{\partial c}{\partial t}$$

This is terrible<sup>21</sup>. Are there some cases when it is not?

$$\begin{aligned} \frac{\partial \bar{e}}{\partial \nabla c} - \frac{s \nabla c}{\rho} &= \\ &= \frac{\partial}{\partial \nabla c} \left( \hat{\psi} - \theta \frac{\partial \hat{\psi}}{\partial \theta} \right) - s \frac{\nabla c}{\rho} = \\ &= \frac{s \nabla c}{\rho} - \theta \frac{\partial}{\partial \theta} \left( \frac{s \nabla c}{\rho} \right) - \frac{s \nabla c}{\rho} = \\ &= -\frac{\theta}{\rho} \nabla c \frac{\partial s}{\partial \theta} = 0 \Leftrightarrow \sigma \neq \sigma(\theta). \end{aligned}$$

<sup>21</sup> The dependency is on  $c, \nabla c, \Delta c$

So when  $\sigma$  the surface stress is constant, one gets

$$\rho \left( \frac{\partial \bar{e}}{\partial \theta} \frac{\partial \theta}{\partial t} + \left( \frac{\partial \bar{e}}{\partial c} - \frac{(\nabla \cdot (s \nabla c))}{\rho} \right) \frac{\partial c}{\partial t} \right) = \nabla \cdot \left( \kappa \frac{\nabla \theta}{\theta} \right)$$

But  $\sigma \neq \sigma(\theta)$  is really *nonphysical*. We see that there is a *fundamental difference* in the case when the surface density depends on temperature - *the equation has a completely different structure!*

**Remark 4.32** (Development of theories). Many times, one develops a model through mechanical assumptions and then try to "extend it thermodynamically", *e.g.* take the parameters (viscosity, moduli) to be temperature-dependent.

But this is wrong.

If one starts within thermodynamic, he ends up with a *totally different* set of equations.  $\lrcorner$

## Cahn-Hilliard-Navier-Stokes-Fourier

This is the case  $\mathbf{j} \neq 0, m = 0$ . The equations are

$$\begin{aligned}\mathbb{T} &= -p\mathbb{I} + \lambda(\nabla \cdot \mathbf{v})\mathbb{I} + 2\nu\mathbb{D} - \mathbb{K}, \\ \mathbf{q} &= -\kappa \frac{\nabla \theta}{\theta} + \boldsymbol{\mu}_c \frac{(\nabla \cdot \mathbf{j})}{\rho}, \\ \mathbf{j} &= -\alpha \theta \nabla \left( \frac{\mu_c}{\theta} \right), \\ \mu_c &= \mu - \frac{(\nabla \cdot \boldsymbol{\mu}_c)}{\theta}.\end{aligned}$$

From these full equations one can obtain several *reductions*

## Cahn-Hilliard

The Cahn-Hilliard model can be derived as follows: for simplicity, let us take  $\rho = \text{const}$ ,  $\mathbf{v} = 0$ ,  $\theta = \text{const}$ . *Mainly, we are not assuming temperature dependence and no advection.*

$$\rho \frac{Dc}{Dt} = \rho \frac{\partial c}{\partial t} = -\nabla \cdot \mathbf{j} = \nabla \cdot (\alpha \nabla \mu_c) = \nabla \cdot \left( \alpha \nabla \left( \mu - \frac{\nabla \cdot \boldsymbol{\mu}_c}{\rho} \right) \right) = \nabla \cdot \left( \alpha \nabla \left( \frac{\partial \psi_1}{\partial \nabla c} \right) - \nabla \cdot (s \nabla c) \right),$$

so if we take  $\alpha = \text{const}$ ,  $s = \text{const}$  we obtain

$$\rho \frac{\partial c}{\partial t} = \alpha \Delta \left( \frac{\partial \psi_1}{\partial c} - s \Delta c \right). \quad (4.33)$$

For comparison, the Allen-Cahn model looks like

$$\rho \frac{\partial c}{\partial t} = -\beta \left( \frac{\partial \psi_1}{\partial c} - s \Delta c \right),$$

where  $\alpha, \beta > 0$ .

## Cahn-Hilliard-Navier-Stokes

This is the case when we omit temperature dependence. Also, we suppose the fluid is incompressible, *i.e.*  $\theta = \text{const}$ ,  $\nabla \cdot \mathbf{v} = 0$ ,  $\rho = \text{const}$ ,  $s = \text{const}$ . The system is

$$\rho \frac{D\mathbf{v}}{Dt} = \nabla \cdot (2\nu \mathbb{D}) - \nabla p + \nabla \cdot (s \nabla c \otimes \nabla c), \quad (4.34)$$

$$\rho \frac{Dc}{Dt} = \alpha \Delta \left( \frac{\partial \psi_1}{\partial c} - s \Delta c \right). \quad (4.35)$$

## 4.2 Allen-Cahn and Cahn-Hilliard as gradient flows

Let us have a Hilbert space  $H$ , a function  $c(t, \mathbf{x}) \in H$  and a functional  $F : \rightarrow \mathbb{R}$ , given as

$$F(c) = \int_{\mathbb{R}^3} \left( f(c) + \frac{s}{2} |\nabla c|^2 \right) d\mathbf{x}.$$

The evolution is called a *gradient flow* if it holds

$$\partial_t c = -k \nabla F. \quad (4.36)$$

where  $\nabla F \in H$  is the *functional derivative* defined as

$$\left\langle \frac{\delta F(c)}{\delta c}, v \right\rangle_{H^*, H} = \frac{d}{ds} (F(c + sv)) \Big|_{s=0} = (\nabla F, v)_{H, H} \quad (4.37)$$

and so  $\frac{\delta F}{\delta c}$  is the distribution representing the Gateaux derivative of  $F$  and  $\nabla F$  is the Riesz representation of  $\frac{\delta F}{\delta c}$ .

Whis is this any useful? Let us compute

$$\frac{d}{dt} F(c)(t) = \left\langle \frac{\delta F}{\delta c}, \partial_t c \right\rangle = (\nabla F, \partial_t c) = -k \|\nabla F\|_H^2 \leq 0,$$

and so one sees

$$\frac{d}{dt} F(c) \leq 0,$$

*i.e.* the evolution of a gradient flow minimizes *the free energy functional*.

## A-C as a gradient flow

We have

$$\langle \delta F(c), v \rangle = \int_{\mathbb{R}^3} (f'(c)v + s \nabla c \cdot \nabla v) dx = \int_{\mathbb{R}^3} (f'(c) - \nabla \cdot (s \nabla c))v dx = (\nabla F, v)_{L_2},$$

and so one sees

$$\partial_t c = -k \left( \frac{\partial \psi_1}{\partial c} - \nabla \cdot (s \nabla c) \right), \quad (4.38)$$

i.e. A-C is a gradient flow in  $L_2$ .

## C-H as a gradient flow

$$\langle \frac{\delta F}{\delta c}, v \rangle = \int_{\mathbb{R}^3} \left( \frac{\partial \psi_1}{\partial c} + s \nabla c \cdot \nabla v \right) dx,$$

let us set  $H = H^{-1}(\mathbb{R}^3)$ , with

$$(u, v)_{H^{-1}} = (\nabla u^*, \nabla v^*)_{L_2},$$

with  $u^*$  being the solution to  $\Delta u^* = u$ . Now

$$\begin{aligned} \langle \frac{\delta F}{\delta c}, v \rangle &= \int_{\mathbb{R}^3} \Delta \left( \frac{\partial \psi_1}{\partial c} \right)^* \Delta v^* + \Delta \nabla \Delta c^* \cdot \nabla \Delta v^* dx = \\ &= \int_{\mathbb{R}^3} \left( \Delta \left( \frac{\partial \psi_1}{\partial c} \right)^* - s \Delta \Delta c^* \right) \Delta v^* dx = \\ &= - \int_{\mathbb{R}^3} \nabla \left( \Delta \left( \frac{\partial \psi_1}{\partial c} \right)^* - s \Delta \Delta c^* \right) \cdot \nabla v^* dx, \end{aligned}$$

and so (with our dot product) the Riesz representation is

$$\langle \frac{\delta F}{\delta c}, v \rangle = \left( -\Delta \left( \frac{\partial \psi_1}{\partial c} \right), v \right)_{H^{-1}},$$

meaning

$$\partial_t c = +k \Delta \left( \frac{\partial \psi_1}{\partial c} - s \Delta c \right),$$

which is exactly the Cahn-Hilliard model.



# 5 Chemical reactions

Our evolution equation for the concentration has been

$$\rho \frac{Dc_\alpha}{Dt} = -\nabla \cdot \mathbf{j}_\alpha + m_\alpha, \alpha = 1, \dots, N,$$

with the constraint

$$\sum_{\alpha=1}^N m_\alpha = 0,$$

representing the *conservation of mass in chemical reactions*. So far, we had

$$\rho \frac{D\eta}{Dt} = \dots - \sum_{\alpha=1}^N m_\alpha \mu_\alpha,$$

and to have this positive, we put

$$m_\alpha = -\beta_\alpha \mu_\alpha,$$

but this approach has a *fundamental weakness*: we have so far ignored that in chemical reactions, the number of atoms of individual types remain unchanged.

**Our goal** is to focus on  $\xi_{\text{chem}} = -\sum_{\alpha=1}^N \mu_\alpha m_\alpha$ , where

$$\mu_\alpha = \frac{\partial \hat{\psi}}{\partial c_\alpha} \left( \theta, \frac{1}{\rho}, c_\alpha \right) = \frac{\partial \hat{g}}{\partial c_\alpha} (\theta, p, c_\alpha),$$

where  $g = \hat{g}(\theta, p, c_\alpha)$  is the *Gibbs potential*.

- *stoichiometry*: mathematical (LA) description of chemical reactions and composition
- *mixture of ideal gases*: we will obtain  $\mu_\alpha$  explicitly,
- *chemical equilibrium*,
- *chemical kinetics*.

## 5.1 Steichiometry

We seek a mathematical description of chemical reactions.

**Definition 5.1** (Molar mass). We define

$$M_\alpha = \sum_{\sigma=1}^Z T_{\sigma\alpha} A^\sigma, \quad (5.2)$$

where  $\sigma = 1, \dots, Z$  are individual types of atoms (*e.g.* O, N, C, ...),  $A^\sigma$  are molar masses of  $\sigma$ -atom *i.e.* the mass of 1 mol,  $T_{\sigma\alpha}$  is the *composition matrix*.

Next up, it will be useful to reformulate  $m_\alpha$  in terms of molar quantites

$$m_\alpha = M_\alpha J^\alpha, \quad (5.3)$$

where  $J^\alpha$  is the *molar rate* in units  $\text{mol}/(\text{m}^3\text{s})$ .

**Lemma 5.4** (Conservation of number of atoms in chemical reactions). It must hold

$$\sum_{\alpha=1}^N T_{\sigma\alpha} J^\alpha = 0, \sigma = 1, \dots, Z. \quad (5.5)$$

Let us realize that from this *axiom* we also obtain the conservation of mass

$$\begin{aligned} \sum_{\alpha=1}^N m_\alpha &= \sum_{\alpha=1}^N M_\alpha J^\alpha = \sum_{\alpha=1}^N \sum_{\sigma=1}^Z T_{\sigma\alpha} A^\sigma J^\alpha = \\ &= \sum_{\sigma=1}^Z A^\sigma \underbrace{\sum_{\alpha=1}^N T_{\sigma\alpha} J^\alpha}_{=0} \equiv 0. \end{aligned}$$

Notice that this means

$$H := \text{rank}(\mathbb{T}) < N, \quad (5.6)$$

*i.e.* the rows of  $\mathbb{T}$  are linearly dependent. Excluding the linearly dependent rows of  $\mathbb{T}$  we obtain the matrix  $\mathbb{S} \in \mathbb{R}^{H \times N}$ .

**Remark 5.7** (No harm done). Realize that the conservation of number of atoms still holds:

↴

$$\sum_{\alpha=1}^N T_{\sigma\alpha} J_{\alpha} = 0 \Leftrightarrow \sum_{\alpha=1}^N S_{\sigma\alpha} J_{\alpha} = 0,$$

and one also has

$$M_{\alpha} = \sum_{\sigma=1}^H S_{\sigma\alpha} \epsilon^{\sigma},$$

with  $\epsilon^{\sigma}$  being the *atomic substances*.<sup>22</sup>

<sup>22</sup> Those are the parts of the mixture that do not react anymore (?).

**Definition 5.8** (Composition and reaction spaces). Let us now denote

$$\mathbf{M} = \sum_{\alpha=1}^N M_{\alpha} \mathbf{e}_{\alpha} \in \mathbb{R}^N,$$

and

$$\mathbf{J} = \sum_{\alpha=1}^N J_{\alpha} \mathbf{e}_{\alpha} \in \mathbb{R}^N,$$

and

$$\mathbf{f}_{\sigma} = \sum_{\alpha=1}^N S_{\sigma\alpha} \mathbf{e}_{\alpha},$$

as the  $\sigma$ -th column of  $\mathbb{S}$  with  $\mathbf{e}_{\alpha}$  being the canonical basis. Denote furthermore

$$W = \text{span} \{ \mathbf{f}_1, \dots, \mathbf{f}_H \},$$

as the *composition space* and

$$V = W^{\perp}, \mathbb{R}^N = V \oplus W,$$

as the *reaction space*.

