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LECTURE NOTES

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Theory of Mixtures

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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 oceans¹, *porous media flows*², 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

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 multi-component continuum theory can be obtained from multi-phase theory through some kind of averaging.

¹ Convection flows due to differences in densities and concentrations.

² This branch is having a renaissance period; a lot of many has been dumped into this.

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, we each of the components can possess a *distinct reference configuration*. This means

$$\mathbf{x} \in \kappa_t(\mathcal{B}) : \mathbf{x} = \chi_1(t, \mathbf{X}_1) = \dots = * \chi(t, \mathbf{X}_n),$$

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 Φ 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 α -component is given as

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

and the eulerien velocity is given as

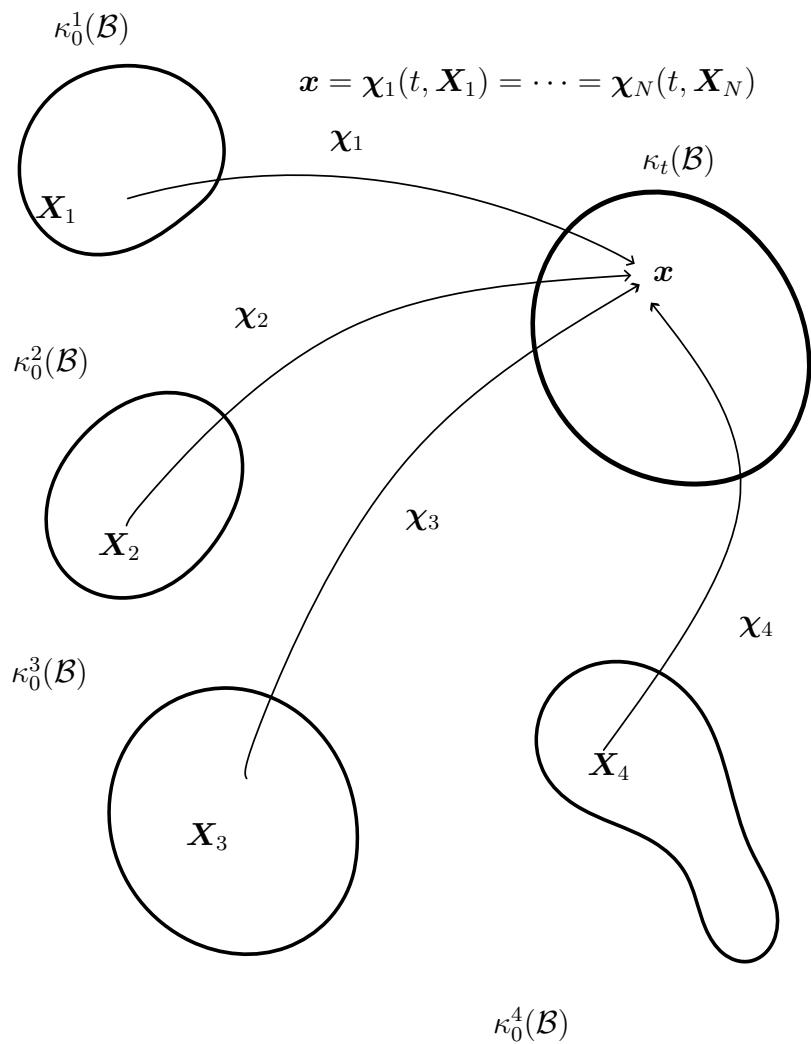


Figure 2.2 / The current configuration is the same for all species, but the referential may differ

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

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:

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

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

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

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 α -component in Ω ,
- $v_\alpha(\Omega)$ us the volume of α -component in Ω .
- ρ is the mixture density,
- ρ_α is the density of α -component,
- c_α is the concetration or the mass fraction of α -component,
- Φ_α is the volume fraction of α -component,
- ρ_α^m is the *good old* material density.

We suppose the mass measure is absolutely continuous³ w.r.t the volume measure, from which follows the existence of the (mass) density⁴.

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

⁴ 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 α -material volume?

