THEORY OF MIXTURES

COURSE LECTURE NOTES

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## Contents

1 Theory of interacting continua - introduction  
2 Reminder of the concepts of classical equilibrium thermodynamics  
   2.1 Physical postulates and mathematical model for a macroscopic system in thermodynamic equilibrium  
   2.2 Examples  
   2.3 Physical interpretation of the mathematical model  
   2.4 Other thermodynamic potentials - Legendre transform  
3 Reminder of some basic concepts of classical continuum thermodynamics and mechanics of single continuum  
   3.1 Basic cornerstones of continuum thermodynamics  
   3.2 Local equilibrium thermodynamics  
      3.2.1 Entropic representation (for fluid mixtures)  
      3.2.2 Energetic representation  
      3.2.3 Other thermodynamic potentials - Enthalpy, Helmholtz and Gibbs free energy  
   3.3 Structure of local equilibrium thermodynamics directly from the local form of fundamental relation  
   3.4 Molar-based quantities  
   3.5 Constitutive theory of continuum thermodynamics  
4 Kinematical description of mixtures  
5 Balance equations  
   5.1 Auxiliary definitions - mass, volume other measures  
   5.2 General form of a balance law in the bulk (in Eulerian description)  
   5.3 Balance of mass  
   5.4 Balance of linear momentum  
   5.5 Balance of angular momentum  
   5.6 Balance of energy (for non-polar mixture of non-polar constituents)  
   5.7 Balance of entropy (Second law of thermodynamics)  
   5.8 Classification of the mixture theories  
6 Class I mixtures  
   6.1 Fick-Navier-Stokes-Fourier model ($\psi = \bar{\psi}(\vartheta, \frac{1}{\rho}, c)$)  
   6.2 Constraints: Incompressibility and Quasi-incompressibility  
      6.2.1 Incompressibility  
      6.2.2 Quasi-incompressibility  
   6.3 Cahn-Hilliard-NSF and Allen-Cahn-NSF model  
   6.4 Allen-Cahn and Cahn-Hilliard models as gradient flows  
   6.5 Chemical reactions  
      6.5.1 Stoichiometry  
      6.5.2 Mixture of ideal gasses  
      6.5.3 Chemical equilibrium  
      6.5.4 Chemical kinetics  
7 Class II mixtures  
   7.1 Balance laws  
   7.2 Interaction forces - structure inferred from balance laws  
   7.3 Interaction forces - macroscopic mechanical analogies  
      7.3.1 Flow around a sphere  
   7.4 Darcy’s law  
      7.4.1 Reduction of two-component momentum balance
1 Theory of interacting continua - introduction

What is a mixture? Oxford English dictionary: mixture: “A product of mixing, a complex unity or aggregate (material or immaterial) composed of various ingredient or constituent parts mixed together”. and goes on as follows:

“... mixed state or condition; co-existence of different ingredients or different groups or classes of things mutually diffused through each other.”

Goal of the course

- Basic understanding of (derivation of) models that might be capable of describing the following processes (examples of mixtures around us):
  - Geophysics - Thermohaline circulation - (convection due to both temperature and concentration variations), Porous media flow - flow of water and transport of solubles through soils, rocks,..., Avalanches, Pollution spreading and transport through environment, Melting of ice and freezing of meltwater in glaciers (phase transitions), Mineral phase transitions in rocks, Generation and extraction of magma, Liquefaction (change of strength of porous water saturated solids under seismic forcing),...
  - Astrophysics - Plasmas and gaseous mixtures in the stars
  - Biology - Flow of tracers/fluids through biological tissues, Processes at cell membranes, Biochemical reactions, Remodulation of bones, Blood coagulation, Cloth formation and dissolution, Flow of blood plasma,...
  - Chemistry - Chemical reactions, Chemical equilibrium, Chemical kinetics
  - Material sciences - Multi-phase flow, Flow of aerosols, dyes, Deformation of composite materials
  - ...

- Understanding of the assumptions required for the derivation of the models and developing framework for their possible generalizations.

- To arrive at three-dimensional thermodynamically consistent material models of mixtures which include temperature effects.

- To understand how the models of Fick, Darcy, Forchheimer, Biot, Brinkman, Allen-Cahn, Cahn-Hilliard and Stephan fit into the general framework of the mixture theory.

- To provide a sufficiently colorful “palette” of material models to cover the real-world processes.
Some names & literature

- Fick (1855), On liquid diffusion.
- Darcy (1856), Les fontaines publiques de la ville de Dijon.
- Truesdell and Toupin (1960), The Classical Field Theories.
- Truesdell and Noll (1965), The non-linear field theories of mechanics.
- Atkin and Craine (1976), Continuum Theories of Mixtures: Applications
- Bowen (1976), Theory of mixtures.
- Truesdell (1984), Rational thermodynamics.
- Müller (1985), Thermodynamics
- Samohýl (1982), Racionální termodynamika chemicky reagujících směsí.
- de Groot and Mazur (1984), Non-equilibrium Thermodynamics.
- Pekař and Samohýl (2014), The thermodynamics of linear fluids and fluid mixtures.
- Bothe and Dreyer (2015), Continuum thermodynamics of chemically reacting fluid mixtures.

Two main approaches within the theory of interacting continua

- **Approach 1** - a concept based on the principle of equi-presence (all components of the mixture are assumed to co-exist simultaneously in each point of the continuum; the foundations of this approach have been laid by Truesdell et al. (e.g. Truesdell and Toupin 1960) and is sometimes referred to as *Continuum mixture theory*.

- **Approach 2** - a concept relying on postulating classical single-component balance laws together with interface conditions at intermediate (sufficiently fine spatial) scale, where components of the mixture are distinguishable (e.g. at the scale of the pore-space in case of porous media flow). This is followed by a suitable averaging procedure, which delivers a continuum-like mixture framework; one of the classical references to this approach is Drew and Passman (1998). This approach is often referred to as *Multi-phase theory*.

In this lecture, we shall mostly rely on the first approach, with the exception of Chapter 8, where foundations of the second approach will be presented.

2 Reminder of the concepts of classical equilibrium thermodynamics

In this section, we first address as a reminder the formal structure of classical equilibrium thermodynamics, following closely Evans’ Lecture notes entropy and PDEs. (Evans 2017). The development of classical physical notions is here performed in a mathematically formal way, a more “physical” introduction to the topic can be found, for example in Callen (1960). In the next chapters, these concepts are used under so-called *assumption of local equilibrium* used to transfer the thermodynamic relation to the realm of continuum physics.
2.1 Physical postulates and mathematical model for a macroscopic system in thermodynamic equilibrium

Let us nevertheless start with the physical postulates (c.f. [Callen, 1960], p. 283-284):

A physical model for a system in thermal equilibrium

- There exist particular states (called equilibrium states) that, macroscopically are characterized completely by the specification of internal energy \( E \) and set of extensive parameters \( X_1, \ldots, X_m \).
- There exists a function (called entropy) of the extensive parameters, defined for all equilibrium states, with the following property: the value assumed by the extensive parameters in the absence of constraints, are those that maximize the entropy over the manifold of equilibrium states.
- The entropy of a composite system is addition over the constituent subsystems (hence the entropy of each system is a homogeneous first order function of the extensive parameters. The entropy is continuous and differentiable and is monotonically increasing function of energy.
- The entropy of any system vanishes in the state for which \( T := \frac{\partial E}{\partial S} = 0 \).

Let us translate these physical postulates into a set of mathematical postulates:

A mathematical model for a system in thermal equilibrium

Let us suppose we are given:

- an open convex subset \( \Sigma \) of \( \mathbb{R}^{m+1} \)
- a \( C^1 \) function \( \hat{S} : \Sigma \rightarrow \mathbb{R} \) such that
  
  \( \hat{S} \) is concave
  
  \( \frac{\partial \hat{S}}{\partial E} > 0 \)
  
  \( \hat{S}(\lambda E, \lambda X_1, \ldots, \lambda X_m) = \lambda \hat{S}(E, X_1, \ldots, X_m) \) \( \lambda > 0 \) (2.1)

We call \( \Sigma \) the state space and \( S \) the entropy of the system.

Let \( E = \hat{E}(S, X_1, \ldots, X_m) \).

Owing to (ii), we can invert relation (2.2) and obtain a \( C^1 \) function \( \hat{E} \) as a function

\( E = \hat{E}(S, X_1, \ldots, X_m) \).

We define:

- Thermodynamic temperature \( T \)
  
  \( T = \hat{T} = \frac{\partial \hat{E}}{\partial S} \) (2.4)

- Generalized force (or pressure)
  
  \( P_k = \hat{P}_k = -\frac{\partial \hat{E}}{\partial X_k} \) (2.5)

Lemma 2.1. (i) The function \( \hat{E} \) is positively homogeneous of degree 1:

\( \hat{E}(\lambda S, \lambda X_1, \ldots, \lambda X_m) = \lambda \hat{E}(S, X_1, \ldots, X_m) \) \( \lambda > 0 \).
The functions \( \hat{T}, \hat{P}_k \) are positively homogeneous of degree 0:

\[
\hat{T}(\lambda S, \lambda X_1, \ldots, \lambda X_m) = \hat{T}(S, X_1, \ldots, X_m) \quad \lambda > 0
\] (2.7)

\[
\hat{P}_k(\lambda S, \lambda X_1, \ldots, \lambda X_m) = \hat{P}_k(S, X_1, \ldots, X_m)
\] (2.8)

These properties will lead to distinguishing so-called **extensive parameters**: \( S, E \) (and also \( X_k \)), which-so-to-speak depend on how “big” the system is and **intensive parameters** \( T, P_k \), which do not depend on the “size” of the system.

**Proof.**

1. Clearly, it must hold for all \( E, X_1, \ldots, X_m \):

\[
E = \hat{E}(\hat{S}(E, X_1, \ldots, X_m), X_1, \ldots, X_m).
\] (2.9)

Thus for all \( \lambda > 0 \):

\[
\lambda E = \hat{E}(\hat{S}(\lambda E, \lambda X_1, \ldots, \lambda X_m), \lambda X_1, \ldots, \lambda X_m)
\]

\[
= \hat{E}(\lambda \hat{S}(E, X_1, \ldots, X_m), \lambda X_1, \ldots, \lambda X_m)
\] (2.10)

due to (2.1)

2. Since \( \hat{S} \) is \( C^1 \), so is \( \hat{E} \). Differentiate (2.6) with respect to \( S \):

\[
\lambda \frac{\partial \hat{E}}{\partial \hat{S}} (\lambda S, \lambda X_1, \ldots, \lambda X_m) = \lambda \frac{\partial \hat{E}}{\partial S}(S, X_1, \ldots, X_m)
\]

\[
T(\lambda S, \lambda X_1, \ldots, \lambda X_m) = T(S, X_1, \ldots, X_m)
\] (2.11)

**Lemma 2.2.** It holds

\[
\frac{\partial \hat{S}}{\partial E} = \frac{1}{T}, \quad \frac{\partial \hat{S}}{\partial X_k} = \frac{P_k}{T} \quad k = 1, \ldots, m
\] (2.12)

**Proof.** We defined \( T = \frac{\partial \hat{E}}{\partial \hat{S}} \) and the function \( \hat{S}(E, X_1, \ldots, X_m) \) as an inverse of \( E = \hat{E}(S, X_1, \ldots, X_m) \). Thus it holds

\[
E = \hat{E}(\hat{S}(E, X_1, \ldots, X_m), X_1, \ldots, X_m).
\] (2.13)

Therefore

\[
1 = \frac{dE}{dE} = \frac{\partial \hat{E}}{\partial \hat{S}} \frac{\partial \hat{S}}{\partial E} \quad \Rightarrow \quad T = \frac{\partial \hat{E}}{\partial \hat{S}} = \left( \frac{\partial \hat{S}}{\partial E} \right)^{-1}.
\] (2.14)

Similarly, by taking a derivative with respect to \( X_k \), we get

\[
0 = \frac{\partial \hat{E}}{\partial \hat{S}} \frac{\partial \hat{S}}{\partial X_k} + \frac{\partial \hat{E}}{\partial X_k} = \frac{P_k}{T} \quad k = 1, \ldots, m.
\] (2.15)

The definitions (2.4) and (2.5) can be summarized by the so-called **Gibbs’s formula**

\[
dE = TdS - \sum_{k=1}^{m} P_k dX_k
\] (2.16)
2.2 Examples

The extensive parameters $X_1, \ldots, X_m$ can represent various physical quantities. Let us discuss some prototypical examples.

1. **Simple fluid.** Possibly the simplest example of an equilibrium thermodynamic system is a homogeneous simple fluid, for which the extensive parameters are:
   - $E$ - internal energy
   - $X_1 = V$ - volume
   - $X_2 = N$ - number of particles

   Consequently, the fundamental thermodynamic relation for such a system reads $S = \hat{S}(E, V, N)$, and the associated intensive parameters are:
   - $T = \frac{\partial \hat{E}}{\partial S}$ - thermodynamic temperature
   - $P_1 = P = -\frac{\partial \hat{E}}{\partial V}$ - pressure
   - $P_2 = -\mu = -\frac{\partial \hat{E}}{\partial N}$ - (molar) chemical potential

   The Gibbs formula for homogeneous simple fluid thus reads
   \[
   dE = TdS - PdV + \mu dN.
   \]

2. **Multicomponent simple fluid.** If the fluid is composed of $N$ constituents, we are in the following setting. The extensive parameters are now:
   - $E$ - internal energy
   - $X_1 = V$ - volume
   - $X_2, \ldots, X_{N+1} = N_1, \ldots, N_N$ - numbers of particles of the individual constituents

   Consequently, the fundamental thermodynamic relation for such a system reads $S = \hat{S}(E, V, N_1, \ldots, N_N)$, and the associated intensive parameters are:
   - $T = \frac{\partial \hat{E}}{\partial S}$ - thermodynamic temperature
   - $P_1 = P = -\frac{\partial \hat{E}}{\partial V}$ - pressure
   - $P_2, \ldots, P_{N+1} : P_{a+1} = -\mu_a = -\frac{\partial \hat{E}}{\partial N_a}$ - chemical potentials $a = 1, \ldots, N$

   The Gibbs formula for such a multicomponent simple fluid thus reads
   \[
   dE = TdS - PdV + \sum_{a=1}^{N} \mu_a dN_a.
   \]

3. **Homogeneous single-component dielectric fluid in a homogeneous electrostatic field** with intensity $\mathbf{E}$. From the principle of virtual work, one can deduce that the change of total energy of the volume filled with the dielectric is
   \[
   dE = TdS - PdV + \mu dN + \int_\Omega \mathbf{E} \cdot d\mathbf{D}.
   \]

   Where $\mathbf{D}$ is the electric induction vector. Assuming a homogenous field, this relation can be written as
   \[
   dE = TdS - PdV + \mu dN + V \mathbf{E} \cdot d\mathbf{D}.
   \]

   For an isotropic linear dielectric body reads $\mathbf{D} = \varepsilon_0 \mathbf{E} + \mathbf{P}$, where $\mathbf{P}$ is the so-called polarization vector and $\varepsilon_0$ is the permittivity of vacuum. Often one introduces a reduced energy $\bar{E} := E - V \frac{\mathbf{E}^2}{8\pi}$ which results
is obtained by subtracting the energy of the electrostatic field (it cannot be however interpreted as intrinsic energy of the dielectric since the value of $E$ is affected by the presence of the dielectric).

The Gibbs relation in terms of $\hat{E}$ reads

$$d\hat{E} = TdS - PdV + \mu dN + V dE : dP$$

and, by introducing the extensive quantity total polarization $\mathcal{P} := PV$, we can rewrite it as

$$d\hat{E} = TdS - \hat{P}dV + \mu dN + E : d\mathcal{P},$$

with $\hat{P} = P + \frac{\partial}{\partial \mathcal{P}} |E|^2 + E \cdot P$, and consider fundamental relation $\hat{E} = \hat{E}(S, V, N, \mathcal{P})$.

### 2.3 Physical interpretation of the mathematical model

Let us spend some time with an attempt of deeper explanation of the mathematical assumptions laid in our model and their physical interpretations and consequences.

- **The assumption** $\frac{\partial S}{\partial E} > 0$ implies $T > 0$, i.e. positivity of the thermodynamic temperature

- **The 1-homogeneity assumption of $\hat{S}$** is equivalent to additivity of entropy over subsystems of an equilibrium system. Indeed, consider a body $\mathcal{B}$ in equilibrium, with internal energy $E$, entropy $S$ and other extensive variables $X_k$, $k = 1, \ldots, m$. Let us consider a subregion $\mathcal{B}^{(1)}$, which represents a $\lambda$ fraction of $\mathcal{B}$, and consequently, its extensive parameters take values: $E^{(1)} = \lambda E$, $X^{(1)}_1 = \lambda X_1, \ldots X^{(1)}_m = \lambda X_m$, and also $S^{(1)} = \lambda S$, due to 1-homogeneity of $\hat{S}$, since

$$S^{(1)} = \hat{S}(E^{(1)}, X^{(1)}_1, \ldots, X^{(1)}_m) = \hat{S}(\lambda E, \lambda X_1, \ldots, \lambda X_m) = \lambda \hat{S}(E, X_1, \ldots, X_m) = \lambda S.$$  

The complementary subregion $\mathcal{B}^{(2)}$ (such that $\mathcal{B} = \mathcal{B}^{(1)} \cup \mathcal{B}^{(2)}$), has extensive parameters $E^{(2)} = (1-\lambda)E$, $X^{(2)}_1 = (1-\lambda)X_1, \ldots X^{(2)}_m = (1-\lambda)X_m$ and thus $S^{(2)} = (1-\lambda)S$ by 1-homogeneity of $\hat{S}$. Consequently, we get $S = S^{(1)} + S^{(2)}$. The argument can be reversed and by assuming additivity of entropy over subsystems of an equilibrium system, we would deduce 1-homogeneity of $\hat{S}$: Take division of $\mathcal{B}$ into $N$ subsystems each of the same size, i.e. $\frac{1}{N}$ fraction of $\mathcal{B}$. By the additivity assumption, it must hold

$$S = \sum_{i=1}^{N} S^{(i)} = N \hat{S} \left( \frac{1}{N} E, \frac{1}{N} X_1, \ldots, \frac{1}{N} X_m \right),$$

which must hold for all $N \in \mathbb{N}$. Using the same argument for subsystems of the size $\frac{M}{N}$, $M \in \{1, \ldots, N\}$, we obtain that $q \hat{S}(E, X_1, X_2, \ldots, X_m) = \hat{S}(qE, qX_1, \ldots, qX_m)$ for all $q \in \mathbb{Q}$, $q > 0$. By the assumption of continuity of $\hat{S}$ and by the density argument of $\mathbb{Q}$ in $\mathbb{R}$, we obtain the desired result.

- On the other hand, we have proven the intensive parameters $T, P_1, \ldots, P_m$, to be 0-homogeneous. This implies that these parameters take the same value irrespective of the size of the subregion, i.e.

$$T = T^{(1)} = T^{(2)} = \ldots, P_k = P^{(1)}_k = P^{(2)}_k = \ldots, k = 1, \ldots, m.$$  

- **Concavity of $\hat{S}$**. Let us now consider two isolated bodies made out of the same substance $\mathcal{B}^{(1)}$ and $\mathcal{B}^{(2)}$ which do not form subregions of one equilibrium system, but each of them is in equilibrium. Let

$$S^{(1)} = \hat{S}(E^{(1)}, X^{(1)}_1, \ldots, X^{(1)}_m) \quad \quad S^{(2)} = \hat{S}(E^{(2)}, X^{(2)}_1, \ldots, X^{(2)}_m)$$

The total entropy of the two systems in this configuration is $S^{(1)} + S^{(2)} = S^{(1)} + S^{(2)}$. If we now combine the two bodies into one (e.g. by allowing transfer of all extensive parameters such as energy, mass, ...) but without doing any work, neither allowing heat transfer from outside, we end up with a system $\mathcal{B}^{(3)}$ with extensive parameters $E^{(3)} = E^{(1)} + E^{(2)}$, $X^{(3)}_k = X^{(1)}_k + X^{(2)}_k$, $k = 1, \ldots, m$. Since irreversible processes may have taken place inside the system $\mathcal{B}^{(3)}$ before it equilibrated, we cannot assume more than

$$S^{(3)} \geq S^{(1)} + S^{(2)}$$
i.e. we assume that the final equilibrium entropy of the joint system is greater or equal than the sum of the two entropies of the originally isolated subsystems. So this means that

\[ S^{(3)} = \hat{S}(E^{(1)} + E^{(2)}, X_1^{(1)} + X_1^{(2)}, \ldots, X_m^{(1)} + X_m^{(2)}) \geq S^{(1)} + S^{(2)} = \hat{S}(E^{(1)}, X_1^{(1)}, \ldots, X_m^{(1)}) + \hat{S}(E^{(2)}, X_1^{(2)}, \ldots, X_m^{(2)}) . \]

This however implies that \( \hat{S} \) is concave, since taking any \( 0 < \lambda < 1 \):

\[ \hat{S} \left( \lambda E^{(1)} + (1-\lambda)E^{(2)}, \lambda X_1^{(1)} + (1-\lambda)X_1^{(2)}, \ldots, \lambda X_m^{(1)} + (1-\lambda)X_m^{(2)} \right) \]

\[ \geq \hat{S} \left( \lambda E^{(1)}, \lambda X_1^{(1)}, \ldots, \lambda X_m^{(1)} \right) + \hat{S} \left( (1-\lambda)E^{(2)}, (1-\lambda)X_1^{(2)}, \ldots, (1-\lambda)X_m^{(2)} \right) \]

\[ = \lambda \hat{S} \left( E^{(1)}, X_1^{(1)}, \ldots, X_m^{(1)} \right) + (1-\lambda) \hat{S} \left( E^{(2)}, X_1^{(2)}, \ldots, X_m^{(2)} \right) \]

where in the last equality, we employed the 1-homogeneity of \( \hat{S} \).

- **Convexity of \( \hat{E} \)** as a consequence of concavity of \( \hat{S} \). Let us take any \( S^{(1)}, X_1^{(1)}, \ldots X_m^{(1)} \) and \( S^{(2)}, X_1^{(2)}, \ldots X_m^{(2)} \) and any \( 0 < \lambda < 1 \). Define

\[ E^{(1)} = \hat{E}(S^{(1)}, X_1^{(1)}, \ldots X_m^{(1)}) \]

\[ E^{(2)} = \hat{E}(S^{(2)}, X_1^{(2)}, \ldots X_m^{(2)}) \]

and thus

\[ S^{(1)} = \hat{S}(E^{(1)}, X_1^{(1)}, \ldots X_m^{(1)}) \]

\[ S^{(2)} = \hat{S}(E^{(2)}, X_1^{(2)}, \ldots X_m^{(2)}) . \]

Since \( \hat{S} \) is concave, it must hold

\[ \hat{S} \left( \lambda E^{(1)} + (1-\lambda)E^{(2)}, \lambda X_1^{(1)} + (1-\lambda)X_1^{(2)}, \ldots, \lambda X_m^{(1)} + (1-\lambda)X_m^{(2)} \right) \]

\[ \geq \lambda \hat{S}(E^{(1)}, X_1^{(1)}, \ldots, X_m^{(1)}) + (1-\lambda) \hat{S}(E^{(2)}, X_1^{(2)}, \ldots, X_m^{(2)}) . \]

Since it holds

\[ E = \hat{E}(S(E, X_1, \ldots, X_m), X_1, \ldots, X_m) \]

and since \( \frac{\partial \hat{E}}{\partial S} = T \geq 0 \), we obtain

\[ \lambda E^{(1)} + (1-\lambda)E^{(2)} = \hat{E} \left( \hat{S}(\lambda E^{(1)} + (1-\lambda)E^{(2)}, \ldots, \lambda X_k^{(1)} + (1-\lambda)X_k^{(2)}, \ldots) \right) \]

\[ \geq \hat{E} \left( \hat{S}(E^{(1)}, X_1^{(1)}, \ldots, X_k^{(1)}, \ldots) + (1-\lambda) \hat{S}(E^{(2)}, X_1^{(2)}, \ldots, X_k^{(2)}, \ldots) \right) \]

\[ = \hat{E}(\lambda S^{(1)} + (1-\lambda)S^{(2)}, \ldots, \lambda X_k^{(1)} + (1-\lambda)X_k^{(2)}, \ldots). \]

So we obtained

\[ \lambda \hat{E}(S^{(1)}, X_1^{(1)}, \ldots, X_m^{(1)}) + (1-\lambda) \hat{E}(S^{(2)}, X_1^{(2)}, \ldots, X_m^{(2)}) \geq \hat{E}(\lambda S^{(1)} + (1-\lambda)S^{(2)}, \ldots, \lambda X_k^{(1)} + (1-\lambda)X_k^{(2)}, \ldots) \]

which implies that \( \hat{E} \) is convex.

- **Entropy maximization and energy minimization** for thermally isolated systems.
  - **Entropy maximization principle** - The equilibrium value of any unconstrained internal parameter is such as to maximize the entropy of the system for the given value of total internal energy.
  - **Energy minimization principle** - The equilibrium value of any unconstrained internal parameter is such as to minimize the energy for the given value of the total entropy.
2.4 Other thermodynamic potentials - Legendre transform

Assume that $H: \mathbb{R}^n \rightarrow (-\infty, +\infty]$ is a convex, lower semicontinuous function, which is proper (i.e. not identically equal to infinity).

**Definition 1.** The Legendre transform of $H(p)$ denoted $H^*(q)$ is defined as

$$H^*(q) = \sup_{p \in \mathbb{R}^n} (p \cdot q - H(p)) \quad (2.17)$$

One can show, that also $H^*(q)$ is convex, lower semicontinuous and proper. Furthermore,

$$(H^*)^* = H \quad (2.18)$$

i.e. $H$ is a Legendre transform of $H^*$, that’s why we call the pair $H, H^*$ as dual convex functions.

Provided that on top of the assumptions before, $H$ is moreover also a $C^2$ and strictly convex, then for each $q \in \mathbb{R}^n$ there exists a unique point $p$ where $(p \cdot q - H(p))$ is maximal, namely the unique point $p$, where

$$q = D_p H(p), \text{ providing relation } q = \hat{q}(p) \quad (2.19)$$

which can be inverted to give

$$p = \hat{p}(q). \quad (2.20)$$

The Legendre transform then reads

$$H^*(q) = \hat{p}(q) \cdot q - H(\hat{p}(q)) \quad (2.21)$$

As a consequence, one obtains also

$$D_q H^*(q) = p + (q - D_p H(p)) D_q \hat{p} = p, \quad (2.22)$$

so to summarize

$$q = D_p H(p) \quad p = D_q H^*(q) \quad (2.23)$$

So far, we have seen $S = \hat{S}(E, X_1, \ldots, X_m)$ and $E = \hat{E}(S, X_1, \ldots, X_m)$. Now Legendre transform is used to define other thermodynamic potentials

- **The Helmholtz free energy** $F$ is

$$F(T, V, \ldots) \overset{\text{def}}{=} \inf_S \hat{E}(S, V, \ldots) - TS \quad (2.24)$$
\begin{itemize}
  \item The enthalpy $H$ is
  \[ H(S,P,\ldots) = \inf_V \hat{E}(S,V,\ldots) + PV \] (2.25)
  \item The Gibbs free energy $G$ is
  \[ G(T,P,\ldots) = \inf_{S,V} \hat{E}(S,V,\ldots) - TS + PV \] (2.26)
\end{itemize}

Assuming $\hat{E}$ is strictly convex and $C^2$ and that the infima are attained at a unique point in the domain of $\hat{E}$, we can rewrite the potentials as

\begin{itemize}
  \item The Helmholtz free energy
  \[ F(T,V,\ldots) = E - TS, \quad \text{where} \quad S = \hat{S}(T,V,\ldots) \quad \text{solves} \quad T = \frac{\partial \hat{E}(S,V,\ldots)}{\partial S} \] (2.27)
  \item The enthalpy
  \[ H(S,P,\ldots) = E + PV, \quad \text{where} \quad V = \hat{V}(S,P,\ldots) \quad \text{solves} \quad P = -\frac{\partial \hat{E}(S,V,\ldots)}{\partial V} \] (2.28)
  \item The Gibbs free energy
  \[ G(T,P,\ldots) = E - TS + PV, \quad \text{where} \quad S = \hat{S}(T,P,\ldots) \quad \text{solves} \quad T = \frac{\partial \hat{E}(S,V,\ldots)}{\partial S}, \quad P = -\frac{\partial \hat{E}(S,V,\ldots)}{\partial V} \] (2.29)
\end{itemize}

Based on the definitions and the assumption $\hat{E}$ is strictly convex and $C^2$, we can prove the following

**Lemma 2.3.**
1. $\hat{E}(S,V,\ldots)$ is locally strictly convex in $(S,V)$
2. $\hat{F}(T,V,\ldots)$ is locally strictly concave in $T$, locally strictly convex in $V$.
3. $\hat{H}(S,P,\ldots)$ is locally strictly concave in $P$, locally strictly convex in $S$.
4. $\hat{G}(T,P,\ldots)$ is locally strictly concave in $(T,P)$.

**Proof.** First, the statement (1) is already assumed hence it is true. To prove (2), let us recall the definition of $F$
\[
\hat{F}(T,V,\ldots) = \hat{E}(\hat{S}(T,V,\ldots),V,\ldots) - T\hat{S}(T,V,\ldots),
\]
with
\[
T = \frac{\partial \hat{E}(\hat{S}(T,V,\ldots),V,\ldots)}{\partial S}\]
This implies
\[
\frac{\partial \hat{F}}{\partial T} = \frac{\partial \hat{E}}{\partial S} \frac{\partial \hat{S}}{\partial T} - \hat{S} - T \frac{\partial \hat{S}}{\partial T} = -\hat{S}(T,V,\ldots),
\]
\[
\frac{\partial \hat{F}}{\partial V} = \frac{\partial \hat{E}}{\partial S} \frac{\partial \hat{S}}{\partial V} + \frac{\partial \hat{E}}{\partial V} - T \frac{\partial \hat{S}}{\partial V} = \frac{\partial \hat{E}}{\partial V}(\hat{S}(T,V,\ldots),V,\ldots) = -\hat{P}(T,V,\ldots)
\]
which implies
\[
\frac{\partial^2 \hat{F}}{\partial T^2} = -\frac{\partial \hat{S}(T,V,\ldots)}{\partial T} = (2.31)
\]
\[
\frac{\partial^2 \hat{F}}{\partial V^2} = -\frac{\partial \hat{P}(T,V,\ldots)}{\partial V} = \frac{\partial^2 \hat{E}}{\partial S \partial V} \frac{\partial \hat{S}(T,V,\ldots)}{\partial V} + \frac{\partial^2 \hat{E}}{\partial V^2} \]
(2.32)
Differentiating (2.30) with respect to $(T, V)$, we obtain
\[
1 = \frac{\partial^2 \hat{E} \partial S(T, V, \ldots)}{\partial S^2} \frac{\partial}{\partial T} + \frac{\partial^2 \hat{E}}{\partial V \partial S}
\]
\[
0 = \frac{\partial^2 \hat{E} \partial S(T, V, \ldots)}{\partial S^2} \frac{\partial}{\partial V} + \frac{\partial^2 \hat{E}}{\partial V \partial S}
\]
Thus (2.31) and (2.32) imply
\[
\frac{\partial^2 F}{\partial T^2} = - \left( \frac{\partial^2 \hat{E}}{\partial S^2} \right)^{-1}
\]
\[
\frac{\partial^2 F}{\partial V^2} = \frac{\partial^2 \hat{E}}{\partial S^2} \left( \frac{\partial^2 \hat{E}}{\partial S \partial V} \right)^2 \left( \frac{\partial^2 \hat{E}}{\partial S^2} \right)^{-1}
\]
and since we assumed that $\hat{E}$ is strictly convex in $(S, V, \ldots)$, it holds
\[
\frac{\partial^2 \hat{E}}{\partial S^2} > 0, \quad \frac{\partial^2 \hat{E}}{\partial V^2} > 0, \quad \left( \frac{\partial^2 \hat{E}}{\partial S^2} \right) \left( \frac{\partial^2 \hat{E}}{\partial S \partial V} \right)^2 \left( \frac{\partial^2 \hat{E}}{\partial S^2} \right)^{-1} > 0,
\]
and thus
\[
\frac{\partial^2 \hat{F}}{\partial T^2} < 0, \quad \frac{\partial^2 \hat{F}}{\partial V^2} > 0.
\]
(2.33)

The remaining two statements are proved analogously.

\begin{proof}
Exercise 1. Prove the statements (3) and (4).
\end{proof}

3 Reminder of some basic concepts of classical continuum thermodynamics and mechanics of single continuum

3.1 Basic cornerstones of continuum thermodynamics

- **A priori homogenization** - continuum mechanics introduces the notion of a material point as a point-wise representative of some sufficiently small/sufficiently large control volume of real material; material properties assigned to such material point are averages (volume/time/stochastic) of the properties of the real material contained in the control volume.

Figure 2: Essential kinematical concept of continuum mechanics - notion of motion $\chi$ of an abstract body $\mathcal{B}$, viewed as a mapping from some reference configuration $\kappa_0(\mathcal{B}) \subset \mathbb{R}^3$ to the current configuration $\kappa_t(\mathcal{B}) \subset \mathbb{R}^3$ at given time $t$. 

11
• Kinematics
  
  Motion - mapping
  \[
  \chi(\cdot,t) : \kappa_0(\mathcal{B}) \rightarrow \kappa_t(\mathcal{B})
  \]  
  \[\mathbb{R}^3 \times \mathbb{R} \rightarrow \mathbb{R}^3 : x = \chi(X,t) \quad x^k = \chi^k(X^K,t), \]  
  which is assumed to be sufficiently smooth and invertible.

  - Spatial gradient
    \[
    \text{Grad}\Phi(X,t) = \frac{\partial\Phi(X,t)}{\partial X}
    \]  
    \[\text{grad}\phi(x,t) = \frac{\partial\phi}{\partial x} \]  

  - Velocity
    \[
    V(X,t) = \frac{\partial\chi}{\partial t} \bigg|_X \quad \text{in Lagrangean description} \tag{3.5}
    \]  
    \[v(x,t) = V(\chi^{-1}(x,t),t) \quad \text{in Eulerian description} \tag{3.6} \]

  - Material time derivative
    \[
    \frac{D}{Dt}\Phi(X,t) = \frac{\partial\Phi(X,t)}{\partial t} \bigg|_X \tag{3.7}
    \]  
    \[
    \frac{D}{Dt}\phi(x,t) = \frac{\partial\phi(\chi^{-1}(x,t),t)}{\partial t} \bigg|_x + v(x,t) \cdot \text{grad}_{x}\phi(x,t) \tag{3.8} \]

  - Deformation gradient
    \[
    \mathcal{F}(X,t) = \frac{\partial\chi(X,t)}{\partial X} \quad (\mathcal{F})^k_i(X) = \frac{\partial\chi^k(X,t)}{\partial X^i} \tag{3.9}
    \]

  - Green deformation tensor
    \[
    C(X,t) = \mathcal{F}^T\mathcal{F} \quad (C)_{IJ} = (\mathcal{F})^I_i(\mathcal{F})^J_j \delta_{ij} \tag{3.10}
    \]  
    \[
    (C)_{IJ} = (\mathcal{F})^I_i(\mathcal{F})^J_j \delta_{ij} \tag{3.11} \]

  - Cauchy deformation tensor
    \[
    c(x,t) = \mathcal{F}^{-T}\mathcal{F}^{-1} \quad (c)_{ij} = (\mathcal{F}^{-1})_I^i(\mathcal{F}^{-1})_J^j \delta_{IJ} \tag{3.12} \]

  - Finger deformation tensor
    \[
    \mathcal{B}(X,t) = \mathcal{F}\mathcal{F}^T \quad (\mathcal{B})^{IJ} = (\mathcal{F})^I_i(\mathcal{F})^J_j \delta^{IJ} \tag{3.15}
    \]  
    \[
    (\mathcal{B})^{IJ} = (\mathcal{F})^I_i(\mathcal{F})^J_j \delta^{IJ} \tag{3.16} \]

  - Piola deformation tensor
    \[
    b(x,t) = \mathcal{F}^{-1}\mathcal{F}^{-T} \quad (b)^{IJ} = (\mathcal{F})^{-1}_I^i(\mathcal{F})^{-1}_J^j \delta^{IJ} \tag{3.17}
    \]  
    \[
    (b)^{IJ} = (\mathcal{F})^{-1}_I^i(\mathcal{F})^{-1}_J^j \delta^{IJ} \tag{3.18} \]

  - Velocity gradient
    \[
    L(x,t) = \text{grad}v \quad (L)_j = \frac{\partial v_j}{\partial x_j} \tag{3.19} \]
Exercise 2. Show that $\dot{\mathbf{F}} = \mathbf{L}\mathbf{F}$.
Exercise 3. Show that $\dot{\mathbf{B}} = \mathbf{L}\mathbf{B} + \mathbf{B}\mathbf{L}^T$.

**Volume and mass measures, constraints**
Consider a mixture body $\Omega$ and let $\mathcal{P} \subset \Omega$ open subset, then we define

$\forall \mathcal{P}$, "nice" $\mathcal{M}(\mathcal{P})$ ... mass contained in $\mathcal{P}$

$\mathcal{V}(\mathcal{P})$ ... volume of $\mathcal{P}$

Constraint: $\forall \mathcal{P}: 0 = \frac{d}{dt} \mathcal{V}(\mathcal{P})$ (using the substitution theorem and identity $\dot{\det(\mathbf{F})} = \text{div} \mathbf{v} \det(\mathbf{F})$), we obtain the incompressibility constraint $0 = \int_{\mathcal{P}} \text{div} \mathbf{v} = 0$, localization gives $\text{div} \mathbf{v} = 0$

**Balance equations (in Eulerian description)**

- **Balance of mass**
  $$\frac{\partial \rho}{\partial t} + \text{div}(\rho \mathbf{v}) = 0,$$
  (3.21)
  where $\rho$ is the density, $\mathbf{v}$ is the velocity.

- **Balance of linear momentum**
  $$\frac{\partial (\rho \mathbf{v})}{\partial t} + \text{div}(\rho \mathbf{v} \otimes \mathbf{v}) = \text{div} \mathbf{T} + \rho \mathbf{b},$$
  (3.22)
  where $\mathbf{T}$ is the Cauchy stress, $\mathbf{b}$ is the intensity of the body forces.

- **Balance of angular momentum (for non-polar continuum)**
  $$\mathbf{T} = \mathbf{T}^T.$$  (3.23)

- **Balance of total energy**
  $$\frac{\partial}{\partial t} \left( \rho \left( e + \frac{1}{2} |\mathbf{v}|^2 \right) \right) + \text{div} \left( \rho \left( e + \frac{1}{2} |\mathbf{v}|^2 \right) \mathbf{v} \right) = \text{div} (\mathbf{T} \mathbf{v} - \mathbf{q}) + \rho \mathbf{b} \cdot \mathbf{v} + \rho r,$$
  (3.24)
  where $e$ is the specific internal energy, and $r$ is the energy supply (e.g. radiation).