**Lemma 5.9** (What lies where.). It holds

$$\mathbf{M} \in W, \mathbf{J} \in V.$$

**Proof.**

$$\mathbf{M} = \sum_{\alpha=1}^N M_{\alpha} \mathbf{e}_{\alpha} = \sum_{\alpha=1}^N \sum_{\sigma=1}^H S_{\sigma\alpha} \epsilon^{\sigma} \mathbf{e}_{\alpha} = \sum_{\sigma=1}^H \epsilon^{\sigma} \sum_{\alpha=1}^N S_{\sigma\alpha} \mathbf{e}_{\alpha} = \sum_{\sigma=1}^H \epsilon^{\sigma} \mathbf{f}_{\sigma} \in W,$$

and

$$\mathbf{f}_{\sigma} \cdot \mathbf{J} = \left( \sum_{\alpha=1}^N S_{\sigma\alpha} \mathbf{e}_{\alpha} \right) \cdot \left( \sum_{\sigma=1}^H J_{\sigma} \mathbf{e}_{\sigma} \right) = \sum_{\alpha=1}^N S_{\sigma\alpha} J_{\alpha} = 0, \forall \sigma = 1, \dots, H,$$

where we have just used the conservations of atoms.  $\square$

**Remark 5.10** (Equivalent formulation of mass conservation).

Equivalently, one can write the conservation of mass in chemical reactions as

$$0 = \mathbf{M} \cdot \mathbf{J} = \left( \sum_{\alpha=1}^N M_{\alpha} \mathbf{e}_{\alpha} \right) \cdot \left( \sum_{\sigma=1}^H J_{\sigma} \mathbf{e}_{\sigma} \right) = \sum_{\alpha} M_{\alpha} J_{\alpha} = \sum_{\alpha} m_{\alpha}.$$

」

$V$  is a vector space, so one can choose a dual basis  $\{\mathbf{g}^P\}_{P=1}^{N-H}$  as the *contravariant basis* of  $V$ , or  $\{\mathbf{g}_P\}_{P=1}^{N-H}$  as the *covariant basis* of  $V$ . The following *orthogonality relations* yield

$$0 = \mathbf{f}_{\sigma} \cdot \mathbf{g}^P = \left( \sum_{\alpha} S_{\sigma\alpha} \mathbf{e}_{\alpha} \right) \cdot \left( \sum_{\rho} P^{P\rho} \mathbf{e}_{\rho} \right) = \sum_{\alpha=1}^N S_{\sigma\alpha} P^{P\alpha}, \sigma = 1, \dots, H, P = 1, \dots, N-H,$$

where the columns of  $P^{P\rho}$  is the *matrice prechodu*. It remains to realize that this yields  $H(N-H)$  relations for  $(N-H)H$  unknown elements of  $\mathbb{P}$ , *i.e.*  $P^{P\alpha}$ .

And so

$$\mathbf{g}^P = \sum_{\alpha=1}^N P^{P\alpha} \mathbf{e}_{\alpha}, p = 1, \dots, N-H.$$

**Example 5.11** (Nitrogen oxides). Let us have two oxides of nitrogen:  $\text{NO}_2, \text{N}_2\text{O}$ . The matrix  $\mathbb{S}$  is  $\mathbb{S} = [1, 2]^{\top}$ .  $\square$

**Example 5.12** (example name).  $N = 3, \alpha = 1 \dots O, \alpha = 2 \dots, O_2, \alpha = 3, \dots, O_3$ . Then  $\mathbb{T} = [1, 2]^\top = \mathbb{S}, H = \text{rank } \mathbb{T} = 1, N - H = 2$ , and so

$$\mathbb{P} = \begin{bmatrix} 1 & 0 & P^{13} \\ 0 & 1 & P^{23} \end{bmatrix}$$

where the remaining components have to satisfy

$$(1, 2, 3) \cdot (1, 0, P^{13}) = 1 + 3P^{13} = 0,$$

and so

$$P^{13} = -\frac{1}{3},$$

and

$$(1, 2, 3) \cdot (0, 1, P^{23}) = 2 + 3P^{23} = 0,$$

and so

$$P^{23} = -\frac{2}{3}.$$

One can take the matrix to be

$$\mathbb{P} = \begin{bmatrix} 3 & 0 & -1 \\ 0 & 3 & -2 \end{bmatrix},$$

and so

$$\begin{aligned} 3O - O_3 &= 0 \Leftrightarrow O_3 \rightarrow 3O_1, \\ 3O_2 - 2O_3 &= 0 \Leftrightarrow 2O_3 \rightarrow 3O_2. \end{aligned}$$

┘

Another possible view is

$$\mathbf{J} \in V \Rightarrow \mathbf{J} = \sum_{\alpha=1}^N J_{\alpha} \mathbf{e}_{\alpha} = \sum_{p=1}^{N-1} J_p \mathbf{g}^p,$$

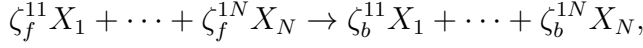
and taking the dot product with  $\mathbf{e}_{\beta}$  we have

$$J_{\beta} = \sum_{p=1}^{N-H} J_p P^{p\beta}, \beta = 1, \dots, N$$

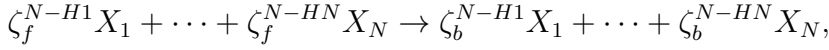
and so the sought quantites in fact are  $J_p, p = 1, \dots, N - H$  and it holds

$$m_\alpha = M_\alpha J_\alpha = \sum_{p=1}^{N-H} M_\alpha P^{p\alpha} J_p, \alpha = 1, \dots, N.$$

Consider now an alternative view: somebody gives us the chemical reactions that take place in the mixture, *i.e.* the reactants and products  $X_1, \dots, X_N$  are known:



...



with  $\zeta_b^{ij}, \zeta_f$  being the *backward/forward* steichiometric coefficients of  $j$  component in  $i$  reaction. The matrix  $\mathbb{P}$  has the elements

$$P^{q\beta} = \zeta_b^{q\beta} - \zeta_f^{q\beta}.$$

Consider now a fixed volume  $V$  and  $N_\alpha(V)$  to be the number of moles in  $V$  of  $\alpha$ -th component. It holds

$$J_q := \frac{1}{P^{q1}} \frac{dN_1(V)}{dt} = \frac{1}{P^{q2}} \frac{dN_2(V)}{dt} = \dots = \frac{1}{P^{qN}} \frac{dN_N(V)}{dt}, q = 1, \dots, N-H. \quad (5.13)$$

*i.e.*  $J_q$  is an invariant of the reaction  $q$ . The quantity  $J_q$  is called the *advancement of  $q$ -th reaction*.

The consequence of this is

$$\zeta^{CH} = -\frac{1}{\theta} \sum_{\alpha=1}^N m_\alpha \mu_\alpha = -\frac{1}{\theta} \sum_{\alpha=1}^N \sum_{q=1}^{N-H} M_\alpha P^{q\alpha} J_q \mu_\alpha = -\frac{1}{\theta} \sum_{q=1}^{N-H} J_q \left( \sum_{\alpha=1}^N M_\alpha \mu_\alpha P^{q\alpha} \right) = -\frac{1}{\theta} \sum_{q=1}^{N-H} J_q \left( \sum_{\alpha=1}^N \mu_\alpha^M P^{q\alpha} \right),$$

where  $\mu_\alpha^M = \mu_\alpha M_\alpha$  is the *molar chemical potential*. We thus can write

$$\zeta^{CH} = -\frac{1}{\theta} \sum_{q=1}^{N-H} J_q A^q,$$

with

$$A^q = \sum_{\alpha=1}^N \mu_\alpha^M P^{q\alpha} = -\frac{1}{\theta} \mathbf{J} \cdot \mathbf{A}.$$

Let us compute the projection of  $\boldsymbol{\mu}^M = (\mu_1^M, \dots, \mu_N^M)$  to  $V$

$$P_V \boldsymbol{\mu}^M = \boldsymbol{\mu}^M \cdot \left( \sum_{p=1}^{N-H} \mathbf{g}^p \otimes \mathbf{g}_p \right) = \sum_p (\mathbf{g}^p \cdot \boldsymbol{\mu}^M) \mathbf{g}_p, \quad (5.14)$$

where

$$\mathbf{g}^p \cdot \boldsymbol{\mu}^M = \sum_{\alpha=1}^N \mu_{\alpha}^M \mathbf{e}_{\alpha} \cdot \mathbf{g}^p = \sum_{\alpha=1}^N \mu_{\alpha}^M P^{p\alpha} = A^p,$$

and so

$$P_V \boldsymbol{\mu}^M = \sum_{p=1}^{N-H} A^p \mathbf{g}_p,$$

and so we see that the *chemical affinity*  $\mathbf{A}$  is the projection of  $\boldsymbol{\mu}^M$  to the reaction subspace  $V$ .

## 5.2 Mixture of ideal gases

Suppose we have a system of  $N$  ideal gases. The state equations are

$$p_{\alpha} = \frac{N_{\alpha} R \theta}{V} = \frac{R \theta}{M_{\alpha}} \frac{n_{\alpha}}{V} = \frac{R}{M_{\alpha}} \theta \rho_{\alpha} = \hat{p}_{\alpha}(\theta, \rho_{\alpha})$$

and so

$$\rho_{\alpha} = \frac{M_{\alpha}}{R \theta} p_{\alpha}.$$

The second equation is

$$e_{\alpha} = \hat{e}_{\alpha} = d_{\alpha} \frac{R \theta}{M_{\alpha}},$$

with  $d_{\alpha}$  being the *equipartitioning constant*. Finally, the entropy is

$$\eta_{\alpha} = \hat{\eta}_{\alpha}(\theta, \rho_{\alpha}) =$$

And so our fundamental relation for Helmholtz:

$$\rho\psi = \sum_{\alpha=1}^N \rho_{\alpha}\psi_{\alpha} = \sum_{\alpha=1}^N \rho_{\alpha}(e_{\alpha} - \theta\eta_{\alpha}) = \sum_{\alpha=1}^N d_{\alpha}\rho_{\alpha} \frac{R\theta}{M_{\alpha}} - \theta \sum_{\alpha=1}^N \left( d_{\alpha}\rho_{\alpha} \frac{R}{M_{\alpha}} \log\left(\frac{\theta}{\theta_0}\right) - \frac{R}{M_{\alpha}} \rho_{\alpha} \log\left(\frac{\rho_{\alpha}}{\rho_{\alpha}^0}\right) + \rho_{\alpha}\eta_{\alpha}^0 \right), \quad (5.15)$$

which is a fundamental relation of the form

$$\rho\psi = \widehat{\rho\psi}(\theta, \rho_{\alpha}).$$

The thermodynamical quantities can be obtained as

$$\begin{aligned} \mu_{\alpha} &= \frac{\partial \widehat{\rho\psi}}{\partial \rho_{\alpha}} = e_{\alpha} - \theta\eta_{\alpha} - \sum_{\beta} \theta \rho_{\beta} \frac{\partial \eta_{\beta}}{\partial \rho_{\alpha}} = e_{\alpha} - \theta\eta_{\alpha} + \frac{R\theta}{M_{\alpha}} = \\ &= \left( e_{\alpha} - \theta\eta_{\alpha} + \frac{p_{\alpha}}{\rho_{\alpha}} \right)(\theta, \rho_{\alpha}) \equiv g_{\alpha}(\theta, \rho_{\alpha}), \end{aligned}$$

and it is natural to express the chemical potential in terms of  $(\theta, p_{\alpha})$ , and so

$$\tilde{\mu}_{\alpha}(\theta, p_{\alpha}) = \mu_{\alpha}(\theta, \hat{\rho}_{\alpha}(p_{\alpha}, \theta)) = \tilde{\mu}_{\alpha}\left(\theta, p \frac{p_{\alpha}}{\rho}\right)$$

From *homework*, we know the *Dalton law* holds:

$$p = \rho^2 \frac{\partial \psi}{\partial \rho} = \sum_{\alpha=1}^N p_{\alpha}, \quad (5.16)$$

which means

$$p = \sum_{\alpha=1}^N p_{\alpha} = R\theta \sum_{\alpha=1}^N \frac{\partial \rho_{\alpha}}{\partial M_{\alpha}}.$$

The natural variable for the chemical potential thus is

$$\frac{p_{\alpha}}{p} = \frac{\frac{\rho_{\alpha}}{M_{\alpha}}}{\sum_{\beta=1}^N \frac{\rho_{\beta}}{M_{\beta}}} = \frac{c_{\alpha}^M}{\sum_{\beta=1}^N \gamma_{\beta}},$$

with

$$c_{\alpha}^M = \frac{\rho_{\alpha}}{M_{\alpha}}. \quad (5.17)$$



Thus we arrive at the relation

$$\mu_\alpha = \mu_\alpha\left(\theta, p \frac{c_\alpha^M}{\sum_{\beta=1}^N c_\beta^M}\right) = \hat{g}_\alpha\left(\theta, p \frac{c_\alpha^M}{\sum_{\beta=1}^N c_\beta^M}\right) = \hat{g}_\alpha(\theta, p) + \frac{R\theta}{M_\alpha} \log\left(\frac{c_\alpha^M}{\sum_{\beta=1}^N c_\beta^M}\right),$$

which can be further manipulated using the fact

$$1 = \sum_\beta c_\beta^M = \sum_\beta \frac{\rho_\beta}{M_\beta} = \frac{1}{R\theta} \sum_\alpha p_\alpha = \frac{p}{R\theta},$$

and so if we set

$$\mu_\alpha^0 = g_\alpha(\theta, p) - \frac{R\theta}{M_\alpha} \log\left(\frac{p}{R\theta}\right),$$

then we obtain

$$\mu_\alpha^M(\theta, p, c_\alpha^M) = \mu_\alpha^{M,0}(\theta, p) + R\theta \log c_\alpha^M \quad (5.18)$$

This condition on the chemical potential is called "*ideal mixing*". In the case of *non-ideal mixing*, the resulting chemical potential would be

$$\mu_\alpha^M - \mu_\alpha^{M,0}(\theta, p) + R\theta \log(a_\alpha(c_\beta^M)),$$

where  $a_\alpha$  is called the *chemical activity* of  $\alpha$ -th component, *i.e.* in the case of ideal mixing  $a_\alpha = c_\alpha$ .