Well, in general

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

where the first term is the non-convective flux of ψ_α , the second term is the production of ψ_α inside Ω_α , the third term is the external supplu of ψ_α and the last in is *the interaction (exchange) of ψ_α 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

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

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*⁵

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 stress,

⁵ 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}_α is the "true interaction force" and $m_\alpha \mathbf{v}_\alpha$ is the change of momentum due to the change of mass⁶

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

$\alpha = 1, \dots, N$

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

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

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}_α is the traction vector exerted on α 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_α 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_α 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

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

let us now set

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

where \mathbf{u}_{α} is the *diffusive⁷ velocity of the component α* . This allows us to write

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

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

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

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

⁷ Kind of a relative velcoity of the component w.r.t the barycenter

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

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

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

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

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 (*mesoscopis*) *internal angular momentum* \mathbf{s}_α called *spin*.

- $\psi_\alpha = (\mathbf{x} \times \rho_\alpha \mathbf{v}_\alpha) + \mathbf{s}_\alpha$,
 - $\Phi^{\psi_\alpha} = \mathbf{x} \times \mathbb{T}_\alpha + \mathbb{M}_\alpha$ ⁸, where \mathbb{M}_α is the *couple stress*,
 - $\xi^{\psi_\alpha} = 0$,
 - $\Sigma^{\psi_\alpha} = \mathbf{x} \times \rho_\alpha \mathbf{b}_\alpha + \rho_\alpha \mathbf{l}_\alpha$, where \mathbf{l}_α is the *spin supply*
 - $\Pi^{\psi_\alpha} = \mathbf{x} \times (m_\alpha \mathbf{v}_\alpha + \mathbf{I}_\alpha) + \mathbf{p}_\alpha$, where \mathbf{p}_α is the interaction couple.
- (8) $(\mathbf{x} \times \mathbb{T}_\alpha)_{ij} = \epsilon_{ikl} x_k (\mathbb{T}_\alpha)_{lj}$

Our balance thus is

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

This can be further manipulated:

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

Our goal is to obtain

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

so

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

⁹

Using 2.13 we see

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

and ϵ_{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

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

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

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

This can be achieved in a *dipole dielectric* for example. □

Our constraint reads as

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

So

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

but since 2.13 we have

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

so in total the constraint reads as

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

Let

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

be the *volumetric velocity*. Assume now¹⁰

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

for some constants K_{α} .

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

Balance of energy

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

Thus the balance takes the form

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

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 ¹¹

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

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}_α and write

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

One can also write 2.28 in the form

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

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

¹¹ 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

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

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

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

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 η_α is the *specific entropy*
- $\Phi^{\psi_\alpha} = \mathbf{q}_{e\alpha}$, 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

$$\partial_t(\rho_\alpha \eta_\alpha) + \nabla \cdot (\rho_\alpha \eta_\alpha \mathbf{v}_\alpha) = -\nabla \cdot \mathbf{q}_\eta + \rho_\alpha r_{\eta\alpha} + \zeta_\alpha + m_\alpha \eta_\alpha + \tilde{\zeta}_\alpha, \quad (2.35)$$

$$\sum_{\alpha=1}^N (m_\alpha \eta_\alpha + \tilde{\zeta}_\alpha) = 0,$$

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

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 ζ_α and $\tilde{\zeta}_\alpha$, *i.e.*, between entropy production and entropy exchange. \square

2.4 Classification of mixture theories

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

¹² 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.

¹² This goes back to *Hutter*.

class IV	class III	class II	class I	quantity
ρ_α	ρ_α	ρ_α	ρ_α	mass
\mathbf{v}_α	\mathbf{v}_α	\mathbf{v}_α	\mathbf{v}	momentum
e_α	e_α	e	e	energy
η_α	η	η	η	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. \square

3 Thermodynamics reminder

3.1 Fundamental relations

Let us begin with the¹³ fundamental thermodynamical relation ¹³ Mistrovská 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 intensive¹⁴ qualities! At least locally...

We have

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

and from 1-homogeneity follows the Euler relation¹⁵

¹⁴ Realize that the temperature, pressure, etc. are defined only in equilibria!