In the framework of continuum thermodynamics, one has to consider also

- **Balance of entropy**
  $$\frac{\partial (\rho \eta)}{\partial t} + \text{div}(\rho \eta \mathbf{v}) + \text{div} \mathbf{q}_\eta = \xi \geq 0,$$
  (3.25)
  where $\eta$ is the specific entropy, $\mathbf{q}_\eta$ is the entropy flux and $\xi$ is the entropy production, which, by the second law of thermodynamics must be non-negative,

**Exercise 4.** Show that (3.21)-(3.24) allow to rewrite (3.24) in a more compact form (balance of internal energy)

$$\rho \dot{e} = \mathbf{T} : \mathbf{D} - \text{div} \mathbf{q} + \rho r.$$  (3.26)

Assuming the body forces $\mathbf{b}$ and energy supply $r$ are given, the balance equations (3.21), (3.22), (3.24) represent system of of 5 evolutionary equations for unknowns $\rho, e, \mathbf{v} = (v_1, v_2, v_3)$, $\mathbf{T} = (T_{11}, T_{12}, T_{13}, T_{22}, T_{23}, T_{33})$, $\mathbf{q} = (q_1, q_2, q_3)$ (14 unknowns), and it is known that it is in general impossible to predict the evolution of the $\mathbf{T}$ and $\mathbf{q}$ from this system knowing the initial state and boundary conditions. It is necessary to provide closure relations - relations describing how $\mathbf{T}$ and $\mathbf{q}$ depend on the mechanical and thermal state of the system.
3.2 Local equilibrium thermodynamics

In this course we shall rarely leave the realm of so called local equilibrium thermodynamics - a thermodynamic theory in which each material point (representing sufficiently small subsystem of the whole system), is assumed to be in local thermodynamic equilibrium. By saying local, we mean, that this equilibrium only concerns the subsystem, but naturally, this material point behaves as an open subsystem, exchanging mass, energy, entropy etc., with the neighbouring points, with which equilibrium may not have been reached.

Based on this idea, we can exploit the notions and relations that have been derived for macroscopic systems in thermodynamic equilibrium and simply apply them on some small representative volume of our system. We will then deduce some local relations, and postulate them to hold point-wise in our continuum model. In the following application we will be exclusively interested in the description of fluid mixtures in the absence of electric and magnetic fields. We shall often tacitly assume this without further emphasizing this point explicitly.

3.2.1 Entropic representation (for fluid mixtures)

So consider this volume element $d\Omega$, assumed to be in thermodynamic equilibrium, for which we apply the formal equilibrium structure, briefly reminded in Section 2. So again, we postulate existence of a function $\hat{S}$ called “entropy”, which is a function of energy of the system, and its extensive variables - in most cases we will restrict ourselves to volume, and masses of individual components of the system:

$$S = \hat{S}(E, V, \mathcal{M}_a).$$

or more precisely

$$S(d\Omega) = \hat{S}(E(d\Omega), V(d\Omega), \mathcal{M}_a(d\Omega)),$$

where $E(d\Omega)$, $V(d\Omega)$ and $\mathcal{M}_a(d\Omega)$ are the energy, volume and masses of component in the subdomain $d\Omega$. The function $\hat{S}$ was postulated (see (2.1)) to be

- positive 1–homogeneous with respect to the extensive variables, meaning

$$\hat{S}(\lambda E, \lambda V, \lambda \mathcal{M}_a) = \lambda \hat{S}(E, V, \mathcal{M}_a) \quad \forall \lambda > 0.$$  

- increasing function of energy

$$\frac{\partial \hat{S}}{\partial E} > 0.$$  

- $\hat{S}$ is concave

From (3.27), we get by differentiating

$$dS = \frac{\partial \hat{S}}{\partial E} dE + \frac{\partial \hat{S}}{\partial V} dV + \sum_{a=1}^{N} \frac{\partial \hat{S}}{\partial \mathcal{M}_a} d\mathcal{M}_a.$$

In chapter 2 we defined the thermodynamic temperature $\vartheta$, thermodynamic pressure $p$ and chemical potentials $\mu_a$ by relations

$$\frac{1}{\vartheta} = \frac{\partial \hat{S}}{\partial E}, \quad \frac{p}{\vartheta} = \frac{\partial \hat{S}}{\partial V}, \quad -\frac{\mu_a}{\vartheta} = \frac{\partial \hat{S}}{\partial \mathcal{M}_a},$$

so we can rewrite (3.31) in the classical form

$$\vartheta dS = dE + p dV - \sum_{a=1}^{N} \mu_a d\mathcal{M}_a.$$  

Differentiating (3.29) w.r.t. $\lambda$ at $\lambda = 1$, we obtained the corresponding Euler relation

$$\hat{S}(E, V, \mathcal{M}_a) = \frac{\partial \hat{S}}{\partial E} E + \frac{\partial \hat{S}}{\partial V} V + \sum_{a=1}^{N} \frac{\partial \hat{S}}{\partial \mathcal{M}_a} \mathcal{M}_a.$$
or, equivalently, using the introduced definitions

\[ \theta S = E + pV - \sum_{a=1}^{N} \mu_a \mathcal{M}_a. \]  

(3.35)

Differentiating (3.35) and using (3.31), we obtained the Gibbs-Duhem relation:

\[ S d \theta = V dp - \sum_{a=1}^{N} \mathcal{M}_a d \mu_a. \]  

(3.36)

Let us now explore the consequences of 1-homogeneity of entropy:

- Let us first take \( \lambda := \frac{1}{\mathcal{M}} \) with \( \mathcal{M} := \sum_{a=1}^{N} \mathcal{M}_a \):

\[ \hat{S} \left( \frac{E}{\mathcal{M}}, \frac{V}{\mathcal{M}}, \mathcal{M}_a \right) = \frac{1}{\mathcal{M}} \hat{S}(E, V, \mathcal{M}_a). \]  

(3.37)

Recognizing in the arguments of the function on the l.h.s., the specific energy \( e \), inverse of density of the mixture \( \frac{1}{\rho} \) and concentrations (mass fractions) \( c_a \), defined as

\[ e \overset{\text{def}}{=} \frac{E}{\mathcal{M}}, \quad \frac{1}{\rho} \overset{\text{def}}{=} \frac{V}{\mathcal{M}}, \quad c_a \overset{\text{def}}{=} \frac{\mathcal{M}_a}{\mathcal{M}} \quad a = 1, \ldots, N, \]  

(3.38)

and observing that the function on the l.h.s. is a specific entropy \( \eta \), we can write this relation as

\[ \frac{1}{\mathcal{M}} \hat{S}(E, V, \mathcal{M}_a) = \eta \overset{\text{def}}{=} \hat{\eta}(e, \frac{1}{\rho}, c_1, \ldots, c_N), \]  

(3.39)

differentiating the last equality yields

\[ d\eta = \frac{\partial \hat{\eta}}{\partial e} de + \frac{\partial \hat{\eta}}{\partial \frac{1}{\rho}} d\left( \frac{1}{\rho} \right) + \sum_{a=1}^{N} \frac{\partial \hat{\eta}}{\partial c_a} dc_a \]  

(3.40)

Dividing the Gibbs-Duhem relation (3.36) by \( \mathcal{M} \), we get

\[ \eta d \theta = \frac{1}{\rho} dp - \sum_{a=1}^{N} c_a d \mu_a. \]  

(3.41)

Dividing the Euler relation (3.35) by \( \mathcal{M} \), we obtain its local form

\[ \theta \eta = e + \frac{p}{\rho} - \sum_{a=1}^{N} \mu_a c_a. \]  

(3.42)

Finally, differentiating (3.42) and subtracting (3.41), we recover the local version of (3.33):

\[ \theta d \eta = de + pd \left( \frac{1}{\rho} \right) - \sum_{a=1}^{N} \mu_a d c_a. \]  

(3.43)

Note that (3.43) implies the following local definitions of temperature, pressure and chemical potential:

\[ \frac{1}{\theta} = \frac{\partial \hat{\eta}}{\partial e} \bigg|_{\frac{1}{\rho}, c_1, \ldots, c_N}, \quad \frac{p}{\theta} = \frac{\partial \hat{\eta}}{\partial \frac{1}{\rho}} \bigg|_{e, c_1, \ldots, c_N}, \quad \approx \frac{\partial \hat{\eta}}{\partial c_a} \bigg|_{e, \frac{1}{\rho}, c_\beta \neq a} \]  

(3.44)
Remark 1. In the definition of $\hat{\eta}$ (3.39) we did not employ the constraint $\sum_{a=1}^{N} c_a = 1$, which follows from the definition of mass fractions $c_a$ in (3.38). Sometimes it is more convenient to employ this constraint when defining the specific entropy $\hat{\eta}$ and eliminate one of the concentrations (without loss of generality $c_N$) and define reduced specific entropy $\bar{\eta}$

$$\hat{\eta}(e, \frac{1}{\rho}, c_1, \ldots, c_{N-1}) = \hat{\eta}(e, \frac{1}{\rho}, c_1, \ldots, c_{N-1}, 1 - \sum_{\beta=1}^{N-1} c_\beta).$$

Immediately, we then obtain the following relations

$$\frac{1}{\theta} = \left. \frac{\partial \hat{\eta}}{\partial e} \right|_{\frac{1}{\rho}, c_1, \ldots, c_{N-1}}, \quad \frac{\rho}{\theta} = \left. \frac{\partial \hat{\eta}}{\partial \rho} \right|_{e, c_1, \ldots, c_{N-1}}, \quad -\frac{\mu_a - \mu N}{\theta} = \left. \frac{\partial \hat{\eta}}{\partial c_a} \right|_{e, \frac{1}{\rho}, c_\beta, \beta = 1, \ldots, N-1 & \beta \neq a}. \quad (3.46)$$

Note that the only difference when employing this reduction arises in the last set of relations, i.e. defining the partial derivatives of $\bar{\eta}$ with respect to reduced (independent) set of concentrations $c_1, \ldots, c_{N-1}$, which define the difference of chemical potentials with respect to the eliminated component.

Clearly one can also employ the constraint in the Gibbs relation (3.43) and get

$$\theta d\eta = de + pd\left(\frac{1}{\rho}\right) - \sum_{a=1}^{N-1} (\mu_a - \mu_N) dc_a. \quad (3.47)$$

If one defines the relative chemical potentials

$$\bar{\mu}_a \overset{\text{def}}{=} \mu_a - \mu N, \quad (3.48)$$

one can simply use the reduced description (i.e. consider $\eta = \hat{\eta}(e, \frac{1}{\rho}, c_1, \ldots, c_{N-1})$) the Gibbs relation as

$$\theta d\eta = de + pd\left(\frac{1}{\rho}\right) - \sum_{a=1}^{N-1} \bar{\mu}_a dc_a. \quad (3.49)$$

Now, let’s consider $\lambda := \frac{1}{V}$. Then 1-homogeneity of $\hat{S}$ yields

$$\hat{S}\left(\frac{E}{V}, 1, \frac{\mathcal{M}_a}{V}\right) = \frac{1}{V} \hat{S}(E, V, \mathcal{M}_a). \quad (3.50)$$

Recognizing in the arguments of the function on the l.h.s., the volume density of energy $\rho e$, and partial density $\rho_a$, and observing that the function on the l.h.s. is a volume density of entropy $\rho \eta$, we can write this relation as

$$\frac{1}{V} \hat{S}(E, V, \mathcal{M}_a) = \rho \eta = \bar{\rho} \eta(\rho e, \rho_1, \ldots, \rho_N), \quad (3.51)$$

donerating the last equality yields

$$d(\rho \eta) = \frac{\partial \rho \eta}{\partial \rho e} d(\rho e) + \sum_{a=1}^{N} \frac{\partial \rho \eta}{\partial \rho_a} d\rho_a. \quad (3.52)$$

Dividing the Gibbs-Duhem relation (3.36) by $V$, we get

$$\rho \eta d\theta = dp - \sum_{a=1}^{N} \rho_a d\mu_a. \quad (3.53)$$

Dividing the Euler relation (3.35) by $V$, we get

$$\partial \rho \eta = \rho e + p - \sum_{a=1}^{N} \mu_a \rho_a. \quad (3.54)$$
Finally, differentiating (3.54) and subtracting (3.53), we recover the local version of (3.33):

$$\theta d(\rho \eta) = d(pe) - \sum_{a=1}^{N} \mu_a d \rho_a .$$

(3.55)

Note that (3.55) implies the following alternative local definitions of temperature, and chemical potential:

$$\frac{1}{\theta} = \frac{\partial \rho \eta}{\partial (pe)} \bigg|_{\rho_a}, \quad -\frac{\mu_a}{\theta} = \frac{\partial \rho \eta}{\partial \rho_a} \bigg|_{pe, \rho \neq a} .$$

(3.56)

**Note:** One might be puzzled now, where has the pressure vanished from our description in (3.55) and (3.56). In this setting we can introduce the pressure through the Euler relation (3.54). A natural question is whether thermodynamic pressure defined in such a manner coincides with (3.44).

**Exercise 5.** Confirm by calculation that two discussed definitions of thermodynamic pressure are compatible. HINT: Assume that you start from fundamental thermodynamic relation $\rho \eta = \rho \eta (pe, \rho_1, \ldots, \rho_N)$ and realize that the introduced definitions imply

$$\dot{\eta} \left( e, \frac{1}{\rho}, c_1, \ldots, c_N \right) = \frac{1}{\mathcal{E}} \dot{S}(E, V, \mathcal{M}_1, \ldots, \mathcal{M}_N) = \frac{V}{\mathcal{M}} \dot{S}(E, V, \mathcal{M}_1, \ldots, \mathcal{M}_N) = \frac{V}{\mathcal{M}} \dot{S} \left( \frac{E}{M}, 1, \frac{V}{M}, \ldots, \frac{V}{M} \right) .$$

(3.57)

Use this relation, define pressure through the Euler relation (3.54) and try to compute what is

$$\theta \frac{\partial \rho \eta}{\partial \frac{1}{\rho}} \bigg|_{e, c_1, \ldots, c_N} = \theta \frac{\partial \rho \eta}{\partial \frac{1}{\rho}} \bigg|_{e, c_1, \ldots, c_N} \left( \frac{\rho}{\rho} \right) \left( pe, \rho_1, \ldots, \rho_N \right) .$$

3.2.2 Energetic representation

Alternatively, using the fact, that $\frac{\partial \dot{S}}{\partial E} = \frac{1}{\theta} > 0$, assuming sufficient smoothness of $\dot{S}$ we could invert (3.27) and write instead

$$E = \dot{E}(S, V, M_a) .$$

(3.57)

This function was proved in [2.1] to be also 1-homogeneous, i.e.

$$\dot{E} \left( S, V, \frac{M_a}{\mathcal{E}}, \frac{\mathcal{M}_a}{\mathcal{M}} \right) = \frac{1}{\mathcal{E}} \dot{E}(S, V, M_a) .$$

(3.58)

Differentiating this relation and comparing with (3.33), we obtained alternative definitions of absolute temperature, pressure and chemical potential:

$$\theta = \frac{\partial \dot{E}}{\partial S}, \quad p = -\frac{\partial \dot{E}}{\partial V}, \quad \mu_a = \frac{\partial \dot{E}}{\partial \mathcal{M}_a} .$$

(3.59)

Both the Euler relation (3.35) and the Gibbs-Duhem relation (3.36) are recovered in the same form, and one can proceed to the local forms as before, by applying the 1-homogeneity w.r.t total mass and total volume. The same form of local Euler and Gibbs-Duhem relations are recovered, plus we obtain the following two sets of alternative definitions:

$$\theta = \frac{\partial \dot{e}}{\partial \eta} \bigg|_{\frac{1}{\rho}, c_1, \ldots, c_N}, \quad -p = \frac{\partial \dot{e}}{\partial \frac{1}{\rho}} \bigg|_{\eta, c_1, \ldots, c_N}, \quad \mu_a = \frac{\partial \dot{e}}{\partial c_a} \bigg|_{\eta, \frac{1}{\rho}, c_{\beta \neq a}}$$

(3.60)

for

$$e = \dot{e}(\eta, \frac{1}{\rho}, c_1, \ldots, c_N) .$$

(3.61)

and

$$\theta = \frac{\partial \rho \dot{e}}{\partial (\rho \eta)} \bigg|_{\rho_a}, \quad \mu_a = \frac{\partial \rho \dot{e}}{\partial \rho_a} \bigg|_{\rho, \rho, \rho_a}$$

(3.62)

for

$$\rho e = \rho \dot{e}(\rho \eta, \rho_1, \ldots, \rho_N) .$$

(3.63)
3.2.3 Other thermodynamic potentials - Enthalpy, Helmholtz and Gibbs free energy

The other thermodynamic potentials can now be obtained as in the classical theory by means of Legendre transform. In particular, we define

- **Thermodynamic potentials associated with \( \hat{\varepsilon}(\eta, \frac{1}{\rho}, c_1, \ldots, c_N) \)**

  - **The specific Helmholtz free energy** \( \psi \) is
    \[
    \psi \left( \theta, \frac{1}{\rho}, c_1, \ldots, c_N \right) \overset{\text{def}}{=} \inf_{\eta} \left\{ \hat{\varepsilon} \left( \eta, \frac{1}{\rho}, c_1, \ldots, c_N \right) - \eta \right\}
    \]
    which for \( \hat{\varepsilon} \) being a \( C^2 \) strictly convex function can be rewritten as
    \[
    \psi \left( \theta, \frac{1}{\rho}, c_1, \ldots, c_N \right) = \hat{\varepsilon} - \eta \]
    where \( \eta = \bar{\eta}(\theta, \frac{1}{\rho}, c_1, \ldots, c_N) \)
    (3.65)
    solves \( \frac{\partial \hat{\varepsilon}}{\partial \eta} = \frac{\partial \bar{\eta}}{\partial \theta} \) (3.66)

  From the above definition, we obtain
  \[
  \frac{\partial \hat{\psi}}{\partial \theta} = \frac{\partial}{\partial \theta} \left( \hat{\varepsilon}(\eta, \frac{1}{\rho}, c_a), \frac{1}{\rho}, c_\beta \right) - \partial \bar{\eta} \left( \theta, \frac{1}{\rho}, c_a \right) = \frac{\partial \hat{\varepsilon}}{\partial \eta} \frac{\partial \eta}{\partial \theta} - \bar{\eta} \frac{\partial \bar{\eta}}{\partial \theta} = -\bar{\eta},
  \]
  \[
  \frac{\partial \hat{\psi}}{\partial c_a} = \frac{\partial}{\partial c_a} \left( \hat{\varepsilon}(\eta, \frac{1}{\rho}, c_a), \frac{1}{\rho}, c_\beta \right) - \partial \bar{\eta} \left( \theta, \frac{1}{\rho}, c_a \right) = \frac{\partial \hat{\varepsilon}}{\partial \eta} \frac{\partial \eta}{\partial c_a} + \frac{\partial \hat{\varepsilon}}{\partial c_a} \frac{\partial \bar{\eta}}{\partial c_a} = \mu_a.
  \]

  In summary, we get relations
  \[
  -\eta = \frac{\partial \hat{\psi}}{\partial \theta} \left. \right|_{\theta, \frac{1}{\rho}, c_1, \ldots, c_N}, \quad -p = \frac{\partial \hat{\psi}}{\partial \rho} \left. \right|_{\theta, \frac{1}{\rho}, c_1, \ldots, c_N}, \quad \mu_a = \frac{\partial \hat{\psi}}{\partial c_a} \left. \right|_{\theta, \frac{1}{\rho}, c_\beta \neq a}
  \]
  (3.67)

  - **The specific enthalpy** \( h \) is
    \[
    h(\eta, \rho, c_1, \ldots, c_N) \overset{\text{def}}{=} \inf_{\hat{\varepsilon}} \left\{ \hat{\varepsilon} \left( \eta, \frac{1}{\rho}, c_1, \ldots, c_N \right) + \frac{\rho}{\rho} \right\}
    \]
    which for \( \hat{\varepsilon} \) a \( C^2 \) strictly convex function gives
    \[
    h(\eta, \rho, c_1, \ldots, c_N) = \hat{\varepsilon} + \frac{\rho}{\rho}
    \]
    where \( \frac{1}{\rho} = \left( \frac{1}{\rho} \right)(\eta, \rho, c_1, \ldots, c_N) \)
    (3.69)
    solves \( -p = \frac{\partial \hat{\varepsilon}}{\partial \rho} \left. \right|_{\eta, \rho, c_1, \ldots, c_N} \) (3.70)

  By analogous computations as for the Helmholtz free energy, we obtain the following expressions for the partial derivatives of enthalpy
  \[
  \theta = \frac{\partial h}{\partial \eta} \left. \right|_{\rho, c_1, \ldots, c_N}, \quad \frac{1}{\rho} = \frac{\partial h}{\partial \rho} \left. \right|_{\eta, c_1, \ldots, c_N}, \quad \mu_a = \frac{\partial h}{\partial c_a} \left. \right|_{\eta, \rho, c_\beta \neq a}
  \]
  (3.71)
Exercise 6. Proof the above relations (3.71).

- **The specific Gibbs free energy** \( \dot{g} \) is

\[
\dot{g}(\theta, p, c_1, \ldots, c_N) \overset{\text{def}}{=} \inf_{\eta, p} \left\{ \dot{c} \left( \eta, \frac{1}{\rho} c_1, \ldots, c_N \right) - \theta \eta + p \rho \right\}
\]  

(3.72)

which for \( \dot{c} \) being a \( C^2 \) strictly convex function can be rewritten as

\[
\dot{g}(\theta, p, c_1, \ldots, c_N) = \dot{c} - \theta \eta + \frac{p}{\rho}
\]  

(3.73)

where \( \eta = \vec{\eta}(\theta, \frac{1}{\rho} c_1, \ldots, c_N) \) solves

\[
\theta = \frac{\partial \dot{c}(\eta, \frac{1}{\rho} c_1, \ldots, c_N)}{\partial \eta},
\]

(3.74)

and

\[
\frac{1}{\rho} \left( \eta, p, c_1, \ldots, c_N \right) \text{ solves } - \frac{\partial \dot{c}(\eta, \frac{1}{\rho} c_1, \ldots, c_N)}{\partial \left( \frac{1}{\rho} \right)}
\]

(3.75)

Consequently, we arrive at the following set of expressions for the partial derivatives of Gibbs’ free energy

\[
-\eta = \frac{\partial \dot{g}}{\partial \theta}_{p, c_1, \ldots, c_N}, \quad \frac{1}{\rho} = \frac{\partial \dot{g}}{\partial p}_{\theta, c_1, \ldots, c_N}, \quad \mu_a = \frac{\partial \dot{g}}{\partial c_a}_{\theta, p, c \neq a}
\]

(3.76)

- **Thermodynamic potentials associated with** \( \vec{\rho}\vec{e}(\rho\eta, \rho_1, \ldots, \rho_N) \)

- **The Helmholtz free energy** (per unit volume) \( \rho\psi \) is

\[
\vec{\rho}\vec{\psi}(\theta, \rho_1, \ldots, \rho_N) \overset{\text{def}}{=} \inf_{\rho\eta} \left\{ \vec{\rho}\vec{e}(\rho\eta, \rho_1, \ldots, \rho_N) - \theta \rho \eta \right\}
\]

(3.77)

which for \( \vec{\rho}\vec{e} \) being a \( C^2 \) strictly convex function can be rewritten as

\[
\vec{\rho}\vec{\psi}(\theta, \rho_1, \ldots, \rho_N) = \vec{\rho}\vec{e} - \theta \rho \eta
\]

where \( \rho \eta = \vec{\eta}(\theta, \rho_1, \ldots, \rho_N) \)

(3.78)

solves

\[
\theta = \frac{\partial \vec{\rho}\vec{e}(\rho\eta, \rho_1, \ldots, \rho_N)}{\partial (\rho \eta)}
\]

(3.79)

- **The enthalpy** (per unit volume) \( \rho h \) is cannot be obtained as a Legendre transform of \( \vec{\rho}\vec{e} \) in this case, but can be defined as

\[
\vec{\rho}h(\rho\eta, \rho_1, \ldots, \rho_N) = \vec{\rho}\vec{e} + p
\]

(3.80)

where \( p \) is given by the Euler relation, i.e. understood as \( (3.42) \), which implies

\[
\vec{\rho}h(\rho\eta, \rho_1, \ldots, \rho_N) = \theta \rho \eta + \sum_{a=1}^{N} \mu_a \rho_a ,
\]

(3.81)

where we understand \( \theta = \frac{\partial \vec{\rho}\vec{e}}{\partial \rho \eta}(\rho\eta, \rho_1, \ldots, \rho_N) \) and \( \mu_a = \frac{\partial \vec{\rho}\vec{e}}{\partial \rho_a}(\rho\eta, \rho_1, \ldots, \rho_N) \).

- Similarly, **the Gibbs free energy** (per unit volume) \( \rho g \) cannot be obtained as a Legendre transform of \( \vec{\rho}\vec{e} \) but can be defined by

\[
\vec{\rho}g(\theta, \rho_1, \ldots, \rho_N) \overset{\text{def}}{=} \vec{\rho}\vec{\psi} + p
\]

(3.82)

where \( p \) is given by the Euler relation \( (3.42) \), meaning

\[
\vec{\rho}g(\theta, \rho_1, \ldots, \rho_N) = \sum_{a=1}^{N} \mu_a \rho_a , \quad \text{where } \mu_a = \frac{\partial \vec{\rho}\vec{\psi}}{\partial \rho_a}.
\]

(3.83)
3.3 Structure of local equilibrium thermodynamics directly from the local form of fundamental relation

In the previous section, we have employed the classical equilibrium thermodynamics applied on some small control volume $d\Omega$ in the continuum, for which we assumed that all the relaxation processes within the control volume have taken place, i.e. should this control volume be suddenly isolated from the rest of the volume, it would not evolve anymore - it would already be in equilibrium.

In continuum mechanics, it would be convenient not to make the digression to the world of macroscopic thermodynamics and not to invoke the associated concepts anymore. In the entropic representation, we have arrived at two possible forms of the local fundamental relation, namely

$$\rho\eta = \hat{\rho}\eta(\rho e, \rho_1, \ldots, \rho_N), \quad (3.84)$$

and

$$\eta = \hat{\eta}(e, \frac{1}{\rho}, c_1, \ldots, c_N) \quad (3.85)$$

We have seen that the Gibbs relations can be directly obtained from these relations by taking a differential (or time derivative). Indeed, taking the time derivative and using the definitions (3.60) and (3.62), we obtain

$$d(\rho\eta) = \frac{1}{\theta} d(\rho e) - \sum_{a=1}^{N} \frac{\mu_a}{\theta} d\rho_a \quad (3.86)$$

and

$$d\eta = \frac{1}{\theta} de + \frac{p}{\theta} d\left(\frac{1}{\rho}\right) - \sum_{a=1}^{N} \frac{\mu_a}{\theta} dc_a \quad (3.87)$$

which are relations (3.55) and (3.43), respectively.

But to arrive at the Euler relations and Gibbs-Duhem relations, we had to rely on the macroscopic equilibrium thermodynamics for some representative volume and employ the 1-homogeneity. Let us show that in fact, the 1-homogeneity is already present in the fundamental relation written as above, and can be directly used to retrieve both the Euler and the Gibbs-Duhem relations. Assume we have the fundamental relation written first as

$$\rho\eta = \hat{\rho}\eta(\rho e, \rho_1) \quad (3.88)$$

and define

$$\hat{\eta}(e, \frac{1}{\rho}, c_1, \ldots, c_N) = \frac{\hat{\rho}\eta(\rho e, \rho c_1, \ldots, \rho c_N)}{\rho} \quad (3.89)$$

Naturally, it holds

$$\rho\hat{\eta} = \hat{\rho}\eta. \quad (3.90)$$

Notice

$$\frac{1}{\theta} \frac{\partial \hat{\rho}\eta}{\partial (\rho e)} = \frac{\partial \hat{\eta}}{\partial e} \quad (3.91)$$

$$\frac{\mu_a}{\theta} \frac{\partial \hat{\rho}\eta}{\partial \rho_a} = \frac{\partial \hat{\eta}}{\partial c_a} \bigg|_{e, \frac{1}{\rho}, c_{\beta \neq a}} \quad (3.92)$$

If we take a material time derivative of (3.90), we obtain

$$\rho\hat{\eta} + \rho\frac{\partial \hat{\eta}}{\partial \dot{e}} + \rho\left(\frac{1}{\rho}\right) \frac{\partial \hat{\eta}}{\partial \left(\frac{1}{\rho}\right)} = \sum_{a=1}^{N} \rho \frac{\partial \hat{\eta}}{\partial \rho_c a} c_a = \frac{\partial \hat{\rho}\eta}{\partial (\rho e)} (\rho e) + \sum_{a=1}^{N} \frac{\partial \hat{\rho}\eta}{\partial \rho_a} \rho_a$$

$$= \frac{\partial \hat{\eta}}{\partial e} (\rho e + \rho \dot{e}) + \sum_{a=1}^{N} \frac{\partial \hat{\eta}}{\partial c_a} (\rho c_a + \rho \dot{c}_a), \quad (3.93)$$

which implies

$$\rho \left( \eta - \frac{1}{\rho} \frac{\partial \hat{\eta}}{\partial \left(\frac{1}{\rho}\right)} - \frac{\partial \hat{\eta}}{\partial e} - \sum_{a=1}^{N} \frac{\partial \hat{\eta}}{\partial c_a} c_a \right) = 0. \quad (3.94)$$
Since this holds for arbitrary \( \dot{\rho} \) and the terms in parenthesis are independent of \( \dot{\rho} \), the parenthesis must be equal to zero. Employing the above definitions of thermodynamic temperature and of the chemical potentials, and defining the thermodynamic pressure as

\[
\frac{p}{\dot{\theta}} = \frac{\partial \hat{\eta}}{\partial \left( \frac{1}{\rho} \right)},
\]

and multiplying by \( \dot{\theta} \), we obtain the Euler relation

\[
\theta \dot{\eta} = e + \frac{p}{\rho} - \sum_{a=1}^{N} \mu_{a} c_{a}.
\]

Differentiating this Euler relation and subtracting the differential of the fundamental relations \( \eta = \hat{\eta}(e, \frac{1}{\rho}, c_{a}) \) and/or \( \rho \eta = \hat{\rho} \eta(\rho, e, \rho_{a}) \), we obtain the Gibbs-Duhem relation

\[
\rho \eta \theta d \theta = dp - \sum_{a=1}^{N} \rho_{a} d \mu_{a}.
\]

### 3.4 Molar-based quantities

Let us also mention an important and practical variant of thermodynamic potentials and their independent variables, based on counting the number of molecules (or moles which are more practical unit in this case). Starting from the fundamental relation (3.27) but expressing now the masses \( M_{a} \) as

\[
M_{a} = n_{a} M_{a},
\]

understood in the sense \( \mathcal{M}_{a}(d\Omega) = n_{a}(d\Omega) M_{a} \),

where \( n_{a}(d\Omega) \) is the number of moles in \( d\Omega \), and \( M_{a} \) is the molar mass of \( a \)th constituent, one can define

\[
S = \tilde{S}(E, V, n_{a}) \overset{\text{def}}{=} \hat{S}(E, V, M_{a} n_{a})
\]

The function \( \tilde{S} \) inherits the positive 1-homogeneity of \( \hat{S} \), i.e.

\[
\tilde{S}(\lambda E, \lambda V, \lambda n_{a}) = \lambda \tilde{S}(E, V, n_{a}) \quad \forall \lambda > 0
\]

and one may now proceed analogously as in the mass-based case by exploiting this 1-homogeneity for two particular weights.

- **λ := \( \frac{1}{n} \)**, with the total molar number \( n \) defined by

\[
n \overset{\text{def}}{=} \sum_{a=1}^{N} n_{a}:
\]

\[
\tilde{S} \left( \frac{E}{n}, \frac{V}{n}, \frac{n_{a}}{n} \right) = \frac{1}{n} \tilde{S}(E, V, n_{a}).
\]

The arguments define molar-based quantities

- **Molar energy** \( e^{M} \)

\[
e^{M} \overset{\text{def}}{=} \frac{E(d\Omega)}{n(d\Omega)},
\]

- **Molar concentration** \( c^{M} \)

\[
c^{M} \overset{\text{def}}{=} \frac{n(d\Omega)}{V(d\Omega)},
\]

- **Molar fractions** \( y_{a}^{M} \)

\[
y_{a}^{M} \overset{\text{def}}{=} \frac{n_{a}(d\Omega)}{n(d\Omega)}, \quad a = 1, \ldots, N.
\]

- **Molar entropy** \( \eta^{M} \) by

\[
\eta^{M} \overset{\text{def}}{=} \frac{S(d\Omega)}{n(d\Omega)}.
\]
Then (3.101) reads

\[ \eta^m = \tilde{\eta}^m(e^m, \frac{1}{c^m}, y^m_1, \ldots, y^m_N) \]  

(3.106)

Going back to definition (3.99), we infer that

\[ \dot{\eta}(e, \frac{1}{\rho}, c_1, \ldots, c_N) = \frac{1}{\mathcal{M}} \dot{\mathcal{S}}(E, V, \mathcal{M}_a) = \frac{1}{\mathcal{M}} \dot{\mathcal{S}}(E, V, n_a) = \frac{n}{\mathcal{M}} \dot{\mathcal{S}} \left( E \left( \frac{V}{n}, \frac{n_a}{n} \right) \right) = \frac{n}{\mathcal{M}} \tilde{\eta}^m(e^m, \frac{1}{c^m}, y^m_n) = \frac{c^m}{\rho} \tilde{\eta}^m(e^m, \frac{1}{c^m}, y^m_n), \]

(3.107)

meaning that

\[ \rho \dot{\eta} = c^m \tilde{\eta}^m. \]

(3.108)

In the same spirit, from (3.102), we conclude

\[ \rho e = c^m e^m. \]

(3.109)

Since

\[ \rho_a = M_a n_a, \]

we obtain

\[ \rho = \sum_{a=1}^{N} \rho_a = \sum_{a=1}^{N} \frac{M_a n_a}{V} = \sum_{a=1}^{N} \frac{M_a c^m_a}{V}, \]

(3.110)

where we introduced molar concentrations \( c^m_a \)

\[ c^m_a \equiv c^m y^m_a \]

(3.111)

which implies the following relations between the corresponding derivatives:

\[ \frac{\partial \tilde{\eta}^m}{\partial e^m} = \frac{\partial \tilde{\eta}}{\partial e}, \quad \frac{\partial \tilde{\eta}^m}{\partial c^m} = \frac{\partial \tilde{\eta}}{\partial \rho}. \]

(3.113)

and finally

\[ \frac{\partial \tilde{\eta}^m}{\partial y^m_\gamma} = M_\gamma \tilde{\eta} + \sum_{\beta=1}^{N} M_{\beta} y^m_\beta \left( \frac{\partial \tilde{\eta}}{\partial e} e^m - e^m M_\gamma + \frac{\partial \tilde{\eta}}{\partial \rho} c^m e^m + \frac{\partial \tilde{\eta}}{\partial c^m} \frac{M_{\beta} y^m_\beta}{\sum_{\beta=1}^{N} M_{\beta} y^m_\beta} \right) + \sum_{\alpha=1}^{N} \frac{M_{\alpha} y^m_\alpha}{\sum_{\beta=1}^{N} M_{\beta} y^m_\beta} \left( \sum_{\beta=1}^{N} M_{\beta} \frac{\partial y^m_\alpha}{\partial c^m} \right) = M_\gamma \tilde{\eta} - \frac{M_\gamma}{\sum_{\beta=1}^{N} M_{\beta} y^m_\beta} \left( e^m + \frac{p}{\rho} - \sum_{\beta=1}^{N} \frac{M_{\beta} y^m_\beta}{\sum_{\beta=1}^{N} M_{\beta} y^m_\beta} \right) \frac{\partial \tilde{\eta}}{\partial e^m} - \frac{\mu_\gamma}{\theta} M_\gamma \]

(3.114)

where in the last equality, we employed the Euler relation (3.42). So defining the molar chemical potential \( \mu^m_a \) by

\[ \mu^m_a \equiv \mu_a M_a, \quad a = 1, \ldots, N, \]

(3.115)
we can summarize the obtained result as
\[
\frac{\partial \hat{\eta}^M}{\partial y_a^M} = \frac{\partial \hat{\eta}}{\partial c_a} M_a = -\frac{\mu_a}{\theta} M_a = -\frac{\mu_a^M}{\theta} \quad a = 1, \ldots, N .
\] (3.116)

With these identities and definitions, we can rewrite the Gibbs, Euler and Gibbs-Duhem relations in terms of molar quantities. In particular, from (3.43), one arrives at
\[
\theta d\eta^M = d e^M + p d \left( \frac{1}{c^M} \right) - \sum_{a=1}^N \mu_a^M d y_a^M \quad \text{Molar Gibbs’ relation.} \quad (3.117)
\]

From (3.42), using (3.108), (3.109), (3.110) and (3.115), one obtains the molar version of the Euler relation
\[
\theta \eta^M = e^M + \frac{p}{c^M} - \sum_{a=1}^N \frac{\mu_a^M}{c^M} y_a^M \quad \text{Molar Euler relation.} \quad (3.118)
\]

Taking a differential of this relation and substracting the molar Gibbs’ relation (3.117), yields the molar version of the Gibbs-Duhem relation
\[
\eta^M d \theta = \frac{1}{c^M} d p - \sum_{a=1}^N y_a^M d \mu_a^M .
\] (3.119)

For the definition of molar counterparts of other thermodynamic potentials and for derivation of relations among them, one proceeds analogously.

**Remark 2.** Similarly as the mass fractions \(c_a\), also the molar fraction \(y_a^M\) are by definition bound by the constraint
\[
\sum_{a=1}^N y_a^M = 1 .
\] (3.120)

In perfect analogy with the transition from \(\hat{\eta}\) to \(\tilde{\eta}\) made in remark 1, we can reduce \(\eta^M\) by eliminating one of the molar fractions using the constraint (3.120) and obtain reduced \(\tilde{\eta}^M\) as
\[
\tilde{\eta}^M \overset{\text{def}}{=} \eta^M \left( e^M, \frac{1}{c^M}, y_1^M, \ldots, y_{N-1}^M, 1 - \sum_{\beta=1}^{N-1} y_{\beta}^M \right) .
\] (3.121)

The consequences, in perfect analogy with the case discussed in remark 1 yields the following relations
\[
\frac{\partial \tilde{\eta}^M}{\partial e^M} = \frac{1}{\theta} , \quad \frac{\partial \tilde{\eta}^M}{\partial \left( \frac{1}{c^M} \right)} = \frac{p}{\theta} , \quad \frac{\partial \tilde{\eta}^M}{\partial y_a^M} = \frac{\mu_a^M - \mu_N^M}{\theta} = -\frac{\tilde{\mu}_a^M}{\theta} , \quad a = 1, \ldots, N - 1 ,
\] (3.122)

where we define
\[
\tilde{\mu}_a^M \overset{\text{def}}{=} \mu_a^M - \mu_N^M , \quad a = 1, \ldots, N - 1 .
\] (3.123)

The molar Gibbs relation can then be written as
\[
\theta d\eta^M = d e^M + p d \left( \frac{1}{c^M} \right) - \sum_{a=1}^{N-1} \tilde{\mu}_a^M d y_a^M .
\] (3.124)

• \(\lambda = \frac{1}{\nu}\)  

23
### 3.5 Constitutive theory of continuum thermodynamics

1. **Assumption of local thermodynamic equilibrium** - we assume that there exists a function \( \eta \) of state variables, one of which is internal energy \( e \), which is continuously differentiable and is increasing w.r.t. energy \( e \). This function is called *specific entropy*. I.e. we assume

\[
\eta = \hat{\eta}(e, y_1, \ldots), \quad \frac{\partial \hat{\eta}}{\partial e} > 0 .
\]  

(3.125a)

(3.125b)

This allows to invert (3.125a) and write

\[
e = \hat{\eta}(\eta, y_1, \ldots) .
\]  

(3.126)

We define thermodynamic temperature \( \vartheta \) by

\[
\vartheta = \frac{\partial \hat{e}}{\partial \eta}.
\]  

(3.127)

2. We assume that \( \dot{y}_i, i \in (1, 2, \ldots) \) is known (we have them from balance equations or from kinematics).