## 5.3 Chemical equilibrium

We have shown that the chemical production of entropy is

$$\zeta^{ch} = -\frac{1}{\theta} \mathbf{J} \cdot \mathbf{A}.$$

It is natural to postulate that *thermodynamical equilibrium* happens when

$$\zeta^{ch\dagger} = 0 = -\frac{1}{\theta^\dagger} \mathbf{J}^\dagger \cdot \mathbf{A}^\dagger. \quad (5.19)$$

<sup>23</sup> One could also assume something else: both vectors being zero, them being perpendicular...

<sup>24</sup> Note that  $\mathbb{P}$  is a constant matrix, so it does not change even in the equilibrium; formally  $\mathbb{P} = \mathbb{P}^\dagger$ .

Our definition <sup>23</sup> of the chemical equilibrium is

$$\mathbf{A}^\dagger = 0,$$

which is equivalent to <sup>24</sup>

$$A^{\dagger p} = 0 \Leftrightarrow \sum_{\alpha} \mu_{\alpha}^{M^\dagger} P^{p\alpha} = 0, p = 1, \dots, N - H.$$

What does this mean? <sup>25</sup>

<sup>25</sup> Recall we are fixing the temperature and pressure, so the chemical equilibrium depends only on the equilibrium of the potentials.

$$0 = \sum_{\alpha=1}^N \left( \mu_{\alpha}^{M^0}(\theta, p) + R\theta \log a_{\alpha} \right)^{\dagger} P^{p\alpha} \Leftrightarrow 0 = \sum_{\alpha=1}^N \mu_{\alpha}^{M^0}(\theta, p) P^{p\alpha} + R\theta \log \left( \prod_{\alpha=1}^N (a_{\alpha}^{\dagger})^{P^{p\alpha}} \right) = 0$$

it is usual to denote

$$\sum_{\alpha=1}^N \mu_{\alpha}^{0M}(\theta, p) \mathbb{P}^{o\alpha} = -R\theta \log K_p(\theta, p), \quad (5.20)$$

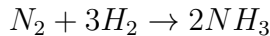
as *equilibrium constants of  $p$ -th reaction*. Our equilibrium requirement yields

$$0 = R\theta \log \left( K_p^{-1} \prod_{\alpha=1}^N (a_{\alpha}^{\dagger})^{\mathbb{P}^{p\alpha}} \right), \quad (5.21)$$

meaning

$$K_p(\theta, p) = \prod_{\alpha=1}^N (a_{\alpha}^{\dagger})^{\mathbb{P}^{p\alpha}}. \quad (5.22)$$

**Example 5.23** (Haber-Bosch synthesis). That is the equation



Let us moreover suppose that the reaction

- runs in a closed container,
- the initial composition is: 1 mole of nitrogen, 3 moles of hydrogen and 0 moles of ammonia,

↴

- the mixing is ideal:  $a_\alpha = c_\alpha^M$ ,
- the pressure  $p$  and temperature  $\theta$  are constant.

What is the equilibrium composition  $Q$ ? Order nitrogen molecule as  $\alpha = 1$ , hydrogen molecule as  $\alpha = 2$  and amoniac molecule as  $\alpha = 3$ , nitrogen as  $\sigma = 1$  and hydrogen as  $\sigma = 2$ .

$$T = \begin{bmatrix} 2 & 0 & 1 \\ 0 & 2 & 3 \end{bmatrix} P = \begin{bmatrix} -1 & -3 & 2 \end{bmatrix}$$

Our equations are

$$\partial_t \rho_\alpha + \nabla \cdot (\rho_\alpha \mathbf{v}_\alpha) = m_\alpha = M_\alpha \mathbb{P}^{1\alpha} J_1,$$

which we integrate over the container  $\Omega$  to obtain

$$\frac{d}{dt} \int_\Omega \rho_\alpha dx + \int_{\partial\Omega} \rho_\alpha \mathbf{v}_\alpha \cdot \mathbf{n} dS = M_\alpha \mathbb{P}^{1\alpha} J_1 V,$$

where  $V = \lambda(\Omega)$  is the volume of  $\Omega$ . Realize that

$$\int_\Omega \rho_\alpha dx = M_\alpha(t, \Omega)$$

and so if integrate this from 0 to  $t$  we can write

$$M_\alpha(t, \Omega) - M_\alpha(0, \Omega) = V M_\alpha \mathbb{P}^{1\alpha} \int_0^t J_1(s) ds,$$

so if we divide this by  $M_\alpha$  the **molar masses** we obtain

$$N_\alpha(t, \Omega) - N_\alpha(t, 0) = V \mathbb{P}^{1\alpha} \int_0^t J_1(s) ds, \alpha = 1, 2, 3,$$

where we have denoted  $N_\alpha(t, \Omega)$  as the number of moles in  $\Omega$  in the time  $t$ . Further manipulation gives

$$\frac{N_\alpha(t, \Omega) - N_\alpha(t, 0)}{\mathbb{P}^{1,\alpha}} = \int_0^t J_1(s) ds,$$

which means

$$\frac{N_{N_2}(t, \Omega) - 1}{-1} = \frac{N_{H_2}(t, \Omega) - 3}{-3} = \frac{N_{NH_3}(t) - 0}{2}, \forall t > 0.$$

↳ And so in equilibrium it must also hold

$$\frac{N_{N_2}^\dagger - 1}{-1} = \frac{N_{H_2}^\dagger - 3}{-3} = \frac{N_{NH_3}^\dagger - 0}{2},$$

which are 2 equations for 3 unknowns :(. But we have also the *mass-action law*:

$$K_1(\theta, p) = (a_{N_2}^\dagger)^{-1} (a_{H_2}^\dagger)^{-3} (a_{NH_3}^\dagger)^2 = \dots = \frac{(N_{NH_3}^\dagger)^2 V^{-2}}{(N_{N_2}^\dagger) (N_{H_2}^\dagger)^3 V^{-4}},$$

and so

$$K_1 V^{-2} = \frac{(N_{NH_3}^\dagger)^2}{(N_{N_2}^\dagger) (N_{H_2}^\dagger)^3}.$$

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## 5.4 Chemical kinetics

There are at least 2 approaches:

- (1) non-linear closures automatically satisfying 2nd law <sup>26</sup>
- (2) reduction of Taylor expansion (rational thermodynamics)

### Rational thermodynamics

<sup>26</sup> Note that mechanical, thermal and chemical effects are all taken to be independent: we suppose the 2nd law holds for every single one of them separately.

$$\begin{aligned} \theta \zeta^{CH} &= - \sum_{\alpha=1}^N m_\alpha \mu_\alpha = - \sum_{p=1}^{N-H} \left( \sum_{\alpha=1}^N \mu_\alpha^m P^{p\alpha} \right) J_p = \\ &= - \sum_{p=1}^{N-H} \sum_{\alpha=1}^N \left( \mu_\alpha^{M0}(\theta, p) + R\theta \log a_\alpha \right) P^{p\alpha} J_p = \\ &= - \sum_{p=1}^{N-H} \left( qty \left( \sum_{\alpha=1}^N \mu_\alpha^{M0} P^{p\alpha} \right) + R\theta \log \left( \prod_{\alpha=1}^N a_\alpha^{P^{p\alpha}} \right) J_p \right) = \\ &= - \sum_{p=1}^{N-H} R\theta \log \left( K_p^{-1} \prod_{\alpha=1}^N a_\alpha^{P^{p\alpha}} \right) J_p, \end{aligned}$$

one can write

$$P^{p\alpha} = \nu_{p\alpha}^b - \nu_{p\alpha}^f,$$

(backward/forward stoich. coefficients), and so

$$\begin{aligned}\theta\zeta^{CH} &= -R\theta \sum_{p=1}^{N-H} \log \left( K_p^{-1}(\theta, p) \frac{\prod_{\alpha=1}^N a_{\alpha}^{\nu_{\alpha p}^b}}{\prod_{\beta=1}^N a_{\beta}^{\nu_{\beta p}^f}} \right) J_p = \\ &= -R\theta \sum_{p=1}^{N-H} \log \left( \frac{k_p^b \prod_{\alpha=1}^{N-H} a_{\alpha}^{\nu_{\alpha p}^b}}{\prod_{\beta=1}^{N-H} \alpha_{\beta}^{\nu_{\beta p}^f}} \right) J_p,\end{aligned}$$

where

$$\frac{k_p^b}{k_p^f} = K_p(\theta, p)^{-1},$$

and so

$$\theta\zeta^{CH} = R\theta \sum_{p=1}^{N-H} \left( \log \left( k_p^f \prod_{\alpha=1}^N a_{\alpha}^{\nu_{\alpha p}^f} \right) - \log \left( k_p^b \prod_{\alpha=1}^N a_{\alpha}^{\nu_{\alpha p}^b} \right) \right) J_p.$$

Let us try to propose a *non-equilibrium mass action law*:

$$J_p = k_p^f \prod_{\alpha=1}^N a_{\alpha}^{\nu_{\alpha p}^f} - k_p^b \prod_{\alpha=1}^N a_{\alpha}^{\nu_{\alpha p}^b} \equiv J_p^f - J_p^b$$

and then from the monotonicity of the logarithm we obtain

$$\zeta^{CH} \geq 0. \quad (5.24)$$

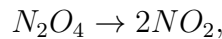
This is in fact beautiful: in equilibrium, we have

$$\zeta^{\dagger} 0 \Leftrightarrow J_p^{\dagger} = 0 \Leftrightarrow J_p^{f\dagger} = J_p^{b\dagger} \Leftrightarrow K_p = \prod_{\alpha=1}^N \left( a_{\alpha}^{\dagger} \right)^{\mathbb{P}^{p\alpha}},$$

and also this has a nice *probabilistic interpretation*:

## Taylor expansion

**Example 5.25** (Nitrogen oxides). Let us come back to the example



↴

↳ that is

$$P = \begin{bmatrix} 2 & -1 \end{bmatrix}$$

and let us look for  $J_1 = \hat{J}_1(\theta, p, a_1, a_2)$ . We use Taylor up to order 2.

$$J_1 = k_{00}a_1^0a_2^0 + k_{10}a_1^1a_2^0 + k_{01}a_2 + k_{11}a_1a_2 + k_{20}a_1^2 + k_{02}a_2^2.$$

We require  $\hat{J}(\mathbf{A}^\dagger) = 0$ , so

$$0 = k_{00} + k_{10}a_1^\dagger + k_{01}a_2^\dagger + k_{11}a_1^\dagger a_2^\dagger + k_{20}(a_1^\dagger)^2 + k_{02}(a_2^\dagger)^2,$$

and also the equilibrium mass action law gives us

$$K_1(\theta, p) = (a_1^\dagger)^2 (a_2^\dagger)^{-1} \Rightarrow a_2^\dagger = K^{-1} (a_1^\dagger)^2,$$

meaning

$$0 = k_{00} + k_{10}a_1^\dagger + k_{01}K_1^{-1}(a_1^\dagger)^2 + k_{11}k_1^{-1}(a_1^\dagger)^3 + k_{20}(a_1^\dagger)^2 + k_{02}K_1^{-2}(a_1^\dagger)^4.$$

From the postulates of rational thermodynamics, this has to be zero  $\forall a_1^\dagger$  and so

$$0 = k_{00} = k_{10} = k_{11} - k_{02},$$

and also

$$k_{01}K_1^{-1} + k_{20} = 0,$$

which gives us

$$J_1 = k_{01}a_2 + k_{20}a_1^2 = k_{01}(a_2 - K_1^{-1}a_1^2).$$

This is *exactly the equilibrium mass action law* and one can identify

$$J_1^f = k_{01}(\theta, p)a_2, J_1^b = K_1^{-1}k_{01}(\theta, p)a_1^2,$$

with

$$J_1 = J_1^f - J_1^b,$$

and also it must hold  $k_{01} \geq 0$ . ┘

# Class II mixtures

In this approach we are taking into account the fact that not only the densities  $\rho_1 \neq \rho_2$ , but also the momenta  $\rho_1 \mathbf{v}_1 \neq \rho_2 \mathbf{v}_2$ , *i.e.* the velocities  $\mathbf{v}_1 \neq \mathbf{v}_2$  are not the same.<sup>27</sup> Note this must mean *there exists a mechanical interaction between the components*.

<sup>27</sup> The same of course holds even for  $N > 2$ .

Important examples of the class II mixtures include

- *porous media flow* (oil industry hydrology, fracking, sewers),
- *bubbly flows*: two phase flows (energetic reactors, chemistry)
- *swelling*: fluid-structure interaction, inporous media<sup>28</sup>

What is our road plan?

- (1) reminder of balances in class II mixtures,
- (2) obtain some *a priori* knowledge about interaction forces *from the balances*,
- (3) forces inferred from investigating the forces *acting on a single particle*,
- (4) **Darcy's law** + generalisations (*Brikman, Forehlheimer*)
- (5) generalised thermodynamical framework

<sup>28</sup> Hydrocephalosis: flow of water in brain tissue - inporous media flow within a viscoelastic setting.