¹⁵ Differentiate w.r.t λ 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

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

$\mathbf{v}, v, v, \mathbf{v}$

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}_α . Let us deal with it by using the *diffusive velocity* and then use some constitutive relations:

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

where we set

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

and so our equation reads as

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

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 begin¹⁶

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

so in fact

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

using the decomposition

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

one obtains

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

Recall the general balance of entropy:

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

¹⁶ 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

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

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

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*

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

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

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

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

$$M + P = \frac{3\lambda + 2\nu}{3} (\nabla \cdot \mathbf{v}), \quad 3\lambda + 2\nu \geq 0,$$

$$\mathbb{T}^d = 2\nu \mathbb{D}^d, \quad \nu \geq 0$$

$$m = -b\mu, \quad \beta \geq 0$$

$$\mathbf{j} = -\alpha \nabla \mu, \quad \mathbf{q} - \mu \mathbf{j} = \kappa \nabla \left(\frac{1}{\theta} \right)$$

$$\mathbf{j} = -\alpha \nabla \left(\frac{\mu}{\theta} \right), \quad \mathbf{q} = \kappa \nabla \left(\frac{1}{\theta} \right) \quad (\text{this one is in fact preferred by statistical physics}).$$

This implies

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

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

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

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

One can see the last relation is very similar 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

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

In the isothermal case, our constitutive relation reads

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

Which is a law in the form

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

exactly similiar 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

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

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*:¹⁷

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

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

¹⁷ 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 Λ 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}_α 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*

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

¹⁸ Gibbs-Duhem works for ∇ also, since that is almost the same like dd .

So we can in fact write (using Gibbs-Duhem¹⁸ 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 $\tau = \tau^T \in \mathbb{R}^{N-1 \times N-1}$ 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 some¹⁹ $\mathbb{f} = \mathbb{f}^\top \in \mathbb{R}^{N \times N}$ symmetric positive semi-definite matrix. This ansatz gives

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

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

¹⁹ 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.

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

and so

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

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

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

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

²⁰

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 ρ 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:

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

↳ 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

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

Plugging this into the balance equations we have

$$\begin{aligned}\rho\frac{D\mathbf{v}}{Dt} &= \nabla M + \nabla \cdot (2\nu\mathbb{D}^d) + \rho\mathbf{b}, \\ \nabla \cdot \mathbf{v} &= r_*(-\beta\mu_* + \nabla \cdot (\alpha\nabla\mu_\alpha)) = r_*(-\beta + \alpha\Delta(\mu_0r_*(M + p))) = \\ &= r_*(-\beta + \alpha\Delta)(\mu(c, \theta) - r_*p(\theta, c)) + r_*^2(\beta - \alpha\Delta)M = \\ &= \gamma(\theta, c) + r_*^2(\beta - \alpha\Delta)M, \quad \lambda > 0, \beta > 0,\end{aligned}$$

concentration equation .

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

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

is the vector *chemical potential*,

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

is the *concentration chemical potential* and

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

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

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

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

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

and so

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

If one chooses the energetic representation

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

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 terrible²¹. Are there some cases when it is not?

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

²¹ The dependency is on $c, \nabla c, \Delta c$

So when σ 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. \square

Cahn-Hilliard-Navier-Stokes-Fourier

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

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

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.

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

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

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

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

Whis is this any useful? Let us compute

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

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 μ_α 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^σ are molar masses of σ -atom *i.e.* the mass of 1 mol, $T_{\sigma\alpha}$ is the *composition matrix*.

Next up, it will be useful to reformulate m_α in terms of molar quantites

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

where J^α 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 ϵ^σ being the *atomic substances*.²²

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 σ -th column of \mathbb{S} with \mathbf{e}_α 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*.

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

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 os mass conservation).

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

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

\square

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 *matice 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: NO_2, N_2O . 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

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

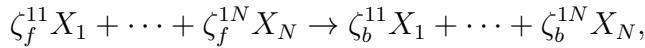
and taking the dot product with \mathbf{e}_β we have

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

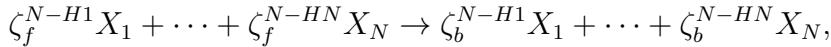
and so the sought quantities in fact are $J_p, p = 1, \dots, N - H$ and it holds

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

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 ζ_b^{ij}, ζ_f being the *backward/forward* stoichiometric 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 α -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_α 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 quantites 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 (θ, p_α) , 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 potentail thus is

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

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_α is called the *chemical activity* of α -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

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

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

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

Our definition²³ of the chemical equilibrium is

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

which is equivalent to²⁴

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

What does this mean? ²⁵

$$0 = \sum_{\alpha=1}^N \left(\mu_{\alpha}^{M0}(\theta, p) + R\theta \log a_{\alpha} \right)^\dagger P^{p\alpha} \Leftrightarrow 0 = \sum_{\alpha=1}^N \mu_{\alpha}^{M0}(\theta, p) P^{p\alpha} + R\theta \log \left(\prod_{\alpha=1}^N (a_{\alpha}^\dagger)^{P^{p\alpha}} \right)$$