Let’s apply material time derivative to (3.126) and multiply by \( \rho \):

\[
\rho \dot{e} = \rho \dot{\eta} + \sum_i \rho \frac{\partial \hat{e}}{\partial y_i} \dot{y}_i ,
\]  

(3.128)

leading to

\[
\rho \dot{\eta} + \text{div} \, q_\eta = \frac{1}{\vartheta} \sum_b J_b \cdot \mathcal{A}_b ,
\]  

(3.129)

where the entropy flux \( q_\eta \) is in many cases related to energy flux \( q \) through \( q_\eta = \frac{q}{\vartheta} \). Second law of thermodynamics (in analogy with the classical equilibrium relation \( dS \geq \frac{dQ}{T} \)) implies

\[
\rho \dot{\eta} + \text{div} \, q_\eta = \xi \geq 0 ,
\]  

(3.130)

that is, the rate of entropy production \( \xi \) is non-negative. We can see that we can identify \( \xi \) with the right-hand side of (3.129). If we succeed in identifying the products \( J_a \cdot \mathcal{A}_a \) in such a way that they represent independent dissipative (=entropy producing mechanisms), we can, for example satisfy the second law by the following choice

3. Setting

\[
J_a = \gamma_a \mathcal{A}_a , \text{ where } \gamma_a \geq 0 \forall a ,
\]  

(3.131)

we obtain

\[
\sum_a J_a \cdot \mathcal{A}_a = \sum_a \gamma_a |\mathcal{A}_a|^2 = \sum_a \frac{1}{\gamma_a} |J_a|^2 \geq 0 ,
\]  

(3.132)

and the validity of the second law of thermodynamics is ensured.

*Note:* The above procedure has many weaknesses, it is rather formal, it may be difficult to identify the products \( J_a \cdot \mathcal{A}_a \), or ensure their independence, ... It serves merely as a possible guide/view at the constitutive theory. It must be supplemented with observations, measurements and further verifications in each particular situation.

**Examples of the above constitutive procedure**

1. **Compressible Navier-Stokes-Fourier (NSF) fluids**

\[
\eta = \hat{\eta}(e, \mathcal{B}) \rightarrow \hat{\eta}(e, \text{tr} (\mathcal{B}), \text{tr} (\mathcal{B}^2), \det (\mathcal{B})) \rightarrow \hat{\eta}(e, \rho) \leftrightarrow e = \hat{e}(\eta, \rho)
\]  

(3.133)

We define

\[
\vartheta = \frac{\partial \hat{\delta}}{\partial \eta} \text{ thermodynamic temperature}, \quad p = \rho^2 \frac{\partial \hat{\delta}}{\partial \rho} \text{ thermodynamic pressure}.
\]  

(3.134)
By the procedure outlined above, we obtain

\[ \rho \dot{e} = \rho \dot{\theta} \ddot{\eta} + \frac{1}{\rho} \rho \dot{\rho} , \]  

(3.135)

and employing the mass balance (3.21) and energy balance (3.26), we arrive at

\[ \rho \dot{\theta} \ddot{\eta} = T : D - \text{div} \mathbf{q} + \rho r + \rho \text{div} \mathbf{v} \]  

(3.136)

We denote the deviatoric (traceless) part of any tensor by \((\cdot)\), i.e. \(A^d = A - \frac{1}{3} \text{tr}(A)I\), and note that

\[ T : D = (T^d + \frac{1}{3} \text{tr} \mathbf{D}) : (D^d + \frac{1}{3} \text{tr} \mathbf{D} I) = T^d : D^d + \frac{1}{3} \text{tr} \mathbf{D} \text{div} \mathbf{v} \]  

(3.137)

The quantity \(m = \frac{1}{3} \text{tr} \mathbf{T}\) is so-called mean normal stress. We have thus arrived at

\[ \rho \dot{\theta} \ddot{\eta} = (p + m) \text{div} \mathbf{v} - \text{div} \mathbf{q} + \rho r . \]  

(3.138)

Dividing by temperature \(\theta\) and rearranging, we obtain

\[ \rho \dot{\eta} + \text{div} \left( \frac{\mathbf{q}}{\theta} \right) - \frac{\rho r}{\theta} = \frac{1}{\theta} \left[ T^d : D^d + (m + p) \text{div} \mathbf{v} - \mathbf{q} \cdot \nabla \theta \right] \]  

(3.139)

Let us set the energy sources equal to zero, i.e. set \(r \equiv 0\). We can see that we have the right-hand side in the desired form of products related to independent processes, which suggests to set

\[ T^d = 2vD^d , \quad v \geq 0 , \]  

(3.140a)

\[ (m + p) = \frac{2v + 3\lambda}{3} \text{div} \mathbf{v} , \quad 2v + 3\lambda \geq 0 , \]  

(3.140b)

\[ \mathbf{q} = -k \nabla \theta , \quad k \geq 0 . \]  

(3.140c)

Putting all together (and setting \(\kappa \equiv \frac{k}{\theta} \geq 0\)), we obtain

\[ T = mI + T^d = -p I + \lambda \text{div} \mathbf{v} I + 2vD \quad \text{Compressible NS fluid,} \]  

(3.141a)

\[ \mathbf{q} = -k \nabla \theta \quad \text{Fourier law.} \]  

(3.141b)

2. **Incompressible NSF fluids**

We add a constraint \(\text{div} \mathbf{v} = 0\), i.e. we consider a material, which in all processes moves isochorically. The derivation is analogous to the compressible case, except the dependence of thermodynamic potential on density, which is now suppressed due to the incompressibility assumption, since from the mass balance (3.21), we have \(\dot{\rho} = 0\), and thus, provided at initial time, \(\rho\) is constant, it remains so during the whole process. Analogously as before, we obtain

\[ \rho \dot{\eta} + \text{div} \left( \frac{\mathbf{q}}{\theta} \right) = \frac{1}{\theta} \left[ T^d : D^d - \mathbf{q} \cdot \nabla \theta \right] + \frac{\rho r}{\theta} \]  

(3.142)

Note that the mean normal stress \(m\) has vanished from the entropy identity, i.e. now we cannot constrain it thermodynamically as before. Constraining ourselves again to simple piece-wise relationships between the entropy producing fluxes and affinities, we obtain

\[ T = mI + 2vD \quad \text{Incompressible NS fluid,} \]  

(3.143)

\[ \mathbf{q} = -k \nabla \theta \quad \text{Fourier law.} \]  

(3.144)

3. **Elastic solid**

Let us consider

\[ \eta = \dot{\eta}(e, \mathcal{B}) \rightarrow e = \dot{e}(\eta, \mathcal{B}) \rightarrow e = \dot{e}(\eta, \text{tr} \mathcal{B}, \text{tr} \mathcal{B}^2, \det \mathcal{B}) , \]  

(3.145)
as a consequence of the principle of material frame indifference. Let us take, for simplicity, only
\[ e = \dot{\varepsilon}(\eta, \rho, \text{tr}\mathcal{B}) , \] (3.146)
and let’s compute
\[ \rho \dot{\varepsilon} = \rho \partial \eta + \frac{1}{\rho} \rho \dot{\rho} + \rho \frac{\partial \dot{\varepsilon}}{\partial \text{tr}\mathcal{B}} \varepsilon = \mu . \] (3.147)

Exercise 7. \( \text{tr}\mathcal{B} = 2 \mathcal{B} : \mathcal{D} \)
Exercise 8. We obtain (verify):
\[ \rho \dot{\eta} + \text{div}\left(\frac{\mathbf{q} \cdot \nabla}{\theta}\right) = \frac{1}{\theta} \left[ (\mathbb{T}^d - 2\mu \mathcal{B}^d) : \mathcal{D}^d + (m + p - \frac{2\mu}{3} \rho \text{tr}\mathcal{B}) \text{div} \mathbf{v} - \mathbf{q} \cdot \nabla \frac{\theta}{\theta} \right] . \] (3.148)

Asserting for a perfectly elastic material that the entropy production is identically zero, we get
\[ \mathbb{T}^d = 2\mu \rho \mathcal{B}^d , \] (3.149)
\[ m = -p + \frac{2\mu}{3} \rho \text{tr}\mathcal{B} , \] (3.150)
\[ \mathbf{q} = 0 , \] (3.151)
i.e.
\[ \mathbb{T} = -p \mathbf{I} + 2\mu \rho \mathcal{B} \quad \text{Neo-Hookean solid} . \] (3.152)

4. Kelvin-Voigt solid \text{FIXME} (add mixture)
\[ \mathcal{D}^d = \frac{1}{2\nu} (\mathbb{T}^d - 2\mu \mathcal{B}^d) \] (3.153)
\[ \text{div} \mathbf{v} = \frac{3}{2\nu + 3\lambda} \left[ m + p + \frac{2\mu}{3} \rho \text{tr}\mathcal{B} \right] \] (3.154)
which implies
\[ \mathbb{T} = -p \mathbf{I} + \lambda \text{div} \mathbf{v} \mathbf{I} + 2\mu \rho \mathcal{B} + 2\nu \mathcal{D} \] (3.155)

Exercise 9. Go through derivation of 3 and 4 for an incompressible material.

5. Burger’s model \text{FIXME}

\textbf{Note:} So far, we were dealing with linear constitutive relations, this assumption can be further relaxed, we will see some examples later.

4 Kinematical description of mixtures

\textbf{Assumption of coexistence (co-occupancy)} In each material point of a mixture with \( N \) components, all the components are present at the same time, see Fig. \[ \text{coexistence} \]

This assumption is a generalization of the continuum hypothesis from the traditional single-component continuum mechanics. It can be justified by the same means - assuming we can distinguish between the components and describe them independently, the averaging procedure over some sufficiently small representative volume allows to assign to each point in a physical space some averaged values of all the field quantities related to the particular component of the mixture.

Realize that instead of a single reference configuration, as in the traditional continuum mechanics, now we have in principle \( N \) independent reference configurations between which we need to distinguish \text{co-occupancy}. Let us assume for simplicity, that all \( N \) reference frames coincide and all the \( N \) spatial frames coincide. We will assume that the two (reference and actual) may differ, and we will distinguish between them (in the component description) by assigning capital letters to the referential and by small letters to the actual description. The particular components of the the mixture will be distinguished by Greek indices.

\[ \text{This has severe implications on the role between the Lagrangian - referential and Eulearian - actual description. The difference is now much bigger than for single component materials in favor of the Eulerian approach.} \]
Figure 3: The assumption of coexistence and generalization of the classical continuum concept of motion. For mixtures with $N$ components, $N$ mappings $\chi_\alpha$, $\alpha = 1, \ldots, N$ are assumed to exist, each being a mapping from a reference configuration of the particular component to the current configuration. One could call the mapping $\chi_\alpha$ the motion of the $\alpha$th component. Each point in the current configuration is thus assumed to be an image of $N$ preimages (material points of the individual mixture components).

Remark 3. Let us note that the mixture concept of co-occupancy can be also extended to a somewhat extreme case, when some of the substances are considered to be locally infinitely diluted. If we considered, for example a liquid and its vapor as the two components of a binary mixture, then we can use the framework of the mixture theory for the description of the motion, development and interaction of macroscopic bubbles of the vapor in the liquid, thinking of the two phases as these end-member cases of the mixture - liquid being the mixture in which the vapor phase is infinitely diluted, and vice-versa, the vapor as the mixture phase, where the liquid is infinitely diluted. This extension of the view makes the mixture concept a very versatile tool for attacking many physical problems.

Motion of $\alpha$th component is traditionally defined as a mapping

$$\chi_\alpha : \mathbb{R}^3 \times \mathbb{R} \rightarrow \mathbb{R}^3,$$

i.e., $x_\alpha = \chi_\alpha(X_\alpha, t)$, $x_\alpha^h = \chi_\alpha^h(X_\alpha^h, t)$, (4.1)

which is assumed to be sufficiently smooth and invertible. In the actual configuration it is natural to look at one particular point in the space-time $(x, t)$, where $x = x_\alpha$, $\alpha = 1, \ldots, N$. To this point there are $N$ corresponding referential points determined by the inverse mappings

$$X_\alpha(x, t) = \chi_\alpha^{-1}(x, t) \quad \alpha = 1, \ldots, N.$$ (4.2)

The assumption of co-occupancy can be then expressed as follows. For any point $x \in \Omega(t) = \text{(current state of mixture)}$, and time $t > 0$, there are material points $X_\alpha$, $\alpha = 1, \ldots, N$, such that $x = \chi_\alpha(X_\alpha, t)$.

With the notion of motion of the $\alpha$th component, we can now introduce the following referential (Lagrangian) and spatial (Eulerian) kinematic quantities:

- **Gradient**

$$\text{Grad}_\alpha \Phi(X_\alpha, t) = \frac{\partial \Phi(X_\alpha, t)}{\partial X_\alpha} \quad \text{referential},$$

$$\text{grad} \phi(x, t) = \frac{\partial \phi}{\partial x} \quad \text{spatial}.$$ (4.3) (4.4)

- **Velocity** of the $\alpha$th component

$$V_\alpha(X_\alpha, t) = \frac{\partial X_\alpha}{\partial t} \bigg|_{X_\alpha} \quad \text{in referential description},$$

$$v_\alpha(x, t) = V_\alpha(\chi_\alpha^{-1}(x, t), t) \quad \text{in spatial description}.$$ (4.5) (4.6)
• **Material time derivative** with respect to the $a$th component

\[
\frac{D_a \Phi(X_a, t)}{Dt} = \left. \frac{\partial \Phi(X_a, t)}{\partial t} \right|_{X_a},
\]

\[
D_a \frac{\phi(x, t)}{Dt} = \left. \frac{\partial \phi(x_a(X_a, t), t)}{\partial t} \right|_{X_a} = \left. \frac{\partial \phi(x, t)}{\partial t} \right|_{x} + v_a(x) \cdot \text{grad}_x \phi(x, t).
\]

• **Deformation gradient** of the $a$th component

\[
F_a(X_a, t) = \frac{\partial X_a(X_a, t)}{\partial X_a}, \quad (F_a)^{ik}_{(a)}(X_a, t) = \frac{\partial X_a^i_k}{\partial X_a^j}
\]

• **right Cauchy-Green stretch tensor** of the $a$th component

\[
C_a(X_a, t) = F_a^T F_a, \quad (C_a)_{IJ} = (F_a)^{ij}_{(a)} (F_a)^{jk}_{(a)} \delta_{IJ}
\]

• **Cauchy deformation tensor** of the $a$th component

\[
c_a(x, t) = F^{-T} F_a^{-1}, \quad (c_a)_{ij} = (F^{-1})^{ij}_{k}(F_a)^{kj}_{(a)} \delta_{IJ}
\]

• **left Cauchy-Green stretch tensor** of the $a$th component

\[
B_a(X_a, t) = F_a^T, \quad (B_a)^{ij}_{(a)} = (F_a)^{ij}_{(a)} \delta^{IJ}
\]

• **Piola deformation tensor** of the $a$th component

\[
b_a(x, t) = F^{-1} F_a^{-T}, \quad (b_a)^{IJ}_{(a)} = (F_a)^{ij}_{(a)} (F^{-1})^{k}_{(a)} \delta^{ij}
\]

• **Velocity gradient** of the $a$th component

\[
L_a(x, t) = \text{grad} v_a, \quad (L_a)^i_j = \frac{\partial v_a^i}{\partial x^j}
\]

Due to the fact that for each material point in the actual configuration there correspond $N$ referential points as preimages of this point in the $N$ reference configurations of individual components, the calculations of even simple kinematic quantities in referential description can become very cumbersome, see also Exercise 10. From this point of view, we find the Eulerian description preferable, and we will formulate all the theory in the actual (Eulerian) configuration. Also, in the following we will consider both the coordinate frame to be Cartesian and we will thus stop distinguishing between the covariant and contravariant components of tensors for simplicity.

**Remark 4.** The fact that we distinguish $N$ different reference configurations has an important impact on the notion of material symmetry. Recall this notion from the basic course on continuum mechanics.

**Exercise 10.** Difficulties with Lagrange description. Since the concept of an $N$-component mixture requires in principle the notion of $N$ different motion mappings and $N$ associated reference configurations, one may expect that Lagrange (referential description) may be more cumbersome than in the case of a single-component material. This is indeed so, let’s demonstrate it on a very simple example. It is natural, for component $a$ of the mixture, to consider some associated field quantity, say $\Psi_a$, which in the simplest case, depends only on $X_a$ and $t$, i.e., we have $\Psi_a = \Psi_a(X_a, t)$. While it is natural to consider $\frac{D \Psi_a}{Dt}$, i.e., material time derivative of $\Psi_a$ following the motion of $a$ material point, one may easily be forced to evaluate also terms of the type $\frac{D \Psi_a}{Dt}$ for $\gamma \neq a$. Switching for a moment to the Eulerian coordinates by considering $\psi_a(x, t) = \Psi_a(X_a, t)$ (with $x = \chi_a(X_a, t)$, it is straightforward to show (try it) that

\[
\frac{D \psi_a}{Dt} = \frac{D \Psi_a}{Dt} = \frac{D \Psi_a}{Dt} = \frac{\partial \psi_a}{\partial t} \left|_x \right. + v_a \cdot \text{grad} \psi_a = \frac{\partial \psi_a}{\partial t} \left|_x \right. + v_a \cdot \text{grad} \psi_a + (v_\gamma - v_a) \cdot \text{grad} \psi_a = \frac{D \psi_a}{Dt} + (v_\gamma - v_a) \cdot \text{grad} \psi_a.
\]

Now try to prove the same statement, i.e. $\frac{D \psi_a}{Dt} \neq \frac{D \Psi_a}{Dt}$ directly from the Lagrangian definition of the material time derivative.

**HINT:** Start by considering $\Psi_a(X_a, t) = \Psi_a(\chi_a^{-1}(x), t) = \Psi_a(\chi_a^{-1}(\chi_a(x), t), t)$. 

28
5 Balance equations

5.1 Auxiliary definitions - mass, volume other measures

We start by defining several useful measures. Consider a mixture body $\Omega$ and let $\mathcal{P} \subset \Omega$ open subset, then we define

- $\mathcal{M}(\mathcal{P})$ . . . mass of the mixture as a whole contained in $\mathcal{P}$,
- $\mathcal{M}_a(\mathcal{P})$ . . . mass of the $a$ component of the mixture contained in $\mathcal{P}$,
- $\mathcal{V}(\mathcal{P})$ . . . volume of the mixture as a whole contained in $\mathcal{P}$,
- $\mathcal{V}_a(\mathcal{P})$ . . . volume of the $a$ component of the mixture contained in $\mathcal{P}$.

Remark 5. The notion of the partial volume $\mathcal{V}_a$ may be a bit puzzling in view of the co-occupancy notion. And indeed, it will become more clear in Chapter 8 when talking about the multiphase theory. It is useful nevertheless to define all these measures in one place. The concept of $\mathcal{V}_a$ should be understood in the following sense. If we exclude solutions, where the mixing among the components happens really at microscopic (molecular) level, and consider a material with internal structure, i.e. material, where after sufficient zooming, we can distinguish the particular components, then the partial volume denotes the volume occupied by individual component.

We postulate the following (and natural) relations of absolute continuity ($\ll$) between the defined measures

1. $\mathcal{M}(\mathcal{P}) \ll \mathcal{V}(\mathcal{P})$. The Radon-Nikodym theorem implies the existence of density $\rho$, such that

$$\mathcal{M}(\mathcal{P}) = \int_{\mathcal{P}} \rho \, dV. \quad (5.1)$$

2. $\mathcal{M}_a(\mathcal{P}) \ll \mathcal{V}(\mathcal{P})$. By the same argument we arrive at partial density $\rho_a$, such that

$$\mathcal{M}_a(\mathcal{P}) = \int_{\mathcal{P}} \rho_a \, dV. \quad (5.2)$$

3. $\mathcal{V}_a(\mathcal{P}) \ll \mathcal{V}(\mathcal{P})$, implying the existence of a volume fraction $\phi_a$ such that

$$\mathcal{V}_a(\mathcal{P}) = \int_{\mathcal{P}} \phi_a \, dV. \quad (5.3)$$

4. $\mathcal{M}_a(\mathcal{P}) \ll \mathcal{M}(\mathcal{P})$, which allows to define the concentration (mass fraction) $c_a$, such that

$$\mathcal{M}_a(\mathcal{P}) = \int_{\mathcal{P}} c_a \, d\mathcal{M} \int_{\mathcal{P}} \rho c_a \, dV. \quad (5.4)$$

5. $\mathcal{M}_a(\mathcal{P}) \ll \mathcal{V}_a(\mathcal{P})$, and thus there exists material (true) partial density $\rho^m_a$ such that

$$\mathcal{M}_a(\mathcal{P}) = \int_{\mathcal{P}} \rho^m_a \, d\mathcal{V}_a \int_{\mathcal{P}} \rho^m_a \phi_a \, dV. \quad (5.5)$$

By comparing (5.2) with (5.4), we obtain

$$c_a = \frac{\rho_a}{\rho}. \quad (5.6)$$

while (5.2) and (5.5) imply

$$\rho_a = \phi_a \rho^m_a. \quad (5.7)$$

Employing the following natural assumption called mass additivity constraint, which simply states that all components of the mixture have been taken into account, i.e.,

$$\sum_{a=1}^{N} \mathcal{M}_a(\mathcal{P}) = \mathcal{M}(\mathcal{P}) \quad (5.8)$$
we obtain
\[
\sum_{a=1}^{N} \rho_a = \rho .
\] (5.9)
This together with (5.6), also implies that
\[
\sum_{a=1}^{N} c_a = 1 .
\] (5.10)

We will sometimes employ also the \textbf{volume additivity constraint}
\[
\sum_{a=1}^{N} \varrho_a(\mathcal{P}) = \varrho(\mathcal{P}) ,
\] (5.11)
from which we obtain (taking into account also (5.3)) that
\[
\sum_{a} \varphi_a = 1 .
\] (5.12)

\textit{Remark 6.} While the \textit{mass additivity constraint} is in fact a natural universal requirement, expressing basically the conservation of mass, the \textit{volume additivity constraint} represents a much stronger assumption which does not hold universally. We know from observation - e.g. by putting salt into water, that volume of the salted water changes only very slightly - in the solution the ions have just occupied voids between the molecules of water and the total volume of the solution has not changed. Examples of cases, where the volume additivity constraint applies are typically materials without interstitial voids.

\subsection*{5.2 General form of a balance law in the bulk (in Eulerian description)}

General form of a balance law for a field quantity \( \psi_a(\mathbf{x},t) \) (some scalar or vectorial of the \( \alpha \) component), assuming that no singular surfaces are present in the bulk, will be postulated in the following integral form
\[
\frac{d}{dt} \int_{\Omega_a(t)} \psi_a \, d\Omega = \int_{\partial \Omega_a(t)} \psi_a \Phi \cdot \mathbf{n} \, dS + \int_{\Omega_a(t)} \psi_a \xi \, d\Omega + \int_{\Omega_a(t)} \psi_a \Sigma \, d\Omega + \int_{\Omega_a(t)} \psi_a \Pi \, d\Omega ,
\] (5.13)
where \( \Omega_a(t) = \chi_a(\Omega_a^0, t) \), and where \( \psi_a \Phi \) is the density of flux of \( \psi_a \) across the boundary \( \partial \Omega_a \) (with outer unit normal \( \mathbf{n} \)), \( \psi_a \xi \) denotes the density of production of \( \psi_a \) inside \( \Omega_a \), \( \psi_a \Sigma \) is the corresponding density of supply (from outside the system) of \( \psi_a \) by interaction with the remaining components of the mixture inside \( \Omega_a \). This integral relation is assumed to hold for any material volume \( \Omega_a(t) \). Note that compared to the analogous statement in single-continuum mechanics, here we have to distinguish the control material volumes corresponding to the individual components since they evolve independently. In the above statement the appropriate material volume is then the one following the motion of the \( \alpha \) component.

The above integral balance law is localized in the standard way, using the Reynolds’ transport theorem and Gauss’ theorem. Assuming for now that the material does not contain any discontinuities, the corresponding local form reads
\[
\frac{\partial \psi_a}{\partial t} + \text{div}(\psi_a \otimes \mathbf{v}_a) - \text{div} \psi_a \Phi - \psi_a \xi - \psi_a \Sigma - \psi_a \Pi = 0 .
\] (5.14)

or, equivalently,
\[
D_a \frac{\psi_a}{Dt} + \psi_a \text{div} \mathbf{v}_a - \text{div} \psi_a \Phi - \psi_a \xi - \psi_a \Sigma - \psi_a \Pi = 0 .
\] (5.15)

A more general case, when material or immaterial discontinuities are present will be discussed later. This way we have formulated a general balance law for a quantity \( \psi_a \). By postulating that the nature of the terms \( \psi_a \Pi \) is truly interactional, we assert that in total, when summed over all components of the mixture these terms add up to zero:
\[
\sum_{a=1}^{N} \psi_a \Pi = 0 ,
\] (5.16)
which leads, by summing (5.14) to the following local form of the balance of quantity $\psi$ over the whole mixture:

$$
\frac{\partial}{\partial t} \sum_{a=1}^{N} \psi_a + \text{div} \left( \sum_{a=1}^{N} \psi_a \otimes \mathbf{v}_a \right) - \text{div} \left( \sum_{a=1}^{N} \psi_a \Phi \right) - \sum_{a=1}^{N} \psi_a \xi - \sum_{a=1}^{N} \psi_a \Sigma = 0 ,
$$

(5.17)

or, equivalently

$$
\sum_{a=1}^{N} \frac{D_a \psi_a}{Dt} + \sum_{a=1}^{N} \psi_a \text{div} \mathbf{v}_a - \text{div} \left( \sum_{a=1}^{N} \psi_a \Phi \right) - \sum_{a=1}^{N} \psi_a \xi - \sum_{a=1}^{N} \psi_a \Sigma = 0.
$$

(5.18)

With this general form of the balance laws for the particular components of the mixture and for the mixture as a whole, we can now proceed to the particular physical balance laws, by merely identifying (or postulating) the corresponding field quantities, their fluxes, productions, supplies and interaction terms.

### 5.3 Balance of mass

Setting $\psi_a = \rho_a$, since the volume in the integral balance law is assumed to be $(\alpha)$-material, there is no flux, i.e. $\rho_a \Phi = 0$, neither is there supply, i.e. $\rho_a \Sigma = 0$, or production $\rho_a \xi = 0$, but due to chemical reactions, or phase transitions, there may be a non-zero transfer of mass of $\alpha$ through conversion process from other components of the mixture. We denote this conversion term as $m_a = \rho_a \Pi$, and the local mass balance for $\alpha$ component of the mixture thus reads

$$
\frac{\partial \rho_a}{\partial t} + \text{div}(\rho_a \mathbf{v}_a) = m_a ,
$$

(5.19)

or equivalently

$$
\frac{D_a \rho_a}{Dt} + \rho_a \text{div} \mathbf{v}_a = m_a ,
$$

(5.20)

The interaction terms - mass exchanges due to chemical reaction (or phase changes) must sum up to zero, when summed over all components of the mixture, so that mass is neither produced, nor destroyed in these reactions, i.e. it must hold

$$
\sum_{a=1}^{N} m_a = 0 .
$$

(5.21)

Consequently, the mass balance for the mixture as a whole, obtained by summing (5.19) over all components, reads

$$
\frac{\partial}{\partial t} \left( \sum_{a=1}^{N} \rho_a \right) + \text{div} \left( \sum_{a=1}^{N} \rho_a \mathbf{v}_a \right) = 0 ,
$$

(5.22)

or, equivalently

$$
\sum_{a=1}^{N} \frac{D_a \rho_a}{Dt} + \sum_{a=1}^{N} \rho_a \text{div} \mathbf{v}_a = 0 .
$$

(5.23)

For all balances for the mixture as a whole, one may attempt to reformulate them in the form of a corresponding single-component body under suitable definition of the whole-mixture properties from the component properties. It is particularly easy in the case of the balance of mass. By (5.9), we already have the natural definition of the total mixture density $\rho$. If we define the mixture velocity as a barycentric velocity through

$$
\mathbf{v} = \frac{1}{\rho} \sum_{a=1}^{N} \rho_a \mathbf{v}_a ,
$$

(5.24)

from (5.22), we arrive at the familiar single-component form of the mass balance for the mixture as a whole

$$
\frac{\partial \rho}{\partial t} + \text{div}(\rho \mathbf{v}) = 0 ,
$$

(5.25)
or, if we define the \textit{barycentric time derivative} as
\[
\frac{D}{Dt} = \frac{\partial}{\partial t} + \mathbf{v} \cdot \text{grad} \mathbf{,}
\] (5.26)

we can write equivalently
\[
\frac{D \rho}{Dt} + \rho \text{div} \mathbf{v} = 0 .
\] (5.27)

\textbf{Remark 7}. Note that according to the previous observation, if we take the single-component form of the balance law as a certain selective rule, the barycentric velocity becomes the privileged definition of the mixture velocity. Also note that alternative formulation might be possible, and is indeed useful in applications, when the weighting functions are not mass fractions, but rather volume fractions, for example.

\textbf{Exercise 11}. Consider an N-component mixture of incompressible fluids, meaning that \( \rho_a = \text{const} \forall a \). Define the mixture velocity alternatively as \( \mathbf{v}^{\phi} = \sum_{\alpha=1}^{N} \phi_\alpha \mathbf{v}_\alpha \), where \( \phi_\alpha = \frac{\rho_\alpha}{\rho_m} \) is the volume fraction of \( \alpha \) component of the mixture. Derive from the local balance law (5.19) the global balance law for the mixture as a whole in terms of this new velocity and show under which conditions is the resultant motion isochoric (=divergence-free).

\subsection*{5.4 Balance of linear momentum}

Setting \( \psi_a = \rho_a \mathbf{v}_a \), since the volume in the integral balance law is assumed to be \( ('(a)\)'-material, there is only momentum flux by action of surface forces represented by the (partial) Cauchy stress tensor \( \mathbb{T}_a \), i.e. \( \rho_a \mathbf{v}_a \phi = \mathbb{T}_a \). The linear momentum supply is realized through long-range body forces (gravity, elmag.) \( \rho_a \mathbf{v}_a \Sigma = \rho_a \mathbf{b}_a \).

We postulate that there is no production of linear momentum \( \rho_a \mathbf{v}_a \xi = 0 \). There is however, a possibility of linear momentum transfer between the components of the mixture by interaction, with a contribution arising from the mass transfer (when there is a mass transfer between two components of the mixture, which are moving, it is necessarily accompanied by a corresponding linear momentum transfer) and another contribution arising from mechanical contact between the constituents represented by interaction forces \( \mathbf{I}_a \).

We thus postulate
\[
\rho_a \mathbf{v}_a \Pi = \mathbf{v}_a m_a + \mathbf{I}_a \quad \alpha = 1, \ldots, N .
\] (5.28)

The local (Eulerian) form of the linear momentum balance for \( \alpha \) component of the mixture thus reads
\[
\frac{\partial (\rho_a \mathbf{v}_a)}{\partial t} + \text{div}(\rho_a \mathbf{v}_a \otimes \mathbf{v}_a) = \text{div} \mathbb{T}_a + \rho_a \mathbf{b}_a + m_a \mathbf{v}_a + \mathbf{I}_a .
\] (5.29)

We can rewrite the left-hand side as
\[
\left( \frac{\partial \rho_a}{\partial t} + \text{div}(\rho_a \mathbf{v}_a) \right) \mathbf{v}_a + \rho_a \frac{D_a \mathbf{v}_a}{Dt} = \rho_a \mathbf{v}_a \mathbf{,}
\]
where the mass balance (5.19) was applied. Thus, we can rewrite the linear momentum balance as follows
\[
\rho_a \frac{D_a \mathbf{v}_a}{Dt} = \text{div} \mathbb{T}_a + \rho_a \mathbf{b}_a + \mathbf{I}_a \quad \alpha = 1, \ldots, N .
\] (5.30)

The corresponding balance of linear momentum is obtained again by summing (5.29) over all components and using the conservation assumption on the interaction terms (5.16), which in our case reads
\[
\sum_{a=1}^{N} (m_a \mathbf{v}_a + \mathbf{I}_a) = 0 ,
\] (5.31)
and, correspondingly, the linear momentum balance for the mixture as a whole reads
\[
\sum_{a=1}^{N} \left( \frac{\partial (\rho_a \mathbf{v}_a)}{\partial t} + \text{div}(\rho_a \mathbf{v}_a \otimes \mathbf{v}_a) \right) = \text{div} \left( \sum_{a=1}^{N} \mathbb{T}_a \right) + \sum_{a=1}^{N} \rho_a \mathbf{b}_a \quad \alpha = 1, \ldots, N .
\] (5.32)
As in the case of the mass balance, we may be interested in whether a corresponding single-component equivalent of the linear momentum balance for the mixture as a whole can be identified. For this purpose, let us express the velocity as
\[ v_\alpha = v + (v_\alpha - v) = v + u_\alpha, \quad \alpha = 1, \ldots, N. \] (5.33)

The term
\[ u_\alpha \overset{\text{def}}{=} v_\alpha - v, \] (5.34)
is called diffusive velocity of the \( \alpha \) component (with respect to the mixture barycentric velocity \( v \)). Using this splitting, the definitions of the barycentric velocity (5.24) and mixture density (5.9), and the fact that \( \sum_{\alpha=1}^{N} \rho_\alpha u_\alpha = 0 \), we can rewrite the left-hand-side of (5.32) as follows
\[ \sum_{\alpha=1}^{N} \left( \frac{\partial (\rho_\alpha v_\alpha)}{\partial t} + \text{div}(\rho_\alpha v_\alpha \otimes v_\alpha) \right) = \sum_{\alpha=1}^{N} \left( \frac{\partial (\rho v)}{\partial t} + \text{div}(\rho v \otimes v) + \text{div}\left( \sum_{\alpha=1}^{N} \rho_\alpha u_\alpha \otimes u_\alpha \right) \right). \]

The first two terms are in the desired form already, we put the the third term on the right-hand side and rewrite (5.32) as
\[ \sum_{\alpha=1}^{N} \left( \frac{\partial (\rho v)}{\partial t} + \text{div}(\rho v \otimes v) \right) = \text{div}\left( \sum_{\alpha=1}^{N} (T_\alpha - \rho_\alpha u_\alpha \otimes u_\alpha) \right) + \sum_{\alpha=1}^{N} \rho_\alpha b_\alpha. \] (5.35)

We thus see, that a natural definition of the mixture stress tensor, is not just the sum of partial stress tensors, but contains also a contribution due to diffusion. This is a typical feature of mixture theory when velocities of the constituents are distinguished. Defining the mixture stress tensor as
\[ \mathbb{T} = \sum_{\alpha=1}^{N} (T_\alpha - \rho_\alpha u_\alpha \otimes u_\alpha), \] (5.36)
and the mixture body force as
\[ \rho b = \sum_{\alpha=1}^{N} \rho_\alpha b_\alpha, \] (5.37)
equation (5.35) takes the form of a traditional single-component linear momentum balance
\[ \frac{\partial (\rho v)}{\partial t} + \text{div}(\rho v \otimes v) = \text{div}\mathbb{T} + \rho b, \] (5.38)
or, with the use of the mixture mass balance (5.27)
\[ \rho \frac{Dv}{Dt} = \text{div}\mathbb{T} + \rho b, \] (5.39)

Exercise 12. Derive the balances of mass and linear momentum for \( \alpha \) component of the mixture in terms of \( \phi_\alpha \) (using the relation: \( \rho_\alpha = \phi_\alpha \rho_m^\alpha \)). Define now the mixture velocity as \( v^\# := \sum_{\alpha=1}^{N} \phi_\alpha v_\alpha \) and derive the balance of linear momentum for the mixture as a whole in terms of this (volume-averaged) velocity.

Remark 8. How should one understand the concept of a partial stress? Can it be obtained intuitively at least in some simple situation? Let us consider a two-component material composed of a porous matrix with connected pores filled with a fluid as in Fig. [4].

Let us consider an equilibrium rest state, in which case the Cauchy stress in the fluid is the isotropic pressure \( T_f^m = -p_f^m \). The superscript “m” refers to the “material” or true value, we used this notation talking about material density, meaning that is the stress state (pressure) that we would measure with a sufficiently small barometer inside an individual pore. What is the corresponding “upscaled” partial fluid stress tensor? Consider a surface element \( dS \) with a normal \( n \) cross-cutting the porous structure. The meaning of the partial fluid Cauchy stress is that \( T_f n dS \) should give the force exerted on the surface \( dS \) by the fluid component. Clearly this is
\[ T_f n dS = T_f^m n dS_f = -p_f^m dS_f, \]
where $dS_f$ is the fraction of the surface $dS$ exposed to the fluid. If we knew everything about the geometric structure of the porous matrix, we could identify a function $\varphi$ depending on the position and on the orientation of the surface that would provide the relation

$$dS_f(x, n) = \varphi_f(x, n) dS .$$

In practice, this information is never available and one has at best information about partial volume, (or porosity) of the particular phase, which we denoted $\phi_\alpha$. For special periodic structures, one can relate the volume fraction and the surface fraction $\phi_\alpha$ and $\varphi_\alpha$, in particular, if we consider parallel tubular pores in our situation, it would hold

$$\varphi_f = \phi_f ,$$

i.e. the two are equal and the surface fraction does not depend on the orientation of the surface. Consequently, one gets

$$T_f = -p_f^m \phi_f I ,$$

i.e. the corresponding “partial pressure” is the true pressure in the fluid times the volume fraction of the fluid component. Relationship of this type involving volume fraction (but sometimes also mass fraction) as the weighting factor between the actual material stress state and the mixture partial stress state are often used in more general situations and for more general geometries, with a tacit understanding that such relationships are approximate.

### 5.5 Balance of angular momentum

We will consider a slightly extended setting with respect to the typical assumptions used in continuum mechanics. There, one typically deals with the so called non-polar materials, in which case the balance of angular momentum merely reduces to the assumption of symmetry of the Cauchy stress tensor. For materials with internal structure, which is often the case for mixtures, one may be forced to adopt a more general view. For example, for a mixture composed of microscopic dispersed spheres of solid in some liquid, apart from translation of the spheres, one must also consider their rotations. This, in the averaged continuum view, gives rise to the notion of intrinsic angular momentum, the so called spin (which is a purely mechanical property in the sense explained above, not to be confused with the quantum mechanical property of microparticles). Materials which possess intrinsic angular momentum (spin) are called polar materials. The theory of continuum mechanics of polar materials goes back to Cosserat brothers (1909) (the theory is sometimes called Cosserat mechanics) and later extended and formalized by Eringen (1967), Toupin (1964) and many others. Here we give a very brief and formal review of this theory, for multi-component materials (mixtures).

Cosserat mechanics introduces several novel concepts into the classical continuum mechanics.

- **Spin** $s_\alpha$ is the internal specific angular moment - $\rho_\alpha s_\alpha d\Omega$ represents the internal angular momentum of the volume element $d\Omega$ - that is, angular momentum hidden in the micro-rotations inside $d\Omega$.

- **Couple stress** $M_\alpha$ - analogy of the Cauchy stress with respect to stress couples. It is introduced analogically as the Cauchy stress, by a tetrahedron argument, looking for the stress couple acting on a surface element and deriving linearity of such mapping with respect to the orientation of the element (given by its unit normal). The stress couple is then given by $M_\alpha \cdot n$
Moreover, we shall also consider some outer specific spin supply term \( I_a \) and interaction couple \( p_a \).