## 6.1 Balance laws

The balance of mass reads

$$\partial_t \rho_\alpha + \nabla \cdot (\rho_\alpha \mathbf{v}_\alpha) = m_\alpha, \quad \sum_{\alpha=1}^N m_\alpha = 0,$$

the balance of linear momentum is

$$\partial_t (\rho_\alpha \mathbf{v}_\alpha) + \nabla \cdot (\rho_\alpha \mathbf{v}_\alpha \otimes \mathbf{v}_\alpha) = \nabla \cdot \mathbb{T}_\alpha + \rho_\alpha \mathbf{b}_\alpha + \mathbf{I}_\alpha + m_\alpha \mathbf{v}_\alpha,$$

with

$$\sum_{\alpha=1}^N (\mathbf{I}_\alpha + m_\alpha \mathbf{v}_\alpha) = \mathbf{0},$$

and a *single* internal energy balance

$$\rho \dot{e} = -\nabla \cdot \mathbf{q} + \mathbb{T} : \mathbb{D} + \rho r,$$

where

$$\mathbb{T} = \sum_{\alpha=1}^N (\mathbb{T}_\alpha - \rho_\alpha \mathbf{u}_\alpha \otimes \mathbf{u}_\alpha).$$

We see that we require extra the constitutive relations for the partial Cauchy stress tensors  $\mathbb{T}_\alpha$  and the interaction forces  $\mathbf{I}_\alpha$ .

## 6.2 Structure of interaction forces

Now we would like to obtain some information about the structure of the interaction forces *just from the balance laws*; this task is difficult on its own, so let us simplify our problem to a *binary mixture*.

Furthermore assume  $m_1 = -m_2 = 0$ , so our balance equations are

$$\begin{aligned} \rho_1 \dot{\mathbf{v}}_1 &= \nabla \cdot \mathbb{T}_1 + \rho_1 \mathbf{b}_+ \mathbf{I}, \\ \rho_2 \dot{\mathbf{v}}_2 &= \nabla \cdot \mathbb{T}_2 + \rho_2 \mathbf{b} - \mathbf{I}. \end{aligned} \quad (6.1)$$

Recall the procedure from ?? : rewrite the balance of mass to have the standard single component form <sup>29</sup>, rewrite the the balance of total momentum using this formulation and identify *something*.

One has  $\mathbf{v}_1 - \mathbf{v}_2 = \mathbf{u}_1 - \mathbf{u}_2$ , and  $\mathbf{j}_\alpha = \rho_\alpha \mathbf{u}_\alpha = \rho c_\alpha \mathbf{u}_\alpha$ , meaning

$$\mathbf{u}_1 = \frac{\mathbf{j}}{\rho c} \quad (6.2)$$

and since  $\mathbf{j}_1 + \mathbf{j}_2 = \mathbf{0}$ , one has

<sup>29</sup> Recall

$$\frac{D}{Dt} = \frac{\partial}{\partial t} + \mathbf{v} \cdot \nabla,$$

and

$$\frac{D_\alpha}{Dt} = \frac{\partial}{\partial t} + \mathbf{v}_\alpha \cdot \nabla,$$

<sup>30</sup> we are taking  $c_1 \equiv c, c_2 = 1 - c$ .



$$\mathbf{j}_2 = -\mathbf{j}_1 \equiv -\mathbf{j} = \rho c_2 \mathbf{u}_2 = \rho(1 - c) \mathbf{u}_2,$$

from which it follows

$$\mathbf{u}_2 = -\frac{\mathbf{j}}{\rho(1 - c)}. \quad (6.3)$$

Let us this compute

$$\mathbf{v}_1 - \mathbf{v}_2 = \mathbf{u}_1 - \mathbf{u}_2 = \frac{\mathbf{j}}{\rho} \left( \frac{1}{c} + \frac{1}{1 - c} \right) = \frac{\mathbf{j}}{\rho c(1 - c)},$$

and so

$$\begin{aligned} \dot{\mathbf{j}} &= \frac{D(\rho c \mathbf{u}_1)}{Dt} = \frac{D(\rho c(\mathbf{v}_1 - \mathbf{v}))}{Dt} = \\ &= \rho \dot{c}(\mathbf{v}_1 - \mathbf{v}) + \rho \dot{c}(\mathbf{v}_1 - \mathbf{v}) + \rho c(\dot{\mathbf{v}}_1 - \dot{\mathbf{v}}), \end{aligned}$$

where

$$\rho c \dot{\mathbf{v}}_1 = \rho c \left( \partial_t \mathbf{v}_1 + (\nabla \mathbf{v}_1) \underbrace{\mathbf{v}}_{=\mathbf{v}_1 - \mathbf{u}_1 = \mathbf{v}_1 - \frac{\mathbf{j}}{\rho c}} \right) = \underbrace{\rho_1 \frac{D_1 \mathbf{v}_1}{Dt}}_{=\nabla \cdot \mathbb{T}_1 - \rho c \mathbf{b} + \mathbf{I}} - \rho c \underbrace{(\nabla \mathbf{v}_1)}_{=\nabla \mathbf{v} + \nabla \left( \frac{\mathbf{j}}{\rho c} \right)} \frac{\mathbf{j}}{\rho c}.$$

Altogether

$$\dot{\mathbf{j}} = -\mathbf{j}(\nabla \cdot \mathbf{v}) - \frac{\nabla \cdot \mathbf{j}}{\rho c} \mathbf{j} + \nabla \cdot \mathbb{T}_1 + \rho c \mathbf{b} + \mathbf{I} - (\nabla \mathbf{v}) \left( \frac{\mathbf{j}}{\rho c} \right) + \nabla \left( \frac{\mathbf{j}}{\rho c} \right) \left( \frac{\mathbf{j}}{\rho c} \right) - c(\nabla \cdot \mathbb{T} + \rho \mathbf{b}),$$

where one can substitute

$$\mathbb{T} = \mathbb{T}_1 + \mathbb{T}_2 + \rho_1 \mathbf{u}_1 \otimes \mathbf{u}_2 + \rho_2 \mathbf{u}_2 \otimes \mathbf{u}_2 = \mathbb{T}_1 + \mathbb{T}_2 - \frac{\mathbf{j} \otimes \mathbf{j}}{\rho c(1 - c)},$$

to obtain

$$\dot{\mathbf{j}} + ((\nabla \cdot \mathbf{v}) \mathbb{I} + \nabla \mathbf{v}) \mathbf{j} + \nabla \cdot \left( \frac{\mathbf{j} \otimes \mathbf{j}}{\rho} \left( \frac{1}{c} - \frac{1}{1 - c} \right) \right) = \nabla \cdot ((1 - c) \mathbb{T}_1 - c \mathbb{T}_2) + \mathbb{T} \nabla c + \mathbf{I}. \quad (6.4)$$

**Remark 6.5** (Maxwell-Catthaneo). One could consider

$$\rho e = \widehat{\rho e}(\rho\eta, \rho_\alpha \mathbf{j}_\alpha),$$

make thermodynamical closures and obtain

$$\tau \partial_t \mathbf{q} = -(\mathbf{q} + \kappa \nabla \theta), \quad (6.6)$$

which is known as the *Maxwell-Catthaneo* equation (law). This is an useful generalisation of the *Fourier law* for very fast processes. Note that this equation leads to a *hyperbolic* heat equation, so in particular there is also the *finite propagation of information*.  $\lrcorner$

Let us take the steady state 6.4 and assume  $\mathbf{v} \approx \mathbf{0}, \mathbf{j} \otimes \mathbf{j} \approx \mathbf{0}, |\mathbf{j}|^2 \approx 0$ :

$$0 = \nabla \cdot ((1 - c)\mathbb{T}_1 + c\mathbb{T}_2) + \mathbb{T} \nabla c + \mathbf{I}.$$

In equilibrium<sup>†</sup>, one must obtain <sup>31</sup>

$$\begin{aligned} \mathbb{T}^\dagger &= -p^\dagger \mathbb{I}, \\ \mathbb{T}_1^\dagger &= -cp^\dagger \mathbb{I}, \\ \mathbb{T}_2^\dagger &= -(1 - c)p^\dagger \mathbb{I}, \end{aligned}$$

which after substitution above yields

$$\mathbf{I}^\dagger = p^\dagger \nabla c. \quad (6.7)$$

One can thus make the assumption

$$\mathbf{I} = -p \nabla c + \text{something},$$

where

$$\text{something}^\dagger = \mathbf{0}.$$

<sup>31</sup> Note that it would be more physical to take the volume fractions instead of mass fractions below.

## 6.3 Interaction forces from macroscopic analogies

### Flow around a sphere

Let us consider the problem of a flow of an incompressible Newtonian fluid around a sphere of radius  $a$ ,

$$\begin{aligned}\nabla \cdot \mathbf{v} &= 0, \\ \partial_t \mathbf{v} + \nabla \cdot (\mathbf{v} \otimes \mathbf{v}) &= -\nabla p + \frac{1}{\text{Re}} \Delta \mathbf{v},\end{aligned}$$

where

$$\text{Re} = \frac{\text{inertial forces}}{\text{viscous forces}} = \frac{|\nabla \cdot (\rho \mathbf{v} \otimes \mathbf{v})|}{|\nabla \cdot (2\mu \mathbb{D})|} = \frac{\frac{1}{L} \rho v^2}{\frac{1}{L^2} \mu v} = \frac{L \rho v}{\mu} = \frac{2a \rho V}{\mu}, \quad (6.8)$$

where  $V$  is some characteristic velocity magnitude. The force acting on the sphere is

$$\mathbf{f} = \int_{\partial\Omega} \mathbb{T} \mathbf{n} \, ds = \mathbf{f}_{\parallel} + \mathbf{f}_{\perp}.$$

But to find  $\mathbf{f}$ , we require  $\mathbb{T}$ , *i.e.* we require  $\mathbb{D}$ , *i.e.* we require the solution  $\mathbf{v}$ .

### Stokes

In some very special cases, like the Stokes problem <sup>32</sup>, we obtain the problem

<sup>32</sup> Spherical symmetry and linearisation

$$\begin{aligned}\nabla \cdot \mathbf{v} &= 0, \\ \frac{1}{\text{Re}} \Delta \mathbf{v} - \nabla p &= \mathbf{0}.\end{aligned} \quad (6.9)$$

This has an analytical solution

$$\mathbf{f}_D = 6\pi a \mu \mathbf{v}_r, \quad (6.10)$$

which is however valid only for very small Reynolds numbers, like  $\text{Re} < 0.2$ .

## Oseen

Another possibility is the *Oseen linearisation*:

$$\nabla \cdot \mathbf{v} = 0, \quad (6.11)$$

$$\mathbf{v}_\infty \cdot \nabla \mathbf{v} = -\nabla p + \frac{1}{\text{Re}} \Delta \mathbf{v}, \quad (6.12)$$

which has the analytical! solution <sup>33</sup>

$$\mathbf{f}_D^{\text{oseen}} = \frac{1}{2} \rho \pi a^2 C_D |\mathbf{v}_r^\infty| \mathbf{v}_r^\infty, \quad (6.13)$$

where the drag coefficient  $C_D$  is given as

$$C_D = \frac{24}{\text{Re}} \left( 1 + \frac{3}{16} \text{Re} \right).$$

This is valid for  $\text{Re} < 3$ , so a *bit* better than Stokes.

## Sheer lift

The fluid flow does not have to be uniform - just because of the gradient of the velocity, the resulting force is known as the *Saffman force*<sup>34</sup>

<sup>34</sup> This is not a drag force, but a lift force!

$$\mathbf{f}_\perp = 6.46 \sqrt{\nu} \rho a^2 \sqrt{\left| \frac{\partial v_r^\infty}{\partial z} \right|} |v_r^\infty| \text{sgn} \left( \frac{\partial v_r^\infty}{\partial z} \right) \mathbf{e}_z. \quad (6.14)$$

## Magnus force

Another known lift is the *Magnus force* acting on a *rotating body*.

$$\mathbf{f}_\perp = -C(|\mathbf{v}_r^\infty|) \boldsymbol{\omega} \times \mathbf{v}_R \quad (6.15)$$

## Non-stationary flows

What about when the flow is not stationary?

### Virtual mass efect

Suppose one wishes to accelerate a ball flowing in a liquid; realize however that in order to accelerate the ball, one has to accelerate also the surrounding fluid! This can be modelled that the ball has a *greater mass*, *i.e.*

$$\mathbf{f}_{\text{virtual mass}} = (m_{\Omega} + m_{\text{vir}}) \dot{\mathbf{v}}_r, \quad (6.16)$$

where  $m_{\Omega}$  is the mass of the ball and  $m_{\text{vir}}$  is the virtual mass. It can be shown

$$m_{\text{vir}} = \frac{2}{3} \pi a^3 \rho_f, \quad (6.17)$$

with  $\rho_f$  being the density of the fluid.<sup>35</sup>

<sup>35</sup> This is *half* of the mass displaced by the incompressible fluid.