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

it is usual to denote

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

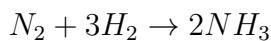
as *equilibrium constants of p-th reaction*. Our equilibrium requirement yields

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

meaning

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

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 amoniac,

↓

- ↳
- the mixing is ideal: $a_\alpha = c_\alpha^M$,
 - the pressure p and temperature θ 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 Ω 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 Ω . Realize that

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

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

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

so if we divide this by M_α 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 Ω 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

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

□

5.4 Chemical kinetics

There are at least 2 approaches:

- (1) non-linear closureas automatically satisfying 2nd law ²⁶
- (2) reduction of Taylor expansion (rational thermodynamics)

Rational thermodynamics

²⁶ 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.

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

one can write

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

(backward/forward stoich. coefficients), and so

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

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

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

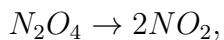
This is in fact beatiful: in equilibrium, we have

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

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.

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

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.²⁷ Note this must mean there exists a mechanical interaction between the components.

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 media²⁸

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

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

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

6.1 Balance laws

The balance of mass reads

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

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}_α and the interaction forces \mathbf{I}_α .

6.2 Structure of interacton 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

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

Recall the procedure from ??: rewrite the balance of mass to have the standard single component form ²⁹, 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

³⁰

$$\mathbf{u}_1 = \frac{\mathbf{j}}{\rho c} \tag{6.2}$$

²⁹ Recall

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

and

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

³⁰ we are taking $c_1 \equiv c, c_2 = 1 - c$.

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

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

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

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

where

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

Altogether

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

where one can substitute

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

to obtain

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

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*. \square

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[†], one must obtain ³¹

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

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

which after substituton 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

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

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 ,

$$\nabla \cdot \mathbf{v} = 0,$$

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

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 problem³², we obtain the problem

³² Spherical symmetry and linearisation

$$\nabla \cdot \mathbf{v} = 0,$$

$$\frac{1}{\text{Re}} \Delta \mathbf{v} - \nabla p = \mathbf{0}. \quad (6.9)$$

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 solution³³

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

³³ Recall that this is the known force

$$\mathbf{F} = -\frac{1}{2} C \rho S |\mathbf{v}|^2 \mathbf{e}.$$

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*³⁴

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

³⁴ This is not a drag force, but a lift force!

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 effect

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_Ω is the mass of the ball and m_{vir} is the virtual mass. It can be shown

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

with ρ_f being the density of the fluid.³⁵

³⁵ This is *half* of the mass displaced by the incompressible fluid.

Basset 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

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

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

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

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

Since $\alpha < 0$, one usually writes

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

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 apart³⁶. Assume the flow regime is stationary, *i.e.* we are interested in the *Poiseulle flow*:

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

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

³⁶ Characteristic pore distance, grain size

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

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 definiton 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

$$\mathbf{v}_f = -\frac{k(\varphi)}{\varphi \mu} \nabla p. \quad ^{37} \text{ And handwaving.}$$

This has been done without gravity, but with some intuition³⁷ 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 Ω_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-dimensinalisation one gets

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

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 Ω ,

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

- the microstructure, *i.e.* the cell of scale ϵ .

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 procedure³⁸ 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

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

and the second equation is

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

Let us now extract the terms of orders of ϵ :

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

This is the formulation of the *cell problem*:

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

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 peridoic 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*,

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

as then the solution would be

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

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

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

where we have defined (obtained!)

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

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

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

i.e.

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

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

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

7 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 Γ separating Ω_+ , Ω_- . 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 Ω_ϵ is the interfacial region ³⁹
It can be then integrated over the whole region Ω_ϵ defined

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

where $S(\xi)$ is the "elevatin surface" that is changing with ξ . 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 can generalise also the fluxes:

³⁹ A strip of (varying) thickness ϵ around the interface.

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

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 transport theorem

One has

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

where $[\varphi] = \varphi^+ - \varphi^-$ is the jump operator and \mathbf{n}_Γ is an unit normal to Γ pointing from Ω_- to Ω_+ and \mathbf{v}_Γ^\perp is the normal velocity of Γ . 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 ψ_Ω through Γ* .