The balance of angular momentum in the local form in Eulerian description is then obtained in our formal balance framework by setting \( \psi_a = \mathbf{x} \times \rho_a \mathbf{v}_a + \rho_a \mathbf{s}_a \), identifying the corresponding non-convective flux as being composed of moment of the partial surface force (expressed through the partial Cauchy stress) plus the couple stress, i.e. by setting \( \mathbf{x} \times \rho_a \mathbf{v}_a + \rho_a \mathbf{s}_a \cdot \Phi = \mathbf{x} \times \mathbf{T}_a + \mathbf{M}_a \), where \( \mathbf{x} \times \mathbf{T}_a \). The angular momentum supply is realized through moment of long-range body forces (gravity, elmag.) plus external spin supply, i.e. we set \( \mathbf{x} \times \rho_a \mathbf{v}_a + \rho_a \mathbf{s}_a \Sigma = \mathbf{x} \times \rho_a \mathbf{b}_a + \rho_a \mathbf{I}_a \). We postulate that there is no production of angular momentum \( \mathbf{x} \times \rho_a \mathbf{v}_a + \rho_a \mathbf{s}_a \xi = 0 \). Angular momentum transfer between the components is possible by interaction, with a contribution arising from (i) moment of interaction forces, (ii) as a result of mass transfer (when there is a mass transfer between two components of the mixture, which have some non-zero angular momentum, it is necessarily accompanied by a corresponding angular momentum transfer) and (iii) another contribution arising from mechanical contact between the constituents realized through interaction couple \( p_a \). We thus postulate

\[
\mathbf{x} \times \rho_a \mathbf{v}_a + \rho_a \mathbf{s}_a \Pi = \mathbf{x} \times (m_a \mathbf{v}_a + \mathbf{I}_a) + p_a + m_a \mathbf{s}_a , \quad \alpha = 1, \ldots, N. 
\]

This leads to the angular balance for polar component \( \alpha \) in the following form:

\[
\frac{\partial}{\partial t} \left( \mathbf{x} \times \rho_a \mathbf{v}_a + \rho_a \mathbf{s}_a \right) + \text{div} \left( \mathbf{x} \times \rho_a \mathbf{v}_a + \rho_a \mathbf{s}_a \right) \mathbf{v}_a = \text{div} \left( \mathbf{x} \times \mathbf{T}_a + \mathbf{M}_a \right) \quad \text{(5.40)}
\]

\[
\begin{align*}
\text{moment of linear momentum} & + \text{spin} \\
\text{moment of surface forces} & + \text{couple stress} \\
\text{moment of body forces} & + \text{external spin supply} \\
\text{moment of interaction forces} & + \text{internal spin exchange} \\
\text{spin exch. due to mass exch.} & , \quad \alpha = 1, \ldots, N. 
\end{align*}
\]

In index notation this reads

\[
\frac{\partial}{\partial t} \left( \epsilon_{ijk} \mathbf{x}_j \rho_a \mathbf{v}_k + \rho_a \mathbf{s}_{ai} \right) + \frac{\partial}{\partial \mathbf{x}_l} \left( \left( \epsilon_{ijk} \mathbf{x}_j \rho_a \mathbf{v}_k + \rho_a \mathbf{s}_{ai} \right) \mathbf{v}_a \right) = \frac{\partial}{\partial \mathbf{x}_l} \left( \epsilon_{ijk} \mathbf{x}_j \mathbf{T}_{akl} + \mathbf{M}_{al} \right) + \epsilon_{ijk} \mathbf{x}_j \mathbf{b}_k + \rho_a \mathbf{l}_{ai} + \epsilon_{ijk} \mathbf{x}_j (m_a \mathbf{v}_a + \mathbf{I}_{ak}) + p_a + m_a \mathbf{s}_{ai}, \quad \alpha = 1, \ldots, N. 
\]

which can be recast to the following form

\[
\epsilon_{ijk} \mathbf{x}_j \left( \frac{\partial (\rho_a \mathbf{v}_a)}{\partial t} + \text{div}(\rho_a \mathbf{v}_a \otimes \mathbf{v}_a) - \text{div} \mathbf{T}_a - \rho_a \mathbf{b}_a - m_a \mathbf{v}_a - \mathbf{I}_a \right) + \frac{\partial (\rho_a \mathbf{s}_{ai})}{\partial t} + \rho_a \epsilon_{ijk} \mathbf{v}_a \mathbf{v}_a j = 0 
\]

\[
+ \frac{\partial}{\partial \mathbf{x}_l} \left( \rho_a \mathbf{s}_{ai} \mathbf{v}_a \mathbf{v}_a \right) = \epsilon_{ijk} \mathbf{T}_{akl} + \frac{\partial \mathbf{M}_{al}}{\partial \mathbf{x}_l} + \rho_a \mathbf{l}_{ai} + p_a + m_a \mathbf{s}_{ai}, \quad \alpha = 1, \ldots, N. 
\]

where \( \epsilon_{ijk} \) is the Levi-Civita permutation symbol. Introducing the vector \( A_a \) is defined as

\[
A_{ai} = \epsilon_{ijk} (\mathbf{T}_a)_{kj}, \quad \alpha = 1, \ldots, N. 
\]

and employing the balance of linear momentum \([5.30]\), we obtain the following local form of the spin balance

\[
\frac{\partial (\rho_a \mathbf{s}_a)}{\partial t} + \text{div}(\rho_a \mathbf{s}_a \otimes \mathbf{v}_a) = \text{div} \mathbf{M}_a + \rho_a \mathbf{l}_a + A_a + p_a + m_a \mathbf{s}_a , \quad \alpha = 1, \ldots, N. 
\]

or, using also the mass balance \([5.19]\):

\[
\rho_a \frac{D_a \mathbf{s}_a}{Dt} = \text{div} \mathbf{M}_a + \rho_a \mathbf{l}_a + A_a + p_a , \quad \alpha = 1, \ldots, N. 
\]

The vector \( A_a \) is closely related with the antisymmetric part of the partial Cauchy stress tensor as can be seen by multiplying \([5.44]\) by \( \epsilon_{ilm} \), (summing over \( i \)) and using the identity

\[
\epsilon_{ijk} \epsilon_{ilm} = \delta_{jl} \delta_{km} - \delta_{jm} \delta_{kl} , 
\]

35
which gives
\[(\Gamma_\alpha)_{ml} - (\Upsilon_\alpha)_{lm} = \varepsilon_{ilm}(A_\alpha)_l, \quad \alpha = 1, \ldots, N.\] (5.48)

In particular, for a mixture of non-polar constituents, i.e. setting \(s_\alpha = 0, M_\alpha = 0, l_\alpha = 0, p_\alpha = 0,\) (5.46) implies
\[A_\alpha = 0 \iff \Gamma_\alpha = \Upsilon_\alpha^T, \quad \alpha = 1, \ldots, N,\] (5.49)

that the partial Cauchy stresses are symmetric.

Now we can formulate the angular balance for the mixture as a whole. Summing (5.45) and postulating in accord with (5.16)
\[\sum_{\alpha=1}^N (\mathbf{x} \times (\mathbf{I}_\alpha + m_\alpha \mathbf{v}_\alpha) + p_\alpha + m_\alpha s_\alpha)) = 0,\] (5.50)

which due to (5.31) implies also
\[\sum_{\alpha=1}^N (p_\alpha + m_\alpha s_\alpha) = 0,\] (5.51)

we obtain
\[\frac{\partial}{\partial t} (\sum_{\alpha=1}^N \rho_\alpha s_\alpha) + \text{div} (\sum_{\alpha=1}^N (\rho_\alpha s_\alpha \otimes \mathbf{v}_\alpha)) = \text{div} (\sum_{\alpha=1}^N M_\alpha) + \sum_{\alpha=1}^N \rho_\alpha l_\alpha + \sum_{\alpha=1}^N A_\alpha .\] (5.52)

Defining the total internal spin of the mixture as a whole as
\[\rho s = \sum_{\alpha=1}^N \rho_\alpha s_\alpha,\] (5.53)

the mixture spin outer supply by
\[\rho l = \sum_{\alpha=1}^N \rho_\alpha l_\alpha,\] (5.54)

vector \(A\) for the mixture as a whole
\[A = \sum_{\alpha=1}^N A_\alpha,\] (5.55)

and the total couple stress of the mixture as a whole by
\[M = \sum_{\alpha=1}^N (M_\alpha - \rho_\alpha s_\alpha \otimes \mathbf{u}_\alpha),\] (5.56)

we arrive at the following single-component form of the spin balance for the mixture as a whole
\[\frac{\partial}{\partial t} (\rho s) + \text{div}(\rho s \otimes \mathbf{v}) = \text{div} M + \rho l + A.\] (5.57)

A possible and sometimes considered case is that of a material, which behaves as a non-polar as a whole, i.e. the mixture Cauchy stress is symmetric, but interaction couples are possible among the constituents, leading to non-symmetry of the partial Cauchy stresses. This can be achieved by neglecting partial spins \((s_\alpha = 0),\) partial couples stresses \((M_\alpha = 0),\) partial spin supplies \((l_\alpha = 0)\) in (5.46), which then reduces to
\[A_\alpha = -p_\alpha, \quad \alpha = 1, \ldots, N.\] (5.58)

or, equivalently in view of (5.48)
\[\Gamma_\alpha - \Upsilon_\alpha^T = p_\alpha, \quad \alpha = 1, \ldots, N.\] (5.59)

where \(p_\alpha\) is the antisymmetric tensor associated with the vector \(p_\alpha\), i.e.
\[(p_\alpha)_{ij} = \varepsilon_{ijk}(p_\alpha)_k, \quad \alpha = 1, \ldots, N.\] (5.60)

In the limit of vanishing interaction couples, we recover the symmetry of the partial Cauchy stresses.

Remark 9. The case described by (5.59) might seem a bit puzzling - we do not consider any spin in the material, yet we consider the interaction couples. Think, for example, of arrangement of molecules, which have some electric dipole moment. As a result of interaction among these electric dipoles, not only forces, but also momenta of forces act among the molecules. If now all the molecules are, for example, fixed in some crystallographic structure, and thus cannot rotate to accommodate to the exerted momenta, we are exactly in the discussed situation - the momenta have to be compensated by the momenta of contact forces. Consequently, this gives rise to the asymmetry of the Cauchy stress tensor.


5.6 Balance of energy (for non-polar mixture of non-polar constituents)

We start with the balance of total energy \( E_\alpha \) for a mixture component. We split the total energy density into a kinetic part and internal energy (with possible further non-trivial structure - e.g. containing potential energy in outer force fields, potential energy due to long-range interaction between the particles of the mixture and ‘thermal’ energy due to thermal thermal motion of the particles of the particular mixture component), that is, we set

\[
\psi_\alpha = \rho_\alpha E_\alpha = \rho_\alpha \left( e_\alpha + \frac{1}{2} |v_\alpha|^2 \right), \quad \alpha = 1, \ldots, N. \tag{5.61}
\]

The total energy flux across a material boundary is composed of the power of surface forces acting there and heat flux, i.e. we set \( \rho_\alpha E_\alpha \Phi = \nabla_a v_\alpha - q_\alpha \), we postulate non-presence of energy production, i.e. we set \( \rho_\alpha E_\alpha \xi = 0 \), and the energy supply is realized through supply of mechanical power and other outer energy supply mechanisms, which we denote \( r_\alpha \), i.e. we set \( \rho_\alpha E_\alpha \Sigma = \rho_a b_\alpha \cdot v_\alpha + \rho_a r_\alpha \). Finally, the energy exchange between the components of the mixture is realized through: (i) mechanical power due to interaction forces, (ii) exchange of energy due to exchange of mass and (iii) the remaining interaction mechanisms denoted \( \varepsilon_\alpha \), i.e we set \( \rho_\alpha E_\alpha \Pi = I_a \cdot v_\alpha + m_a \left( e_\alpha + \frac{|v_\alpha|^2}{2} \right) + \varepsilon_\alpha \). With such choices, for the mixture constituents \( \alpha = 1, \ldots, N \) the total energy balance reads:

\[
\begin{align*}
\frac{\partial}{\partial t} \left( \rho_\alpha \left( e_\alpha + \frac{|v_\alpha|^2}{2} \right) \right) + \nabla \cdot \left( \rho_\alpha \left( e_\alpha + \frac{|v_\alpha|^2}{2} \right) v_\alpha \right) &= \nabla \cdot (\nabla_a v_\alpha - q_\alpha) \\
\quad + \rho_a b_\alpha \cdot v_\alpha + I_a \cdot v_\alpha + \rho_a r_\alpha + \varepsilon_\alpha + m_a \left( e_\alpha + \frac{|v_\alpha|^2}{2} \right), \quad \alpha = 1, \ldots, N. \tag{5.62}
\end{align*}
\]

where we summarize: \( e_\alpha \) is the internal specific energy of \( \alpha \) component, \( q_\alpha \) is the (partial) heat flux of the \( \alpha \) component, \( r_\alpha \) represent the specific energy sources (e.g. radiation) corresponding to \( \alpha \) component, \( \varepsilon_\alpha \) is the interaction energy term representing the rate of energy exchange between \( \alpha \) component and the rest of the mixture due to internal processes in the material. We can see three novel terms (w.r.t. the classical single-continuum theory - cf. (3.24)) on the right-hand side of (5.62), namely \( I_a \cdot v_\alpha, \varepsilon_\alpha, m_a \left( e_\alpha + \frac{|v_\alpha|^2}{2} \right) \). All these terms are interaction terms representing energy exchange between \( \alpha \) component and the rest of the mixture due to internal processes in the mixture. From this point of view, all these three terms could be absorbed into one interaction term, say \( \varepsilon_\alpha \). Nevertheless, we choose to explicitly impose the given structure of these terms, since we can a-priori pin out two particular of all the energy exchange mechanisms. The first one - the term \( I_a \cdot v_\alpha \) corresponds to the work performed by the interaction (e.g. frictional) forces \( I_a \), the second term \( m_a \left( e_\alpha + \frac{|v_\alpha|^2}{2} \right) \) represents the energy transfer directly related to mass transfer \( m_a \). To explicitly expand the interaction terms as we did is motivated merely by the aim to arrive at simple relation for the internal energy balance which will follow.

The interaction energy terms must again sum up to zero, i.e. we assert

\[
\sum_{\alpha=1}^N \left( \varepsilon_\alpha + I_a \cdot v_\alpha + m_a \left( e_\alpha + \frac{|v_\alpha|^2}{2} \right) \right) = 0. \tag{5.63}
\]

We will now derive a more compact form of the energy balance starting from (5.62) by getting rid of the kinetic energy contribution. Taking a scalar product of the partial linear momentum balance (5.30) with \( v_\alpha \), we obtain

\[
\rho_\alpha \left( \frac{\partial}{\partial t} \frac{|v_\alpha|^2}{2} + v_\alpha \cdot \nabla \frac{|v_\alpha|^2}{2} \right) = \nabla \cdot (\nabla_a v_\alpha - \nabla_a \cdot v_\alpha) + \rho_a b_\alpha \cdot v_\alpha + I_a \cdot v_\alpha. \tag{5.64}
\]

Now the left-hand side of (5.62) can be written as follows (using also (5.19) and (5.64)):

\[
\text{(LHS) of (5.62)} = \left( \frac{\partial \rho_\alpha}{\partial t} + \nabla \cdot (\rho_\alpha v_\alpha) \right) \left( e_\alpha + \frac{|v_\alpha|^2}{2} \right) + \rho_a \left( \frac{\partial e_\alpha}{\partial t} + v_\alpha \cdot \nabla e_\alpha \right) + \rho_a \left( \frac{\partial \frac{|v_\alpha|^2}{2} + v_\alpha \cdot \nabla |v_\alpha|^2}{2} \right) = m_a \left( e_\alpha + \frac{|v_\alpha|^2}{2} \right) + \rho_a \left( \frac{\partial e_\alpha}{\partial t} + v_\alpha \cdot \nabla e_\alpha \right) + \nabla \cdot (\nabla_a v_\alpha - \nabla_a \cdot v_\alpha) + \rho_a b_\alpha \cdot v_\alpha + I_a \cdot v_\alpha. \tag{5.65}
\]

37
Comparing with (5.62), we obtain
\[
\rho_a \left( \frac{\partial e_a}{\partial t} + \mathbf{v}_a \cdot \nabla e_a \right) = -\nabla \cdot \mathbf{q}_a + \nabla \cdot (\nabla \cdot \rho_a \mathbf{v}_a + \rho_a \mathbf{r}_a + \epsilon_a) , \quad a = 1, \ldots, N . \tag{5.66}
\]
or, using again the mass balance (5.19):
\[
\frac{\partial (\rho_a e_a)}{\partial t} + \text{div}(\rho_a e_a \mathbf{v}_a) = -\mathbf{q}_a + \nabla \cdot (\nabla \cdot \rho_a \mathbf{v}_a + \rho_a \mathbf{r}_a + \epsilon_a + m_a e_a) , \quad a = 1, \ldots, N . \tag{5.67}
\]

The balance of total energy for the mixture as a whole is obtained by summing the partial balances (5.62) over all components of the mixture, employing (5.63). We arrive at
\[
\frac{\partial}{\partial t} \left( \sum_{a=1}^{N} \rho_a \left( e_a + \frac{\mathbf{v}_a^2}{2} \right) \right) + \text{div} \left( \sum_{a=1}^{N} \rho_a \left( e_a + \frac{\mathbf{v}_a^2}{2} \right) \mathbf{v}_a \right) = \text{div} \left( \sum_{a=1}^{N} (\mathcal{T}_a \mathbf{v}_a - \mathbf{q}_a) \right) + \sum_{a=1}^{N} \rho_a \mathbf{b}_a \cdot \mathbf{v}_a + \sum_{a=1}^{N} \rho_a \mathbf{r}_a \tag{5.68}
\]
Since energy is additive, the natural definition of the total specific energy of the mixture \(E\) is
\[
\rho E = \sum_{a=1}^{N} \rho_a E_a = \sum_{a=1}^{N} \rho_a \left( e_a + \frac{\mathbf{v}_a^2}{2} \right) . \tag{5.69}
\]
We expand the kinetic energy terms
\[
\sum_{a=1}^{N} \rho_a \left( \frac{\mathbf{v}_a^2}{2} \right) = \sum_{a=1}^{N} \frac{1}{2} \rho_a (\mathbf{v} + \mathbf{u}_a) \cdot (\mathbf{v} + \mathbf{u}_a) = \rho \frac{\mathbf{v}^2}{2} + \mathbf{v} \cdot \sum_{a=1}^{N} \rho_a \mathbf{u}_a + \sum_{a=1}^{N} \rho_a \left( \frac{\mathbf{u}_a^2}{2} \right) , \tag{5.70}
\]
and thus
\[
\rho E = \sum_{a=1}^{N} \rho_a e_a + \frac{1}{2} \sum_{a=1}^{N} \rho_a |\mathbf{u}_a|^2 + \frac{1}{2} \rho |\mathbf{v}|^2 . \tag{5.71}
\]
Let us rewrite (5.68) using the definition of \(E\) and splitting the velocity \(\mathbf{v}_a = \mathbf{v} + \mathbf{u}_a\) and the definition of the mixture body force (5.37). We obtain
\[
\frac{\partial (\rho E)}{\partial t} + \text{div} \left( \rho E \mathbf{v} + \sum_{a=1}^{N} \rho_a E_a \mathbf{u}_a \right) = \text{div} \left( \sum_{a=1}^{N} \mathcal{T}_a \mathbf{v} + \sum_{a=1}^{N} \mathcal{T}_a \mathbf{u}_a - \sum_{a=1}^{N} \mathbf{q}_a \right) + \sum_{a=1}^{N} \rho_a \mathbf{b}_a \cdot \mathbf{v}_a + \sum_{a=1}^{N} \rho_a \mathbf{r}_a , \tag{5.72}
\]
Let us recall how we defined the total mixture stress \(\mathcal{T}\) in (5.36) and rewrite the term on the right-hand side of (5.72)
\[
\text{div} \left( \sum_{a=1}^{N} \mathcal{T}_a \mathbf{v} \right) = \text{div}(\mathcal{T} \mathbf{v}) + \text{div} \left( \sum_{a=1}^{N} \rho_a \mathbf{u}_a \otimes \mathbf{u}_a \right) \mathbf{v} , \tag{5.73}
\]
and on the left-hand side we rewrite the term
\[
\text{div} \left( \sum_{a=1}^{N} \rho_a E_a \mathbf{u}_a \right) = \text{div} \left( \sum_{a=1}^{N} \rho_a e_a \mathbf{u}_a \right) + \text{div} \left( \sum_{a=1}^{N} \rho_a \frac{1}{2} (\mathbf{v} + \mathbf{u}_a) \cdot (\mathbf{v} + \mathbf{u}_a) \mathbf{u}_a \right) \frac{1}{|\mathbf{v}|^2 + |\mathbf{u}_a|^2 + 2 \mathbf{v} \cdot \mathbf{u}_a} \tag{5.74}
\]
Plugging (5.73) and (5.74) into (5.72) and noticing that the last terms in both equations cancel out, after slight rearranging of the terms, we arrive at
\[
\frac{\partial (\rho E)}{\partial t} + \text{div}(\rho E \mathbf{v}) = \text{div}(\mathcal{T} \mathbf{v}) - \sum_{a=1}^{N} \left( \mathbf{q}_a - \mathcal{T}_a \mathbf{u}_a + \rho_a (e_a + \frac{1}{2} |\mathbf{u}_a|^2) \mathbf{u}_a \right) + \rho \mathbf{b} \cdot \mathbf{v} + \sum_{a=1}^{N} (\rho_a \mathbf{r}_a + \rho_a \mathbf{b}_a \cdot \mathbf{u}_a) . \tag{5.75}
\]
We can see that provided we define the mixture heat flux \( q \) as
\[
q = \sum_{a=1}^{N} \left( q_a - \mathbb{T}_a u_a + \rho_a (e_a + \frac{1}{2} |u_a|^2) u_a \right),  \tag{5.76}
\]
and the mixture energy sources \( r \) as
\[
\rho r = \sum_{a=1}^{N} \left( \rho_a r_a + \rho_a b_a \cdot u_a \right),  \tag{5.77}
\]
we obtain the single-component form of the total mixture energy balance
\[
\frac{\partial (\rho E)}{\partial t} + \text{div}(\rho E \mathbf{v}) = \text{div}(\mathbb{T} \mathbf{v}) - \text{div} q + \rho \mathbf{b} \cdot \mathbf{v} + \rho r.  \tag{5.78}
\]
It remains to identify the condensed form (the internal energy balance) by subtracting the mixture kinetic energy balance. Multiplying the mixture linear momentum balance \((5.36)\) by \( \mathbf{v} \), we get
\[
\mathbf{v} \cdot \left( \frac{\partial \rho}{\partial t} + \text{div}(\rho \mathbf{v}) \right) + \rho \left( \frac{\partial |\mathbf{v}|^2}{\partial t} + \mathbf{v} \cdot \nabla |\mathbf{v}|^2 \right) = \text{div}(\mathbb{T} \mathbf{v}) - \mathbf{T} : \mathbf{v} + \rho \mathbf{b} \cdot \mathbf{v}, \tag{5.79}
\]
or, using the mass balance again on the left-hand side
\[
\frac{\partial \ |\mathbf{v}|^2}{\partial t} + \text{div}(\rho \mathbf{v} |\mathbf{v}|^2) = \text{div}(\mathbb{T} \mathbf{v}) - \mathbf{T} : \mathbf{v} + \rho \mathbf{b} \cdot \mathbf{v}, \tag{5.80}
\]
We subtract this identity from \((5.78)\) and obtain
\[
\frac{\partial}{\partial t} \left( \sum_{a=1}^{N} \rho_a (e_a + \frac{|u_a|^2}{2}) \right) + \text{div} \left( \mathbf{v} \left( \sum_{a=1}^{N} \rho_a (e_a + \frac{|u_a|^2}{2}) \right) \right) = \mathbf{T} : \mathbf{v} - \text{div} q + \rho r, \tag{5.81}
\]
which suggests to introduce the internal energy \( e \) of the mixture as
\[
\rho e = \sum_{a=1}^{N} \rho_a (e_a + \frac{|u_a|^2}{2}), \tag{5.82}
\]
in which case the reduced energy balance (internal energy balance) for the mixture as a whole reduces to its traditional single-component form
\[
\frac{\partial (\rho e)}{\partial t} + \text{div}(\rho e \mathbf{v}) = \mathbf{T} : \mathbf{v} - \text{div} q + \rho r, \tag{5.83}
\]
or, using the mixture mass balance \((5.27)\)
\[
\frac{De}{Dt} = \mathbf{T} : \mathbf{v} - \text{div} q + \rho r.  \tag{5.84}
\]
Sometimes it is also useful to consider the balance obtained by summation of \((5.67)\):
\[
\frac{\partial (\sum_{a=1}^{N} \rho_a e_a)}{\partial t} + \text{div} \left( \sum_{a=1}^{N} \rho_a e_a \mathbf{v}_a \right) = - \text{div} \left( \sum_{a=1}^{N} q_a + \sum_{a=1}^{N} \mathbb{T}_a : \mathbf{v}_a + \sum_{a=1}^{N} \rho_a r_a + \sum_{a=1}^{N} \mathbf{I}_a : \mathbf{v}_a - \sum_{a=1}^{N} m_a e_a \right), \tag{5.85}
\]
Using the constraint on the interaction terms \((5.63)\), we can rewrite this relation as
\[
\frac{\partial (\sum_{a=1}^{N} \rho_a e_a)}{\partial t} + \text{div} \left( \sum_{a=1}^{N} \rho_a e_a \mathbf{v}_a \right) = - \text{div} \left( \sum_{a=1}^{N} q_a + \sum_{a=1}^{N} \mathbb{T}_a : \mathbf{v}_a + \sum_{a=1}^{N} \rho_a r_a - \sum_{a=1}^{N} \mathbf{I}_a : \mathbf{v}_a - \sum_{a=1}^{N} m_a \frac{|\mathbf{v}_a|^2}{2} \right), \tag{5.86}
\]
This can still be simplified as follows:

\[
\sum_{a=1}^{N} I_a \cdot v_a + \sum_{a=1}^{N} m_a \frac{|v_a|^2}{2} = \left( \sum_{a=1}^{N} m_a + v \cdot \sum_{a=1}^{N} (I_a + m_a v_a) + \sum_{a=1}^{N} I_a \cdot u_a + \sum_{a=1}^{N} m_a \frac{|u_a|^2}{2} \right) = 0
\]

\[
= \sum_{a=1}^{N} I_a \cdot u_a + \sum_{a=1}^{N} m_a \frac{|u_a|^2}{2} .
\]

Using this relation in (5.88), we can rewrite it as

\[
\frac{\partial (\sum_{a=1}^{N} \rho_a e_a)}{\partial t} + \text{div} \left( \sum_{a=1}^{N} \rho_a e_a v_a \right) = -\text{div} \sum_{a=1}^{N} q_a + \sum_{a=1}^{N} I_a : \nabla v_a + \sum_{a=1}^{N} \rho_a r_a - \sum_{a=1}^{N} I_a \cdot u_a - \sum_{a=1}^{N} m_a \frac{|u_a|^2}{2} .
\]

(5.88)

5.7 Balance of entropy (Second law of thermodynamics)

Setting \( \psi_a = \rho_a \eta_a \), where \( \eta_a \) is the partial specific entropy of \( \alpha \) component, denoting the partial entropy flux as \( \rho_a \eta_a \Phi = q_{\eta_a} \), considering entropy exchange due to mass exchange and other mechanism denoted by \( \xi \), i.e. setting \( \rho_a \eta_a \Pi = m_a \eta_a + \xi_a \) and denoting the entropy production \( \rho_a \eta_a \xi = \zeta_a \), and the entropy supply by \( \rho_a \eta_a \Sigma = \rho_a r_{\eta_a} \), the balance of entropy for a particular \( \alpha \) component of the mixture reads

\[
\frac{\partial (\rho_a \eta_a)}{\partial t} + \text{div} (\rho_a \eta_a v_a) = -\text{div} q_{\eta_a} + \xi_a + \check{\xi}_a + m_a \eta_a + \rho_a r_{\eta_a} , \hspace{1cm} \alpha = 1, \ldots, N .
\]

(5.89)

As in the case of energy balance, we have explicitly split the entropy exchange into two terms: \( \check{\xi}_a \) and \( m_a \eta_a \), the second one corresponding to entropy exchange due to mass exchange between the components of the mixture. The interaction exchange terms must by definition sum up to zero, i.e. we assert

\[
\sum_{a=1}^{N} (\check{\xi}_a + m_a \eta_a) = 0 .
\]

(5.90)

The statement of the second law of thermodynamics for a particular component would be postulate of non-negativity of the partial entropy productions:

\[
\zeta_a \geq 0 , \quad \alpha = 1, \ldots, N .
\]

(5.91)

Balance of entropy for the mixture as a whole is obtained again by summing up the partial entropy balances (5.89) over all component of the mixture, with the use of (5.90), we obtain:

\[
\frac{\partial}{\partial t} \left( \sum_{a=1}^{N} \rho_a \eta_a \right) + \text{div} \left( \sum_{a=1}^{N} (\rho_a \eta_a v_a) \right) = -\text{div} \left( \sum_{a=1}^{N} q_{\eta_a} + \rho_a \eta_a u_a \right) + \sum_{a=1}^{N} \xi_a + \sum_{a=1}^{N} \rho_a r_{\eta_a} .
\]

(5.92)

This expression suggests to identify

\[
\rho \eta = \sum_{a=1}^{N} \rho_a \eta_a ,
\]

(5.93)

\[
q_{\eta} = \sum_{a=1}^{N} (q_{\eta_a} + \rho_a \eta_a u_a) ,
\]

(5.94)

\[
\xi = \sum_{a=1}^{N} \xi_a ,
\]

(5.95)

\[
\rho r_{\eta} = \sum_{a=1}^{N} \rho_a r_{\eta_a} .
\]

(5.96)

in which case, we recover the traditional single-component entropy balance:

\[
\frac{\partial (\rho \eta)}{\partial t} + \text{div} (\rho \eta v) = -\text{div} q_{\eta} + \xi + \rho r_{\eta} ,
\]

(5.97)
or, using (5.27)
\[
\frac{\rho}{Dt} \frac{D\eta}{D\xi} = -\text{div}q_\xi + \zeta + \rho r_\eta,
\]
and the statement of the second law of thermodynamics in view of (5.95) and (5.91) reads
\[
\zeta \geq 0.
\]

5.8 Classification of the mixture theories

Certain classification of the mixture theories is possible based on the chosen complexity at the level of balance laws. The motivation is that we do not always need to distinguish between the constituents at all levels. As an example, we can be interested in describing the evolution of concentrations of dispersed tracers in a solvent, that is, to solve the balances of mass for all constituents, but concerning the mechanical and thermal behavior, we are only concerned with the behavior of the mixture as a whole, that is not considering individual balances. Similarly, we can proceed to further levels by increasing the complexity, giving rise to the following classification:

Following the classification introduced by Hutter and Jöhnk (2004), we divide the mixtures based on the descriptive level into four classes, depending on whether partial component-wise properties of the mixture are formulated, or just properties of the mixture as a whole are considered:

<table>
<thead>
<tr>
<th>Class IV</th>
<th>Class III</th>
<th>Class II</th>
<th>Class I</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\rho_\alpha$</td>
<td>$\rho_\alpha$</td>
<td>$\rho_\alpha$</td>
<td>$\rho_\alpha$</td>
</tr>
<tr>
<td>$v_\alpha$</td>
<td>$v_\alpha$</td>
<td>$v_\alpha$</td>
<td>$v$</td>
</tr>
<tr>
<td>$e_\alpha$</td>
<td>$e_\alpha$</td>
<td>$e$</td>
<td>$e$</td>
</tr>
<tr>
<td>$\eta_\alpha$</td>
<td>$\eta$</td>
<td>$\eta$</td>
<td>$\eta$</td>
</tr>
</tbody>
</table>

Class I. $N$ balances of mass for constituents, one balance of linear momentum for the mixture as a whole and one balance of energy and entropy for the mixture as a whole. Typical examples of class I mixtures: Fickian systems, dissolved species in solvent, mixtures of dilute gases, pollution in air, water, ...

Class II. $N$ balances of mass for individual components, $N$ balances of linear momentum for components, but only one balance of energy and entropy for the mixture as a whole. Typical examples: Flow of fluids in porous media (Darcy, Forchheimer, Brinkman), partial melting and melt extraction in geological materials, chemical reactors (bubbly flow), ...

Class III. $N$ balances of mass, $N$ balances of lin. momentum and $N$ balances of energy, one balance of entropy for the mixture as a whole. Typical examples: Plasmas, Systems of melt + matrix far from equilibrium: need to distinguish different temperatures of the species, ...

In principle, one can consider balances of entropy at the level of individual constituents, i.e the Class IV mixtures. Such formulation is, however, not often met in practice, where in most cases, the second law can be reasonably formulated only for the mixture as a whole.

6 Class I mixtures

As defined in the previous section, within the Class I mixture theory, we employ the partial mass balances for the mixture constituents, but consider only linear momentum, angular momentum, energy (and entropy) balance for the mixture as a whole. The system of governing equations (without entropy balance which will
be employed later in the constitutive theory for class I mixtures) reads

\[
\frac{\partial \rho_a}{\partial t} + \text{div}(\rho_a \mathbf{v}_a) = m_a, \quad \alpha = 1, \ldots, N, \quad \tag{6.1a}
\]

\[
\sum_a m_a = 0, \quad \tag{6.1b}
\]

\[
\frac{\partial (\rho \mathbf{v})}{\partial t} + \text{div}(\rho \mathbf{v} \otimes \mathbf{v}) = \text{div} \mathbf{T} + \rho \mathbf{b}, \quad \tag{6.1c}
\]

\[
\mathbf{T} = \mathbf{T}^T, \quad \tag{6.1d}
\]

\[
\frac{\partial}{\partial t} \left( \rho \left( e + \frac{|\mathbf{v}|^2}{2} \right) \right) + \text{div} \left( \rho \left( e + \frac{|\mathbf{v}|^2}{2} \right) \mathbf{v} \right) = \text{div} (\mathbf{T} \mathbf{v} - \mathbf{q}) + \rho \mathbf{b} \cdot \mathbf{v} + \rho r, \quad \tag{6.1e}
\]

where

\[
\rho = \sum_a \rho_a, \quad \rho \mathbf{v} = \sum_{a=1}^N \rho_a \mathbf{v}_a. \quad \tag{6.2}
\]

This is still not the final form, since these equations contain the partial velocities \( \mathbf{v}_a \), for which we do not have any evolution equations within the Class I, (we only have one eq. for the barycentric velocity \( \mathbf{v} \)). Let us thus rewrite the system (6.1) by introducing the diffusive fluxes (with respect to barycenter)

\[
\mathbf{j}_a = \rho_a (\mathbf{v}_a - \mathbf{v}), \quad \alpha = 1, \ldots, N. \quad \tag{6.3}
\]

and rewrite the system (6.1) as follows

\[
\frac{\partial \rho_a}{\partial t} + \text{div}(\rho_a \mathbf{v}) = m_a - \text{div} \mathbf{j}_a, \quad \alpha = 1, \ldots, N, \quad \tag{6.3a}
\]

\[
\sum_a m_a = 0, \quad \tag{6.3b}
\]

\[
\frac{\partial (\rho \mathbf{v})}{\partial t} + \text{div}(\rho \mathbf{v} \otimes \mathbf{v}) = \text{div} \mathbf{T} + \rho \mathbf{b}, \quad \tag{6.3c}
\]

\[
\mathbf{T} = \mathbf{T}^T, \quad \tag{6.3d}
\]

\[
\frac{\partial}{\partial t} \left( \rho \left( e + \frac{|\mathbf{v}|^2}{2} \right) \right) + \text{div} \left( \rho \left( e + \frac{|\mathbf{v}|^2}{2} \right) \mathbf{v} \right) = \text{div} (\mathbf{T} \mathbf{v} - \mathbf{q}) + \rho \mathbf{b} \cdot \mathbf{v} + \rho r. \quad \tag{6.3e}
\]

This system of equations is now perceived as a system for unknowns \( \rho_a, \mathbf{v}, e \), which needs to be complemented by constitutive equations determining \( \mathbf{T}, m_a, \mathbf{q} \) and \( \mathbf{j}_a \), i.e. we ignore the structure (6.2) and determine \( \mathbf{j}_a \) constitutively. We only need to bear in mind that any constitutive relations for \( \mathbf{j}_a \) must satisfy the constraint

\[
\sum_{a=1}^N \mathbf{j}_a = \mathbf{0}, \quad \tag{6.4}
\]

which on the level (6.2) follows directly from the definition (of the barycentric velocity).

Instead of using the set of independent variables \( \rho_a, \mathbf{v}, e \), we can equivalently work in terms of variables \( c_a, \rho, \mathbf{v}, e \) (we could also start with another equivalent set containing e.g. the volume fractions \( \phi_a \)), where, let us remind

\[
c_a = \frac{\rho_a}{\rho}. \quad \tag{6.5}
\]

Let us evaluate the material time derivative of \( c_a \) with respect to barycentric velocity and multiply by \( \rho \)

\[
\rho \dot{c}_a = \rho \frac{\partial c_a}{\partial t} + \rho \mathbf{v} \cdot \nabla c_a = \frac{\partial (pc_a)}{\partial t} + \text{div} (pc_a \mathbf{v}) = \frac{\partial}{\partial t} \left( \rho \frac{\partial c_a}{\partial t} + \rho \mathbf{v} \cdot \nabla c_a \right) = \rho \frac{\partial c_a}{\partial t} + \text{div} (pc_a \mathbf{v}) = \rho \frac{\partial c_a}{\partial t} + \text{div} (pc_a \mathbf{v}) = \frac{\partial (pc_a)}{\partial t} + \text{div} (pc_a \mathbf{v}),
\]

we arrive at the following evolution equation for concentration \( c_a \):

\[
\rho \dot{c}_a + \text{div} \mathbf{j}_a = m_a, \quad \alpha = 1, \ldots, N. \quad \tag{6.5}
\]

Note that since \( \sum_{a=1}^N c_a = 1 \), and \( \sum_{a=1}^N \mathbf{j}_a = \mathbf{0} \), only \( N - 1 \) equations from (6.5) are independent. To obtain a system equivalent with (5.25), we must accompany (6.5), with the mixture mass balance (5.19).
The system of governing equations for class I mixtures, written in terms of concentrations reads

\[
\begin{align*}
\rho \dot{c}_a &= m_a - \text{div} j_a, \quad \alpha = 1, \ldots, N, \quad (6.6a) \\
\sum_a m_a &= 0, \quad (6.6b) \\
\sum_a j_a &= 0, \quad (6.6c) \\
\frac{\partial \rho}{\partial t} + \text{div}(\rho v) &= 0, \quad (6.6d) \\
\rho \dot{\rho} &= -\rho \text{div} v, \quad (6.6e) \\
T &= T^T, \quad (6.6f) \\
\rho \dot{E} &= \text{div}(\rho v - \mathbf{q}) + \rho \mathbf{b} \cdot \mathbf{v} + \rho r. \quad (6.6g)
\end{align*}
\]

In the following, we will proceed in the similar manner as for the single continuum, i.e. starting from a fundamental thermodynamic relation for the Helmholtz free energy \( \psi = \hat{\psi}(\theta, \frac{1}{\rho}, c_1, \ldots, c_N) \), or its reduced form \( \psi = \bar{\psi}(\theta, \frac{1}{\rho}, c_1, \ldots, c_{N-1}) \), and we will attempt to derive the constitutive relations. We will moreover also discuss how to impose various additional constraint (incompressibility,...) into these models and discuss their consequences.