### Besset force

When the particle is accelerating, there exists another force called the *Basset force*

$$\mathbf{f}_b = -6\pi a^2 \sqrt{\pi\mu} \int_{-\infty}^t \frac{1}{\sqrt{t-s}} \dot{\mathbf{v}}_r(s) ds. \quad (6.18)$$

### Buyoancy force

An approximation can be made when one suppose hydrostatic conditions and Taylor expansion

$$\begin{aligned} \mathbf{f}_b &= \int_{\partial\Omega} -p \mathbf{n} \mathbf{n} ds = - \int_{\partial\Omega} (p(0) + \nabla p(0) \cdot \mathbf{x}) \mathbf{n} ds = \\ &= -p(0) \underbrace{\int_{\partial\Omega} \mathbf{n} ds}_{=0} - \nabla p(0) \cdot \underbrace{\int_{\partial\Omega} \mathbf{x} \otimes \mathbf{n} ds}_{=\mathbb{I}} = -\nabla p(0) \cdot \mathbb{I} V_{\Omega}, \end{aligned}$$

### Inspiration

We have seen there are many many interactions between the fluid and some particles - *i.e.* there can be many interactions between the mixture components.

How can one include these effects in the balance laws? Assume the ansatz

$$\mathbf{I} \propto \underbrace{\alpha_1(\mathbf{v}_f - \mathbf{v}_s)}_{\text{drag}} + \underbrace{\alpha_2 \mathbb{D}(\mathbf{v}_f)(\mathbf{v}_f - \mathbf{v}_s)}_{\text{shear lift}} + \underbrace{\alpha_3(\omega(\mathbf{v}_f) - \omega(\mathbf{v}_s))(\mathbf{v}_f - \mathbf{v}_s)}_{\text{Magnus force}}$$

with  $\mathbf{v}_f$  being the velocity of the fluid and  $\mathbf{v}_s$  being the velocity of the solid (or some particle), and  $\omega(\mathbf{v})$  is the skew-symmetric part of  $\nabla \mathbf{v}_f$ .

We are yet to include the virtual mass effect. That is however troublesome, we require the force to be objective. It can be shown that it holds

$$\mathbf{a}_1^* - \mathbf{a}_2^* = \mathbb{Q}(t)(\mathbf{a}_1 - \mathbf{a}_2) + 2\dot{\mathbb{Q}}(t)(\mathbf{v}_1 - \mathbf{v}_2),$$

where the last term corresponds to the Coriolis force. It can be shown that the only *objective relative accelerations* have the form

$$\mathbf{a}_{12} = \frac{D_2 \mathbf{v}_1}{Dt} - \frac{D_1 \mathbf{v}_2}{Dt} + (1 - \lambda)(\nabla(\mathbf{v}_2 - \mathbf{v}_1))(\mathbf{v}_1 - \mathbf{v}_2), \lambda \in \mathbb{R}. \quad (6.19)$$

In our model, we assume  $\lambda = 1$  only, so the total interaction becomes

$$\mathbf{I} \propto \underbrace{\alpha_1(\mathbf{v}_f - \mathbf{v}_s)}_{\text{drag}} + \underbrace{\alpha_2 \mathbb{D}(\mathbf{v}_f)(\mathbf{v}_f - \mathbf{v}_s)}_{\text{shear lift}} + \underbrace{\alpha_3(\omega(\mathbf{v}_f) - \omega(\mathbf{v}_s))(\mathbf{v}_f - \mathbf{v}_s)}_{\text{Magnus force}} + \quad (6.20)$$

$$+ \underbrace{\left( \alpha_4 \left( \frac{D_f}{Dt} \{ \mathbf{v}_s \} - \frac{D_s \mathbf{v}_f}{Dt} \right) \right)}_{\text{virtual mass effect}} + \underbrace{(\alpha_5 \nabla \varphi)}_{\text{diffusion}} + p \nabla \varphi \quad (6.21)$$

## 6.4 Darcy law

In the following we will show 3 ways one can obtain the Darcy law

- (1) reduction of the governing equations,
- (2) from macroscopic analogies and physical intuition,
- (3)

## Reduction derivation

Assume that the mixture is a binary mixture of fluid  $f$  and solid  $s$ . What we will do:

- ignore  $\mathbf{v}_s = \mathbf{0}$ ,
- neglect fluid inertia  $\dot{\mathbf{v}}_2 = \mathbf{0}$ ,
- ignore most viscous effects:  $\mathbb{T}_f = -p_f \mathbb{I} = -p\varphi \mathbb{I}$ ,
- assume drag only in the interaction force  $\mathbf{I} = \alpha \left( \mathbf{v}_f - \underbrace{\mathbf{v}_s}_{=\mathbf{0}} \right) + p \nabla \varphi$ .

In total, from the balance of momentum for the fluid one has

$$0 = -\nabla(p\varphi) + \rho_f^m \varphi \mathbf{g} + \alpha \mathbf{v}_f + p \nabla \varphi - \varphi \nabla p - p \nabla \varphi,$$

so one has

$$\alpha \mathbf{v}_f = \varphi \nabla p - \rho_f^m \varphi \mathbf{g} = \varphi \left( \nabla p_f^{\text{pore}} - \rho_f^m \mathbf{g} \right).$$

Since  $\alpha < 0$ , one usually writes

$$\tilde{\alpha} \mathbf{v}_f = -\varphi \left( \nabla p_f^{\text{pore}} - \rho_f^m \mathbf{g} \right), \quad (6.22)$$

with  $\tilde{\alpha} > 0$ , the *drag coefficient*. This is the *Darcy law*.

## Macroscopic analogy

Let us show another derivation of the Darcy law, springing from some *macroscopic analogy*.

Imagine the fluid solid system can be imagined as a slab with periodic circular channels of radius  $a$  that are  $d$  apart<sup>36</sup>. Assume the flow regime is stationary, *i.e.* we are interested in the *Poiseuille flow*:

<sup>36</sup> Characteristic pore distance, grain size

$$\mathbf{j} = -\frac{\pi}{8\mu} a^4 \nabla p, \quad (6.23)$$

where  $\mathbf{j}$  is the volume flux in  $\text{m}^3/\text{s}$ . But this works for a straight channel; what if it is curved? It can be shown:

$$\mathbf{j} = -\frac{\pi a^4}{8\mu X} \nabla p, \quad (6.24)$$

where  $X$  is the *tortuosity*, *i.e.* some geometric factor. Define now

$$\tilde{\mathbf{j}} = \frac{\mathbf{j}}{d^2},$$

and the volume fraction will be proportional to

$$\varphi \propto \left( \frac{a^2}{d^2} \right).$$

We thus see

$$\tilde{\mathbf{j}} \propto \frac{a^4}{d^2} \frac{\nabla}{\mu} \propto \frac{d^2 \varphi^2 \nabla p}{\mu},$$

in a straight channel; in a curved one we would have

$$\tilde{\mathbf{j}} = -\frac{d^2 \varphi}{X} \frac{\nabla p}{\mu}, \quad (6.25)$$

which can be further simplified upon the definition of the *permeability of the environment*

$$k(\varphi) = \frac{d^2 \varphi^2}{X},$$

to the form

$$\tilde{\mathbf{j}} = -\frac{k(\varphi)}{\mu} \nabla p.$$

Since it holds

$$\tilde{\mathbf{j}} = \varphi_f \mathbf{v}_f,$$

we obtain

$$\mathbf{v}_f = -\frac{k(\varphi)}{\varphi \mu} \nabla p.$$

<sup>37</sup> And handwaving.



This has been done without gravity, but with some intuition <sup>37</sup> one can infer

$$\mathbf{v}_f = -\frac{k(\varphi)}{\varphi\mu} (\nabla p - \rho_f^m \mathbf{g}). \quad (6.26)$$

We see that our previously obtained Darcy 6.22 suggests

$$\frac{\varphi}{\alpha_1} = \frac{k(\varphi)}{\varphi\mu_j}.$$

Very often, the permeability has the form

$$k(\varphi) = k_0 \varphi^n,$$

for usually  $n \in [2, 3]$ .

## Homogenization

Imagine that the structure of the material is such that there are many *cells* with radius  $a$  and dimension  $d$ . For simplicity, assume again that the system is only a binary mixture of a fluid and a solid and it holds

$$\Omega_f = \bigcup_i \Omega_f^i,$$

$$\Omega_s = \bigcup_i \Omega_s^i,$$

*i.e.* the region occupied by the fluid and solid consists of some cells. In these regions, we wish to solve the Stokes problem:

$$\begin{aligned} \nabla \cdot \mathbf{v} &= 0, \\ -\nabla p + \mu \Delta \mathbf{v} &= 0, \end{aligned}$$

in  $\Omega_g$  and  $\mathbf{v} = \mathbf{0}$  at  $\partial\Omega_g$ . To actually get somewhere, we introduce some scaling

$$\mathbf{v} = [\mathbf{v}] \tilde{\mathbf{v}},$$

with  $\tilde{\mathbf{v}} = O(1)$ . For Darcy

$$[\mathbf{v}_f] = \frac{d^2}{\mu} \frac{\delta p}{l}.$$

After non-dimensionalisation one gets

$$\frac{1}{l} \nabla \cdot ([\tilde{\mathbf{v}}_f] \tilde{\boldsymbol{\rho}}) = 0,$$

and so it must hold all the time

$$\nabla \cdot \tilde{\mathbf{v}}_f = 0.$$

The momentum equation then becomes

$$0 = \frac{[\delta p]}{l} (-\tilde{\nabla} \tilde{p}) + \frac{\mu}{l^2} \frac{d^2}{\mu l} [\delta p] \tilde{\Delta} \tilde{\mathbf{v}}_f,$$

which begs for the definition

$$\epsilon = \frac{d}{l} \ll 1,$$

as then

$$-\tilde{\nabla} \tilde{p} + \epsilon^2 \tilde{\Delta} \tilde{\mathbf{v}},$$

with

$$\tilde{\mathbf{v}} = 0.$$

Drop the tildas now and write

$$\begin{aligned} \nabla \cdot \mathbf{v}_\epsilon &= 0, \\ -\nabla p_\epsilon + \epsilon^2 \Delta \mathbf{v}_\epsilon &= 0, \end{aligned}$$

in  $\Omega_{f_\epsilon}$  and  $\mathbf{v}_\epsilon = \mathbf{0}$  on  $\partial\Omega_{f_\epsilon}$ . To proceed we need some kind of *scale separation*:

- the macroscale  $\Omega$ ,

<sup>38</sup> A very dirty one: the variable is discrete, which gets forgotten very often.

- the microstructure, *i.e.* the cell of scale  $\epsilon$ .

This can be done in the following way: from  $\psi_\epsilon(t, \mathbf{x}) : \Omega \times (0, T) \rightarrow \mathbb{R}$  we go for  $\psi_\epsilon(t, \mathbf{x}_0, \boldsymbol{\xi})$ , with  $\boldsymbol{\xi} \in \Omega_{\text{cell}}$ . The procedure<sup>38</sup> is

$$\psi_\epsilon(t, \mathbf{x}_0, \boldsymbol{\xi}) = \psi_\epsilon(t, \mathbf{x}_0 + \epsilon \boldsymbol{\xi}).$$

Then the useful quantity is

$$\langle \rho \rangle(t, \mathbf{x})_{\text{cell}} = \frac{1}{|\Omega_{\text{cell}}|} \int_{\Omega_{\text{cell}}} \rho_\epsilon(t, \mathbf{x}, \boldsymbol{\xi}) d\boldsymbol{\xi},$$

and furthermore do a *asymptotic power series expansion*

$$\psi_\epsilon(t, \mathbf{x}) = \sum_{i=0}^{\infty} \epsilon^i \psi_\epsilon^{(i)}(t, \mathbf{x}, \boldsymbol{\xi}).$$

Finally, realize that

$$\nabla_{\mathbf{x}} \psi_\epsilon(t, \mathbf{x}) \rightarrow \left( \nabla_{\mathbf{x}} + \frac{1}{\epsilon} \nabla_{\boldsymbol{\xi}} \right) \psi_\epsilon(t, \mathbf{x}, \boldsymbol{\xi}),$$

and so we are ready to rewrite the equations using

$$\mathbf{v}_\epsilon(t, \mathbf{x}) = \sum_{i=0}^{\infty} \epsilon^i \mathbf{v}_\epsilon^{(i)}(t, \mathbf{x}, \boldsymbol{\xi}),$$

$$p_\epsilon(t, \mathbf{x}) = \sum_{i=0}^{\infty} \epsilon^i p_\epsilon^{(i)}(t, \mathbf{x}, \boldsymbol{\xi}),$$

to the form

$$\left( \nabla_{\mathbf{x}} + \frac{1}{\epsilon} \nabla_{\boldsymbol{\xi}} \right) \cdot \left( \mathbf{v}^{(0)} + \epsilon \mathbf{v}^{(1)} + \dots \right) = 0,$$

and the second equation is

$$0 = - \left( \nabla_{\mathbf{x}} + \frac{1}{\epsilon} \nabla_{\boldsymbol{\xi}} \right) \left( p^{(0)} + \epsilon p^{(1)} + \dots \right) + \epsilon^2 \left( \nabla_{\mathbf{x}} + \frac{1}{\epsilon} \nabla_{\boldsymbol{\xi}} \right) \cdot \left( \nabla_{\mathbf{x}} + \frac{1}{\epsilon} \nabla_{\boldsymbol{\xi}} \right) \left( \mathbf{v}^{(0)} + \epsilon \mathbf{v}^{(1)} \right).$$