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. \square

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 curvature⁴⁰

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

Surface Gauss theorem

That is the equation

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

Localized form of balance laws

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

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

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

Surface mass balance

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

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. \square

Surface momentum balance

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

Jump conditions

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

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

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.

⁴¹

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

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.

where σ is the surface tension. Then one has

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

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.⁴²

⁴² This can be examined, for example the *wine tears*.

⁴³ The notation is of course totally misleading.

Stefan condition

Let us derive the jump condition for the total energy in the case⁴³

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

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

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

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

⁴⁴ 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 ⁴⁴ 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 known⁴⁵

$$\langle \chi_\alpha \rangle = \Phi_\alpha,$$

⁴⁵

$$\langle \chi_\alpha \rangle = \frac{1}{\lambda(B(\mathbf{x}, \delta))} \int_{B(\mathbf{x}, \delta)} \chi_\alpha(t, \mathbf{x} + \mathbf{z}) d\mathbf{z}$$

$$\langle \chi_\alpha \rho \rangle = \frac{m_\alpha}{V} = \rho_\alpha.$$

This procedure will be very interesting⁴⁶ We must however give meaning to⁴⁷

$$\begin{aligned} \int_{\mathbb{R}^3 \times \mathbb{R}} \partial_t \xi_\alpha) \varphi(t, \mathbf{x}) d\mathbf{x} dt &= - \int_{\mathbb{R}^3 \times \mathbb{R}} \chi_\alpha \partial_t \varphi d\mathbf{x} dt = \\ &- \int_{\mathbb{R}} \int_{\Omega_\alpha(t)} \partial_t \varphi d\mathbf{x} dt = - \int_{\mathbb{R}} \frac{d}{dt} \int_{\Omega_\alpha(t)} \varphi d\mathbf{x} dt = \\ &= - \int_{\mathbb{R}} \frac{d}{dt} \left(\int_{\Omega_\alpha(t)} d\mathbf{x} + \int_{\Omega_\alpha} \varphi \mathbf{v}_{\partial\Omega_\alpha} \cdot \mathbf{n} dS + \int_{\mathbb{R}} \int_{\partial\Omega_\alpha} \varphi \mathbf{v}_\Gamma \cdot \mathbf{n} dS dt \right) = \\ &= \int_{\mathbb{R}} \int_{\partial\Omega_\alpha(t)} \varphi \mathbf{v}_\Gamma \cdot \mathbf{n} dS dt, \end{aligned}$$

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 δ_Γ 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}_Γ is the outer unit normal to⁴⁸ $\partial\Omega_\alpha$. We will also need

⁴⁶ We will *e.g.* obtain the exact interaction forces.

⁴⁷ This is the problem of multiplication of general distributions.

⁴⁸ This means that the characteristic function rises in the direction to Ω_α

the *topological equation*

$$\partial_t \chi_\alpha + \tilde{\mathbf{v}}_\Gamma \cdot \nabla \chi_\alpha = 0, \quad (7.24)$$

where

$$\begin{aligned} \int_{\mathbb{R}^3 \times \mathbb{R}} (\tilde{\mathbf{v}}_\Gamma \cdot \nabla \chi_\alpha) \varphi \, d\mathbf{x} \, dt &= - \int_{\mathbb{R}^3 \mathbb{R}} (\nabla \cdot (\tilde{\mathbf{v}}_\Gamma) \varphi) \, d\mathbf{x} \, dt = - \int_{\mathbb{R}} \int_{\Omega_\alpha} \nabla \cdot (\tilde{\mathbf{v}}_\Gamma \varphi) \, d\mathbf{x} \, dt = \\ &= - \int_{\mathbb{R}} \int_{\partial \Omega_\alpha} \mathbf{v}_\Gamma \cdot \mathbf{n}_\Gamma \varphi \, dS \, dt. \end{aligned}$$