We will in the following, for simplicity, for a while consider only a special case of a binary mixture, i.e. the case \( N=2 \). Since we know that

\[
\sum_{a=1}^N c_a = 1 \Rightarrow c_1 + c_2 = 1, \quad \text{and thus } c_2 = 1 - c_1,
\]

denoting \( c \overset{\text{def}}{=} c_1, \quad m \overset{\text{def}}{=} m_1 = 1 - m_2, \quad j_1 \overset{\text{def}}{=} -j_2, \) we obtain the following system

\[
\begin{align*}
\rho \dot{c} + \text{div} j &= m, \quad (6.7a) \\
\dot{\rho} &= -\rho \text{div} v, \quad (6.7b) \\
\rho v &= \text{div} \mathbb{T} + \rho \mathbf{b}, \quad (6.7c) \\
\mathbb{T} &= \mathbb{T}^T, \quad (6.7d) \\
\rho \dot{E} &= \text{div}(\mathbb{T} v - \mathbf{q}) + \rho \mathbf{b} \cdot \mathbf{v} + \rho r. \quad (6.7e)
\end{align*}
\]

or using the reduced form of the energy balance (internal energy balance):

\[
\begin{align*}
\rho \dot{c} + \text{div} j &= m, \quad (6.8a) \\
\dot{\rho} &= -\rho \text{div} v, \quad (6.8b) \\
\rho v &= \text{div} \mathbb{T} + \rho \mathbf{b}, \quad (6.8c) \\
\mathbb{T} &= \mathbb{T}^T, \quad (6.8d) \\
\rho \dot{E} &= \mathbb{T} : \nabla v - \text{div} \mathbf{q} + \rho r. \quad (6.8e)
\end{align*}
\]

We will now investigate the following special cases of binary Class I mixtures based on various choices and constraints on the constitutive equations, which will allow to derive as special cases the constitutive models of Fick, Cahn-Hilliard, Allen-Cahn and their generalizations. Throughout most of this chapter, we will be work with fundamental relation for the Helmholtz free energy, see (3.64) in order to work with a natural set of variables involving thermodynamic temperature \( \theta \), density \( \rho \) concentrations \( c_a \). Particular choices of the fundamental relation for \( \psi \) will lead to several classical models

1. \( \psi = \bar{\psi}(\theta, \frac{1}{\rho}, c) \) \( \Rightarrow \textbf{Fick-Navier-Stokes-Fourier model} \)
2. \( \psi = \bar{\psi}(\theta, \frac{1}{\rho}, c, \nabla c), \ j \neq 0, \ m=0 \) \( \Rightarrow \textbf{Cahn-Hilliard-Navier-Stokes-Fourier model} \)
3. \( \psi = \bar{\psi}(\theta, \frac{1}{\rho}, c, \nabla c), \ j=0, \ m \neq 0 \) \( \Rightarrow \textbf{Allen-Cahn-Navier-Stokes-Fourier model} \)
6.1 Fick-Navier-Stokes-Fourier model \( (\psi = \bar{\psi}(\bar{\theta}, \frac{1}{\rho}, c)) \)

We start from the fundamental relation for the Helmholtz free energy

\[
\psi = e - \theta \eta = \bar{\psi}(\bar{\theta}, \frac{1}{\rho}, c),
\]

where, for simplicity, we work with the reduced form of the fundamental relation (denoted by the bar symbol) which reflects the fact that one of the concentrations was eliminated. Taking a time derivative, and recalling (3.67)²

\[
-\eta = \frac{\partial \bar{\psi}}{\partial \bar{\theta}}, \quad -p = \frac{\partial \bar{\psi}}{\partial \frac{1}{\rho}}, \quad \mu = \frac{\partial \bar{\psi}}{\partial c},
\]

we obtain using the balances of mass and energy (setting for simplicity the energy sources equal to zero \( r = 0 \)):

\[
\rho \dot{\theta} \eta = \mathbb{T} : \mathbb{D} - \text{div} \mathbf{q} + p \text{div} \mathbf{v} - \mu m + \mu \text{div} \mathbf{j},
\]

or, equivalently

\[
\rho \dot{\theta} \eta = \mathbb{T}^d : \mathbb{D}^d + (m + p) \text{div} \mathbf{v} - \mu m - \text{div}(\mathbf{q} - \mu \mathbf{j}) - \mathbf{j} \cdot \nabla \mu.
\]

Dividing (6.11) by temperature and absorbing the term \( \frac{1}{\bar{\theta}} \) in the divergence term, we obtain the balance of entropy in the following form

\[
\rho \dot{\eta} + \text{div} \left( \frac{\mathbf{q} - \mu \mathbf{j}}{\bar{\theta}} \right) = \frac{1}{\bar{\theta}} \left[ \mathbb{T}^d : \mathbb{D}^d + (m + p) \text{div} \mathbf{v} - (\mathbf{q} - \mu \mathbf{j}) \cdot \nabla \frac{\partial \bar{\psi}}{\partial \theta} - \mathbf{j} \cdot \nabla \mu - \mu m \right].
\]

If we want to identify independent entropy-producing mechanism and provide piece-wise linear closures, we now have more options, how to treat the terms involving \( \mathbf{j} \cdot \nabla \theta \). Let us consider two end-member variants.

**Variant A**

Assuming the terms in (6.12) represent these mutually independent mechanism, if we restrict ourselves as before to only linear relations, we obtain constitutive closures in the form

\[
\mathbb{T}^d = 2v \mathbb{D}^d, \quad m + p = \frac{2v + 3\lambda}{3} \text{div} \mathbf{v},
\]

\[
\mathbf{q} - \mu \mathbf{j} = -\kappa \frac{\nabla \theta}{\bar{\theta}}, \quad \mathbf{j} = -\alpha \nabla \mu, \quad m = -\beta \mu,
\]

where for \( v \geq 0, 2v + 3\lambda \geq 0, \kappa \geq 0, \alpha \geq 0, \beta \geq 0 \), we obtain that automatically the entropy production is non-negative, i.e. \( \frac{\xi}{\bar{\theta}} \geq 0 \) and we obtain the final form of the constitutive relations

\[
\mathbb{T} = -pl + \lambda \text{div} \mathbf{v} + 2v \mathbb{D}, \quad \mathbf{j} = -\alpha \nabla \mu, \quad \mathbf{q} = -\kappa \frac{\nabla \theta}{\bar{\theta}} + \mu \mathbf{j}, \quad m = -\beta \mu.
\]

²Note that based on our definitions from Sec. 3.2.2 for a binary mixture we would have \( \psi = \psi(\bar{\theta}, \frac{1}{\rho}, c_1, c_2) \), with the definition of the chemical potential as \( \mu = \frac{\partial \bar{\psi}}{\partial c} \). Since in this section, we defined our Helmholtz energy as \( \bar{\psi}(\bar{\theta}, \frac{1}{\rho}, c_1, 1 - c_2) \), we can see that in fact \( \mu = \frac{\partial \bar{\psi}}{\partial c} = \frac{\partial \bar{\psi}}{\partial c_1} - \frac{\partial \bar{\psi}}{\partial c_2} = \mu_1 - \mu_2 \), that is the “chemical potential” we are working with is in fact the difference between the chemical potentials of the two component of the mixture.
Note that if $\psi = \bar{\psi}_0(\vartheta, \frac{1}{\rho}) + \bar{\psi}_1(c)$, we obtain $\mu = \bar{\psi}_1'$
\[
j = -\alpha \bar{\psi}_1''(c) \nabla c ,
\]
and the evolution equation for concentration reads
\[
\rho \frac{\partial c}{\partial t} - \alpha \text{div}(\bar{\psi}_1''(c) \nabla c) = -\beta \bar{\psi}_1' .
\]
The relation (6.15), written in the more general form
\[
j = -k(c) \nabla c ,
\]
represents the Fick’s law - analogy of Fourier’s law of heat conduction relating the heat flux and the temperature gradient.

**Remark 10.** Note that should $\bar{\psi}_1$ be quadratic (and convex) in $c$, the evolution equation for concentration reads
\[
\rho \frac{\partial c}{\partial t} - \beta \bar{\psi}_1' \nabla c - \beta \bar{\psi}_1' \nabla c = -\beta \bar{\psi}_1' ,
\]
where $k_1 \geq 0$ and $k_2$ are constants. This is an example of the so-called advection-diffusion-reaction equation (the three terms corresponding to these three mechanisms).

**Remark 11.** A perhaps more realistic, despite still rather special example could be considered as following. Let’s have a binary mixture, composed of substance $A$ which is highly diluted in substance $B$ which in turn represents vast majority of the mixture. Let’s assume that mass conversion (reaction) between the two substances is possible, i.e. reaction $A \rightarrow B$ takes place. Let, for simplicity, the molar masses of both substances be the same (equal to $M$). Then, as we shall see later, we can write the chemical potential $\mu = \mu_A - \mu_B = (\mu_0^A - \mu_0^B)(\vartheta, \rho) + \frac{R \vartheta}{M} (\ln c_A - \ln(1-c_A)) = (\mu_0^A - \mu_0^B)(\vartheta, \rho) + \frac{R \vartheta}{M} \ln c_A$, the last equality due to the assumption of diluteness. With the same piece-wise linear closure relations as before, and assuming some given isothermal conditions and neglecting volume changes of the mixture as a whole (i.e. $\vartheta=\text{const.}, \rho=\text{const}$), we obtain the following evolution equation for concentration $c \overset{\text{def}}{=} c_A$:
\[
\rho \frac{\partial c}{\partial t} - \frac{R}{M} \text{div}(\bar{\psi}_1''(c) \nabla c) = -\beta \left( (\mu_0^A - \mu_0^B)(\vartheta, \rho) + \frac{R \vartheta}{M} \ln c \right) ,
\]
we could consider $a_0 > 0$ and $\alpha = a_0 c \geq 0$, which yields
\[
\rho \frac{\partial c}{\partial t} - \alpha_0 \frac{\partial}{\partial c} \Delta c = -\beta \left( (\mu_0^A - \mu_0^B)(\vartheta, \rho) + \frac{R \vartheta}{M} \ln c \right) .
\]
On the left-hand side, we obtained the classical advection-diffusion operator. The term on the right-hand side represents the rate of the reaction and, while $\beta \geq 0$, the bracket does not have any a-priori given sign. Its sign, which determines whether the reaction goes forward or backward, depends on whether the concentration is larger or smaller than the actual equilibrium composition (such $c$ for which the bracket is zero). This equilibrium value, as we can infer, can be a very intricate function of temperature and pressure (and it typically is the case in real-world chemical reactions).

**Variant B**

Alternatively, we can rewrite (6.12) as follows
\[
\rho \frac{\partial \eta}{\partial t} + \text{div} \left( \frac{q - \mu j}{\vartheta} \right) = \frac{1}{\vartheta} \left[ \text{T}^d : \text{D}^d + (m + p) \text{div} \mathbf{v} - \frac{\vartheta}{\vartheta} \mu m \right] - j \cdot \nabla \left( \frac{\mu}{\vartheta} \right) .
\]
\[\text{(6.19)}\]
Assuming now the grouped terms represent the individual entropy-producing mechanisms, ignoring the possible mutual couplings (cross-effects), for a class of piece-wise linear closure relations, we obtain:

\[
\begin{align*}
T^d &= 2v\nabla^d, \\
m + p &= \frac{2v + 3\lambda}{3} \text{div} \mathbf{v}, \\
\mathbf{q} &= -\kappa \frac{\nabla \theta}{\theta}, \\
\mathbf{j} &= -\alpha \left(1 - \delta\right) \frac{\nabla \left(\mu \theta\right)}{\theta} + \delta \nabla \mu, \\
m &= -\beta \mu.
\end{align*}
\]

(6.20a) (6.20b) (6.20c) (6.20d) (6.20e)

where for \( v \geq 0, 2v + 3\lambda \geq 0, \kappa \geq 0, \alpha \geq 0, \beta \geq 0, \) we obtain that automatically the entropy production is non-negative, i.e. \( \xi \geq 0 \) and we obtain the final form of the constitutive relations

\[
\begin{align*}
T &= -p + \lambda \text{div} \mathbf{v} + 2v, \\
\mathbf{j} &= -\alpha \left(1 - \delta\right) \frac{\nabla \left(\mu \theta\right)}{\theta} + \delta \nabla \mu, \\
\mathbf{q} &= -\kappa \frac{\nabla \theta}{\theta}, \\
m &= -\beta \mu.
\end{align*}
\]

(6.21a) (6.21b) (6.21c) (6.21d)

**Variant C**

Alternatively, if we want to remain indecisive as for the splitting, we can introduce the following convex combination for a free parameter \( \delta \in (0, 1) \), use the following identity

\[
-\mathbf{j} \cdot \nabla \mu + \mu \mathbf{j} \cdot \nabla \theta = -\mathbf{j} \cdot \left(\delta \nabla \mu + (1-\delta) \nabla \left(\frac{\mu}{\theta}\right)\right) + \delta \mu \mathbf{j} \cdot \nabla \frac{\theta}{\theta}
\]

(6.22)

with the help of which, we can rewrite \( (6.12) \) as follows

\[
\rho \dot{\eta} + \text{div} \left(\frac{\mathbf{q} - \delta \mu \mathbf{j}}{\theta}\right) = \frac{1}{\theta} \left[ T^d : \nabla^d + (m + p) \text{div} \mathbf{v} - (\mathbf{q} - \delta \mu \mathbf{j}) \cdot \nabla \frac{\theta}{\theta} - \mathbf{j} \cdot \left(\delta \nabla \theta \left(\frac{\mu}{\theta}\right) + \delta \nabla \mu\right) - \mu m \right].
\]

(6.23)

Assuming now the grouped terms represent the individual entropy-producing mechanisms, ignoring the possible mutual couplings (cross-effects), for a class of piece-wise linear closure relations, we obtain:

\[
\begin{align*}
T^d &= 2v\nabla^d, \\
m + p &= \frac{2v + 3\lambda}{3} \text{div} \mathbf{v}, \\
\mathbf{q} - \delta \mu \mathbf{j} &= -\kappa \frac{\nabla \theta}{\theta}, \\
\mathbf{j} &= -\alpha \left(1 - \delta\right) \frac{\nabla \left(\mu \theta\right)}{\theta} + \delta \nabla \mu, \\
m &= -\beta \mu.
\end{align*}
\]

(6.24a) (6.24b) (6.24c) (6.24d) (6.24e)

where for \( v \geq 0, 2v + 3\lambda \geq 0, \kappa \geq 0, \alpha \geq 0, \beta \geq 0, \) we obtain that automatically the entropy production is non-negative, i.e. \( \xi \geq 0 \) and we obtain the final form of the constitutive relations

\[
\begin{align*}
T &= -p + \lambda \text{div} \mathbf{v} + 2v, \\
\mathbf{j} &= -\alpha \left(1 - \delta\right) \frac{\nabla \left(\mu \theta\right)}{\theta} + \delta \nabla \mu, \\
\mathbf{q} &= -\kappa \frac{\nabla \theta}{\theta} + \delta \mu \mathbf{j}, \\
m &= -\beta \mu.
\end{align*}
\]

(6.25a) (6.25b) (6.25c) (6.25d)
Remark 12. In all cases the chemical reaction rates were written simply as \( m = -\beta \mu \). This is, however, very unrealistic in real applications. Chemical reactions typically require non-linear closures, we will investigate chemical reactions in more detail in Sec. 6.5.4.

6.2 Constraints: Incompressibility and Quasi-incompressibility

Our starting system of governing equations is still

\[
\begin{align*}
\rho \dot{c} &= -\text{div} \mathbf{j} + m, \\
\dot{\rho} &= -\rho \text{div} \mathbf{v}, \\
\rho \mathbf{v} &= \text{div} \mathbf{T} + \rho \mathbf{b}, \\
\mathbf{T} &= \mathbf{T}^T, \\
\rho \dot{\mathbf{e}} &= \mathbf{T} : \mathbb{D} - \text{div} \mathbf{q}.
\end{align*}
\]

Starting from the same (i.e. compressible) constitutive assumptions as before, and by just plugging (6.27) into (6.10), we arrive at

\[
\rho \theta \dot{\eta} = \mathbf{T}^d : \mathbb{D}^d - \text{div} \mathbf{q} - \mu m + \mu \text{div} \mathbf{j}.
\]  

From here we can proceed in the same lines as in the compressible case and obtain the three variants A,B,C. In particular, for variant C (A and B follow setting \( \delta = 1 \) and \( 0 \), respectively), we get:

\[
\begin{align*}
\mathbf{T}^d &= 2 \nu \mathbb{D}^d, \\
\mathbf{q} - \delta \mu \mathbf{j} &= -\kappa \frac{\nabla \theta}{\theta}, \\
\mathbf{j} &= -\alpha \left( (1-\delta) \theta \nabla \left( \frac{\mu}{\theta} \right) + \delta \nabla \mu \right), \\
m &= -\beta \mu.
\end{align*}
\]

As we can see the entropy inequality no longer provides any information about the isotropic part of the Cauchy stress tensor (mean normal stress \( m \equiv \frac{1}{3} \text{tr} \mathbf{T} \)). Therefore, concerning the final closures, we can only write,

\[
\begin{align*}
\mathbf{T} &= m \mathbf{I} + 2 \nu \mathbb{D}^d, \\
\mathbf{j} &= -\alpha \left( (1-\delta) \theta \nabla \left( \frac{\mu}{\theta} \right) + \delta \nabla \mu \right), \\
\mathbf{q} &= -\kappa \frac{\nabla \theta}{\theta} + \delta \mu \mathbf{j}, \\
m &= -\beta \mu,
\end{align*}
\]

where now the mean-normal stress \( m \) is a constitutively undetermined variable, which has to be sought by solving the corresponding initial-boundary value problem.
6.2.2 Quasi-incompressibility

The quasi-incompressibility will be a certain assumption of explicit relation between the mixture density and concentration, i.e.

\[ \rho = \rho(c). \]  \hfill (6.31)

Taking time derivative of (6.31) and using (6.26a) and (6.26b), we obtain relation

\[ \text{div} \, \mathbf{v} = \left( \frac{1}{\rho(c)} \right)' \left( m - \text{div} \, \mathbf{j} \right). \]  \hfill (6.32)

Let us remind that we have in mixture the following measures \( \rho_\alpha \) (partial density), \( c_\alpha \) (concentration), \( \phi_\alpha \) (volume fraction), \( \rho_{m\alpha} \) (true material density) and let us now assume that the following assumptions hold in the material:

(P1) mass additivity constraint \( \mathcal{M}(\mathcal{P}) = \sum_{a=1}^{N} \mathcal{M}_a(\mathcal{P}) \), which implies \( \rho = \sum_{a=1}^{N} \rho_a \),

(P2) volume additivity constraint \( \mathcal{V}(\mathcal{P}) = \sum_{a=1}^{N} \mathcal{V}_a(\mathcal{P}) \), which implies \( \sum_{a} \phi_a = 1 \),

(P3) \( \rho_{m\alpha} \) are constant for all \( \alpha = 1, \ldots, N \).

Under the assumptions (P1)–(P3) we obtain for an N-component mixture the following expression for \( \frac{1}{\rho} \) in terms of concentrations \( c_\alpha \) and (constant) material densities \( \rho_{m\alpha} \)

\[ \frac{1}{\rho}(c_1, \ldots, c_N) = \sum_{a=1}^{N} \frac{c_a}{\rho_{m_a}} \]  \hfill (6.33)

which follows immediately if we write down the volume additivity constraint as

\[ 1 = \sum_{a=1}^{N} \phi_a = \sum_{a=1}^{N} \frac{\rho_a}{\rho_{m_a}} = \rho \sum_{a=1}^{N} \frac{c_a}{\rho_{m_a}}. \]  \hfill (6.34)

In particular, for a binary mixture, we get

\[ \frac{1}{\rho(c)} = \frac{c}{\rho_1^m} + \frac{1-c}{\rho_2^m}. \]  \hfill (6.35)

We have demonstrated that the assumption \( \rho_{m\alpha}^m \) constant + volume additivity \( \Rightarrow \) Quasi-incompressibility. In the following we will be using this stronger assumption, so that not only there is some relation between \( \rho \) and \( c_\alpha \), but that the particular formula (6.33) holds.

Coming back to the binary mixture, having \( \rho_1^m, \rho_2^m \in \mathbb{R}^+ \), \( \rho_2^m > \rho_1^m \), we can explicitly compute

\[ \left( \frac{1}{\rho(c)} \right)' = \left( \frac{\rho_2^m - \rho_1^m}{\rho_1^m \rho_2^m} \right) \text{def} = r > 0, \]  \hfill (6.36)

and our quasi-incompressible constraint thus reads

\[ \text{div} \, \mathbf{v} = r(m - \text{div} \, \mathbf{j}). \]  \hfill (6.37)

**Exercise 13.** How does analogue of (6.37) look like for a \( N \)-component quasi-incompressible mixture from?

**Solution:**

\[ \text{div} \, \mathbf{v} = \sum_{a=1}^{N} \frac{m_a - \text{div} \, \mathbf{j}_a}{\rho_{m_a}}. \]

Let us discuss the constraint (6.37) a bit more. The terms involved are connected with three dissipative processes - roughly speaking \( \text{div} \, \mathbf{v} \) corresponds to compaction of the material, \( \text{div} \, \mathbf{j} \) to diffusion and \( m \) to mass conversion by reactions (chemical, phase transitions). Let’s get back to our constitutive procedure. Starting from the internal energy in the “Fickian” form for simplicity \( \psi = \tilde{\psi}(\theta, \rho, c) \). We can again obtain the following balance

\[ \rho \partial \eta = \mathbf{I} : \mathbf{D}^d + (\mathbf{m} + p) \text{div} \, \mathbf{v} - \mu \mathbf{m} + \mu \text{div} \, \mathbf{j} - \text{div} \, \mathbf{q}. \]  \hfill (6.38)

Now we want to plug in the constraint (6.37), the question is how? There are several possibilities
(A) “Compaction is a dependent mechanism”: we substitute in (6.38) for $\text{div} \mathbf{v}$ from (6.37)

(B) “Compaction is an independent mechanism”: we substitute in (6.38) for $m - \text{div} \mathbf{j}$ from (6.37)

(C) Both mechanisms are present and (to-some extent) independent

**Variant A**

Substituting from (6.37) into (6.38) for $\text{div} \mathbf{v}$ gives us

$$
\rho \partial_t \eta = T^d : \mathbf{D}^d - (\mu - r_*(m+p))m + (\mu - r_*(m+p)) \text{div} \mathbf{j} - \text{div} \mathbf{q}.
$$

(6.39)

Denoting auxiliary “chemical potential”

$$
\tilde{\mu} \overset{\text{def}}{=} \mu - r_*(m+p),
$$

(6.40)

and comparing with the incompressible Fick-NSF case (6.28), we see, we are in fact in the same setting, only with $\mu$ replaced by $\tilde{\mu}$. We can immediately “copy-and-paste” the closure relations:

$$
T^d = 2v^d, \quad \mathbf{q} - \delta \tilde{\mathbf{p}} = -\kappa \frac{\partial}{\partial} \mathbf{q},
$$

(6.41a)

$$
\mathbf{j} = -\alpha \left( (1-\delta) \frac{\partial}{\partial} \left( \frac{\mu}{\partial} \right) + \delta \nabla \tilde{\mu} \right),
$$

(6.41b)

$$
\mathbf{q} = -\kappa \frac{\partial}{\partial} \mathbf{q} + \delta (\mu - r_*(m+p)) \mathbf{j},
$$

(6.41c)

$$
m = -\beta \tilde{\mu},
$$

(6.41d)

for some $\delta \in (0,1)$. Writing explicitly the final closures, we get for some $\nu \geq 0$, $\alpha \geq 0$, $\kappa \geq 0$, $\beta \geq 0$:

$$
T = m + 2v^d, \quad \mathbf{j} = -\alpha \left( (1-\delta) \frac{\partial}{\partial} \left( \frac{\mu}{\partial} \right) + \delta \nabla (\mu - r_*(m+p)) \right),
$$

(6.42a)

$$
\mathbf{q} = -\kappa \frac{\partial}{\partial} \mathbf{q} + \delta (\mu - r_*(m+p)) \mathbf{j},
$$

(6.42b)

$$
m = -\beta (\mu - r_*(m+p)).
$$

(6.42c)

It is instructive to look at the structure of the balance equations after plugging in these closures. Let us, for simplicity, consider an isothermal setting and write down the balances of mass and momentum. We obtain

$$
\text{div} \mathbf{v} = r_*(-\beta + \alpha \Delta)(\mu - r_*(m+p)) ,
$$

(6.43a)

$$
\rho \mathbf{v} = \nabla m + \text{div}(2v^d),
$$

(6.43b)

$$
\rho \dot{c} - \text{div}(a^2 \nabla (\mu - r_*(m+p))) = -\beta (\mu - r_*(m+p)).
$$

(6.43c)

These are 5 equations for 5 unknowns $\mathbf{v}$, $c$, $m$, and the system should be understood in the sense, that in relations for both $\mu$ and $p$, density was substituted from the constraint (6.31), i.e. $\mu = \tilde{\mu}(c)$, $p = \tilde{p}(c)$, it is more elucidating to rewrite the system as follows

$$
\text{div} \mathbf{v} = r_2^2 (\beta - \alpha \Delta)m + r_*(-\beta + \alpha \Delta)(\mu - r_*(\tilde{p}))(c) ,
$$

(6.44a)

$$
\rho \mathbf{v} = \nabla m + \text{div}(2v^d),
$$

(6.44b)

$$
\rho \dot{c} - \text{div}(a^2 \nabla (\mu - r_*(\tilde{p}))(c)) + \beta (\mu - r_*(\tilde{p}))(c) = r_*(\beta - \alpha \Delta)m.
$$

(6.44c)

**Remark 13.** (Mathematical remark on quasi-incompressibility) The incompressible Navier-Stokes system reads (with $\rho = 1$ since this is a mathematical remark):

$$
\text{div} \mathbf{v} = 0
$$

(6.45)

$$
\frac{\partial \mathbf{v}}{\partial t} + \text{div}(\mathbf{v} \otimes \mathbf{v}) = \nabla m + v \Delta \mathbf{v}
$$

(6.46)
R. Temam in his “1st book on NSEs in the West” (J. Málek) replaced this system by the following quasi-compressible approximation

$$\text{div} \mathbf{v}^\varepsilon = -\varepsilon \Delta m \quad (6.47)$$

$$\frac{\partial \mathbf{v}^\varepsilon}{\partial t} + \text{div}( \mathbf{v}^\varepsilon \otimes \mathbf{v}^\varepsilon ) = \nabla m^\varepsilon + \nu \Delta \mathbf{v}^\varepsilon \quad (6.48)$$

Let us inspect the advantages of such a system in terms of a-priori estimates. Multiplying the momentum eq. by $\mathbf{v}$, we get:

$$\frac{d}{dt} \| \mathbf{v}^\varepsilon \|^2_{L^2(\Omega)} + \| \nabla \mathbf{v}^\varepsilon \|^2_{L^2(\Omega)} + \varepsilon \| \Delta \mathbf{m}^\varepsilon \|^2_{L^2(\Omega)} = 0 \quad (6.49)$$

Substituting in the last term from (6.45), integrating over $\Omega$ and assuming all the boundary integrals vanish, we obtain

$$\frac{d}{dt} \| \mathbf{v}^\varepsilon \|^2_{L^2(\Omega)} + \| \nu \nabla \mathbf{v}^\varepsilon \|^2_{L^2(\Omega)} + \varepsilon \| \nabla \mathbf{m}^\varepsilon \|^2_{L^2(\Omega)} = 0 \quad (6.50)$$

Integrating over time from 0 to some $T$, we see, that in this case, one obtains apart from the standard estimates on velocity ($\mathbf{v}^\varepsilon \in L^2((0,T),H^1(\Omega)) \cap L^\infty((0,T),L^2(\Omega))$), for a fixed $\varepsilon$, we get also $\nabla \mathbf{m}^\varepsilon \in L^2((0,T),L^2(\Omega))$, suggesting the usefulness of the concept of mathematical quasi-compressibility.

Now inspecting (6.44a), we can see that the structure of the r.h.s. with respect to $m$ is analogous (with $\varepsilon \sim a r^2_\star$). This indicates that the mathematical concept can interpreted in terms of the physical notion of quasi-incompressibility, which we have defined.

**Variant B**

Substituting from (6.37) into (6.61) for $m - \text{div} \mathbf{j}$ gives us

$$\rho \dot{\eta} = \mathcal{T}^d : \mathbf{D}^d + (m + (p - r_{\star \mu}) \text{div} \mathbf{v} - \text{div} \mathbf{q} \quad (6.51)$$

Denoting

$$\tilde{p} \overset{\text{def}}{=} p - r_{\star \mu} \quad (6.52)$$

and comparing with (3.136), we can see the same structure as for compressible NSF system. We can again “copy-and-paste” the corresponding closure relations (3.140), only with $p$ replaced by $\tilde{p}$:

$$\mathcal{T}^d = 2\nu \mathbf{D}^d \quad , \quad \nu \geq 0 \quad (6.53a)$$

$$\frac{2\nu + 3\lambda}{3} \text{div} \mathbf{v} \quad , \quad 2\nu + 3\lambda \geq 0 \quad (6.53b)$$

$$\mathbf{q} = -k \nabla \frac{\Theta}{\theta} \quad , \quad k \geq 0 \quad (6.53c)$$

Putting all together (and setting $\kappa \overset{\text{def}}{=} \frac{k}{\rho} \geq 0$), we obtain

$$\mathcal{T} = -(p - r_{\star \mu}) \| + \lambda \text{div} \mathbf{v} \| + 2\nu \mathbf{D} \quad , \quad (6.54a)$$

$$\mathbf{q} = -k \nabla \frac{\Theta}{\theta} \quad (6.54b)$$

The chemical potential is assumed to be expressed now as a function of $\eta$ and $\rho$, obtained by substituting for $c$ from inversion of (6.31). Again, in the isothermal setting, we can write down the balances of mass and momentum

$$\rho \dot{\rho} = \rho \text{div} \mathbf{v} = 0 \quad , \quad (6.55)$$

$$\rho \mathbf{v} = \nabla (p - r_{\star \mu})(\Theta, \rho) + \nabla (\lambda \text{div} \mathbf{v}) + \text{div}(2\nu \mathbf{D}) \quad , \quad (6.56)$$

so it is indeed compressible NSF system, only with a modified definition of the thermodynamic pressure. Concentration is obtained from $\rho$ (solution of the corresponding IBVP) simply by inverting relation the incompressibility constraint (6.31).
Remark 14. Let us shortly comment on some interesting mathematical properties of the system (6.55): Assuming ideal mixing contribution of concentration to the chemical potential, we can write (up to some constants, but this is mathematical detour):
\[ \mu(c) = (\ln(c) - \ln(1-c)) \]
(6.57)
Assuming without loss of generality \( \rho_2^m \geq \rho_1^m \) and setting \( \rho_2^m = 1 \), \( \rho^m \overset{\text{def}}{=} \rho_1^m \), we get \( r* = \frac{1-\rho^m}{\rho^m} \implies \frac{1}{\rho^*} = 1 + r* \) and \( \hat{c}(\rho) = \frac{\rho r* + (\rho - 1)}{\rho r*} \). Hence
\[ \mu(c(\rho)) = \ln\left(1 + \frac{1}{r*} \right) - \ln(1 - \rho) \implies \rho \in \left(\frac{1}{1 + r*}, 1\right) \]
(6.58)
so in the quasi-incompressible setting, we obtain structure formally similar to compressible Navier-Stokes equations, but due to arising singular pressure, we obtain boundedness of density \( \rho \), which otherwise is not guaranteed in the compressible case.

Variant C

If we want to keep both mechanisms present, we will split
\[
\begin{align*}
v &= v_A + v_B, \\
j &= j_A + j_B, \\
m &= m_A + m_B,
\end{align*}
\]
(6.59a)
(6.59b)
(6.59c)
and we will assume that both sets A and B satisfy the constraint, i.e.
\[
\begin{align*}
\text{div} v_A &= r_* (m_A - \text{div} j_A), \\
\text{div} v_B &= r_* (m_B - \text{div} j_B).
\end{align*}
\]
(6.60a)
(6.60b)
We write the initial balance as
\[
\rho \frac{\partial \eta}{\partial t} = \mathbb{T}^d : D^d + (m + p)(\text{div} v_A + \text{div} v_B) - (m_A + m_B) \mu + (\text{div} j_A + \text{div} j_B) \mu - \text{div} q,
\]
(6.61)
and we substitute for \( \text{div} v_A \) from (6.60a) and for \( m_B - \text{div} j_B \) from (6.60b). We obtain
\[
\rho \frac{\partial \eta}{\partial t} = \mathbb{T}^d : D^d - \text{div} q - (\mu - r_* (m + p))(m_A - \text{div} j_A) + (m + p - r_*^{-1} \mu) \text{div} v_B.
\]
(6.62)
Denoting as before
\[
\begin{align*}
\tilde{\mu} &\overset{\text{def}}{=} \mu - r_* (m + p), \\
\tilde{\rho} &\overset{\text{def}}{=} p - r_*^{-1} \mu,
\end{align*}
\]
(6.63a)
(6.63b)
we obtain
\[
\rho \frac{\partial \eta}{\partial t} = \mathbb{T}^d : D^d - \text{div} q + (m + \tilde{\rho}) \text{div} v_B - \tilde{\mu} m_A + \tilde{\mu} \text{div} j_A,
\]
(6.64)
and comparing with the compressible Fick-NSF case (6.10), we see, we are in fact in the same setting, only with \( v, j, m, p, \) and \( \mu \) replaced by \( v_B, j_A, m_A, \tilde{\rho} \) and \( \tilde{\mu} \), respectively. We can immediately “copy-and-paste” the closure relations:
\[
\begin{align*}
\mathbb{T}^d &= 2v \mathbb{D}^d, \\
m + \tilde{\rho} &= \frac{2v + 3\lambda}{3} \text{div} v_B, \\
q - \delta \tilde{\mu} j_A &= -\kappa \frac{\nabla \theta}{\theta}, \\
j_A &= -\alpha \left((1 - \delta) \Theta \frac{\nabla \tilde{\mu}}{\Theta} + \delta \nabla \tilde{\mu}\right), \\
m_A &= -\beta \tilde{\mu},
\end{align*}
\]
(6.65a)
(6.65b)
(6.65c)
(6.65d)
(6.65e)
where \( \nu, 2\nu + 3\lambda, \alpha, \beta \geq 0 \), we obtain that automatically the entropy production is non-negative, i.e. \( \zeta \geq 0 \). We can not identify the full closures, (e.g. for \( j \) or \( m \)), but the given ones allow to close the system of balances.

Consider again, an isothermal setting, for simplicity. Now can compute

\[
\text{div} \, \mathbf{v} = \text{div} \, \mathbf{v}_A + \text{div} \, \mathbf{v}_B = r_* (m_A - \text{div} \, j_A) + \text{div} \, \mathbf{v}_B
\]

\[
= r_* (-\beta \tilde{\mu} + \text{div} \, (\alpha \nabla \tilde{\mu})) + \frac{3}{2\nu + 3\lambda} r_* (m + \tilde{p}) , \tag{6.66}
\]

\[
m - \text{div} \, j = (m_A - \text{div} \, j_A) + r_*^{-1} \text{div} \, \mathbf{v}_B
\]

\[
= -\beta \tilde{\mu} + \text{div} \, (\alpha \nabla \tilde{\mu}) + r_*^{-1} \frac{3}{2\nu + 3\lambda} (m + \tilde{p}) . \tag{6.67}
\]

### 6.3 Cahn-Hilliard-NSF and Allen-Cahn-NSF model

Motivation: The Cahn-Hilliard and Allen-Cahn models are one of the simplest models which allows to describe a phenomena of phase-separation, i.e. spontaneous separation of two component of a binary mixture into distinct macroscopic phases. They are typical representatives of the class of the so-called diffuse interface models. These models allow to deal with multi-phase continua without the necessity to track and explicitly capture the behaviour of the interfaces between the phases. In the diffuse interface framework, the interfaces are described intrinsically as regions of steep gradient of some order parameter (e.g. concentration). This viewpoint is also more physical, true interfaces between phases or between different materials exhibit, in fact, some transition layers (with typical thickness of few molecular diameters).

History - capillarity effects - Young (1805); van der Waals (1893); Korteweg (1901); Cahn and Hilliard (1958, 1959); Lowengrub and Truskinowsky (1998). The crucial conceptual idea behind the models of Cahn-Hilliard and Allen-Cahn is (in the simplest two-component setting) related to the variational (minimization) problem for the free energy functional \( F \) of the form:

\[
F = \int_\Omega f(c) + \frac{\sigma}{2} |\nabla c|^2 \, dx . \tag{6.68}
\]

The first term - called phobic term, typically looks as in Fig.5 the second term \( \sim |\nabla c|^2 \) is called phyllic term. The coefficient \( \sigma \) is proportional to the surface tension and is non-negative.

![Figure 5: Typical “double-well” structure of the phobic part of the free energy in the Allen-Cahn and Cahn-Hilliard models.](image)

As we will see, both the Cahn-Hilliard and the Allen-Cahn model can be viewed as certain evolution equations, that ensure minimization of the free-energy functional. Since the phobic part has two local minima, the system subject to such evolution will try to separate into the two phases corresponding to these two minima \( (c = 0 \text{ and } c = 1) \) for the case depicted in Fig.5, thereby the name phobic. On its own, this term would lead to a separation into regions with \( c = 1 \) and \( c = 0 \), with arbitrarily fine structure, depending on the initial conditions. Consequently, there would be lot of “interfaces” i.e. regions at the contact of these
two types of regions, with a very steep (in the limit infinite) gradient of concentration. This situations is prevented by the presence of the second term - phylic term - which penalizes the occurrence of such regions with high gradients and during the evolution is thus responsible for the so-called coarsening - i.e. tendency of the system to evolve in such a manner that the amount of interfaces between the phases is minimal. How such an evolution can look like can be seen, for example on the snapshots in Fig.6.

Let us first present the “historical” form of the various equations related to the problems of phase separation and phase change.

**Figure 6:** Example of numerical simulation of a model of Cahn-Hilliard type. The evolution starts from a random distribution (top left corner) and continues to the right by separation into two almost pure phases and gradual coarsening and coalescence (second line from left to right).


\[
\frac{\partial c}{\partial t} - \frac{\Delta(f'(c) - \sigma \Delta c)}{4\text{th order operator}!!} = 0 , \quad (6.69a)
\]

can be extended to take into account mechanical coupling with flow (Cahn-Hilliard-Navier-Stoke model), e.g. [Lowengrub and Truskinowsky](1998):

\[
\frac{\partial (\rho v)}{\partial t} + \text{div}(\rho v \otimes v) - \text{div}(2\nu \mathbb{D}(v)) + \nabla(p(\rho) - \lambda \text{div} v) + \text{div}(\sigma \nabla c \otimes \nabla c) = 0 , \quad (6.70a)\text{ Korteweg-like stress}
\]

\[
\frac{\partial (\rho c)}{\partial t} + \text{div}(\rho c v) - \Delta(f'(c) - \sigma \Delta c) = 0 . \quad (6.70b)
\]


- “order parameter” \( c \) leads to

\[
\frac{\partial c}{\partial t} = -\alpha f'(c) + \alpha \sigma \Delta c , \quad (6.71)
\]

(first term - responsible for conversion of one phase to another, second term - diffusion term, penalization of the interface). Original Allen-Cahn (Fourier) system (for unknown \( c \) and \( \vartheta \)):

\[
\frac{\partial c}{\partial t} - \beta \Delta c + \alpha f'(c) = 0 , \quad (6.72a)
\]

\[
\frac{\partial}{\partial t} (\gamma \vartheta + \lambda c) - \text{div}(\kappa \nabla \vartheta) = 0 . \quad (6.72b)
\]
- describing eg. advance interface between phases, i.e. surface of ice during melting occurring at the surface.

\[ \partial_t \gamma(\theta) - \text{div}(\kappa(\theta) \nabla \theta)) = 0. \] (6.73)

Natural questions:
1. What is the “order parameter”
2. Balance equations of single continuum - where does the equation for \( c \) come from?
3. Are these models O.K. from thermodynamic point of view?
4. How to include mechanical effects?
5. How to include thermal effects?
6. What are natural BC's for such class of models?
7. Is \( \alpha \sigma \Delta c \) in A-C model indeed connected with diffusive flux?

We will be able to provide answers to these questions and derive such class of models in a thermodynamically consistent manner in a quite simple setting of binary mixtures in the Class I framework. Our approach will also in natural way allow to include thermal phenomena.