Let us now extract the terms of orders of  $\epsilon$ :

$$\begin{aligned}\epsilon^1 : \nabla_\xi \cdot \mathbf{v}^{(0)}(t, \mathbf{x}, \xi) &= 0, \\ \epsilon^1 : \nabla_\xi p^{(0)}(t, \mathbf{x}, \xi) &= 0 \Leftrightarrow p^{(0)}(t, \mathbf{x}, \xi) = p^{(0)}(t, \mathbf{x}), \\ \epsilon^0 : -\nabla_x p^{(0)} - \nabla_\xi p^{(1)} + \triangle_\xi \mathbf{v}^{(0)} &= 0.\end{aligned}$$

This is the formulation of the *cell problem*:

$$\begin{aligned}\nabla_\xi \cdot \mathbf{v}^{(0)} &= 0, \\ \triangle_\xi \mathbf{v}^{(0)} - \nabla_\xi p^{(1)} &= \nabla_x p^{(0)}(t, \xi),\end{aligned}$$

inside  $\Omega_{\text{cell}}(\mathbf{x})$  with the boundary conditions

$$\mathbf{v}^{(0)} = \mathbf{0}, \text{ on } \partial\Omega_{\text{cell}}^f \setminus \partial\Omega_{\text{cell}},$$

and periodic BC's on  $\partial\Omega_{\text{cell}}$ . We see that if we solve *three cell problems* with the RHS of  $\mathbf{e}_\alpha, \alpha = 1, 2, 3$  the basis vectors of  $\mathbb{R}^3$ , we can solve any virtually any problem - it is *linear*,

$$\begin{aligned}\nabla_\xi \cdot \mathbf{v}^{(0)} &= 0, \\ \triangle_\xi \mathbf{v}^{(0)} - \nabla_\xi p^{(1)} &= \mathbf{e}_\alpha,\end{aligned}$$

as then the solution would be

$$-\sum_{\alpha=1}^3 \mathbf{v}_\alpha^{(0)}(t, \mathbf{x}, \xi) \left( \frac{\partial p^{(0)}(t, \mathbf{x})}{\partial x^\alpha} \right),$$

with  $\mathbf{v}^{(0)}$  solving the special problem. What are we interested in is then in fact

$$\begin{aligned}\langle \mathbf{v}^{(0)}(t, \mathbf{x}, \xi) \rangle (t, \mathbf{x}) &= \frac{1}{|\Omega_{\text{cell}}|} \int_{\Omega_{\text{cell}}} \mathbf{v}^{(0)}(t, \mathbf{x}, \xi) d\xi = \\ &= -\sum_{i=1}^3 \langle \mathbf{v}_\alpha^{(0)} \rangle (t, \mathbf{x}) \left( \frac{\partial p^{(0)}(t, \mathbf{x})}{\partial x^i} \right) = -\frac{\mathbb{k}(t, \mathbf{x}, \varphi)}{\mu\varphi} \nabla_x p^{(0)},\end{aligned}$$

where we have defined (obtained!)

$$\mathbb{k} = \mu\varphi \sum_{i=1}^3 \langle \mathbf{v}_\alpha^{(0)} \rangle \otimes \mathbf{e}_\alpha,$$

as the *permeability tensor*.

## Well problem

Two neighbours have a well near the fence and one of them uses a lot of water. How does the water level of the underground water pool changes?

The balance of mass

$$\partial_t \rho_f + \nabla \cdot (\rho_f \mathbf{v}_f) = 0,$$

can be recast as

$$\partial_t (\varphi \rho_f^m) + \nabla \cdot (\varphi \rho_f^m \mathbf{v}_f) = 0,$$

where

$$\varphi \mathbf{v}_f = -\frac{k_0 \varphi^2}{\mu} (\nabla p - \rho_f^m \mathbf{g}) = -\frac{k_0 \varphi^2}{\mu} \rho_f^m g \nabla \left( \frac{p}{\rho_f^m g} + z \right),$$

where

$$h = \left( \frac{p}{\rho_f^m g} + z \right)$$

It can be shown that the continuity equation in fact gives

$$F(p) \frac{\partial h}{\partial t} - K \rho_f^m \Delta h = 0.$$

The stationary case of this is  $\Delta h = 0$ . How to interpret this? The levels of equal pressure are  $z = \hat{z}(r)$ , *s.t.*  $p(r, z(r)) = \text{const}$ , *i.e.*

$$h(r, z(r)) = \frac{p(r, z(r))}{\rho_f^m g} + \hat{z}(r).$$

In cylindrical coordinates  $(z, r)$  with the assumption  $\frac{\partial h}{\partial z} = 0$  one has

$$\Delta h = \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial h}{\partial r} \right) = 0,$$

this can be manipulated by integrating from 0 to some  $h(r)$

$$0 = \int_0^{h(r)} \frac{\partial}{\partial r} \left( r \frac{\partial h}{\partial r} \right) dz = \frac{\partial}{\partial r} \int_0^{h(r)} r \frac{\partial h}{\partial r} dr - \frac{\partial h}{\partial r} h \frac{\partial h}{\partial r} = 0,$$

from which it follows

$$rh \frac{dh}{dr} = \text{const} = Q,$$

meaning

$$\frac{d^2 h}{dr^2} = \frac{Q}{2\pi r},$$

*i. e.*

$$h^2(r_2) - h^2(r_1) = 2Q \log \left( \frac{r_2}{r_1} \right).$$

$$-\nabla p = \frac{\mu}{k} \mathbf{v}_r + \mu' \triangle \mathbf{v} \quad (6.27)$$

$$\varphi v_f + O|\mathbf{v}_f| \mathbf{v}_f = -\frac{k(\varphi)}{\varphi \mu} \left( \nabla p - \rho_f^m \mathbf{g} \right) \quad (6.28)$$

# Multi-phase continuum thermodynamics

This is the approach where we assume that the region is occupied by regions of *different species*, that are not *mixed on a molecular level*. This is a more physically sound approach:

- one can formulate balance laws on the interfaces
- the *multicomponent* theory can be obtained by some kind of averaging

Our starting point must be a generalisation of the *classical* continuum mechanics to a setting with *active interfaces*, or discontinuities (*passive interfaces*)

## 7.1 General balance laws with interfaces

Assume the presence of (active) interfaces  $\Gamma$  separating  $\Omega_+, \Omega_-$ . Then one can take e.g density and define its excess as

$$\rho_\Gamma^E = \begin{cases} \rho - \rho^+, & \text{in } \Omega_+, \\ \rho - \rho^-, & \text{in } \Omega_- \end{cases}. \quad (7.1)$$

We see that  $\text{supp } \rho_\Gamma^E \subset \Omega_\epsilon$ , where  $\Omega_\epsilon$  is the interfacial region <sup>39</sup>

It can be then integrated over the whole region  $\Omega_\epsilon$  defined

<sup>39</sup> A strip of (varying) thickness  $\epsilon$  around the interface.

$$\rho_\Gamma = \int_{-\epsilon}^{\epsilon} \int_{S(\xi)} \rho_\Gamma^E dS(\xi) d\xi,$$

where  $S(\xi)$  is the "elevatin surface" that is changing with  $\xi$ . and it can be shown that this is equal to

$$\rho_\Gamma = \int_\Gamma \int_{-\epsilon}^{\epsilon} (1 - \kappa_1)(1 - \kappa_2) \rho_\Gamma^E d\xi dS, \quad (7.2)$$

where  $\kappa_i(\xi)$  are the principal curvatures of the surface.

In this manner one cane generalise also the fluxes:

$$\mathcal{F}^\psi = \int_{S_+ \cup S_i} \Phi_\Omega^\psi dS + \int_{\partial\Gamma} \Phi_\Gamma^\psi \cdot \mathbf{n}_\gamma dl, \quad (7.3)$$

and the production

$$\mathcal{P}^\psi \int_{\Omega_+ \cup \Omega_i} \xi_\Omega^\psi dx + \int_\Gamma \xi_\Gamma^\psi dS, \quad (7.4)$$

and the supply

$$\mathcal{S}^\psi = \int_{\Omega_+ \cup \Omega_i} \Sigma_\Omega^\psi dx + \int_\Gamma \Sigma_\Gamma^\psi dS. \quad (7.5)$$

We then postulate

$$\frac{d\psi}{dt} = -\mathcal{F}^\psi + \mathcal{P}^\psi + \mathcal{S}^\psi, \forall \Omega \text{ control volumes.} \quad (7.6)$$

To manipulate further, we require some advanced tools

## Generalization of some theorems

### Reynolds theorem

One has

$$\frac{d}{dt} \int_{\Omega_+ \cup \Omega_i} \psi_\Omega dx = \int_{\Omega_+ \cup \Omega_i} \left( \frac{\partial \psi_\Omega}{\partial t} + \nabla \cdot (\psi_\Omega \otimes \mathbf{v}) \right) dx + \int_\Gamma [\psi_\Omega \otimes (\mathbf{v} - \mathbf{v}_\Gamma^\perp \mathbf{n}_\Gamma)] dS, \quad (7.7)$$

where  $[\varphi] = \varphi^+ - \varphi^-$  is the jump operator and  $\mathbf{n}_\Gamma$  is a unit normal to  $\Gamma$  pointing from  $\Omega_-$  to  $\Omega_+$  and  $\mathbf{v}_\Gamma^\perp$  is the normal velocity of  $\Gamma$ . The interpretation of  $[\psi_\Omega \otimes (\mathbf{v} - \mathbf{v}_\Gamma^\perp \mathbf{n}_\Gamma)] \cdot \mathbf{n}_\Gamma$  is thus the *relative flux of  $\psi_\Omega$  through  $\Gamma$* .

**Remark 7.8** (Material surfaces). Recall that the surfaces in general *need not be material!* Meaning they do not have to evolve (deform) with the material - there can be nontrivial relative movement of the bulk and the surface.  $\lrcorner$

### Gauss theorem

That is

$$\int_{S_+ \cup S_-} \Phi_\Omega^\psi \cdot \mathbf{n} dS = \int_{\Omega_+ \cup \Omega_i} \nabla \cdot \Phi_\Omega^\psi dx + \int_\Gamma [\Phi_\Omega^\psi] \mathbf{n}_\Gamma dS, \quad (7.9)$$

again, we see that there is a jump operator.



### Surface Reynolds transport theorem

Finally, one requires the surface analog for the Reynolds transport theorem:

$$\frac{d}{dt} \int_{\Gamma} \psi_{\Gamma} dS = \int_{\Gamma} \left( \frac{D_{\Gamma} \psi_{\Gamma}}{Dt} + \psi_{\Gamma} \operatorname{div}_{\Gamma} \mathbf{v}_{\Gamma} - 2K_{\Gamma} \psi_{\Gamma} \mathbf{v}_{\Gamma}^{\perp} \right) dS, \quad (7.10)$$

where  $K$  is the mean curvature<sup>40</sup>

### Surface Gauss theorem

That is the equation

$$\int_{\Gamma} \operatorname{div}_{\Gamma} \mathbf{t}_{\Gamma} dS = \int_{\partial \Gamma} \mathbf{t}_{\Gamma} \cdot \boldsymbol{\nu}_{\Gamma} \cdot d\mathbf{l}. \quad (7.11)$$

### Localized form of balance laws

Finally, using the localization arguments, one can obtain the form in the nonsingular points

$$\frac{\partial \Psi_{\Omega}}{\partial t} + \nabla \cdot (\psi_{\Omega} \otimes \mathbf{v} + \boldsymbol{\Phi}_{\Omega}^p) - \xi^{\psi} - \Sigma^{\psi} = 0, \quad (7.12)$$

$$\frac{D_{\Gamma} \psi_{\Gamma}}{Dt} + \psi_{\Gamma} \operatorname{div}_{\Gamma} \mathbf{v}_{\Gamma}^{\parallel} - 2K_{\Gamma} \psi_{\Gamma} \mathbf{v}_{\Gamma}^{\perp} + \operatorname{div}_{\Gamma} \boldsymbol{\Phi}_{\Gamma}^{\psi} - \xi_{\Gamma}^{\psi} - \Sigma_{\Gamma}^{\psi} = - \left[ \boldsymbol{\Phi}_{\Omega}^{\psi} + \boldsymbol{\Psi}_{\Omega}^{\psi} \otimes (\mathbf{v} - \mathbf{v}_{\Gamma}^{\perp} \mathbf{n}_{\Gamma}) \right] \mathbf{n}_{\Gamma} \quad (7.13)$$

### Surface mass balance

$$\frac{D_{\Gamma} \rho}{Dt} + \rho_{\Gamma} (\operatorname{div}_{\Gamma} \mathbf{v}_{\Gamma}^{\parallel} - 2K_{\Gamma} \mathbf{v}_{\Gamma}^{\perp}) = - \left[ \rho (\mathbf{v} - \mathbf{v}_{\Gamma}^{\perp} \mathbf{n}_{\Gamma}) \right] \cdot \mathbf{n}_{\Gamma} \quad (7.14)$$

**Example 7.15** (Balloon inflation). Assume the case  $\mathbf{v}_{\Gamma}^{\parallel} = 0$ ,  $\mathbf{n} \cdot \mathbf{v} = v_{\Gamma}^{\perp}$ . Then the evolution becomes

$$\frac{\partial \rho_{\Gamma}}{\partial t} = 2K_{\Gamma} \mathbf{v}_{\Gamma}^{\perp} = - \frac{2}{R} \mathbf{v}_{\Gamma}^{\perp}.$$

Remember that when a balloon inflates, you can see the walls thinning. ┘

<sup>40</sup>  $K = \frac{1}{2} g^{\beta\alpha} b_{\beta\alpha}$  where  $g^{\beta\alpha}$  is the dual metric surface tensor and  $b_{\beta\alpha} = \Gamma_{\beta\alpha}^3$  is the Christoffel symbol.