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 χ_α 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_Γ^α is the value from "inside of Ω_α " 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

$$\begin{aligned} \int_{\mathbb{R}^3 \times \mathbb{R}} \partial_t(\chi_\alpha f) \varphi \, d\mathbf{x} \, dt &= - \int_{\mathbb{R}^3 \times |R|} \chi_\alpha f \partial_t \varphi \, d\mathbf{x} \, dt = \\ &= - \int_{\mathbb{R}} \int_{\Omega_\alpha} f \partial_t \varphi \, d\mathbf{x} \, dt = - \int_{\mathbb{R}} \int_{\Omega_\alpha} \partial_t(f \varphi) \, d\mathbf{x} \, dt + \int_{\mathbb{R}} \int_{\Omega_\alpha} (\partial_t \varphi) f \, d\mathbf{x} \, dt = \\ &= - \int_{\mathbb{R}} \frac{d}{dt} \left(\int_{\Omega_\alpha} f \varphi \, d\mathbf{x} \right) dt + \int_{\mathbb{R}} \int_{\partial \Omega_\alpha} f_\Gamma^\alpha f \mathbf{v}_\Gamma \cdot \mathbf{n} \, dS \, dt \int_{\mathbb{R}^3 \times \mathbb{R}} (\chi_\alpha \partial_t f) \varphi \, d\mathbf{x} \, dt = \\ &= 0 + \int_{\mathbb{R}^3 \times \mathbb{R}} (\partial_t \chi_\alpha f_\Gamma^\alpha + \chi_\alpha \partial_t f) \varphi \, d\mathbf{x} \, dt, \end{aligned}$$

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_Γ^α 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

$$\begin{aligned} \partial_t(\chi_\alpha \psi) - \left(\tilde{\psi}_\Gamma^\varphi \partial_t \chi_\alpha \right) + \nabla \cdot (\chi_\alpha \psi_\Omega \mathbf{v}) - \left((\psi_\Omega \tilde{\mathbf{v}})_\gamma^\alpha \cdot \nabla \chi_\alpha \right) + \\ + \nabla \cdot \left(\chi_\alpha \Phi_\Omega^\psi \right) - \Phi_{\Omega,\Gamma}^{\tilde{\alpha}} \cdot \nabla \chi_\alpha - \chi_\alpha \Pi_\Omega^\psi - \chi_\alpha \xi_\Omega^\psi = 0. \end{aligned}$$

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**: i 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

$$\begin{aligned} & \partial_t \langle \psi_\Omega \chi_\alpha \rangle + \nabla \cdot (\langle \psi_\Omega \chi_\alpha \mathbf{v} \rangle) + \nabla \cdot (\chi_\alpha \Phi_\Omega^\psi) + \\ & - \langle \chi_\alpha^\psi \Pi_\Omega^\psi \rangle - \langle \chi_\alpha \xi_\Omega^\psi \rangle = \langle (\psi_\Omega)_\Gamma^\alpha \partial_t \chi_\alpha + (\tilde{\psi}_\Omega \mathbf{v}_\Omega)_\Gamma^\alpha \cdot \nabla \chi_\alpha \rangle + \tilde{\Phi}_\Omega^\alpha \cdot \nabla \chi_\alpha, \end{aligned}$$

where the last term can be manipulated as

$$\langle (\tilde{\psi}_\Omega)_\Gamma^\alpha (\tilde{\mathbf{v}})_\Gamma^\alpha - \tilde{\mathbf{v}}_\Gamma \cdot \nabla \chi_\alpha + (\tilde{\Phi})_{\Omega\Gamma}^\alpha \cdot \nabla \chi_\alpha \rangle,$$

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 ρ 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_α . We have obtained new expressions for m_α .

Momentum balance

$$\begin{aligned} \partial_t \langle \chi_\alpha \rho \mathbf{v} \rangle + \nabla \cdot (\langle \chi_\alpha \rho \mathbf{v} \otimes \mathbf{v} \rangle) - \nabla \cdot (\langle \chi_\alpha \mathbb{T}_\Omega \rangle) - \langle \chi_\alpha \rho \mathbf{b} \rangle = \\ = \left\langle \left((\tilde{\rho}_\Omega)_\Gamma^\alpha (\tilde{\mathbf{v}}_\Omega)_\Gamma^\alpha \otimes ((\tilde{\mathbf{v}}_\Omega)_\Gamma^\alpha - \tilde{\mathbf{v}}_\Gamma) - (\tilde{\mathbb{T}}_\Omega)_\Gamma^\alpha \right) \cdot \nabla \chi_\alpha \right\rangle, \end{aligned}$$

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 exactly the expression we obtained in the chapter about *Darcy law*.