Again, the system of balance equations (neglecting for simplicity the energy sources, i.e. \( r = 0 \)) reads:

\[
\begin{align*}
\rho \dot{c} + \text{div} j &= m, \quad (6.74a) \\
\dot{\rho} + \rho \text{div} \mathbf{v} &= 0, \quad (6.74b) \\
\rho \mathbf{v} &= \text{div} \mathbf{T} + \rho \mathbf{b}, \quad (6.74c) \\
\mathbf{T} &= \nabla \bar{\psi}, \quad (6.74d) \\
\rho \dot{\mathbf{e}} &= \mathbf{T} : \mathbb{D} - \text{div} \mathbf{q}, \quad (6.74e)
\end{align*}
\]

where \( \rho = \rho_1 + \rho_2 \) and \( c = \rho_1/\rho \). Let us now assume the fundamental relation for the Helmholtz free energy in the following form

\[ \psi = \bar{\psi}(\theta, \rho, c, \nabla c), \]

and let us compute the material time derivative

\[ \dot{\psi} = \frac{\partial \bar{\psi}}{\partial \theta} \dot{\theta} + \frac{\partial \bar{\psi}}{\partial \rho} \dot{\rho} + \frac{\partial \bar{\psi}}{\partial c} \dot{c} + \frac{\partial \bar{\psi}}{\partial \nabla c} \cdot \dot{\nabla c}. \] (6.75)

Using the already defined quantities: thermodynamic pressure \( p = \rho^2 \frac{\partial \bar{\psi}}{\partial \rho} \), chemical potential \( \mu = \frac{\partial \bar{\psi}}{\partial c} \) and relation \( -\eta = \frac{\partial \bar{\psi}}{\partial \theta} \), and employing also the thermodynamic relation \( \psi = e - \theta \eta \), we get:

\[ \rho \dot{\theta} \eta = \rho \dot{e} - p \frac{\dot{\rho}}{\rho} - \mu \dot{c} - \mu_c \cdot \nabla c, \] (6.76)

where we defined a new quantity

\[ \mu_c \overset{\text{def}}{=} \rho \frac{\partial \bar{\psi}}{\partial \nabla c}. \] (6.77)

In the following, we shall consider the following more explicit form of \( \psi \):

\[ \psi = \psi_0(\theta, \rho) + \frac{\psi_1(\theta, c)}{\rho} + \frac{\tau(\theta)}{2 \rho} |\nabla c|^2. \] (6.78)
Then it holds

$$p = \rho^2 \frac{\partial \psi_0}{\partial \rho} - \psi_1 - \frac{s(\theta)}{2} |\nabla c|^2,$$

(6.79a)

$$\mu = \frac{1}{\rho} \frac{\partial \psi_1}{\partial \epsilon},$$

(6.79b)

$$\mu_\epsilon = s(\theta) |\nabla c|.$$ 

(6.79c)

A particular example of function \( \psi \) is as follows:

$$\psi = \psi_0(\theta, \rho) + \frac{12\sigma(\theta)\epsilon^2(1-c)^2}{\epsilon \rho} + \frac{3}{4\rho} \sigma(\theta) \epsilon |\nabla c|^2,$$

(6.80)

i.e. we have \( \psi_1 = \frac{12\sigma c^2(1-c)^2}{\epsilon}, \) \( s = \frac{3}{2}\sigma \epsilon \). With such choice of parameters, \( \sigma \) represents the surface tension between the two materials (interpreted as corresponding surface free energy density of the interaction between the two materials) and \( \epsilon \) is a parameter characterizing the (equilibrium) thickness of the transition zone.

**Remark 15.** Motivation for this particular choice comes from a formula used in the literature for the free energy functional (e.g. Boyer and Lapuerta, 2006)

$$\mathcal{F}_{\sigma, \epsilon} = \int_{\Omega} \rho \psi_1 \, dx.$$

The first term \( \rho \psi_1 = 12\frac{\sigma c^2(1-c)^2}{\epsilon} \) has a double-well structure with two local minima at \( c = 0 \) and \( c = 1 \). In the process of minimization of \( \mathcal{F}_{\sigma, \epsilon} \), where the minimum corresponds to an equilibrium of the system, this term is thus responsible for separation of the material into the two “phases”. The second terms is non-negative penalty term measuring the “volume of interfaces”, in the minimization process this term is responsible for the so-called coarsening, i.e. growth of spatial scale of the two-phase structures. This particular formula has several beautiful properties, namely it allows to give the parameter \( \sigma \) a precise physical meaning - identify it with the surface density of energy stored in the interfacial zone = surface tension.

To see this, let us consider only one-dimensional case in the whole \( \mathbb{R} \), and let us minimize the free energy

$$\min_{\epsilon > 0} \int_{-\infty}^{\infty} 12\frac{\sigma}{\epsilon^2}(1-c)^2 + \frac{3}{4}\sigma \epsilon |c'|^2 \, dx,$$

(6.81)

with the additional constraint \( \lim_{x \to -\infty} c(x) = 0 \), \( \lim_{x \to +\infty} c(x) = 1 \) (i.e. “one phase on the left, the other on the right”). The corresponding Euler-Lagrange equation for the minimizer \( c_0(x) \) reads (try as an exercise):

$$-\frac{3}{2}\sigma \epsilon c''(x) + 24\frac{\sigma}{\epsilon} c_0(1-c_0)(1-2c_0) = 0,$$

$$\lim_{x \to -\infty} c_0(x) = 0,$$

$$\lim_{x \to +\infty} c_0(x) = 1.$$

An analytical solution of this equation can be found and it reads

$$c_0(x) = \frac{1}{2} \left( 1 + \tanh \left( \frac{2x}{\epsilon} \right) \right),$$

(6.82)

from where we can see that the parameter \( \epsilon \) has the interpretation of a intrinsic length scale for the thickness of the interface. Finally, computing the total energy corresponding to the found solution, we get

$$\int_{-\infty}^{\infty} 12\frac{\sigma}{\epsilon} c_0^2(1-c_0)^2 + \frac{3}{4}\sigma \epsilon |c_0'|^2 \, dx = \sigma.$$

(6.83)

Let us assume that in a 3-dimensional case we can zoom in the vicinity of the interface obtaining a locally planar geometry. Taking now the 1-d solution as an approximation of the equilibrium concentration with \( x \) now representing the distance along the normal to the interface, the obtained result indicates that \( \sigma \) would be energy of the interface integrated over the whole interface, which is nothing but the surface energy density assigned to the interface. This quantity is in physics denoted as the surface tension.
Exercise 15. Captures the average interfacial energy density (surface tension) in the interfacial region and merely wants to have a model that ensures phase separation and appropriately often sufficient, especially if one is not interested in accurate description of the concentration distribution \(\vartheta\).

Remark 16. The polynomial form of the phobic part of the free energy used above is in fact not very physical. A more physical relation is obtained by considering an ideal solution theory, in which case the corresponding phobic part of the potential reads

\[
\psi_1 = \omega_1 c(1-c) + \omega_2 k \vartheta \ln c + (1-c) \ln(1-c),
\]

(6.84)

where \(\omega_1, \omega_2\) are some parameters, \(k\) is the Boltzmann constant. The polynomial approximation is however often sufficient, especially if one is not interested in accurate description of the concentration distribution in the interfacial region and merely wants to have a model that ensures phase separation and appropriately captures the average interfacial energy density (surface) tension.

Exercise 15. From the balance (6.74a), obtain evolution equation for \(\nabla c\):

\[
\nabla c = -(\nabla v)^T \nabla c + \nabla \left( \frac{m - \operatorname{div} j}{\rho} \right).
\]

(6.85)

Proceeding further, and plugging into (6.76) balances of mass (6.74a), (6.74b), and relation (6.85), we obtain

\[
\rho \dot{\vartheta} = T^d : D^d + (m + p) \nabla v - \nabla q - \mu (m - \operatorname{div} j) + (\mu_c \otimes \nabla c) : (\nabla v)^T - \mu_c \cdot \nabla \left( \frac{m - \operatorname{div} j}{\rho} \right),
\]

(6.86)

Exercise 16. The dependence of the Helmholtz free energy \(\bar{\psi}(\vartheta, \rho, c, \nabla c)\) on \(\nabla c\) must, by the principle of material frame indifference, reduce to dependence only on the modulus of \(\nabla c\), i.e. \(\psi = \bar{\psi}(\vartheta, \rho, c, |\nabla c|)\). Show that in that case the dyadic product \(\mu_c \otimes \nabla c\) is a symmetric tensor.

We employ the identity

\[
\mu_c \cdot \nabla \left( \frac{m - \operatorname{div} j}{\rho} \right) = \operatorname{div} \left( \frac{m - \operatorname{div} j}{\rho} \mu_c \right) - \frac{(m - \operatorname{div} j)}{\rho} \operatorname{div} \mu_c
\]

(6.87)

We substitute from (6.87) into (6.86) and introduce the Korteweg tensor \(\kappa\)

\[
\kappa = \mu_c \otimes \nabla c,
\]

(6.88)

and obtain

\[
\rho \dot{\vartheta} = (T^d + \kappa^d) : D^d + \left( m + p + \frac{\operatorname{tr} \kappa}{3} \right) \nabla v - \nabla q - \mu \frac{m - \operatorname{div} j}{\rho} \mu_c - \frac{(m - \operatorname{div} \mu_c)}{\rho} m
\]

\[
+ \left[ \mu - \frac{\operatorname{div} \mu_c}{\rho} \right] \nabla j,
\]

(6.89)

Denoting

\[
\mu_c := \left( \mu - \frac{\operatorname{div} \mu_c}{\rho} \right),
\]

(6.90)

dividing (6.89) by \(\vartheta\) and rearranging, we obtain the balance of entropy in the form

\[
\rho \dot{\vartheta} + \operatorname{div} \left( \frac{q + m - \operatorname{div} j}{\rho} - \mu_c \cdot \nabla \vartheta \right)
\]

\[
= \frac{1}{\vartheta} \left( T^d + \kappa^d ight) : D^d + \left( m + p + \frac{\operatorname{tr} \kappa}{3} \right) \nabla v - \mu_c m - \left( \frac{q + m - \operatorname{div} j}{\rho} - \mu_c \cdot \nabla \vartheta \right) - \nabla \vartheta - \nabla \mu_c
\]

With the terms involving \(j\) we now have the same choice as in the Fickian case. Using the same identity as before:

\[
-j \cdot \nabla \mu_c + \mu_c j \cdot \nabla \vartheta = -j \cdot \left[ \delta \nabla \mu_c + (1-\delta) \nabla \left( \frac{\mu_c}{\vartheta} \right) \right] + \delta \mu_c j \cdot \nabla \vartheta,
\]

(6.91)
for some $\delta \in (0,1)$, we arrive at the final form of the entropy balance:

$$\rho \dot{\eta} + \text{div} \left( q + \frac{m - \text{div} j}{\rho} \mu_c - \mu_c j \right) = \frac{1}{\delta} \left( \langle T^d + \psi^d \rangle : D^d + \left( m + p + \frac{\text{tr} K}{3} \right) \text{div} \mathbf{v} - \mu_c m - \left( q + \frac{m - \text{div} j}{\rho} \mu_c - \delta \mu_c j \right) \cdot \nabla \theta - j \cdot \left( \delta \nabla \mu_c + (1-\delta) \theta \nabla \left( \frac{\mu_c}{\theta} \right) \right) \right). $$

(6.92)

Now we will consider two particular situations

**Allen-Cahn-NSF model**

Consider first the case $j = 0$, $m \neq 0$. Consider piece-wise linear closure relations, we obtain from (6.92):

$$\begin{align*}
\mathbb{T}^d + \psi^d & = 2v \mathbb{D}^d , \\
\rho + p + \frac{\text{tr} K}{3} & = \frac{2v + 3\lambda}{3} \text{div} \mathbf{v} , \\
m & = -\beta \mu_c , \\
q + \frac{m}{\rho} \mu_c & = -\kappa \nabla \theta .
\end{align*}$$

(6.93a)-(6.93d)

for $v \geq 0$, $3\lambda + 2v \geq 0$, $\beta \geq 0$, $\kappa \geq 0$, the second law of thermodynamics is automatically satisfied, i.e. the r.h.s. of (6.92) representing the entropy production is non-negative. These closures can be rewritten as

$$\begin{align*}
T & = -p \mathbb{I} + \lambda \text{div} \mathbf{v} \mathbb{I} + 2v \mathbb{D} - \psi^d , \\
m & = -\beta \left( \mu - \frac{\text{div} \mu_c}{\rho} \right) , \\
q & = -\kappa \frac{\nabla \theta}{\theta} - \frac{m}{\rho} \mu_c ,
\end{align*}$$

(6.94a)-(6.94c)

or, for our particular choice of the Helmholtz free energy (6.78), using (6.79), we obtain

$$\begin{align*}
T & = -\rho \frac{\partial \psi_0}{\partial \rho} - \psi_1 - \frac{s(\theta)}{2} |\nabla c|^2 + \lambda \text{div} \mathbf{v} \mathbb{I} + 2v \mathbb{D} - s(\theta)\nabla c \otimes \nabla c , \\
m & = -\beta \left( \frac{\partial \psi_1}{\partial c} - \text{div}(s(\theta)\nabla c) \right) , \\
q & = -\kappa \frac{\nabla \theta}{\theta} + \frac{\beta s(\theta)}{\rho^2} \left( \frac{\partial \psi_1}{\partial c} - \text{div}(s(\theta)\nabla c) \right) \nabla c .
\end{align*}$$

(6.95a)-(6.95c)

**Reduction: Allen-Cahn - Fourier model**

In order to compare with the original Allen-Cahn system, let us consider a special situation $\mathbf{v} = 0$. Consequently from (6.74b), $\rho = \rho_0$, which we set to be constant for simplicity. Let us also ignore the mechanical coupling, i.e. the balance of momentum, and let us write down the balance equation for concentration (6.74a) and for internal energy (6.74e). Plugging in the constitutive relations (6.95), we obtain

$$\begin{align*}
\rho \frac{\partial c}{\partial t} & = \frac{\beta}{\rho} \text{div}(s\nabla c) + \frac{\beta}{\rho} \frac{\partial \psi_1}{\partial c} = 0 , \\
\rho \frac{\partial e}{\partial t} & = \text{div} \left( \kappa \frac{\nabla \theta}{\theta} - \frac{\beta s(\theta)}{\rho^2} \left( \frac{\partial \psi_1}{\partial c} - \text{div}(s(\theta)\nabla c) \right) \nabla c \right) = 0 .
\end{align*}$$

(6.96a)-(6.96b)

It remains to express $e$ in terms of $\psi$, but that is easy. We know from the definition of the Helmholtz potential that

$$\bar{e}(\theta, \rho, c, \nabla c) = \psi + \partial \eta = \bar{\psi}(\theta, \rho, c, \nabla c) - \theta \frac{\partial \bar{\psi}(\theta, \rho, c, \nabla c)}{\partial \theta} ,$$

57
where we used (3.64). For our choice of Helmholtz free energy (6.78), this yields
\[ \bar{\psi} = \frac{1}{\rho} \left( \frac{\partial \tilde{e}}{\partial \bar{\psi}} + 1 \left( \frac{\partial \tilde{e}}{\partial \bar{\psi}} + \frac{1}{2} \left( s - \frac{\partial \tilde{e}}{\partial s} \right) |\nabla c|^2 \right), \] (6.97)
so unless \( s \) and \( s \) are linear functions of temperature, dependence of \( c \) and \( \nabla c \) persists also in \( e \). Differentiating \( e(\theta, \rho, c, \nabla c) \)) in (6.96b), we obtain (using \( \rho = \text{const} \) and \( \mathbf{v} = \mathbf{0} \)):
\[ \rho \left( \frac{\partial \tilde{e}}{\partial \theta} \frac{\partial \theta}{\partial t} + \frac{\partial \tilde{e}}{\partial \theta} \frac{\partial \bar{c}}{\partial t} + \frac{\partial \tilde{e}}{\partial \bar{c}} \frac{\partial \nabla c}{\partial t} \right) - \text{div} \left( \kappa \frac{\nabla \theta}{\theta} - \frac{\beta s}{\rho^2} \left( \frac{\partial \psi_1}{\partial \bar{c}} - \text{div} (s \nabla c) \right) \nabla c \right) = 0, \] (6.98)
which can be with the aid of (6.96a) written in the following form
\[ \rho \left( \frac{\partial \tilde{e}}{\partial \theta} \frac{\partial \theta}{\partial t} + \left[ \frac{\partial \tilde{e}}{\partial \bar{c}} - \text{div} (s \nabla c) \rho \right] \frac{\partial \nabla c}{\partial \theta} \right) - \text{div} \left( \kappa \frac{\nabla \theta}{\theta} \right) = 0. \] (6.99)
If we denote \( \bar{\gamma} = \rho \frac{\partial \tilde{e}}{\partial \theta} \) and the differential operator (!) \( \bar{\lambda} = \rho \left[ \frac{\partial \tilde{e}}{\partial \bar{c}} - \text{div} (s \nabla c) \rho \right] \frac{\partial \nabla c}{\partial \theta} \), assuming further that \( s \) is constant (!) and denoting \( \bar{\alpha} = \bar{\beta} s \), we can write the derived system in the form
\[ \frac{\partial \bar{c}}{\partial t} - \bar{\alpha} \Delta c + \bar{\beta} \frac{\partial \psi_1}{\partial \bar{c}} = 0, \] (6.100a)
\[ \frac{\partial}{\partial t} (\bar{\gamma} \theta + \bar{\lambda} c) - \text{div} (\bar{\kappa} \nabla \theta) = 0, \] (6.100b)
which is the original Allen-Cahn (Fourier) system, cf. (6.72). We can see that the main difference is, that our \( \bar{\lambda} \) is not a parameter or function, but it is a differential operator, because of the term \( \frac{\partial \tilde{e}}{\partial \bar{c}} - \frac{s \nabla c}{\rho} \). Expressing this term explicitly from (6.97), we obtain
\[ \frac{\partial \tilde{e}}{\partial \bar{c}} - \frac{s \nabla c}{\rho} = \frac{1}{\rho} \left( 0, \kappa \right) \frac{\partial \tilde{e}}{\partial \bar{c}} = 0, \] (6.101)
under our assumption that \( s \) is constant, \( \bar{\lambda} \) thus reduces to a function (still depending on \( \Delta c \), however).

**Cahn-Hilliard - NSF model**

Assuming now in contrast to the Allen-Cahn model situation, \( \mathbf{j} \neq \mathbf{0} \), but setting \( m = 0 \), we obtain from (6.92) assuming piece-wise linear closure relations
\[ (\mathbf{T} + \mathbf{K})^d = 2 \nu \mathbf{D}^d, \] (6.102a)
\[ \text{tr} \mathbf{K} + m = \frac{2 \nu + 3 \lambda}{3} \text{div} \mathbf{v}, \] (6.102b)
\[ \mathbf{q} - \frac{\text{div} \mathbf{j}}{\rho} \mathbf{\mu}_c = -\delta \left( \mu - \frac{\text{div} \mathbf{u}_c}{\rho} \right) \mathbf{j} = -\kappa \frac{\nabla \theta}{\theta}, \] (6.102c)
\[ \mathbf{j} = -\beta \left( \delta \nabla \mu_c + (1 - \delta) \nabla \left( \frac{\mu_c}{\theta} \right) \right). \] (6.102d)
which choice, under the assumption \( \nu \geq 0, 2 \nu + 3 \lambda \geq 0, \kappa \geq 0, \beta \geq 0 \) implies that the second law is automatically satisfied (the entropy production is non-negative). The closure relations can be rewritten as follows
\[ \mathbf{T} = -\rho \mathbf{I} + \lambda \text{div} \mathbf{v} \mathbf{D} + \mathbf{K}, \] (6.103a)
\[ \mathbf{q} = -\kappa \frac{\nabla \theta}{\theta} + \frac{\text{div} \mathbf{j}}{\rho} \mathbf{\mu}_c + \delta \left( \mu - \frac{\text{div} \mathbf{u}_c}{\rho} \right) \mathbf{j}, \] (6.103b)
\[ \mathbf{j} = -\beta \left[ \nabla \left( \mu - \frac{\text{div} \mathbf{u}_c}{\rho} \right) \right] - (1 - \delta) \left( \mu - \frac{\text{div} \mathbf{u}_c}{\rho} \right) \nabla \theta. \] (6.103c)
Plugging these equations into the balance laws (6.74), we obtain the explicit form of the Cahn-Hilliard-NSF model.
Reduction: Cahn-Hilliard - NS model

Such system is already quite complex and thus, for the sake of simplicity, let us consider simpler isothermal setting and let us investigate the balances of mass and momentum. Considering $\beta$ constant, we obtain

$$\frac{\partial (\rho v)}{\partial t} + \text{div}(\rho v \otimes v) - \text{div} 2\nu \Delta v + \nabla(p - \lambda \text{div} v) + \text{div}(s\nabla c \otimes \nabla c) = 0 ,$$  \hspace{0.5cm} (6.104a) $$\rho + \rho \text{div} v = 0 ,$$  \hspace{0.5cm} (6.104b) $$\frac{\partial (\rho c)}{\partial t} + \text{div}(\rho vc) - \beta \Delta \left(\frac{\mu - \text{div}(s\nabla c)}{\rho}\right) = 0 .$$  \hspace{0.5cm} (6.104c)

Reduction: Cahn-Hilliard model

In 1954 the original system of Cahn-Hilliard equations was derived with the additional assumption $v = 0$ (Note that in that case assuming $\rho(\cdot, t = 0) = \rho_0$ constant implies that $\rho(\cdot, t) = \rho_0 \forall t \geq 0$). In this case, inspecting the equation for concentration, we obtain

$$\frac{\partial c}{\partial t} - \beta \Delta \left(\frac{\partial \psi_1}{\partial c} - s \Delta c\right) = 0 ,$$  \hspace{0.5cm} (6.105)

with $\beta = \frac{\beta}{\rho}$, which is the original form of the Cahn-Hilliard equation.

Remark 17. Lowengrub and Truskinowsky (1998) obtained a model with an incompressibility assumption $\text{div} v = 0$ and so-called quasi-incompressibility (which has been discussed in Sec. 6.2), assuming dependence $\rho = \rho(c)$.

Remark 18. Instead of the initial assumption on the fundamental thermodynamic relation of the form $\psi = \psi(\theta, \rho, c, \nabla c)$ we could have started from e.g. $\psi = \psi(\theta, \rho, \rho_1, \nabla \rho_1)$, for details see Heida et al. (2012).

6.4 Allen-Cahn and Cahn-Hilliard models as gradient flows

Both the Allen-Cahn and Cahn-Hilliard systems can be derived as so-called gradient flows (e.g. Cowan, 2004). The idea behind is to postulate evolution of some field quantity (concentration $c$ in our example), provided we are given corresponding energy functional $\mathcal{F}$ on some Hilbert space $\mathcal{H}$ as the following abstract ODE on this Hilbert space:

$$\frac{\partial c}{\partial t} = -k \text{grad}^X \mathcal{F} , \quad k \geq 0 ,$$  \hspace{0.5cm} (6.106)

where the symbol $\text{grad}^X \mathcal{F}$ denotes $X$-constrained gradient, is understood in the sense

$$(\text{grad}^X \mathcal{F}, v)_{\mathcal{H}} = \left(\frac{\delta \mathcal{F}}{\delta c}, v\right)_{\mathcal{H}, \mathcal{H}} = \left.d \frac{\delta \mathcal{F}}{\delta c}\right|_{v = 0} (c + sv) , \quad \forall v \in X \subset \mathcal{H} ,$$  \hspace{0.5cm} (6.107)

i.e. as a Riesz representant of the constrained differential (we assume that $\mathcal{F}$ is Fréchet differentiable, the derivative thus being a member of $\mathcal{H}^\prime$). An important feature of such setting is that such gradient flow produce evolution of $c$ in such a manner that the associated energy $\mathcal{F}(c)$ decreases in time. Indeed, assuming sufficient regularity of all objects to justify the calculation, and ignoring for a moment the constraint space $X$, we get formally

$$\frac{d}{dt} \mathcal{F}(c(t)) = \left(\frac{\delta \mathcal{F}}{\delta c}, \frac{\partial c}{\partial t}\right)_{\mathcal{H}, \mathcal{H}} = \left(\text{grad} \mathcal{F}, \frac{\partial c}{\partial t}\right)_{\mathcal{H}, \mathcal{H}} = -k \| \text{grad} \mathcal{F}(c(t)) \|_{\mathcal{H}}^2 \leq 0 .$$  \hspace{0.5cm} (6.108)

Such evolution thus tends to evolve the system to a local (global) energetic minimum.

Let us consider the energy functional in the form corresponding to the concentration-dependent part of energy (6.78):

$$\mathcal{F} \overset{\text{def}}{=} \int_{\Omega} \psi_1 + \frac{s}{2} |\nabla c|^2 dx ,$$  \hspace{0.5cm} (6.109)

then we obtain (formally, provided all the formulae make sense):

$$\left(\frac{\delta \mathcal{F}}{\delta c}, v\right)_{\mathcal{H}, \mathcal{H}} = \int_{\Omega} \frac{\partial \psi_1}{\partial c} v + s \nabla c \cdot \nabla v dx$$  \hspace{0.5cm} (6.110)

The two cases - Allen-Cahn and Cahn-Hilliard models will now differ only by the choice of the corresponding Hilbert space. Since we are interested in the original A-C and C-H setting, we consider $s$ constant.
• **Allen-Cahn**: \( \mathcal{H} = L^2(\Omega), X = C_c^\infty(\Omega) \)

Seeking for a representative in \( L^2(\Omega) \) is easy, just using the Green theorem, we get

\[
\left\langle \frac{\delta \mathcal{F}}{\delta c}, v \right\rangle_{L^2(\Omega), L^2(\Omega)} = \left( \frac{\partial \psi_1}{\partial c} - s \Delta c, v \right)_{L^2(\Omega)}, \tag{6.111}
\]

i.e. the sought gradient is

\[
\text{grad}^X_{L^2} \mathcal{F}(c) = \frac{\partial \psi_1}{\partial c} - s \Delta c. \tag{6.112}
\]

Taking \( k = \tilde{\beta} \), the corresponding gradient flow is thus

\[
\frac{\partial c}{\partial t} + \tilde{\beta} \frac{\partial \psi_1}{\partial c} - \tilde{\beta} s \Delta c = 0, \tag{6.113}
\]

which is the original Allen-Cahn equation for concentration, cf. \((6.100a)\).

• **Cahn-Hilliard**: \( \mathcal{H} = H^{-1}(\Omega) = (H^1_0)^*, X = C_c^\infty(\Omega) \)

The inner product in \( H^{-1} \) is defined as follows

\[
(u, v)_{H^{-1}} \overset{\text{def}}{=} \langle \nabla u^*, \nabla v^* \rangle_{L^2(\Omega)}, \tag{6.114}
\]

where the starred functions are associates of the unstarred in the sense of the unique solution of the following problem:

\[
\begin{align*}
\Delta u^* &= u \quad \text{in } \Omega, \\
u^* &= 0 \quad \text{at } \partial \Omega,
\end{align*}
\]

i.e. formally, \( u^* = \Delta^{-1} u \). So the sought \( \text{grad}^X_{H^{-1}} \mathcal{F} \) should satisfy

\[
\begin{align*}
(\text{grad}^X_{H^{-1}} \mathcal{F}, v)_{H^{-1}} &= \langle \nabla (\text{grad}^X_{H^{-1}} \mathcal{F}), \nabla v^* \rangle_{L^2} = \left\langle \frac{\delta \mathcal{F}}{\delta c}, \nabla v^* \right\rangle_{\mathcal{H}^*, \mathcal{H}} = \int_\Omega \frac{\partial \psi_1}{\partial c} \Delta u^* + s \nabla c \cdot \nabla v^* \, dx \\
&= \int_\Omega \frac{\partial \psi_1}{\partial c} \Delta u^* + s \nabla c \cdot \nabla v^* \, dx = \int_\Omega \nabla \frac{\partial \psi_1}{\partial c} \cdot \nabla v^* + s \nabla \Delta c^* \cdot \nabla v^* \, dx \\
&= \int_\Omega \left\{ -\Delta \left( \frac{\partial \psi_1}{\partial c} \right)^* + (s \Delta^2 c^*) \right\} \cdot \nabla v^* \, dx = \left( -\Delta \frac{\partial \psi_1}{\partial c} + s \Delta^2 c, v \right)_{H^{-1}},
\end{align*}
\]

and thus the corresponding gradient flow reads, taking again \( k = \tilde{\beta} \):

\[
\frac{\partial c}{\partial t} - \tilde{\beta} \Delta \left( \frac{\partial \psi_1}{\partial c} - s \Delta c \right) = 0, \tag{6.115}
\]

which is the original Cahn-Hilliard equation for concentration, cf. \((6.105)\).

### 6.5 Chemical reactions

**Motivation** We remain within the Class I with the balance equations, i.e. we consider the following system of balance equations:

\[
\begin{align*}
\frac{\partial \rho}{\partial t} + \text{div}(\rho \mathbf{v}) &= 0, \quad \tag{6.116a} \\
\rho \mathbf{c}_a + \text{div} \mathbf{j}_a &= m_a, \quad a = 1, \ldots, N, \quad \tag{6.116b} \\
\sum_a c_a &= 1, \quad \sum_{a=1}^N \mathbf{j}_a = 0, \quad \sum_{a=1}^N m_a = 0, \quad \tag{6.116c} \\
\frac{\partial (\rho \mathbf{v})}{\partial t} + \text{div}(\rho \mathbf{v} \otimes \mathbf{v}) &= \text{div} \mathbb{T} + \rho \mathbf{b}, \quad \tag{6.116d} \\
\mathbb{T} &= \mathbb{T}^T, \\
\frac{\partial (\rho E)}{\partial t} + \text{div}(\rho E \mathbf{v}) &= \text{div}(\mathbb{T} \mathbf{v} - \mathbf{q}) + \rho \mathbf{b} \cdot \mathbf{v}, \quad \tag{6.116f}
\end{align*}
\]
and in this whole chapter we will solely focus on the reaction term \( m_a \). In the previous text we have already provided closure relations for \( m_a \), but we merely restricted ourselves to linear closures of the type \( m_a = -\beta_a \mu_a \). Let us briefly recall what we were doing (for the simplest “Fickian” setting). We considered an \( N \)-component mixture with specific internal or free Helmholtz/Gibbs’ energy in the form

\[
e = \hat{e}(\eta, \rho, c_\alpha), \quad \psi = \hat{\psi}(\theta, \rho, c_\alpha), \quad g = \hat{g}(\theta, p, c_\alpha),
\]

and by the standard procedure (taking time derivative and plugging the balance laws), we obtained the entropy balance in the form

\[
\rho \dot{\eta} + \text{div} \left( q - \sum_{\alpha=1}^{N} j_{\alpha} \mu_\alpha \right) = \frac{1}{\theta} \left[ T^d : \nabla^d + (m + p) \text{div} \mathbf{v} - \left( q - \sum_{\alpha=1}^{N} j_{\alpha} \mu_\alpha \right) \cdot \nabla \theta - \sum_{\alpha=1}^{N} j_{\alpha} \cdot \nabla \mu_\alpha - \sum_{\alpha=1}^{N} m_a \mu_a \right]. \tag{6.117}
\]

We will focus on the last term in the dissipation, which we will call chemical dissipation and denote \( \xi^{\text{CH}} \).

Ignoring for the moment again any possible cross-effects and assuming thus independence of the chemical reactions on the remaining dissipative processes, we will be interested in ensuring the non-negativity of chemical contribution to entropy production, i.e. in ensuring validity of

\[
0 \leq \xi^{\text{CH}} = -\sum_{\alpha} m_a \mu_a, \tag{6.118}
\]

where we recall the definition of the chemical potential

\[
\mu_\alpha = \left. \frac{\partial \hat{e}}{\partial c_\alpha} \right|_{\eta, \rho, c_\beta \neq \alpha} = \left. \frac{\partial \hat{\psi}}{\partial c_\alpha} \right|_{\theta, \rho, c_\beta \neq \alpha} = \left. \frac{\partial \hat{g}}{\partial c_\alpha} \right|_{\theta, p, c_\beta \neq \alpha}, \tag{6.119}
\]

depending on the set of independent thermodynamic variables we want to work with. The linear relations, which one might be tempted to impose, i.e. \( m_a = -\beta_a \mu_a \) (no summation), s.t. \( \beta \geq 0 \) are quite inapplicable in practice. In chemistry in particular, one needs to step out of the realm of linear force-flux relations to capture the kinetics realistically.

Another deficiency of such type of constitutive closure is that in the process of its derivation, we haven’t at any stage employed the information about the atomic/molecular structure of the matter, in particular the fact that in chemical reactions, only bonds between the atoms and molecules become disrupted or created, but the atoms themselves do not transform (unlike in nuclear reactions). This additional assumption of conservation of atoms or some of their combinations, will impose additional restrictions on the sought constitutive theory, stronger than the assumption of the conservation of mass in the reactions \( \sum_{\alpha=1}^{N} m_a = 0 \). Our aim will be to enforce this statement/observation formally into our theory and we will see the important consequences it will have on the closure relations and also on the notion of chemical equilibrium.

We will focus on the following topics

- **Stoichiometry** (= mathematical description of chemical reactions, using the apparatus of linear algebra).

- **Mixture of ideal gases** as the simplest possible mixture model will serve us to identify explicitly the form of the chemical potential and to infer its general structure in more general cases.

- **Chemical equilibrium** will be studied as a special process in which there is no dissipation due to reactions, and we will derive the **equilibrium mass action law**

- Outside the equilibrium we will study **chemical kinetics**, i.e. look for constitutive relations for the reaction rates.

### 6.5.1 Stoichiometry

Stoichiometry is a discipline providing the *mathematical description of chemical reactions*. Let us assume that we are dealing with a \( N \)-component mixture with components indexed by \( \alpha = 1, \ldots, N \). Let us assume that all the components are composed of a set of \( Z \) different elements, for which we shall use index \( \sigma = 1, \ldots, Z \).
Definition 2 (Molar mass). Let us remind the basic unit of atomic substances 1 mole $\pm 6,022 \times 10^{23}$ of units and let us define the molar mass of $\alpha$ component of the mixture as

$$M_\alpha = \sum_{\sigma=1}^{Z} T_{\sigma \alpha} \mathcal{A}_\sigma, \quad \alpha = 1, \ldots, N.$$  \hfill (6.120)

where $\mathcal{A}_\sigma$ denotes the atomic (molar) mass of the “element” $\sigma$ and $T$ is a matrix the columns of which captures the composition of each component in terms of the present elements.

Definition 3 (Molar production of $\alpha$ component). Let us define the molar production $J_\alpha$ as follows

$$m_\alpha = M_\alpha J_\alpha \quad \text{(no summation)} , \quad \alpha = 1, \ldots, N.$$  \hfill (6.121)

Clearly $J_\alpha$ expresses the amount of number of moles of $\alpha$ component that are produced (or consumed) during all ongoing chemical reactions per unit time and per unit volume of the mixture.

Theorem 6.1 (Conservation of number of atoms in chemical reactions). In chemical reactions, the atomic structure of the mass by definition does not change, we can express this with the use of the above definitions as follows

$$\sum_{\alpha} T_{\sigma \alpha} J_\alpha = 0 , \quad \sigma = 1, \ldots, Z.$$  \hfill (6.122)

Naturally, conservation of number of atoms is much stronger assumption than conservation of total mass during the reactions, not surprisingly we can prove

Lemma 6.2. Conservation of number of atoms implies conservation of mass in chemical reactions.

Proof. \footnote{Remark 19. Note by inspecting (6.122) that if the matrix $T_{\sigma \alpha}$ has rank equal to $N$, then it must hold $J_\sigma = 0, \forall \alpha$, which means that no chemical reactions take place. For chemically reacting system, we must therefore have rank($T_{\sigma \alpha}$)<N .}

$$\sum_{\alpha=1}^{N} m_\alpha = \sum_{\alpha=1}^{N} M_\alpha J_\sigma = \sum_{\alpha=1}^{N} \sum_{\sigma=1}^{Z} T_{\sigma \alpha} \mathcal{A}_\sigma J_\sigma = \sum_{\sigma=1}^{Z} \mathcal{A}_\sigma \sum_{\alpha=1}^{N} T_{\sigma \alpha} J_\alpha = 0 ,$$

which is the desired statement - sum of mass productions over all component of the mixture is zero.

Let us assume, in view of the previous remark that $H \stackrel{\text{def}}{=} \text{rank}(T)<N$. By excluding linearly dependent rows, we can construct from matrix $T_{\sigma \alpha} \in \mathbb{R}^{Z \times N}$ sub-matrix $S_{\sigma \alpha} \in \mathbb{R}^{H \times N}$ and it holds

$$\sum_{\alpha=1}^{N} T_{\sigma \alpha} J_\sigma = 0 , \quad \sigma = 1, \ldots, Z \iff \sum_{\alpha=1}^{N} S_{\sigma \alpha} J_\sigma = 0 , \quad \sigma = 1, \ldots, H.$$  \hfill (6.123)

and for the molar masses

$$M_\alpha = \sum_{\sigma=1}^{Z} T_{\sigma \alpha} \mathcal{A}_\sigma = \sum_{\sigma=1}^{H} S_{\sigma \alpha} \mathcal{A}_\sigma ,$$  \hfill (6.124)

where $\mathcal{A}_\sigma$ is so-called atomic substance (certain linear combination of atoms $\mathcal{A}_\sigma$). In view of this, a minimal version of the conservation law for atoms concerns only the independent atomic substances.

Let us have $N$ components of the mixture, and let us introduce an $N$-dimensional linear vector space $\mathcal{V}$ with an orthonormal basis $\{ \mathbf{e}_\alpha \}_{\alpha=1}^{N}$, $\mathbf{e}_\sigma = \mathbf{e}_\alpha, \forall \alpha$. Let us define the vector of molar masses $\mathbf{M}$

$$\mathbf{M} = \sum_{\alpha=1}^{N} M_\alpha \mathbf{e}_\alpha ,$$  \hfill (6.125)

and the vector of molar reaction speed $\mathbf{J}$:

$$\mathbf{J} = \sum_{\alpha=1}^{N} J_\alpha \mathbf{e}_\alpha .$$  \hfill (6.126)
Let us further define $H$ linearly independent vectors

$$f_{a} \overset{\text{def}}{=} \sum_{a=1}^{N} S_{\sigma a} e^{a}, \quad \sigma = 1, \ldots, H,$$  \hspace{1cm} (6.127)

where $H$ is the number of linearly independent rows of matrix $S$ and let us define subspace $W \overset{\text{def}}{=} \text{span}(f_{a})_{a=1}^{H}$. Its orthogonal complement, denoted $V$ represents the so-called reaction subspace of $W$:

$$W = \mathcal{W} \oplus V, \quad V \perp W.$$  \hspace{1cm} (6.128)

It holds $M \in W$ and $J \in V$. Indeed

$$M = \sum_{a=1}^{N} M_{a} e^{a} = \sum_{a=1}^{H} S_{\sigma a} e^{a} = \sum_{a=1}^{H} \sum_{\alpha=1}^{N} S_{\sigma a} e^{a} \in W.$$  \hspace{1cm} (6.129)

Furthermore, as a direct consequence of the law of conservation of atomic substances, we get

$$J \cdot f_{a} = \left( \sum_{a=1}^{N} J^{a} e^{a} \right) \cdot \left( \sum_{a=1}^{H} S_{\sigma a} e^{a} \right) = \sum_{a=1}^{H} J^{a} S_{\sigma a} = 0, \quad \sigma = 1, \ldots H,$$  \hspace{1cm} (6.130)

i.e. $J \in W^\perp = V$.