### Surface momentum balance

$$\frac{D_\Gamma(\rho_\Gamma \mathbf{v}_\Gamma)}{Dt} + \rho_\Gamma \mathbf{v}_\Gamma (\operatorname{div}_\Gamma \mathbf{v}_\Gamma^\perp - 2K_\Gamma v_\Gamma^\perp) - \operatorname{div}_\Gamma \mathbb{T}_\Gamma - \rho_\Gamma \mathbf{b}_\Gamma = -[\rho \mathbf{v} \otimes (\mathbf{v} - v_\Gamma^\perp \mathbf{n}_\Gamma) - \mathbb{T}] \cdot \mathbf{n}_\Gamma. \quad (7.16)$$

### Jump conditions

Assume the special case when  $\psi_\Gamma = \Phi_\Gamma^\psi = \xi_\Gamma^\psi = \Sigma_\Gamma^\psi = 0$ . On  $\Gamma$  one has

$$[\Phi_\Omega^\psi + \psi_\Omega \otimes (\mathbf{v} - v_\Gamma^\perp \mathbf{n}_\Gamma)] \cdot \mathbf{n}_\Gamma = 0,$$

so for mass in particular one has

$$[\rho(\mathbf{v} - v_\Gamma^\perp \mathbf{n}_\Gamma)] \cdot \mathbf{n}_\Gamma = 0, \quad (7.17)$$

and for the momentum

$$[\mathbb{T} - \rho \mathbf{v} \otimes (\mathbf{v} - v_\Gamma^\perp \mathbf{n}_\Gamma)] \cdot \mathbf{n}_\Gamma = 0, \quad (7.18)$$

which means

$$[\mathbb{T}] \cdot \mathbf{n}_\Gamma = [\rho \mathbf{v} \otimes (\mathbf{v} - v_\Gamma^\perp \mathbf{n}_\Gamma)] \cdot \mathbf{n}_\Gamma \quad (7.19)$$

$$= [\mathbf{v}] \rho (\mathbf{v} - v_\Gamma^\perp \mathbf{n}_\Gamma) \cdot \mathbf{n}_\Gamma, \quad (7.20)$$

*i.e. the traction vector need not be continuous!* in general. However, in the case of *material discontinuities*, one has  $\mathbf{v} \cdot \mathbf{n}_\Gamma = v_\Gamma^\perp$  and the *traction vector* is continuous.

### Surface tension

There however exists a special case: *interface with surface tension*. Then one has

$$\rho_\Gamma = 0, \mathbb{T}_\Gamma = \sigma \mathbb{I}_\Gamma = \sigma (\mathbb{I} - \mathbf{n}_\Gamma \otimes \mathbf{n}_\Gamma),$$

where  $\sigma$  is the surface tension. Then one has

$$\operatorname{div}_\Gamma \mathbb{T}_\Gamma = \operatorname{div}_\Gamma (\sigma \mathbb{I}_\Gamma) = \nabla_\Gamma \sigma - \sigma \operatorname{div}_\Gamma (\mathbf{n}_\Gamma \otimes \mathbf{n}_\Gamma) = {}^{41} \nabla_\Gamma \sigma + 2K_\Gamma \sigma \mathbf{n}_\Gamma$$

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$$\operatorname{div}_\Gamma (\mathbf{n}_\Gamma \otimes \mathbf{n}_\Gamma) = (\nabla_\Gamma \mathbf{n}_\Gamma \cdot \mathbf{n}_\Gamma) + \mathbf{n}_\Gamma (\operatorname{div}_\Gamma \mathbf{n}_\Gamma)$$

and we have

$$\nabla_\Gamma \mathbf{n}_\Gamma \cdot \mathbf{n}_\Gamma = 0$$

, because the vectors are orthogonal and

$$\mathbf{n}_\Gamma (\operatorname{div}_\Gamma \mathbf{n}_\Gamma) = -2K_\Gamma$$

from our definition of the mean curvature.

Let us furthermore consider only material interfaces, *i.e.*  $\mathbf{v} \cdot \mathbf{n}_\Gamma = v_\Gamma^\perp$ . Then

$$[\mathbb{T}] \cdot \mathbf{n}_\Gamma - \operatorname{div}_\Gamma \mathbb{T}_\Gamma = -\nabla_\Gamma \sigma - 2K_\Gamma \sigma \mathbf{n}_\Gamma.$$

If we take the normal component of this, we obtain

$$[\mathbf{n}_\Gamma \cdot \mathbb{T} \mathbf{n}_\Gamma] = -2K_\Gamma \sigma,$$

but since  $\mathbb{T} = -p\mathbb{I} + \mathbb{S}$ , we have

$$[p] = 2K_\Gamma \sigma = \frac{-2\sigma}{R},$$

*i.e.* we have recovered

$$p^- - p^+ = \frac{2\sigma}{R}, \quad (7.21)$$

the *Laplace Young condition*.

What about the tangent component? One has

$$[(\mathbf{t})_\tau] = -\nabla_\Gamma \sigma.$$

Suppose we are dealing with the mixture of a liquid and its gas; then the gas tangent traction is *negligible* and one has

$$(\mathbf{t})_\tau^{\text{liquid}} = \nabla_\Gamma \sigma,$$

and since

$$(\mathbf{t}_\tau)^{\text{liquid}} = (2\eta \mathbb{D} \mathbf{n}_\Gamma)_\tau,$$

we have obtained

$$(2\eta \mathbb{D}) \mathbf{n}_\Gamma)_\tau = \nabla_\Gamma \sigma.$$

This is called the *Marangoni effect*: the liquid is forced to flow by the gradient of surface tension.<sup>42</sup>

<sup>42</sup> This can be examined, for example the *wine tears*.

<sup>43</sup> The notation is of course totally misleading.

### Stefan condition

Let us derive the jump condition for the total energy in the case<sup>43</sup>

$$\rho_\Gamma = \mathbf{q}_\Gamma = \mathbb{T}_\Gamma = 0.$$

From our general law, we have

$$\left[ \rho \left( e + \frac{1}{2} |\mathbf{v}|^2 \right) (\mathbf{v} - v_\Gamma^\perp \mathbf{n}_\Gamma) - \mathbf{v} \cdot \mathbb{T} + \mathbf{q} \right] \cdot \mathbf{n}_\Gamma = 0.$$

Decompose

$$\mathbb{T} = -p_{th} \mathbb{I} + \mathbb{S},$$

and let us make some assumptions:

- $[\rho (\mathbf{v} - v_\Gamma^\perp \mathbf{n}_\Gamma)] \cdot \mathbf{n}_\Gamma = 0,$
- $[\mathbb{T}] \mathbf{n}_\Gamma = [\mathbf{v}] \rho (\mathbf{v} - v_\Gamma^\perp \mathbf{n}_\Gamma) \cdot \mathbf{n}_\Gamma - \nabla_\Gamma \sigma - 2K_\Gamma \sigma \mathbf{n}_\Gamma,$
- $[p_{th}] = 0.$

We than have

$$0 = [\mathbf{q}] \cdot \mathbf{n}_\Gamma = -[\mathbf{v} \cdot (p_{th} \mathbb{I} + \mathbb{S}) \cdot \mathbf{n}_\Gamma] + \left[ \rho \left( e + \frac{1}{2} |\mathbf{v}|^2 \right) (\mathbf{v} - v_\Gamma^\perp \mathbf{n}_\Gamma) \right] \cdot \mathbf{n}_\Gamma,$$

and with our assumption on the continuity of the pressure we obtain

$$\begin{aligned} [p_{th} \mathbf{v}] \cdot \mathbf{n}_\Gamma &= [p_{th} (\mathbf{v} - v_\Gamma^\perp \mathbf{n}_\Gamma)] \cdot \mathbf{n}_\Gamma = \left[ \frac{p_{th}}{\rho} \rho (\mathbf{v} - v_\Gamma^\perp \mathbf{n}_\Gamma) \right] \cdot \mathbf{n}_\Gamma = \\ &= \left[ \frac{p_{th}}{\rho} \right] \rho (\mathbf{v} - v_\Gamma^\perp \mathbf{n}_\Gamma) \cdot \mathbf{n}_\Gamma. \end{aligned}$$

It is customary to define

$$\dot{m} = \rho (\mathbf{v} - v_\Gamma^\perp \mathbf{n}_\Gamma) \cdot \mathbf{n}_\Gamma$$

as some kind of a mass flux. In total, we have

<sup>44</sup> Which often is - think of the solidifying of a water body.

$$0 = [\mathbf{q}] \cdot \mathbf{n}_\Gamma + \left[ \left( e + \frac{p_{th}}{\rho} \right) \right] \dot{m} = -[\mathbf{v} \cdot \mathbb{S}] \mathbf{n}_\Gamma + \left[ \frac{1}{2} |\mathbf{v}|^2 \right] \dot{m},$$

and if we now assume the transport velocity is negligible <sup>44</sup> and manipulate

$$[\mathbf{v} \cdot \mathbb{S}] \mathbf{n}_\Gamma = [\mathbf{v}]_\tau (\mathbb{S} \mathbf{n}_\Gamma)_\tau + [(\mathbb{S} \mathbf{n})_n \mathbf{v}].$$

Most often the normal jump is negligible and the tangential components aswell (these are for example friction forces)

$$[\mathbf{q}] \cdot \mathbf{n}_\Gamma + [h] \dot{m} \approx 0,$$

where  $h = e + \frac{p}{\rho}$  is the specific enthalpy. Realize that the jump of enthalpy is the latent heat  $L$ , and so one obtains

$$[\mathbf{q}] \cdot \mathbf{n}_\Gamma + L \dot{m} \approx 0. \quad (7.22)$$

## "Blurring"

We are able to describe the continuum precisely on a detailed level; but is this description compatible with the previous *molecular mixing* theory?

Suppose  $\Omega = \Omega_1 \cup \Omega_2, \Gamma = \overline{\Omega_1} \cap \overline{\Omega_2}, \Omega_1 \cap \Omega_2 = \emptyset$ . In each  $\Omega_\alpha, \alpha = 1, 2$  we have some balance equations:

$$\partial_t \psi_\alpha + \nabla \cdot (\psi_\alpha \mathbf{v}_\alpha) + \nabla \cdot \Phi_\Omega^{\psi_\alpha} - \Pi_\Omega^{\psi_\alpha} - \xi_\Omega^{\psi_\alpha} = 0,$$

and at the interface  $\Gamma_{\alpha\beta}$  we have

$$\frac{D_\Gamma \psi_{\alpha\beta}^\Gamma}{Dt} + \psi_{\alpha\beta}^\Gamma \left( \operatorname{div}_\Gamma \mathbf{v}_\Gamma^\parallel - 2K_\Gamma \mathbf{v}_\Gamma^\perp \right) + \operatorname{div}_\Gamma^\psi \Phi_\Gamma^{\alpha\beta} - \Pi_\Gamma^{\alpha\beta\psi} - \xi_\Gamma^{\alpha\beta\psi} = - \left( \Phi_\Omega^\psi + \Psi_\Omega \otimes (\mathbf{v} - \mathbf{v}_\Gamma^\perp \mathbf{n}_\Gamma) \right) \cdot \mathbf{n}_\Gamma,$$

where the meaning of the terms is either *known* or can be *guessed*.

Define now the *characteristic function* of each phase

$$\chi_\alpha(t, \mathbf{x}) = \begin{cases} 1, & \mathbf{x} \in \Omega_\alpha(t), \\ 0, & \mathbf{x} \notin \Omega_\alpha(t). \end{cases}$$

Or, to make the math more sensible. we can take some *mollification* of the characteristic function, *i.e.*  $\chi_\alpha^\epsilon(t, \mathbf{x})$ . The goal is now to write the *local, detailed* evolution equations as  $\chi_\alpha^\epsilon(t, \mathbf{x})$  times the *global, less detailed* evolution.

Define the average

$$\langle \varphi \rangle_V = \frac{1}{\lambda(B(\mathbf{x}, \delta))} \int_{B(\mathbf{x}, \delta)} \varphi(\mathbf{x} + \mathbf{z}) \, d\mathbf{z}, \quad (7.23)$$

and realize that some averages are in fact known<sup>45</sup>

$$\langle \chi_\alpha \rangle = \Phi_\alpha,$$

$$\langle \chi_\alpha \rho \rangle = \frac{m_\alpha}{V} = \rho_\alpha.$$

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$$\langle \chi_\alpha \rangle = \frac{1}{\lambda(B(\mathbf{x}, \delta))} \int_{B(\mathbf{x}, \delta)} \chi_\alpha(t, \mathbf{x} + \mathbf{z}) \, d\mathbf{z}$$

This procedue will be very interesting<sup>46</sup> We must however give meaning to<sup>47</sup>

<sup>46</sup> We will *e.g.* obtain the exact interaction forces.