Remark 20. The statement just proved implies immediately conservation of mass in chemical reactions. Indeed, we have

$$0 = J \cdot M = \left( \sum_{a=1}^{N} J^{a} e^{a} \right) \cdot \left( \sum_{a=1}^{H} M_{a} e^{a} \right) = \sum_{a=1}^{H} M_{a} J^{a} = \sum_{a=1}^{N} m^{a} = 0.$$  \hspace{1cm} (6.131)

Let now $(g^{p})_{p=1}^{N-H}$ be the basis of the reaction space $V$

$$g^{p} = \sum_{a=1}^{N} P^{pa} e^{a} \implies P^{pa} = g^{p} \cdot e^{a}.$$  \hspace{1cm} (6.132)

and let $(g^{q})_{q=1}^{N-H}$ be the associated dual base in the sense:

$$g^{p} \cdot g^{q} = \delta^{p}_{q}, \quad \forall p, q = 1, \ldots, N-H.$$  \hspace{1cm} (6.133)

with $P^{pa}$ the corresponding expansion coefficients in the $(e^{a})_{a=1}^{N}$ basis. The orthogonality relation between $V$ and $W$ then can be rewritten as:

$$0 = f_{a} \cdot g^{q} = \left( \sum_{a=1}^{N} S_{\sigma a} e^{a} \right) \cdot \left( \sum_{b=1}^{N} P^{qb} e^{b} \right) = \sum_{a=1}^{N} S_{\sigma a} P^{qa} \quad \forall q = 1, \ldots, N-H, \forall \sigma = 1, \ldots H.$$  \hspace{1cm} (6.134)

Since $M \in W$, it must hold

$$0 = M \cdot g^{q} = \left( \sum_{a=1}^{N} M_{a} e^{a} \right) \cdot \left( \sum_{a=1}^{N} P^{qa} e^{a} \right) = \sum_{a=1}^{N} M_{a} P^{qa}, \quad \forall q = 1, \ldots, N-H.$$  \hspace{1cm} (6.135)

The above relation, when the molar masses are replaced with the symbol of the reacting molecules (or atoms) represents transcription of the $N-H$ independent chemical reactions, with the $i$-th rows of the matrix $P$ corresponding to the stoichiometric coefficients of $i$-th (independent) chemical reaction.

Remark 21. It is customary to interpret the molecules with positive stoichiometric entry in $P$ as reaction products and write them on the right-hand side of a chemical reaction, and molecules with negative corresponding entry in $P$ as reactants and write them on the left-hand side of the chemical reaction.
Example: Let us consider a binary mixture of molecules of NO\(_2\) and N\(_2\)O\(_4\):

\[
N = 2: \alpha = 1\ldots\text{NO}_2, \\
\alpha = 2\ldots\text{N}_2\text{O}_4,
\]

\[
Z = 2: \sigma = 1\ldots\text{N}, \\
\sigma = 2\ldots\text{O}.
\]

Then our newly defined quantities read as follows:

\[
T = \begin{pmatrix} 1 & 2 \\ 2 & 4 \end{pmatrix}, \\
S = (1 \ 2).
\]

The orthogonal subspace is generated e.g. by \(P = (2, -1)\), from where we can directly read the stoichiometric coefficients of the corresponding reaction:

\[
2\text{NO}_2 - \text{N}_2\text{O}_4 = 0 \iff \text{N}_2\text{O}_4 \rightarrow 2\text{NO}_2.
\]

Example: Let us consider a ternary mixture of atomic oxygen O, molecular oxygen \(\text{O}_2\), and ozone molecules \(\text{O}_3\):

\[
N = 3: \alpha = 1\ldots\text{O}, \\
\alpha = 2\ldots\text{O}_2, \\
\alpha = 3\ldots\text{O}_3,
\]

\[
Z = 1: \sigma = 1\ldots\text{O}.
\]

Then our newly defined quantities read as follows:

\[
T = [1 \ 2 \ 3], \\
S = (1 \ 2 \ 3),
\]

i.e. \(H = 1, N-H = 2\). To find the orthogonal complement in general can be achieved by the following simple trick (in chemistry sometimes called as Hooyman method):

**Remark 22.** Let the rank of \(S\) be \(H\). Let us look for \(P\) in the following special form

\[
P = \begin{pmatrix}
1 & 0 & \ldots & 0 & p^{1N-H+1} & \ldots & p^{1N} \\
0 & 1 & \ldots & 0 & p^{2N-H+1} & \ldots & p^{2N} \\
0 & 0 & \ddots & 0 & \vdots & \ddots & \vdots \\
0 & 0 & \ldots & 1 & p^{N-RN-H+1} & \ldots & p^{N-HN}
\end{pmatrix}
\]

i.e. unit matrix of dimension \(N-H\) complemented with \(H \times (N-H)\) unknowns, and we are solving the following orthogonality relation:

\[
\sum_{\sigma=1}^{N} S_{\sigma \alpha} P^{\sigma \alpha} = 0 \quad \sigma = 1, \ldots, H, \quad q = 1, \ldots, N-H,
\]

which represent \(H \times (N-H)\) independent equations.

In our particular example, we look for \(P\) in the form

\[
P = \begin{pmatrix}
1 & 0 & p^{13} \\
0 & 1 & p^{23}
\end{pmatrix}
\]

and the orthogonality relations are

\[
S_{11}P^{11} + S_{12}P^{12} + S_{13}P^{13} = 0 \\
S_{11}P^{21} + S_{12}P^{22} + S_{13}P^{23} = 0 \Rightarrow 1 + 3P^{13} = 0 \\
2 + 3P^{23} = 0 \Rightarrow P = \begin{pmatrix} 1 & 0 & -1 \\ 0 & 1 & -2 \end{pmatrix},
\]

64
or, equivalently

\[ P = \begin{bmatrix} 3 & 0 & -1 \\ 0 & 3 & -2 \end{bmatrix}, \]

which corresponds to the following two independent chemical reactions:

\[ \text{O}_3 \rightarrow 3\text{O}, \]
\[ 2\text{O}_3 \rightarrow 3\text{O}_2. \]

These are the independent reactions of the system in the sense that any other reaction can be written as a linear combination of these ones. (This also includes inverse reactions, naturally). The choice of independent reactions is by no means unique, of course.

**Exercise 17.** Consider a 6-component mixture with reactants CH₄, O₂, CO₂, H₂O, CO and H₂. Identify the stoichiometric matrices \( T_{\sigma\alpha} \), and \( S_{\sigma\alpha} \) and using the ansatz for the reaction matrix as in remark (22) above, identify the set of independent chemical reactions in this system.

Since \( J \in \mathcal{V} \), we have

\[ J = \sum_{p=1}^{N-H} J_p g_p = \sum_{a=1}^{N-H} J_p P^p a e_a, \tag{6.135} \]

i.e.

\[ J^a = \sum_{q=1}^{N-H} J_q P^q a. \tag{6.136} \]

The above expression determines the molar reaction rate for \( a \) component in terms of independent chemical reactions. Plugging this relation back into (6.121), yields a standard formula for the reaction rates in chemistry literature:

\[ m_a = \sum_{q=1}^{N-H} M_a P^q a J_q \tag{6.137} \]

**Remark 23.** Let us reinspect the above formula from a different perspective. Let us assume that we are a priori given the information about the chemical reactions that take place in the system. Let the system of \( N-H \) independent chemical reactions be

\[
\begin{align*}
\zeta_f^{1,1} X_1 + a_f^{1,2} X_2 + \cdots + \zeta_f^{1,N} X_N \rightleftharpoons & \zeta_b^{1,1} X_1 + \zeta_b^{1,2} X_2 + \cdots + \zeta_b^{1,N} X_N, \\
\zeta_f^{2,1} X_1 + \zeta_f^{2,2} X_2 + \cdots + \zeta_f^{2,N} X_N \rightleftharpoons & \zeta_b^{2,1} X_1 + \zeta_b^{2,2} X_2 + \cdots + \zeta_b^{2,N} X_N, \\
& \vdots \\
\zeta_f^{N-H,1} X_1 + \zeta_f^{N-H,2} X_2 + \cdots + \zeta_f^{N-H,N} X_N \rightleftharpoons & \zeta_b^{N-H,1} X_1 + \zeta_b^{N-H,2} X_2 + \cdots + \zeta_b^{N-H,N} X_N,
\end{align*}
\]

where \( X_1, \ldots, X_N \) are the components and \( \zeta_f^{q,\beta}, \zeta_b^{q,\beta} \) are the forward and backward stoichiometric coefficients of \( q \)-th reaction. Denoting \( P^{q\beta} = \zeta_f^{q,\beta} - \zeta_b^{q,\beta} \), and considering a fixed reacting (unit) volume, with the \( \mathcal{N}(X_1), \ldots, \mathcal{N}(X_N) \), the numbers of moles of the individual species, we can see that in each (\( q \)-th) reaction it must hold

\[
\frac{1}{P^{q1}} \frac{d\mathcal{N}(X_1)}{dt} = \frac{1}{P^{q2}} \frac{d\mathcal{N}(X_2)}{dt} = \cdots = \frac{1}{P^{qN}} \frac{d\mathcal{N}(X_N)}{dt} \overset{\text{def}}{=} J_q, \quad q = 1, \ldots, N-H. \tag{6.138}
\]

Consequently, the amount of species \( X_a \) produced or consumed per unit of time and unit of volume in \( q \)-th reaction is \( M_a P^{q\alpha} J_q \), with \( J_q \) denoting the so called rate of advancement of the \( q \)-th reaction. Summing for each component these contributions over all \( N-H \) independent chemical reactions, we obtain formula (6.137), and we can indeed see that the interpretation of \( P^{q\alpha} \) as stoichiometric coefficients of independent chemical reactions occurring advancing with the rates \( J_q \) is meaningful.
Let us return to the chemical dissipation rate and let’s employ the stoichiometry. We have

\[ \zeta^\text{CH} = - \sum_a m_a \mu_a = - \sum_a J^a \bar{M}_a \mu_a = - \sum_a J^a \bar{p}_a^M \mu_a = - J \cdot \bar{\mu}^M \]  

(6.139)

where we introduced the molar chemical potential and the associated vector

\[ \bar{\mu}^M_a \overset{\text{def}}{=} M_a \mu_a, \quad \bar{\mu}^M = \sum_{a=1}^N \mu_a^M e^a. \]  

(6.140)

We denote the (unique) projections of \( \bar{\mu}^M \) into the reaction space \( \mathcal{V} \) and its orthogonal complement \( \mathcal{W} \) as \( A \) and \( B \):

\[ \bar{\mu}^M = \frac{A}{\in \mathcal{V}} + \frac{B}{\in \mathcal{W}}, \]  

(6.141)

and we call \( A \) vector of chemical affinity. We find the components of \( A \) explicitly from the definition, i.e. as the projection:

\[ A = \mu^M \cdot \sum_{q=1}^{N-H} g^q g_q = \sum_{a=1}^N \mu^M_a e^a \cdot \sum_{q=1}^{N-H} g^q g_q = \sum_{q=1}^{N-H} (\sum_{a=1}^N \mu^M_a p^{qa}) g_q = \sum_{q=1}^{N-H} A^q g_q, \]  

(6.142)

hence for the contravariant components of \( A \) (w.r.t to the basis \( \{ g_q \} \)) reads

\[ A^q = \sum_{a=1}^N \mu^M_a p^{qa}, \quad q = 1, \ldots, N - H. \]  

(6.143)

Since we already know that \( J \in \mathcal{V} \) and \( \mathcal{W} \perp \mathcal{V} \), it holds

\[ \zeta^\text{CH} = - J \cdot \bar{\mu}^M = - J \cdot A = - \sum_{q=1}^{N-H} J^q A^q. \]  

(6.144)

This is one of the crucial outcomes of the stoichiometry, i.e. of considering the atomic composition of matter - it is not the whole chemical potential, but only its projection to the reaction subspace - the chemical affinity, that drives the chemical reactions and determines the chemical reaction rates.

So in order to comply with the second law of thermodynamics, we will require \( J \cdot A \leq 0 \) and we will look for constitutive relations for \( J \). In order to do so, we shall first inspect how affinity and molar chemical potential look like for a special, though in some sense very representative case of the so-called ideal gas mixture.

### 6.5.2 Mixture of ideal gasses

In a mixture of ideal gasses with common temperature, each component behaves as an ideal gas, in particular we have the following state equations

- Partial pressures:
  \[ p_a = \hat{p}_a(\theta, \rho_a) = \frac{R \theta}{M_a} \rho_a \quad \implies \quad \rho_a = \hat{\rho}_a(\theta, p_a) = \frac{M_a}{R \theta} p_a, \quad a = 1, \ldots, N, \]  

(6.145)

where \( R \) is the universal gas constant (\( R = 8.3144598 \) J K\(^{-1}\) mol\(^{-1}\)).

- Specific internal energy
  \[ e_a = \hat{e}_a(\theta) = z_a \frac{R \theta}{M_a} + \beta_a, \quad a = 1, \ldots, N, \]  

(6.146)

where \( \beta_a \) are constants and \( z_a \) is the “equi-partitioning” term (e.g. \( \frac{3}{2} \) for a monoatomic gas).
• Entropy

$$\eta_a = \hat{\eta}_a(\theta, \rho_a) = z_a \frac{R}{M_a} \ln \theta - \frac{R}{M_a} \ln \rho_a + \gamma_a, \quad a = 1, \ldots, N,$$

(6.147)

where $\gamma_a$ are constants.

Note that we don’t have any of the thermodynamic potentials in its natural variables. But we can construct Helmholtz free energy of the mixture as a whole $\tilde{\psi}(\theta, \rho_a) = \tilde{\psi}(\rho, \theta, c_a)$ from these. Assuming $pe = \sum_{a=1}^{N} \rho_a e_a$ (i.e. ignoring the diffusive kinetic energy terms in (5.82) and setting the mixture entropy in accord with (5.93)) as $\rho \eta = \sum_{a=1}^{N} \rho_a \eta_a$, we can compute

$$\rho \psi = \sum_{a} \rho_a \psi_a = \sum_{a} \rho_a (e_a - \theta \eta_a) = \sum_{a} \rho_a \left( z_a \frac{R \theta}{M_a} + \hat{\beta}_a \right) - \rho_a \theta \left( z_a \frac{R}{M_a} \ln \theta - \frac{R}{M_a} \ln \rho_a + \gamma_a \right).$$

(6.148)

Now we can evaluate the chemical potential $\mu_a$:

$$\mu_a = \left. \frac{\partial \rho \psi(\theta, \rho_1, \ldots, \rho_N)}{\partial \rho_a} \right|_{\theta, \rho \neq \rho_a} = \left( z_a \frac{R \theta}{M_a} + \hat{\beta}_a \right) - \theta \left( z_a \frac{R}{M_a} \ln \theta - \frac{R}{M_a} \ln \rho_a + \gamma_a \right) + \frac{R \theta}{M_a} \hat{\beta}_a.$$

Inverting the relation for $p_a = \hat{\rho}_a(\theta, \rho_a)$ from (6.145), and writing $\rho_a = \hat{\rho}_a(\theta, p_a)$, and defining function $\hat{g}_a$ (specific Gibbs’ free energy also called free enthalpy of (pure) a component) as follows:

$$\hat{g}_a(\theta, p_a) = \hat{e}_a(\theta, p_a) - \theta \hat{\eta}_a(\theta, p_a) + \frac{p_a}{\hat{\rho}_a(\theta, p_a)},$$

(6.149)

we can see that we obtained relation

$$\mu_a = \hat{g}_a(\theta, p_a),$$

(6.150)

with the notion $\hat{e}(\theta, p_a) \stackrel{\text{def}}{=} \hat{e}(\theta, \hat{\rho}_a(\theta, p_a))$, and $\hat{\eta}(\theta, p_a) \stackrel{\text{def}}{=} \hat{\eta}(\theta, \hat{\rho}_a(\theta, p_a))$.

We would like to replace the partial pressures with the total pressure of the mixture, so that we have the chemical potential expressed in terms of $\theta$, $p$, which are typically experimentally well-accessible and well-controllable quantities.

Exercise 18. Confirm for our Helmholtz free energy (6.145), that the Dalton’s law holds, i.e. defining the thermodynamic pressure as always according to $p = \rho \frac{\partial e_a}{\partial \rho}$, yields

$$p = \sum_{a=1}^{N} p_a.$$  

(6.151)

Let us now recall the definition of molar concentration (see (3.111))

$$c_a^M \stackrel{\text{def}}{=} \frac{\rho_a}{M_a} = \lim_{|V| \to 0+} \frac{\mathcal{M}_a(V)}{|V|} = \lim_{|V| \to 0+} \frac{n_a(V)}{|V|},$$

(6.152)

where $n_a(V)$ is the number of moles of substance $a$ in the volume $V$ of the mixture. Hence the name of the quantity. So now we can rewrite

$$\mu_a = \hat{g}_a(\theta, p_a) = \hat{g}_a(\theta, p \frac{p_a}{p}) = \hat{g}_a \left( \theta, p \frac{c_a^M}{\sum_{\beta=1}^{N} c_\beta^M} \right), \quad a = 1, \ldots, N,$$

where we employed (6.145) in order to substitute for $\frac{p_a}{p}$.

Exercise 19. Verify that

$$\hat{g}_a \left( \theta, p \frac{c_a^M}{\sum_{\beta=1}^{N} c_\beta^M} \right) = \hat{g}_a(\theta, p) + \frac{R \theta}{M_a} \ln \left( \frac{c_a^M}{\sum_{\beta=1}^{N} c_\beta^M} \right), \quad a = 1, \ldots, N.$$

Hint: $p$ in fact only appears in the expression for entropy $\hat{\eta}_a(\theta, \bullet) = \hat{\eta}(\theta, \hat{\rho}_a(\theta, \bullet))$ and in the fraction $\frac{p_a}{\hat{\rho}_a(\theta, \bullet)}$.
1. \[
\frac{xp}{\hat{\rho}_a(\theta, xp)} = \frac{R \theta}{M_a} \quad \forall x ,
\]

2. \[
\ln \hat{\rho}_a \left( \theta, p \frac{c_a^M}{\sum_{\beta=1}^N c_{\beta}^M} \right) = \ln \left( \frac{M_a}{R \theta} \frac{c_a^M}{\sum_{\beta=1}^N c_{\beta}^M} \right) = \ln \left( \frac{M_a}{R \theta} p \right) + \ln \left( \frac{c_a^M}{\sum_{\beta=1}^N c_{\beta}^M} \right) .
\]

So we summarize that we obtained

\[
\mu_a = \hat{\mu}_a(\theta, p, c_a^M) = \hat{g}_a(\theta, p) + \frac{R \theta}{M_a} \ln \left( \frac{c_a^M}{\sum_{\beta=1}^N c_{\beta}^M} \right) , \quad a = 1, \ldots, N . \tag{6.154}
\]

We can rewrite it a bit more as follows. Using

\[
\sum_{\beta=1}^N c_{\beta}^M = \sum_{\beta=1}^N \frac{p_{\beta}}{M_{\beta}} = \frac{1}{R \theta} \sum_{\beta=1}^N p_{\beta} = \frac{p}{R \theta} , \tag{6.155}
\]

so that we can absorb

\[
\mu_a = \hat{g}_a(\theta, p) - \frac{R \theta}{M_a} \ln \left( \frac{p}{R \theta} \right) + \frac{R \theta}{M_a} \ln c_a^M , \quad a = 1, \ldots, N , \tag{6.156}
\]

i.e.

\[
\mu_a(p, \theta, c_a^M) = \mu_a^0(p, \theta) + \frac{R \theta}{M_a} \ln c_a^M , \quad a = 1, \ldots, N , \tag{6.157}
\]

or in terms of the molar potential

\[
\mu_a(p, \theta, c_a^M) = \mu_a^0(p, \theta) + R \theta \ln c_a^M , \quad a = 1, \ldots, N . \tag{6.158}
\]

Remark 24. This expression is widely used, despite being slightly confusing. While \(c_a^M\) is a dimensionless quantity as an argument of the logarithm, \(c_a^M\) is not. One should always keep in mind original formula (6.157), when working with (6.158).

The expression (6.158) is a characteristic formula for the chemical potential of so-called ideal solutions. Despite we derived it for a very special model of ideal mixture of gasses, the applicability of this formula is in fact very large and holds in many practical situations. In cases, when ideality of the solution is no-longer a viable approximation, a generalization of such formula is used, introducing the so-called activity \(a_a(c_a^M)\):

\[
\mu_a(p, \theta, a_a(c_a^M)) = \mu_a^0(p, \theta) + R \theta \ln a_a(c_a^M) , \quad a = 1, \ldots, N . \tag{6.159}
\]

In the ideal case, activity \(a_a = c_a^M\). Another popular notion is the so-called activity coefficient \(\gamma_a\) defined as \(a_a = \gamma_a(c_a^M)c_a^M\), being one in ideal solutions.

6.5.3 Chemical equilibrium

In this chapter we will use the explicit form of the chemical potential which we obtained in the previous section in order to investigate a special class of chemical process - the chemical equilibrium. We have seen that the chemical dissipation reads

\[
\xi^{\text{CH}} = - \mathbf{J} \cdot \mathbf{A} , \tag{6.160}
\]

In equilibrium, which we will denote by symbol \(^+\), no dissipation takes place, i.e. \(\xi^{\text{CH}^+} = 0\). This implies that either

\[
\mathbf{J}^+ = \mathbf{0} , \quad \text{or } A^+ = \mathbf{0} . \tag{6.161}
\]
Here, we postulate the chemical equilibrium to be the process in which

\[ A^+ = 0 \quad \text{and} \quad J^+(A^+) = 0 \]  

(6.162)

Let us investigate the first condition \( A^+ = 0 \) that is

\[ 0 = \sum_{q=1}^{N-H} (A^q)^+ \mathbf{g}_q = \sum_{q=1}^{N-H} N_{\alpha}^\mathbf{0} P^{\mathbf{q}a} \mathbf{g}_q = \sum_{q=1}^{N-H} \left( \sum_{\alpha=1}^N \left( \mu_{\alpha}^{\mathbf{0}a} + R \theta \ln \alpha_{\alpha}^{\mathbf{a}} \right) P^{\mathbf{q}a} \right) \mathbf{g}_q , \]

so it must hold

\[ \sum_{\alpha=1}^N \left( \mu_{\alpha}^{\mathbf{0}a} + R \theta \ln \alpha_{\alpha}^{\mathbf{a}} \right) P^{\mathbf{q}a} = 0 \quad q = 1, \ldots, N-H . \]  

(6.164)

Let us define the so called equilibrium constant \( K_q(\theta, p) \)

\[ K_q(\theta, p) = \prod_{\alpha=1}^N (\alpha_{\alpha}^{a})^{P_{\mathbf{e}a}} , \quad q = 1, \ldots, N-H . \]  

(6.166)

Exercise 20. Let us consider the following reaction, called Haber-Bosch synthesis of amonic:

\[ N_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3 , \]

which takes place in a closed container. Let the initial composition of the mixture be as follows:

\[ n_{N_2} = 1 \text{ mole} , \]
\[ n_{\text{H}_2} = 3 \text{ moles} , \]
\[ n_{\text{NH}_3} = 0 \text{ moles} . \]

What is the resultant equilibrium composition of the mixture provided we know the equilibrium constant of the reaction at the given pressure and temperature?

Solution: So we have \( N = 3 (\alpha = 1 \sim N_2, \alpha = 2 \sim \text{H}_2, \alpha = 3 \sim \text{NH}_3) \) and \( Z = 2 (\sigma = 1 \sim N, \sigma = 2 \sim O). \) The matrix \( T \) thus reads

\[ T = \begin{pmatrix} 2 & 0 & 1 \\ 0 & 2 & 3 \end{pmatrix} \]

\[ H = \text{rank}(T) = 2 , \]

i.e. \( S = T \), and thus \( P \) matrix has rank 1 and it can be picked e.g. as

\[ P = \begin{pmatrix} -1 & -3 & 2 \end{pmatrix} , \]

which indeed corresponds to the considered reaction \( N_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3 \), the only independent reaction in the system. Now the balances mass read

\[ \frac{\partial r_\alpha}{\partial t} + \text{div} r_\alpha v_\alpha = m_\alpha , \quad \alpha = 1, 2, 3. \]

Let us integrate these relations over the container \( \Omega \), the volume of which is \( V \), and employ the assumption of closedness of the container \( \Rightarrow v_\alpha \cdot n = 0, \forall \alpha \) at \( \partial \Omega \). We get, assuming \( m_\alpha \) to be uniform in \( \Omega \):

\[ \frac{\partial \mathcal{M}_\alpha(\Omega, t)}{\partial t} = V m_\alpha = V M_\alpha P^{1a} J_1(t) , \quad \alpha = 1, 2, 3 , \]

with \( \mathcal{M}_\alpha(\Omega, t) \) the total mass of \( \alpha \) component in \( \Omega \) at time \( t \). Dividing by molar masses \( M_\alpha \) and integrating w.r.t time from the initial time \( t=0 \) to arbitrary \( t \geq 0 \):

\[ \frac{n_\alpha(\Omega, t)}{P^{1a}} - \frac{n_\alpha(\Omega, 0)}{P^{1a}} = V \int_0^t J_1 dt \quad \alpha = 1, 2, 3 , \]

advancement of reaction 69
where \( n_\alpha(\Omega, t) \) in the number of moles of \( \alpha \) component in \( \Omega \) at time \( t \). When interested in the **equilibrium composition**, we do not need to know \( J_1 \) i.e. the chemical kinetics. We can eliminate the common (unknown) advancement of reaction and write

\[
\frac{n_1(\Omega, t)}{P^{11}} - \frac{n_1(\Omega, 0)}{P^{11}} = \frac{n_2(\Omega, t)}{P^{12}} - \frac{n_2(\Omega, 0)}{P^{12}} = \frac{n_3(\Omega, t)}{P^{13}} - \frac{n_3(\Omega, 0)}{P^{13}},
\]

which are two (!) independent reactions for 3 unknowns \( n_1(\Omega, t), n_2(\Omega, t), n_3(\Omega, t) \). In particular, for the equilibrium values, using the initial conditions, the two independent relations (switching from indexing by numbers to stoichiometric labels for better clarity) read

\[
\begin{align*}
n^+_2 - 1 &= -\frac{n^+_{\text{NH}_3}}{2}, \\
n^+_3 - 1 &= -\frac{n^+_{\text{NH}_3}}{2}.
\end{align*}
\]

The missing relation, available only in equilibrium (!) is the equilibrium mass action law, which in this case reads:

\[
\left(\frac{c^+_{\text{NH}_3}}{c^+_2}\right)^2 = K_1(\theta, p).
\]

Expressing

\[
n^+_a = V(c^+_a), \quad a = 1, 2, 3,
\]

we get

\[
\frac{\left(n^+_{\text{NH}_3}\right)^2}{n^+_2 \left(n^+_3\right)^3} = \frac{1}{V^2} K_1(\theta, p).
\]

Solution of this nonlinear algebraic system yields the equilibrium composition.

### 6.5.4 Chemical kinetics

So far we have only investigated equilibrium process (chemical equilibrium), in which \( J^+ = 0, A^+ = 0 \). Now we will finally investigate the actual chemical reaction, i.e. the case when \( J \neq 0 \). We will discuss two approaches.

**Taylor expansion constrained by equilibrium relations** In the first approach we will proceed in several consequent steps:

1. We perform ansatz of the molar reaction rates in the form of a Taylor expansion (around zero), in activities or in molar concentrations.
2. We employ equilibrium mass action law and condition of equilibrium in order to reduce the number of coefficients of the expansion.
3. We constrain the reduced form by investigating the validity of the second law.

Let us attempt to clarify the whole procedure first on a simple example and then come back to the general case. Consider again two molecules: \( \text{NO}_2 (\alpha=1) \) and \( \text{N}_2\text{O}_4 (\alpha=2) \). We already know, that only one independent reaction may take place, e.g. \( \text{N}_2\text{O}_4 \rightarrow 2\text{NO}_2 \), in which case the reaction matrix reads \( P = (2, -1) \). Let us now look for the corresponding rate of this reaction \( J_1 \) in the form

\[
J_1 = J_1(\theta, p, a_1, a_2).
\]

In equilibrium, the concentrations must satisfy the mass action law:

\[
K_1(\theta, p) = (a_1^+)^2 (a_2^+)^{-1}, \quad (6.167)
\]

70
with $K_1$ the corresponding equilibrium constant. Let us look for $J_1$ in the form of a polynomial of maximal degree $D = 2$ in the two activity coefficients $a_1, a_2$ i.e. let the ansatz for the reaction kinetics be

$$J_1 = k_{00} + k_{10}a_1 + k_{01}a_2 + k_{20}(a_1)^2 + k_{11}a_1a_2 + k_{02}(a_2)^2,$$  \hspace{1cm} (6.168)

where the coefficients $k_{ij}$ may, possibly still depend on pressure and temperature, but do no longer depend on activities. Let us now employ the equilibrium assumptions $J_1(a^+) = 0$:

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

$$= k_{00} + k_{10}a_1^+ + k_{01}K_1^{-1}(a_1^+)^2 + k_{20}(a_1^+)^2 + k_{11}a_1^+K_1^{-1}(a_1^+)^2 + k_{02}K_1^{-2}(a_1^+)^4,$$

where in the second equality, we substituted from the mass action law for $a_2^+$. By collecting the terms of same power in $a_1^+$, and realizing that the equilibrium concentrations of $a_1^+$ are arbitrary (can be arbitrarily varied by the choice of initial concentrations, for example), all the coefficients at all powers of $a_1^+$ must be zero. We get the following constraints on the coefficients of the polynomial

$$k_{00} = 0, \quad k_{10} = 0, \quad k_{01}K_1^{-1} + k_{20} = 0, \quad k_{11} = 0, \quad k_{02} = 0.$$

Plugging now back to the original ansatz formula for $J_1$ \textbf{(6.168)} we obtain

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

Finally, let us check whether, or under which conditions this satisfies the second law. I.e. let us inspect

$$\xi^{CH} = -J_1A^1 .$$

Let us evaluate the affinity $A^1$:

$$A^1 = \sum_{a=1}^{N} \mu^d_{a}P^{1a} = (2\mu_1^0 - \mu_2^0) + R\vartheta \ln \left( \frac{a_2^2}{a_2} \right) = R\vartheta \ln \left( K_1^{-1} \frac{a_2^2}{a_2} \right) .$$

and thus

$$\xi^{CH} = -k_{01}(a_2 - K_1^{-1}a_1^+)^2R\vartheta \ln \left( K_1^{-1} \frac{a_2^2}{a_2} \right) = k_{01}R\vartheta \ln \left( a_2 - K_1^{-1}a_1^+ \right) \left( \ln(a_2) - \ln(K_1^{-1}a_1^+) \right) .$$

and thus we see, thanks to the fact that logarithm is a monotone increasing function, that

$$\xi^{CH} \geq 0 \iff k_{01} \geq 0 .$$

So, under the assumption $k_{01} \geq 0$, we obtained a thermodynamically consistent description of reaction kinetics of the reaction $N_2O_4 \rightarrow 2 NO_2$ in the form

$$J_{N_2O_4 \rightarrow 2NO_2} = k(a_{N_2O_4} - K_1^{-1}a_{NO_2}^2) .$$

Note that the sign of the parenthesis depends on which “side” from the equilibrium given by the eq. mass action law the system is. If we have more products than corresponding to equilibrium, the parenthesis becomes negative, and the reaction goes backwards. So kinetics describes in fact both cases - the forward and backward reaction simultaneously, which is sometimes expressed by writing the reaction as $N_2O_4 \rightleftharpoons 2 NO_2$ and we shall thus write

$$J_{N_2O_4 \rightleftharpoons 2NO_2} = k(a_{N_2O_4} - K_1^{-1}a_{NO_2}^2) .$$

In reality both equations the forward and the backward one happen simultaneously and it is only the overall balance of these two processes which determines whether in total the number of “reactants” decreases and number of “products” increases (i.e. reaction goes forwards) or the other way around (reaction goes backwards). The definition of reactants and products is thus only formal and depends on our choice of the independent chemical reaction (i.e. the choice of matrix $P$). Structure of the formula for reaction rate which we obtained reflects this idea of two reactions happening simultaneously: the forward reaction (dissociation
of $\text{N}_2\text{O}_4$) with the rate $J_f = k_f a_{\text{N}_2\text{O}_4}^2$ and the backward reaction (synthesis of $\text{NO}_2$) with the rate $J_b = k_b a_{\text{NO}_2}^2$, where $k_f$ and $k_b$ are kinetic parameters of the forward and backward reactions, which satisfy $\frac{k_f}{k_b} = K$, $K$ being the equilibrium constant of the reaction. This type of chemical kinetics is quite generic and is sometimes referred to as “non-equilibrium mass action law”.

Let us consider now still one reaction, but with more reactants and products. For a reaction of the form

$$\sum_{1}^{N} \xi_{f}^i X_i + \sum_{1}^{N} \xi_{b}^i X_i \rightarrow \sum_{1}^{N} \zeta_{f}^i X_i + \sum_{1}^{N} \zeta_{b}^i X_i$$

where $X_1, \ldots, X_N$ are the reacting species and $\xi_{f}^{i}, \xi_{b}^{i}$ are the forward and backward stoichiometric coefficients, we recall the sign convention $P^{1\beta} = \xi_{b}^{i} - \xi_{f}^{i}$, i.e. “products” having positive stoichiometric coefficients, “reactants” having negative ones. Let us look for the reaction kinetics in the form of a polynomial of degree $D$ in the chemical activities, i.e.

$$J_1 = \sum_{\nu=0}^{Q} k_{\nu} \prod_{a=1}^{N} a_{a}^{\nu a}, \quad \text{s.t. multi-indices } \nu_{\beta} \text{ satisfy } \sum_{a=1}^{N} \nu_{\beta a} \leq D \quad \forall \beta=1, \ldots, Q,$$

where

$$Q = \sum_{k=0}^{D} \frac{(N+k-1)!}{(N-1)!k!},$$

by this formula we mean the following:

$$J_1 = k_{0\ldots0}$$

$$+ k_{10\ldots0}a_1 + k_{010\ldots0}a_2 + \cdots + k_{00\ldots01}a_N$$

$$+ k_{110\ldots0}a_1a_2 + k_{101\ldots0}a_1a_3 \ldots + \cdots.$$

In equilibrium, it must hold

$$0 = \sum_{\nu=0}^{Q} k_{\nu} \prod_{a=1}^{N} (a_{a}^{+})^{\nu_{\alpha a}},$$

and for the given reaction, we also have the equilibrium mass action law in the form

$$K_1 = \prod_{a=1}^{N} (a_{a}^{+})^{p_{1a}}.$$

Let us from here express

$$a_{a}^{+} = K_1^{\frac{1}{N}} \prod_{a=1}^{N-1} (a_{a}^{+})^{-\frac{p_{1a}}{N-1}},$$

and let us substitute for $a_{a}^{+}$ from here to (6.173):

$$0 = \sum_{\beta=0}^{Q} k_{\nu} \prod_{a=1}^{N-1} (a_{a}^{+})^{v_{\beta a} - \frac{p_{1a}}{N}} v_{\beta N} = \sum_{\beta=0}^{Q} k_{\nu} K_1^{\frac{1}{N}} \prod_{a=1}^{N} (a_{a}^{+})^{v_{\beta a} - \frac{p_{1a}}{N}} v_{\beta N}.$$

Now there are two possibilities, each power $v_{\beta a} - \frac{p_{1a}}{N} v_{\beta N}$ either occurs exactly once, or there are multiple of them in the expansion. In the first case, the corresponding coefficient $k_{\nu} v_{\beta}$ must be identically zero. In the second case, let us have

$$v_{\beta a} - \frac{p_{1a}}{N} v_{\beta N} = v_{k_1 a} - \frac{p_{1a}}{N} v_{k_1 N}$$

$$= v_{k_2 a} - \frac{p_{1a}}{N} v_{k_2 N}$$

$$\vdots$$

$$= v_{k_s a} - \frac{p_{1a}}{N} v_{k_s N}$$

(6.177)
for some $\kappa_1, \ldots, \kappa_k$. Now all such $v_{\kappa N}$ must differ from each other and from $v_{\beta N}$, for otherwise, the above relation would imply equality of the whole multi-indices whenever they would have the same $N$-th component, and since each multi-index is unique in the original expansion, this is not possible. We can rewrite the relations (6.177) as

$$v_\beta - v_{\kappa_1} = P^1 v_{\beta N} - v_{\kappa_1 N} / p_{1N},$$
$$v_\beta - v_{\kappa_2} = P^1 v_{\beta N} - v_{\kappa_2 N} / p_{1N},$$
$$\vdots$$
$$v_\beta - v_{\kappa_k} = P^1 v_{\beta N} - v_{\kappa_k N} / p_{1N},$$

(6.178)

i.e. all such multi-indices differ by a non-zero multiple of the reaction vector $P^1$. So now the equilibrium relation (6.176) reads

$$0 = \sum \text{groups} \left( k v_{\kappa N} P_{1N} + k v_{\kappa_1} K_{1N} + \ldots + k v_{\kappa_k} K_{1N} \right) \prod_{\alpha=1}^{N} \left( a_{1}^{\alpha} \gamma_{\alpha} - \frac{p_{1N}^{\alpha}}{p_{1N}} v_{\beta N} \right),$$

where the first sum is over groups of terms with the same multi-indices. Consequently, we obtain the following relations for the coefficients

$$k v_\beta = -k v_{\kappa_1} K_{1N} \ldots - k v_{\kappa_k} K_{1N}$$

Plugging these relations back to (6.177), we can group terms as before and write

$$J_1 = \sum \text{groups} \left\{ k v_{\kappa_1} \prod_{\alpha=1}^{N} a_{\alpha}^{\gamma_{\alpha}} + k v_{\kappa_1} \prod_{\alpha=1}^{N} a_{\alpha}^{\gamma_{\alpha}} + \ldots + k v_{\kappa_k} \prod_{\alpha=1}^{N} a_{\alpha}^{\gamma_{\alpha}} \right\}$$
$$= \sum \text{groups}_{\alpha=1}^{N} a_{\alpha}^{\gamma_{\alpha}} \left\{ k v_{\kappa_1} \prod_{\alpha=1}^{N} a_{\alpha}^{\gamma_{\alpha}} + k v_{\kappa_1} \prod_{\alpha=1}^{N} a_{\alpha}^{\gamma_{\alpha}} + \ldots + k v_{\kappa_k} \prod_{\alpha=1}^{N} a_{\alpha}^{\gamma_{\alpha}} \right\}$$
$$= \sum \text{groups}_{\alpha=1}^{N} a_{\alpha}^{\gamma_{\alpha}} \left\{ k v_{\kappa_1} \left( \prod_{\alpha=1}^{N} a_{\alpha}^{\gamma_{\alpha}} + K_{1} \prod_{\alpha=1}^{N} a_{\alpha}^{\gamma_{\alpha}} \right) \right\} \ldots + k v_{\kappa_k} \left( \prod_{\alpha=1}^{N} a_{\alpha}^{\gamma_{\alpha}} + K_{1} \prod_{\alpha=1}^{N} a_{\alpha}^{\gamma_{\alpha}} \right),$$

where for the second equality, we employed relations (6.178). This kinetic formula complies with our equilibrium assumptions, since each factor in the round brackets vanishes in equilibrium. The resultant formulae represent the generic form of the non-equilibrium mass action law for one reaction expanded about zero to degree $D$. The exponents of the type $\gamma_{\alpha} v_{\kappa N} - v_{\beta N}$ are not a-priori neither positive nor whole numbers. Provided $P_{1N} = \pm 1$ (which can always be achieved by suitable normalization), one can group the terms with positive and negative coefficients (which now are whole numbers), and using the formula $x^{k} - y^{k} = (x - y)(x^{k-1} + x^{k-2} y + \ldots + x y^{k-2} + y^{k-1})$, we obtain the form

$$J_1 = \mathcal{P}_1(a_1, \ldots, a_N) \left( \prod_{\alpha=1}^{N} a_{\alpha}^{\gamma_{\alpha}} - K_{1} \right) + \mathcal{P}_2(a_1, \ldots, a_N) \left( \prod_{\alpha=1}^{N} a_{\alpha}^{\gamma_{\alpha}} - K_{1} \right)^{-1},$$

(6.179)

where $\mathcal{P}_1$ and $\mathcal{P}_2$ are functions of $a_1, \ldots, a_N$. Employing again the forward and backward stoichiometric coefficients, i.e. writing $P^{1a} = \frac{1}{b} \gamma_{\alpha}^{1a} - \gamma_{\beta}^{1a}$, we can further write

$$J_1 = \left\{ \mathcal{P}_2 \prod_{\alpha=1}^{N} a_{\alpha}^{-\gamma_{\alpha}^{1a}} - K_1 \mathcal{P}_1 \prod_{\alpha=1}^{N} a_{\alpha}^{-\gamma_{\alpha}^{1a}} \right\} \left( \prod_{\alpha=1}^{N} a_{\alpha}^{\gamma_{\alpha}^{1a}} - K_1 \prod_{\alpha=1}^{N} a_{\alpha}^{\gamma_{\alpha}^{1a}} \right)^{-1},$$

(6.180)

or, in short

$$J_1 = k(a_1, \ldots, a_N) \left( \prod_{\alpha=1}^{N} a_{\alpha}^{\gamma_{\alpha}^{1a}} - K_1 \prod_{\alpha=1}^{N} a_{\alpha}^{\gamma_{\alpha}^{1a}} \right),$$

(6.181)
where on the right-hand side we again recognize the products corresponding to forward and backward reactions, respectively. Denoting the forward kinetic coefficient \( k_f = k \) and the backward coefficient \( k_b = kK_1^{-1} \), we obtain as in the example the kinetics of the reaction in the form

\[
J_1 = k_f (a_1, \ldots, a_N) \prod_{a=1}^N a_a^{c_{1a}} - k_b (a_1, \ldots, a_N) \prod_{a=1}^N a_a^{c_{1a}}.
\]

(6.182)

It remains to inspect the validity of the second law. The affinity

\[
A^1 = \sum_{\alpha=1}^N \mu_{1\alpha} p_{1\alpha} - R \theta \ln \left( \prod_{\alpha=1}^N a_{\alpha}^{p_{1\alpha}} \right) = \sum_{\alpha=1}^N \mu_{1\alpha} p_{1\alpha} + R \theta \ln \left( \prod_{\alpha=1}^N a_{\alpha}^{p_{1\alpha}} \right),
\]

and thus, using (6.179),

\[
\xi^{CH} = -J_1 A^1 = -R \theta \varphi_1 (a_1, \ldots, a_N) \left( \prod_{\alpha=1}^N a_{\alpha}^{p_{1\alpha}} - K_1 \right) \left( \ln \prod_{\alpha=1}^N a_{\alpha}^{p_{1\alpha}} - \ln K_1 \right)
\]

\[
+ R \theta \varphi_2 (a_1, \ldots, a_N) \left( \prod_{\alpha=1}^N a_{\alpha}^{p_{1\alpha}} - K_1^{-1} \right) \left( \ln \prod_{\alpha=1}^N a_{\alpha}^{p_{1\alpha}} - \ln K_1^{-1} \right),
\]

(6.183)

by monotone increasing property of logarithm, we thus see that a sufficient condition for the requirement \( \xi^{CH} \geq 0 \) is \( \varphi_1 \leq 0 \& \varphi_2 \geq 0 \), which is the sought constraint on the functions \( \varphi_1, \varphi_2 \). Let us come back to the general case a let us look for \( J \) in the form of a polynomial of maximum degree \( D \) in chemical activities.

\[
J = \sum_{\beta=0}^Q k_{\beta} \prod_{\alpha=1}^N a_{\alpha}^{v_{\beta\alpha}}, \quad \text{s.t. multi-indices } v_{\beta} \text{ satisfy } \sum_{\alpha=1}^N v_{\beta\alpha} \leq D \quad \forall \beta = 1, \ldots, Q,
\]

(6.184)

where

\[
Q = \sum_{k=0}^D \frac{(N+k-1)!}{(N-1)k!}.
\]

(6.185)

Let us note that the coefficients \( k_{v_{\beta}} \) can still depend on temperature, pressure, etc, but no-longer on activities \( a_{\alpha} \) (or molar concentrations \( c_{\alpha} \)) in the ideal case.