<sup>47</sup> This is the problem of *multiplication* of general distributons.

$$\begin{aligned} \int_{\mathbb{R}^3 \times \mathbb{R}} \partial_t \xi_\alpha \varphi(t, \mathbf{x}) \, d\mathbf{x} \, dt &= - \int_{\mathbb{R}^3 \times \mathbb{R}} \chi_\alpha \partial_t \varphi \, d\mathbf{x} \, dt = \\ &= - \int_{\mathbb{R}} \int_{\Omega_\alpha(t)} \partial_t \varphi \, d\mathbf{x} \, dt = - \int_{\mathbb{R}} \frac{d}{dt} \int_{\Omega_\alpha(t)} \varphi \, d\mathbf{x} \, dt = \\ &= - \int_{\mathbb{R}} \frac{d}{dt} \left( \int_{\Omega_\alpha(t)} d\mathbf{x} + \int_{\Omega_\alpha} \varphi \mathbf{v}_{\partial\Omega_\alpha} \cdot \mathbf{n} \, dS + \int_{\mathbb{R}} \int_{\partial\Omega_\alpha} \varphi \mathbf{v}_\Gamma \cdot \mathbf{n} \, dS \, dt \right) = \\ &= \int_{\mathbb{R}} \int_{\partial\Omega_\alpha(t)} \varphi \mathbf{v}_\Gamma \cdot \mathbf{n} \, dS \, dt, \end{aligned}$$

where  $\varphi(t, \mathbf{x}) \in \mathcal{D}(\mathbb{R}^3 \times \mathbb{R})$ . Next, we need

$$\begin{aligned} \int_{\mathbb{R}^3 \times \mathbb{R}} (\nabla_i \chi_\alpha) \, d\mathbf{x} \, dt &= - \int_{\mathbb{R}^3 \times \mathbb{R}} \chi_\alpha \chi_\alpha \frac{\partial \varphi}{\partial x_i} \, d\mathbf{x} \, dt - \int_{\mathbb{R}} \int_{\Omega_\alpha} \frac{\partial \varphi}{\partial x_i} \, d\mathbf{x} \, dt = \\ &= - \int_{\mathbb{R}} \int_{\partial\Omega_\alpha} \varphi \mathbf{n}_i \, dS \, dt = \\ &= \int_{\mathbb{R}^3 \times \mathbb{R}} \varphi (-n_{i\Gamma} \delta_\Gamma) \, d\mathbf{x} \, dt, \end{aligned}$$

where  $\delta_\Gamma$  is the Dirac delta with  $\text{supp } \delta_\Gamma = \Gamma \subset \mathbb{R}^2$ . Next we use

$$\nabla \chi_\alpha = -\mathbf{n}_\Gamma \delta_{\partial\Omega_\alpha},$$

where  $\mathbf{n}_\Gamma$  is the *outter unit normal* to<sup>48</sup>  $\partial\Omega_\alpha$ . We will also need

<sup>48</sup> This means that the characteristic function rises in the direction to  $\Omega_\alpha$

the *topological equation*

$$\partial_t \chi_\alpha + \tilde{\mathbf{v}}_\Gamma \cdot \nabla \chi_\alpha = 0, \quad (7.24)$$

where

$$\begin{aligned} \int_{\mathbb{R}^3 \times \mathbb{R}} (\tilde{\mathbf{v}}_\Gamma \cdot \nabla \chi_\alpha) \varphi \, d\mathbf{x} \, dt &= - \int_{\mathbb{R}^3 \times \mathbb{R}} (\nabla \cdot (\tilde{\mathbf{v}}_\Gamma) \varphi) \, d\mathbf{x} \, dt = - \int_{\mathbb{R}} \int_{\Omega_\alpha} \nabla \cdot (\tilde{\mathbf{v}}_\Gamma \varphi) \, d\mathbf{x} \, dt = \\ &= - \int_{\mathbb{R}} \int_{\partial \Omega_\alpha} \mathbf{v}_\Gamma \cdot \mathbf{n}_\Gamma \varphi \, dS \, dt. \end{aligned}$$

Next next, we need to give *meaning* to

$$\nabla_i(\chi_\alpha f), \partial_t(\chi_\alpha f).$$

This is a **problem**: both  $f$  and  $\chi_\alpha$  are not continuous, *i.e.* their derivatives are distributions; we *cannot use a simple Leibniz formula*.

$$\begin{aligned} \int_{\mathbb{R}^3 \times \mathbb{R}} \nabla_i(\chi_\alpha f) \varphi \, d\mathbf{x} \, dt &= - \int_{\mathbb{R}} \int_{\mathbb{R}^3} \chi_\alpha f (\nabla_i \varphi) \, d\mathbf{x} \, dt = - \int_{\mathbb{R}} \int_{\Omega_\alpha} f \frac{\partial \varphi}{\partial x_i} \, d\mathbf{x} \, dt = \\ &= \int_{\mathbb{R}} \int_{\Omega_\alpha} \frac{\partial f}{\partial x_i} \, d\mathbf{x} \, dt = - \int_{\mathbb{R}} \int_{\partial \Omega_\alpha} f_\Gamma^\alpha n_i \varphi \, dS \, dt = \int_{\mathbb{R}^3 \times \mathbb{R}} (\chi_\alpha \nabla_i f) \varphi \, d\mathbf{x} \, dt + \int_{\mathbb{R}^3 \times \mathbb{R}} (f_\Gamma^\alpha \nabla \chi_\alpha) \varphi \, d\mathbf{x} \, dt \end{aligned}$$

where  $f_\Gamma^\alpha$  is the value from "inside of  $\Omega_\alpha$ " the function is discontinuous. Meaning that

$$\nabla_i(f \chi_\alpha) = \chi_\alpha \nabla_i f + f_\Gamma^\alpha \nabla \chi_\alpha.$$

And for the time derivative we obtain

$$\begin{aligned} \int_{\mathbb{R}^3 \times \mathbb{R}} \partial_t(\chi_\alpha f) \varphi \, d\mathbf{x} \, dt &= - \int_{\mathbb{R}^3 \times \mathbb{R}} \chi_\alpha f \partial_t \varphi \, d\mathbf{x} \, dt = \\ &= - \int_{\mathbb{R}} \int_{\Omega_\alpha} f \partial_t \varphi \, d\mathbf{x} \, dt = - \int_{\mathbb{R}} \int_{\Omega_\alpha} \partial_t(f \varphi) \, d\mathbf{x} \, dt + \int_{\mathbb{R}} \int_{\Omega_\alpha} (\partial_t \varphi) \varphi \, d\mathbf{x} \, dt = \\ &= - \int_{\mathbb{R}} \frac{d}{dt} \left( \int_{\Omega_\alpha} f \varphi \, d\mathbf{x} \right) dt + \int_{\mathbb{R}} \int_{\partial \Omega_\alpha} f_\Gamma^\alpha \mathbf{v}_\Gamma \cdot \mathbf{n} \, dS \, dt + \int_{\mathbb{R}^3 \times \mathbb{R}} (\chi_\alpha \partial_t f) \varphi \, d\mathbf{x} \, dt = \\ &= 0 + \int_{\mathbb{R}^3 \times \mathbb{R}} (\partial_t \chi_\alpha f_\Gamma^\alpha + \chi_\alpha \partial_t f) \varphi \, d\mathbf{x} \, dt, \end{aligned}$$

and so in total

$$\partial_t(\chi_\alpha f) = \chi_\alpha \partial_t f + (\partial_t \chi_\alpha) f_\Gamma^\alpha.$$

Note that we are in fact working with the *smooth extension* of  $f_\Gamma^\alpha$  rather than the function itself (which is defined only on the boundary), so we in fact are in the case of *Dirac times a smooth function*.

Finally, the evolution equation can be then rewritten as

$$\chi_\alpha \left( \partial_t \varphi + \nabla \cdot (\varphi \mathbf{v}) + \nabla \cdot \Phi_\Omega^\psi - \Pi_\Omega^\psi - \xi_\Omega^\psi \right) = 0 \quad (7.25)$$

or equivalently

$$\begin{aligned} \partial_t(\chi_\alpha \psi) - \left( \tilde{\psi}_\Gamma^\varphi \partial_t \chi_\alpha \right) + \nabla \cdot (\chi_\alpha \psi_\Omega \mathbf{v}) - \left( (\psi_\Omega \tilde{\mathbf{v}})_\gamma^\alpha \cdot \nabla \chi_\alpha \right) + \\ + \nabla \cdot (\chi_\alpha \Phi_\Omega^\psi) - \Phi_{\Omega, \Gamma}^\alpha \cdot \nabla \chi_\alpha - \chi_\alpha \Pi_\Omega^\psi - \chi_\alpha \xi_\Omega^\psi = 0. \end{aligned}$$

As for averaging, we have multiple options

- ensemble averaging (over configurations in the phase space)
- time averaging (throughout evolution)
- volume averaging (our introduced)

What properties do we require?

- *linearity*:  $\langle c_1 f_1 + c_2 f_2 \rangle = c_1 \langle f_1 \rangle + c_2 \langle f_2 \rangle$ ,
- *perfect filter property*:  $\langle f_1 \langle f_2 \rangle \rangle = \langle f_1 \rangle \langle f_2 \rangle$ .

We see that linearity holds for all of them, but *e.g.* the *perfect filter property does not hold for volume averaging*. And there is a bigger problem also, we would want

$$\begin{aligned} \langle \partial_t f \rangle &= \partial_t \langle f \rangle, \\ \langle \partial_i f \rangle &= \partial_i \langle f \rangle. \end{aligned}$$

Note that *e.g.* the second requirement **does not hold in general**: it can have lots of discontinuities on the LHS, which produce diracs in the differentiation, but the RHS is nicely smooth.

Not everything is lost. It can be shown that for *volume averaging*, it holds



$$\langle \chi_\alpha \nabla_i f \rangle_V = \nabla_i \langle \chi_\alpha f \rangle_V + \langle f_\Gamma^\alpha \nabla_i \chi_\alpha \rangle_V. \quad (7.26)$$

This allows us to do the volume averaging of the balance equations to obtain

$$\begin{aligned} & \partial_t \langle \psi_\Omega \chi_\alpha \rangle + \nabla \cdot (\langle \psi_\Omega \chi_\alpha \mathbf{v} \rangle) + \nabla \cdot (\chi_\alpha \Phi_\Omega^\psi) + \\ & - \langle \chi_\alpha^\psi \Pi_\Omega^\psi \rangle - \langle \chi_\alpha \xi_\Omega^\psi \rangle = \langle (\psi_\Omega)_\Gamma^\alpha \partial_t \chi_\alpha + (\psi_\Omega \tilde{\mathbf{v}}_\Omega)_\Gamma^\alpha \cdot \nabla \chi_\alpha \rangle + \tilde{\Phi}_{\Omega\Gamma}^\alpha \cdot \nabla \chi_\alpha, \end{aligned}$$

where the last term can be manipulated as

$$\langle (\tilde{\varphi}_\Omega)_\Gamma^\alpha (\tilde{\mathbf{v}})_\Gamma^\alpha - \tilde{\mathbf{v}}_\Gamma \cdot \nabla \chi_\alpha + (\tilde{\Phi})_{\Omega\Gamma}^\alpha \cdot \nabla \chi_\alpha \rangle,$$

where we have used the topological equation. Recognizing the volume fraction  $\Phi_\alpha = \langle \chi_\alpha \rangle$  we can recover the known expressions as *phasic averages*

$$\bar{\varphi}_\alpha \Phi_\alpha = \langle \chi_\alpha \varphi_\Omega \rangle,$$

so for  $\rho$  we obtain

$$\frac{1}{\lambda(B)} \int_{B_\alpha} \rho \, dx = \left( \frac{1}{\lambda(B)} \int_{B_\alpha} \rho \, dx \right) \left( \frac{\lambda(B_\alpha)}{\lambda(B)} \right) = \rho_\alpha^m \Phi_\alpha.$$

We see a second option would be to use the mass-weighted average

$$\hat{\varphi}_\alpha \bar{\rho}_\alpha \Phi_\alpha = \langle \chi_\alpha \rho \varphi_\Omega \rangle.$$

Let us recover some known equations.

### Mass balance

$$\partial_t \langle \chi_\alpha \rho \rangle + \nabla \cdot (\langle \chi_\alpha \rho \mathbf{v} \rangle) = \langle (\tilde{\rho}_\Omega)_\Gamma^\alpha ((\tilde{\mathbf{v}}_\Omega)_\Gamma^\alpha - \tilde{\mathbf{v}}_\Gamma) \cdot \nabla \chi_\alpha \rangle.$$

Realize now that the LHS is  $\partial_t (\Phi_\alpha \bar{\rho}_\alpha) + \nabla \cdot (\Phi_\alpha \bar{\rho}_\alpha \hat{\mathbf{v}}_\alpha) = m_\alpha$ , so *also the RHS* must be  $m_\alpha$ . We have obtained new expressions for  $m_\alpha$ .

### Momentum balance

$$\begin{aligned} \partial_t \langle \chi_\alpha \rho \mathbf{v} \rangle + \nabla \cdot (\langle \chi_\alpha \rho \mathbf{v} \otimes \mathbf{v} \rangle) - \nabla \cdot (\langle \chi_\alpha \mathbb{T}_\Omega \rangle) - \langle \chi_\alpha \rho \mathbf{b} \rangle = \\ = \left\langle \left( (\tilde{\rho}_\Omega)_\Gamma^\alpha (\tilde{\mathbf{v}}_\Omega)_\Gamma^\alpha \otimes \left( (\tilde{\mathbf{v}}_\Omega)_\Gamma^\alpha - \tilde{\mathbf{v}}_\Gamma \right) - \left( \tilde{\mathbb{T}}_\Omega \right)_\Gamma^\alpha \right) \cdot \nabla \chi_\alpha \right\rangle, \end{aligned}$$

and so again taking the time derivative and manipulating we obtain *something*. It is interesting that the RHS will be

$$-p_\Gamma^\alpha \nabla \Phi_\alpha + \mathbf{I}_\alpha^{\text{drag}},$$

which is exatly the expression we obtained in the chapter abut *Darcy law*.