Analysis such as the one in the example above can be performed for the general polynomial ansatz.

**Exercise 21.** Try the same polynomial ansatz as in the above example for reaction \( N_2O_4 \rightarrow 2NO_2 \), but this time for linear (\( D=1 \)) and cubic (\( D=3 \)) case. Can you still recast the result to the form given by the non-equilibrium mass action law? (Result: for \( D=1 \) we get \( J_1 = 0 \), for \( M = 3 \) one has \( J_1 = (k_{11} + k_{12}a_1 + k_{22}a_2) (a_2 - K_1^{-1}a_2^2) \).

For a system with \( N \) reacting components in which \( N-H \) independent reactions take place:

\[
\begin{align*}
\zeta_{f}^{1.1}X_1 + a_f^{1.2}X_2 + \cdots + \zeta_{f}^{1.N}X_N & \rightleftharpoons \zeta_{b}^{1.1}X_1 + \zeta_{b}^{1.2}X_2 + \cdots + \zeta_{b}^{1.N}X_N, \\
\zeta_{f}^{2.1}X_1 + \zeta_{f}^{2.2}X_2 + \cdots + \zeta_{f}^{2.N}X_N & \rightleftharpoons \zeta_{b}^{2.1}X_1 + \zeta_{b}^{2.2}X_2 + \cdots + \zeta_{b}^{2.N}X_N, \\
& \vdots \\
\zeta_{f}^{N-H.1}X_1 + \zeta_{f}^{N-H.2}X_2 + \cdots + \zeta_{f}^{N-H.N}X_N & \rightleftharpoons \zeta_{b}^{N-H.1}X_1 + \zeta_{b}^{N-H.2}X_2 + \cdots + \zeta_{b}^{N-H.N}X_N,
\end{align*}
\]

where \( X_1, \ldots, X_N \) are the reacting species and \( \zeta_{f}^{p,\beta}, \zeta_{b}^{p,\beta} \) are the forward and backward stoichiometric coefficients of \( p \)-th reaction, respectively with the sign convention \( p^{\beta} = \zeta_{b}^{p,\beta} - \zeta_{f}^{p,\beta} \). One can now proceed in the same spirit as in the case of one reaction. I.e., apply the \( N-H \) independent equilibrium mass action laws

\[
K_q = \prod_{\alpha=1}^N (\alpha_a^{p,\beta})^{q}, \quad q = 1, \ldots, N-H,
\]

(6.186)

to express certain \( N-H \) equilibrium activities in terms of the remaining \( H \) ones. By plugging these relations into the polynomial ansatz for equilibrium, one arrives at relations among the coefficients, some of which
must be identically zero, some, being linearly dependent. Finally, these relations are used outside equilibrium for the polynomial ansatz, and, one arrives at formulae of the form
\[ J = \cdots + k \nu_r \prod_{a=1}^{N} a^{Y_a} \left( \prod_{\gamma=1}^{N} a^{(Y_{\gamma r} - Y_{\gamma s})} - K \right) + \ldots, \]
which is a typical term in the final expansion. By the same procedure as before, one can show that the coefficient \( \nu_r - \nu_s \) is some linear combination of the stoichiometric coefficients of the chosen independent reactions, i.e. coefficients of some possible chemical reaction, and \( K \) is the corresponding equilibrium constant of this reaction. It is not straightforward to discuss the constraints implied by the second law on the coefficients of these formulae in the general case, one has to inspect case-by-case (in the same spirit as for one reaction).

**Non-linear closure based on the structure of the chemical contribution to entropy production automatically satisfying the second law.** An alternative to the procedure just described above is more in the spirit we are used to - we start from inspecting the structure of the chemical dissipation contribution to the entropy production and infer directly certain closure relation which will automatically satisfy the second law of thermodynamics.

Let us recall the chemical dissipation term in the entropy production
\[ \xi^{\text{CH}} = - \sum_{a=1}^{N} m_a \mu_a = - \sum_{a=1}^{N} \sum_{q=1}^{N-H} M_a \mu_a P^{qa} J_q = - \sum_{a=1}^{N} \sum_{q=1}^{N-H} \mu_a P^{qa} \frac{\partial}{\partial a} J_q \]

Expressing the stoichiometric coefficients as differences of the corresponding backward and forward contributions, i.e.
\[ P^{qa} = \xi^q_b - \xi^q_f, \quad q = 1, \ldots, N - H, \]
we obtain
\[ \xi^{\text{CH}} = - R \theta \sum_{q=1}^{N-H} \ln \left( K_q^{-1} \prod_{a=1}^{N} a^{\xi^q_b} \right) J_q \]

where \( k^q_f, k^q_b \) are such that
\[ \frac{k^q_b}{k^q_f} = K_q^{-1}, \quad q = 1, \ldots, N - H. \]

The revealed structure of \( \xi^{\text{CH}} \) shows that a constitutive closure
\[ J_q = k^q_f \prod_{a=1}^{N} a^{\xi^q_f} - k^q_b \prod_{a=1}^{N} a^{\xi^q_b}, \quad q = 1, \ldots, N - H, \]
automatically satisfies \( \xi^{\text{CH}} \geq 0 \) due to the fact that logarithm is monotonously increasing function. The two terms in \( \xi^{\text{CH}} \) can be interpreted as the molar reaction rates of the forward and backward reaction. Note that in equilibrium, these two really cancel out due to the equilibrium mass action law, and the equilibrium reaction rate is thus zero.

**Add remark about non-constant reaction coefficients**
**Add remark about elementary and non-elementary chemical reactions**
7 Class II mixtures

Motivation

- Porous media flow
- Swelling of muscles, diffusion of species (nutrients, drugs) through muscles
- ...

Reminder: N balances of mass for N components of the mixture, N balances of momentum for N components of mixture, One balance of energy and entropy for the mixture as a whole.

Note: fundamental problem with specification of boundary conditions

This frame is very useful for derivation and understanding of simplified models of the type Darcy, Brinkman, Forchheimer, Biot

Plan:

- Balance laws and identification of quantities that need to be specified by constitutive relations.
- Constitutive relations for $\psi$, $\xi$ in close analogy with relations for single-component continuum (i.e. working with quantities related to the mixture as a whole).
- Derivation of constitutive relations.

7.1 Balance laws

Balance laws in class II comprise the balances of mass for individual component, balances of momenta for individual components, and one balance of energy for the mixture as a whole.

\[
\frac{\partial \rho_a}{\partial t} + \text{div} (\rho_a \mathbf{v}_a) = m_a , \quad a=1,\ldots,N ,
\]

\[
\sum_{a=1}^{N} m_a = 0 ,
\]

\[
\frac{\partial (\rho_a \mathbf{v}_a)}{\partial t} + \text{div} (\rho_a \mathbf{v}_a \otimes \mathbf{v}_a) = \text{div} \mathbf{T}_a + \rho_a \mathbf{b}_a + \mathbf{I}_a + m_a \mathbf{v}_a , \quad a = 1,\ldots,N ,
\]

\[
\sum_{a=1}^{N} \mathbf{I}_a + m_a \mathbf{v}_a = 0 ,
\]

\[
\mathbf{T}_a = \mathbf{I}_a , \quad a=1,\ldots,N ,
\]

\[
\frac{\partial}{\partial t} \left( \rho \left( e + \frac{\mathbf{v}^2}{2} \right) \right) + \text{div} \left( \rho \left( e + \frac{\mathbf{v}^2}{2} \right) \mathbf{v} \right) = \text{div} (\mathbf{T} \mathbf{v} - \mathbf{q}) + \rho \mathbf{b} \cdot \mathbf{v} + \rho r .
\]

The terms in these balances, which are novel with respect to the system of balance equations for Class I, and for which now constitutive closures must be provided, are the partial Cauchy stresses $\mathbf{T}_a$ and the new interaction forces $\mathbf{I}_a$.

7.2 Interaction forces - structure inferred from balance laws

A lot about the possible structure of the interaction force can be gained by investigating macroscopic mechanical interaction in two typical situations - (i) flow of fluid around obstacles and (ii) flow of fluid through channels. Before doing so, let us gain some information about the interaction force just by rewriting the momentum balances in a slightly different manner. Let us consider a binary mixture, for simplicity. For Class I mixtures, we have derived in Sec. 6 two equivalent sets of mass balances, one in terms of partial densities $\rho_a$, the other in terms of the mixture density $\rho$, which had the classical single-component form and was supplemented with evolution equations for the $N-1$ independent concentrations. In Section 5.4, we have shown that in Class II, we can arrive at single-component balance of momentum for the mixture as a whole, which, under suitable definition of the mixture Cauchy stress and mixture body forces, has the same form as in the case of a single-component continuum. One might be interested whether we can supplement this
equation with a set of equations for some $N-1$ quantities, such that the final system would be equivalent with the system of for the partial linear momenta. This is indeed so. Let us consider a binary, non-reacting mixture (i.e. setting $m_{\alpha} = 0$) for simplicity. The two momentum balances then read

\[ \frac{\partial (\rho_1 \mathbf{v}_1)}{\partial t} + \text{div} (\rho_1 \mathbf{v}_1 \otimes \mathbf{v}_1) = \text{div} \mathbb{T}_1 + \rho_1 \mathbf{b}_1 + \mathbf{I}, \]  
\[ \frac{\partial (\rho_2 \mathbf{v}_2)}{\partial t} + \text{div} (\rho_2 \mathbf{v}_2 \otimes \mathbf{v}_2) = \text{div} \mathbb{T}_2 + \rho_2 \mathbf{b}_2 - \mathbf{I}, \]  

where we denoted $\mathbf{I} = -\mathbf{I}_2$. Equivalently, assuming moreover ($\mathbf{b}_1 = \mathbf{b}_2$ - which hold, for example if the body force is gravity), the two momentum balances read

\[ \rho_1 \frac{D_1 \mathbf{v}_1}{Dt} = \text{div} \mathbb{T}_1 + \rho_1 \mathbf{b} + \mathbf{I}, \]  
\[ \rho_2 \frac{D_2 \mathbf{v}_2}{Dt} = \text{div} \mathbb{T}_2 + \rho_2 \mathbf{b} - \mathbf{I}, \]  

reminding the definition of the convective time derivative with respect to the $\alpha$ component $\frac{D_{\alpha}}{Dt} = \frac{\partial}{\partial t} + [\mathbf{v}] \cdot \mathbf{\nabla} v_{\alpha}$. As we already know, by adding (7.2a) and (7.2b), with the definitions of mixture density $\rho = \rho_1 + \rho_2$ mixture velocity $\mathbf{v} = \frac{1}{\rho} (\rho_1 \mathbf{v}_1 + \rho_2 \mathbf{v}_2)$, mixture body force $\mathbf{b} = \frac{1}{\rho} (\rho_1 \mathbf{b}_1 + \rho_2 \mathbf{b}_2)$ we get the momentum balance in the standard single-component form

\[ \frac{\partial (\rho \mathbf{v})}{\partial t} + \text{div} (\rho \mathbf{v} \otimes \mathbf{v}) = \text{div} \mathbb{T} + \rho \mathbf{b}, \quad \text{or using the mass balance} \quad \frac{D\mathbf{v}}{Dt} = \text{div} \mathbb{T} + \rho \mathbf{b}, \]  

provided that we define the mixture stress tensor as $\mathbb{T} = \mathbb{T}_1 + \mathbb{T}_2 - \rho_1 \mathbf{u}_1 \otimes \mathbf{u}_1 - \rho_2 \mathbf{u}_2 \otimes \mathbf{u}_2$, where $\mathbf{u}_\alpha = \mathbf{v}_\alpha - \mathbf{v}$, $\alpha = 1, 2$ are the diffusive velocities. Now we want a complementary evolution equation, which would give us together with the total momentum balance (7.4) an equivalent system to the system (7.2). The quantity complementary to the mixture velocity $\mathbf{v}$ can be for example the relative velocity between the components $\mathbf{v}_1 - \mathbf{v}_2$. Observing

\[ \mathbf{v}_1 - \mathbf{v}_2 = \mathbf{u}_1 - \mathbf{u}_2 = \frac{j_1}{\rho c} - \frac{j_2}{\rho (1-c)} = \frac{j_1}{\rho c (1-c)}, \]  

(wher we used $j_1 + j_2 = 0$), we can equivalently choose $\mathbf{j} = j_1$ as complementary variable to $\mathbf{v}$ instead of $\mathbf{v}_1 - \mathbf{v}_2$. Let us now investigate the evolution equation for $\mathbf{j}$.

\[ \frac{D \mathbf{j}}{Dt} = \frac{D}{Dt} \left( \rho c (\mathbf{v}_1 - \mathbf{v}) \right) = \rho c (\mathbf{v}_1 - \mathbf{v}) + \rho c (\mathbf{v}_1 - \mathbf{v}) + \rho c \left( \frac{D\mathbf{v}_1}{Dt} - \frac{D\mathbf{v}}{Dt} \right), \]  

Using the mass balances in the form

\[ \rho = -\rho \text{div} \mathbf{v}, \]  
\[ \rho c = -\text{div} \mathbf{j}, \]  

realizing that

\[ \rho c \frac{D\mathbf{v}_1}{Dt} = \rho c \left( \frac{\partial \mathbf{v}_1}{\partial t} + [\mathbf{v}] \cdot \mathbf{\nabla} \mathbf{v}_1 \right) = \rho c \left( \frac{\partial \mathbf{v}_1}{\partial t} + [\mathbf{v}] \cdot \mathbf{\nabla} \mathbf{v}_1 \right) - \rho c [\mathbf{\nabla} \mathbf{v}_1] \mathbf{u}_1 = \rho c \frac{D\mathbf{v}_1}{Dt} - [\mathbf{\nabla} \mathbf{v}_1] \mathbf{j}, \]  

\[ \text{7.3a} \left[ \text{div} \mathbb{T}_1 + \rho c \mathbf{b} + \mathbf{I} \right] - [\mathbf{\nabla} \mathbf{v}_1] \mathbf{j} = \left[ \text{div} \mathbb{T}_1 + \rho c \mathbf{b} + \mathbf{I} \right] - [\mathbf{\nabla} \mathbf{v} - \left[ \frac{j}{\rho c} \right] \mathbf{j} \right] \mathbf{j} \]  

and employing the momentum balance for the mixture as a whole (7.4) we can recast (7.8) to the form

\[ \frac{D \mathbf{j}}{Dt} = -\mathbf{j} \text{div} \mathbf{v} - \frac{j}{\rho c} \text{div} \mathbf{j} + \text{div} \mathbb{T}_1 + \mathbf{I} - [\mathbf{\nabla} \mathbf{v}] \mathbf{j} - \left[ \frac{j}{\rho c} \right] \mathbf{\nabla} \left[ \frac{j}{\rho c} \right] \mathbf{j} \mathbf{j} - c \text{div} \mathbb{T}. \]  

Let us further express

\[ \mathbb{T} = \mathbb{T}_1 + \mathbb{T}_2 - \frac{j_1}{\rho c} - \frac{j_2}{\rho (1-c)} = \mathbb{T}_1 + \mathbb{T}_2 - \frac{j}{\rho} \left( \frac{1}{c} + \frac{1}{1-c} \right) = \mathbb{T}_1 + \mathbb{T}_2 - \frac{j}{\rho c(1-c)}, \]  

77
which, when plugged into (7.11) yields

\[
\frac{Dj}{Dt} = -(\text{div}vI + (\nabla v)I)j + I \cdot \text{div} \left( \frac{j \otimes j}{\rho c} \right) + (1-c)\text{div} T_1 - c \text{div} T_2 + c \text{div} \left( \frac{j \otimes j}{\rho c(1-c)} \right)
\]

\[
= -(\text{div}vI + (\nabla v)I)j + I \cdot \text{div} \left( \frac{j \otimes j}{\rho} \right) \left( \frac{1}{c} - \frac{1}{1-c} \right) + (1-c)\text{div} T_1 - c \text{div} T_2 - \left( \frac{j \otimes j}{\rho c(1-c)} \right) \cdot \nabla c
\]

\[
= -(\text{div}vI + (\nabla v)I)j + I \cdot \text{div} \left( \frac{j \otimes j}{\rho} \right) \left( \frac{1}{c} - \frac{1}{1-c} \right) + \text{div}((1-c)T_1 - cT_2) + \frac{T_1 + T_2 - \left( \frac{j \otimes j}{\rho c(1-c)} \right)}{\gamma} \cdot \nabla c.
\]  

(7.13)

So to summarize we have shown that the complementary balance to the mixture momentum balance (7.4) for the binary non-reactive mixture can be written in the form of an evolution equation for diffusive flux \( j \) in the form

\[
\dot{j} + ((\text{div}vI + (\nabla v)I)j + \text{div} \left( \frac{1}{\rho} \left( \frac{1}{c} - \frac{1}{1-c} \right) j \otimes j \right)) = \text{div}((1-c)T_1 - cT_2) + \nabla c + I.
\]  

(7.14)

**Remark 25.** One can show (FIXME reference), that under some conditions this evolution equation reduces to Fick’s law \( j = -k \nabla c \), or in fact to its “Maxwell-Cattaneo” form. Maxwell-Cattaneo equation is so called extended thermodynamics counterpart of the classical Fourier law for heat transfer: \( T = \frac{\partial q}{\partial t} + q = -k \nabla \theta \). This equation yields for very small \( \tau \) a very fast relaxation of \( q \) to the stationary form given by the classical Fourier law \( q = -k \nabla \theta \), but formally, it completely changes the mathematical character of the associated energy-balance – heat equation, making it hyperbolic instead of parabolic. Such form of the heat law thus solves the paradox of infinite speed of propagation of heat, known for the parabolic Fourier law.

Let us now neglect in equation (7.14) the non-linear terms \( j \otimes j \), \( (\text{div}vI)j \), \( (\nabla v)Ij \), and consider on top of it its stationary limit. We arrive at

\[
0 \approx \text{div}((1-c)T_1 - cT_2) + \nabla c + I,
\]  

(7.15)

in equilibrium, the partial Cauchy stresses reduce only to isotropic parts - partial pressures, for a binary fluid mixture, these can be shown to be of the form

\[
T_1 = -p_1 I = -c p I,
\]

\[
T_2 = -p_2 I = -(1-c) p I,
\]  

(7.16)

where \( p \) is the “mixture pressure”. Under such assumptions, we obtain equilibrium relation

\[
I = p \nabla c,
\]  

(7.17)

This is quite an important result: the interaction force, contains term \( p \nabla c \) and essentially reduces to it in equilibrium. This will be confirmed also in a different (thermodynamic) framework in Section 7.6.

### 7.3 Interaction forces - macroscopic mechanical analogies

What other terms except the equilibrium term \( p \nabla c \) can be part of the interaction force? We will employ macroscopic considerations, studying first the problem of flow of a fluid around a sphere and also the problem of flow of a fluid through channels.

#### 7.3.1 Flow around a sphere

Let us consider flow around a sphere (located in the origin) with radius \( a \), in a velocity field only perturbed by the presence of the sphere, which at infinity reads \( \mathbf{v}^\infty = (v_r, 0, 0) \), \( v_r \) being the relative velocity between the fluid (at infinity) and the sphere. In the dimensionless form, the balance of momentum becomes the Navier-Stokes equation

\[
\frac{\partial \mathbf{v}}{\partial t} + \text{div}(\mathbf{v} \otimes \mathbf{v}) = -\nabla p + \frac{1}{Re} \Delta \mathbf{v},
\]  

(7.18)
where \( Re \) is the Reynolds’ number given here as \( Re = \frac{\text{inertial forces}}{\text{viscous forces}} = \frac{\text{div}(\rho_f v \otimes v)}{\text{div}(\mu_f \Omega)} = \frac{\rho_f v^2}{\mu_f} \sim 2a \rho_f v_r \mu_f, \) \( \mu_f \) being the dynamic viscosity of the fluid. We are now interested in the total force exerted on the sphere by the fluid

\[
f = \int_{\partial \Omega} \mathbf{n} \mathbf{d} a .
\] (7.19)

Several approximations are now considered

1. **Stokes problem** - is an approximation valid provided we can neglect the inertial terms on the l.h.s. (i.e. for slow laminar flows with small \( Re \)), it reads

\[
0 = -\nabla p + \frac{1}{Re} \Delta \mathbf{v} ,
\] (7.20)

an analytical solution exists and the drag force is given by the famous Stokes formula

\[
f_{D}^{\text{Stokes}} = 6 \pi a \mu_f \mathbf{v}_r ,
\] (7.21)

valid approximately for \( Re \leq 0.2 \).

**Remark 26.** To gain some insight, for a 1mm sphere immersed in water with viscosity and density \( \mu = 10^{-3} \text{Pa s}, \rho_f = 10^3 \text{kg m}^{-3}, \) Reynolds’ number 0.2 corresponds to relative flow velocities \( v_r = \frac{Re \mu_f}{2a \rho_f} = 10^{-4} \text{ms}^{-1}! \)

2. **Oseen correction** - valid for slightly higher \( Re \) (up to \( Re \sim 2 \)), is

\[
\mathbf{v}_r^{\infty} \cdot \nabla \mathbf{v} = -\nabla p + \frac{1}{Re} \Delta \mathbf{v} ,
\] (7.22)

can also be solved analytically and yields the drag force

\[
f_{D}^{\text{Oseen}} = \frac{1}{2} \rho \pi a^2 C_D |\mathbf{v}_r| \mathbf{v}_r ,
\] (7.23)

with the drag coefficient

\[
C_D = \frac{24}{Re} \left( 1 + \frac{3}{16} Re \right) ,
\] (7.24)

where \( C_D = 24/Re \) corresponds to for the Stokes’ formula.

3. **Slip shear lift** - if the imposed flow field to which the sphere is immersed is not uniform, but if there is a horizontal gradient \( \frac{\partial \mathbf{v}}{\partial z} \neq 0 \), and if the sphere is not allowed to rotate additionally to the drag force a lift force (Saffman, 1965,1968) arises in the direction perpendicular to the flow \( \mathbf{v}_r^{\infty} \). The force is

\[
f_{L}^{\text{Shear lift}} = f_L \mathbf{e}_z = 6.46 \sqrt{\mu_f \rho_f a^2} \sqrt{\left| \frac{\partial \mathbf{v}_r}{\partial z} \right| v_r |\mathbf{v}_r| \text{sgn} \left( \frac{\partial \mathbf{v}_r}{\partial z} \right)} \mathbf{e}_z .
\] (7.25)

4. **Spin lift (Magnus force)** - if the sphere is rotating with a given angular rotational vector \( \mathbf{\omega} \) additional force is exerted

\[
f_{L}^{\text{Magnus}} = -C(v_r) \mathbf{\omega} \times \mathbf{v}_r^{\infty} ,
\] (7.26)

where \( C(v_r) \) is a lift parameter.

**Remark 27.** This force is responsible of many famous goals in soccer, when mastered, it can be a diabolically devious weapon in table tennis, it is used in airsoft guns to extend their reach, but was also used for “serious” purposes to drive ships equipped with rotating cylinders instead of sails.

5. **Virtual mass effect** - so far we considered only stationary cases, if the sphere would be accelerating in the fluid, or the other way round, if the surrounding flow was not stationary, the sphere would apart from the classical inertial force be subjected to additional drag force due to the necessity to accelerate the flow of the surrounding fluid (a phenomenon known to anybody who has ever been paddling in a canoe). A typical form of the total force associated with acceleration is then

\[
f_{D}^{\text{virtual mass}} = (m_s + m_{vm}) \mathbf{a}_{12} ,
\] (7.27)

where \( m_s \) is the mass of the sphere (this is the classical inertial term), and the virtual mass \( m_{vm} \) for a sphere reads \( m_{vm} = \frac{1}{2} \rho_f \frac{4}{3} \pi a^3 \) and \( \mathbf{a}_{12} \) is the relative acceleration between the two phases.
Remark 28. What is the class of relative accelerations, which are objective (frame indifferent)? An analysis in the context of two-phase flow has been done by reference Drew (1979) showing that a general frame-indifferent class of relative accelerations between two phases is of the following form:

\[
\mathbf{a} = \frac{\partial (\mathbf{v}_f - \mathbf{v}_s)}{\partial t} + \nabla (\mathbf{v}_f - \mathbf{v}_s) \mathbf{v}_f + (1 - \lambda) \nabla \mathbf{v}_f + (\lambda - 2) \nabla \mathbf{v}_s \quad (7.28)
\]

The derivation proceeds as follows. Consider the change of frame described by a general time-dependent translation and rotation, i.e. by the mapping \( \mathbf{x}^*(t) = \mathbf{Q}(t)(\mathbf{x}(t) - \mathbf{x}_0) + \mathbf{y}(t) \), \( t^* = t + t' \), where \( t' \in \mathbb{R} \) and \( \mathbf{Q}(t)\mathbf{Q}^T(t) = \mathbf{Q}(t)^T\mathbf{Q}(t) = \mathbf{I} \). Let us consider two continua and in each of them pick a material particle, say \( \mathbf{X}_1 \) and \( \mathbf{X}_2 \), their motion being described by the mappings \( \mathbf{x}_1(\mathbf{X}_1, t) \) and \( \mathbf{x}_2(\mathbf{X}_2, t) \) giving velocities

\[
\mathbf{v}_a = \frac{D_a \mathbf{x}_a(\mathbf{X}_a, t)}{D t}, \quad a = 1, 2.
\]

In the starred frame, these velocities read

\[
\mathbf{v}_a^*(\mathbf{X}_a, t^*) = \frac{\partial \mathbf{x}_a^*(\mathbf{X}_a, t^*)}{\partial t^*} = \mathbf{Q}(t)\mathbf{v}_a(\mathbf{X}_a, t) + \mathbf{Q}(t)\mathbf{x}_a(\mathbf{X}_a, t) + \dot{\mathbf{y}}(t), \quad \alpha = 1, 2. \quad (7.29)
\]

Taking time derivatives of the velocities yields accelerations

\[
\mathbf{a}_a = \frac{D_a \mathbf{v}_a(\mathbf{X}_a, t)}{D t}, \quad a = 1, 2,
\]

and their transformations read

\[
\mathbf{a}_a^*(\mathbf{X}_a, t^*) = \frac{\partial \mathbf{v}_a^*(\mathbf{X}_a, t^*)}{\partial t^*} = \mathbf{Q}(t)\mathbf{a}_a(\mathbf{X}_a, t) + 2\mathbf{Q}(t)\mathbf{v}_a(\mathbf{X}_a, t) + \mathbf{Q}\mathbf{x}_a(\mathbf{X}_a, t) + \ddot{\mathbf{y}}(t), \quad \alpha = 1, 2. \quad (7.30)
\]

Switching from reference description to spatial, i.e. defining two spatial velocity fields

\[
\mathbf{v}_a(\mathbf{x}, t) \overset{\text{def}}{=} \mathbf{v}_a(\mathbf{X}_a^{-1}(\mathbf{x}, t), t) \quad \alpha = 1, 2,
\]

and accelerations

\[
\mathbf{a}_a(\mathbf{x}, t) \overset{\text{def}}{=} \mathbf{a}_a(\mathbf{X}_a^{-1}(\mathbf{x}, t), t) \quad \alpha = 1, 2,
\]

eq. \((7.29)\) and \((7.30)\), then read

\[
\mathbf{v}_a^*(\mathbf{x}^*, t^*) = \mathbf{Q}(t)\mathbf{v}_a(\mathbf{x}, t) + \mathbf{Q}(t)\mathbf{x} + \dot{\mathbf{y}}(t), \quad \alpha = 1, 2, \quad (7.31)
\]

\[
\mathbf{a}_a^*(\mathbf{x}^*, t^*) = \mathbf{Q}(t)\mathbf{a}_a(\mathbf{x}, t) + 2\mathbf{Q}(t)\mathbf{v}_a(\mathbf{x}, t) + \ddot{\mathbf{x}} + \dot{\mathbf{y}}(t), \quad \alpha = 1, 2. \quad (7.32)
\]

These relations imply that relative velocity is an objective vector, since it transforms as

\[
(\mathbf{v}_1^* - \mathbf{v}_2^*)(\mathbf{x}^*, t^*) = \mathbf{Q}(t)(\mathbf{v}_1 - \mathbf{v}_2)(\mathbf{x}, t), \quad (7.33)
\]

but also that relative acceleration is not an objective vector, since

\[
(\mathbf{a}_1^* - \mathbf{a}_2^*)(\mathbf{x}^*, t^*) = \mathbf{Q}(t)(\mathbf{a}_1 - \mathbf{a}_2)(\mathbf{x}, t) + 2\mathbf{Q}(t)(\mathbf{v}_1 - \mathbf{v}_2)(\mathbf{x}, t). \quad (7.34)
\]

The troublemaker is the Coriolis term \( 2\mathbf{Q}(\mathbf{v}_1 - \mathbf{v}_2) \). In order to come up with an objective measure of mutual acceleration, let us take the spatial gradient of \((7.31)\) using \( \text{grad}(\cdot) = \text{grad}^*(\cdot)\mathbf{Q} \), expressing

\[
\dot{\mathbf{Q}} = \text{grad}^* \mathbf{v}_a^*(\mathbf{x}^*, t^*) \mathbf{Q}(t) - \mathbf{Q}(t)\text{grad} \mathbf{v}_a(\mathbf{x}, t), \quad \alpha = 1, 2.
\]

Since for the same quantity \( \dot{\mathbf{Q}} \), we have two expressions (for \( \alpha = 1, 2 \)), let us take their affine combination with some parameter \( \lambda \in \mathbb{R} \) and express

\[
2\mathbf{Q}(t)(\mathbf{v}_1 - \mathbf{v}_2) = 2(1 - \lambda)\{\text{grad}^* \mathbf{v}_1^*(\mathbf{x}^*, t^*) \mathbf{Q}(t) - \mathbf{Q}(t)\text{grad} \mathbf{v}_1(\mathbf{x}, t)\}(\mathbf{v}_1 - \mathbf{v}_2))
\]

\[
+ 2\lambda \{\text{grad}^* \mathbf{v}_2^*(\mathbf{x}^*, t^*) \mathbf{Q}(t) - \mathbf{Q}(t)\text{grad} \mathbf{v}_2(\mathbf{x}, t)\}(\mathbf{v}_1 - \mathbf{v}_2). \quad (7.35)
\]
Substituting (7.35) into (7.34) yields after some manipulation

\[
\frac{D_t^1}{D_t^*} \mathbf{v}_1 - \frac{D_t^2}{D_t^*} \mathbf{v}_2 - ([\nabla^* \mathbf{v}_1](\mathbf{v}_1^* - \mathbf{v}_2^*) - [\nabla^* \mathbf{v}_2^*](\mathbf{v}_1^* - \mathbf{v}_2^*)) + (1 - \lambda) [\nabla(\mathbf{v}_2^* - \mathbf{v}_1^*)](\mathbf{v}_1^* - \mathbf{v}_2^*) = \mathbf{Q}(t) \left\{ \frac{D_t^1}{D_t^*} \mathbf{v}_1 - \frac{D_t^2}{D_t^*} \mathbf{v}_2 - ([\nabla \mathbf{v}_1](\mathbf{v}_1 - \mathbf{v}_2) - [\nabla \mathbf{v}_2](\mathbf{v}_1 - \mathbf{v}_2)) + (1 - \lambda) [\nabla(\mathbf{v}_2 - \mathbf{v}_1)](\mathbf{v}_1 - \mathbf{v}_2) \right\},
\]

i.e. the quantity on the left-hand side transforms as an objective vector. The expression can be recast to the following form of the objective relative acceleration

\[
a_{12} = \left( \frac{D_t^1}{D_t^*} \mathbf{v}_1 - [\nabla \mathbf{v}_1](\mathbf{v}_1 - \mathbf{v}_2) \right) - \left( \frac{D_t^2}{D_t^*} \mathbf{v}_2 + [\nabla \mathbf{v}_2](\mathbf{v}_1 - \mathbf{v}_2) \right) + (1 - \lambda) [\nabla(\mathbf{v}_2 - \mathbf{\mathbf{v}_1})](\mathbf{v}_1 - \mathbf{v}_2),
\]

which is equivalent to (7.28). Another equivalent forms is

\[
a_{12} = \frac{D_t^2 \mathbf{v}_1}{D_t^*} - \frac{D_t^1 \mathbf{v}_2}{D_t^*} + (1 - \lambda) [\nabla(\mathbf{v}_2 - \mathbf{v}_1)](\mathbf{v}_1 - \mathbf{v}_2).
\]

Postulating the form of the virtual mass force as between the fluid and dispersed phase (droplets, bubbles, ...) as

\[ f_{D}^{\text{virtual mass}} = \rho_i C_{vm} \mathbf{a}_{12}, \]

the analysis of two cases with extreme values of the volume fractions of the dispersed phase yields the corresponding \( \lambda \) values: very low volume fraction of the dispersed phase, i.e. \( \lim_{\phi \to 0} \) corresponds to \( \lambda = 2 \), while the other extreme \( \lim_{\phi \to 1} \) implies \( \lambda = 0 \). For an intermediate value \( \lambda = 1 \) one gets a relatively simple and symmetric form

\[
a_{12} = \frac{D_t^2 \mathbf{v}_1}{D_t^*} - \frac{D_t^1 \mathbf{v}_2}{D_t^*}.
\]

6. **Basset force** - results from the viscous flow field created by the particle when accelerating, or equivalently, in an unsteady flow (Basset, 1888). For a laminar unsteady flow around a sphere the force reads

\[
\mathbf{f}_B^{\text{Basset}} = -6 \rho a^2 \sqrt{\pi \mu_f} \int_{t_0}^{t} \frac{1}{\sqrt{t - t'}} \frac{d\mathbf{v}_r}{dt'} dt'.
\]

7. **Buoyancy** can be computed simply in the hydrostatic approximation

\[
\left( f_L^{\text{buoyancy}} \right)_i = -\int_{\partial \Omega} \rho_n d\mathbf{a} = -p(0) \int_{\partial \Omega} n_i d\mathbf{a} = -\frac{\partial p}{\partial x_j}(0) \int_{\partial \Omega} x_j n_i d\mathbf{a} + \ldots = -\frac{\partial p}{\partial x_i}(0) \int_{\Omega} dx + \ldots,
\]

where \( (0) \) is some mid-value which gives the buoyancy lift force

\[
\mathbf{f}_L^{\text{buoyancy}} \approx -\nabla p \mathbf{V}_\Omega.
\]

For a fluid in hydrostatic equilibrium \( \nabla p = -\rho_f \mathbf{g} e_z \), and combined with the gravity force exerted on the sphere itself

\[
\mathbf{f}^{\text{gravity}} = -\rho_s \mathbf{V}_\Omega \mathbf{g} e_z,
\]

the combined force gravity+buoyancy reads

\[
\mathbf{f}_L^{\text{gravity+buoyancy}} = -(\rho_s - \rho_f) \mathbf{V}_\Omega \mathbf{g} e_z.
\]

These interaction mechanisms can now be used to construct continuum counterparts of the interaction force between a solid phase composed of small particles (moving with velocity \( \mathbf{v}_s \)) dispersed in a liquid phase moving with velocity \( \mathbf{v}_f \). The procedure is essentially to prescribe the force as \( \phi_s \mathbf{f}_s^{\text{particle}} \) (where \( \phi_s \) is the volume fraction of the solid phase), simultaneously replacing all kinematic quantities by their suitably chosen continuum counterparts. In constructing the individual terms one must also respect the basic principles of continuum constitutive theory such as principle of material frame indifference. Consequently, the following formulas can be identified
If we use $\rho v$ with velocity force, the following ansatz can be found in the literature for interaction force between solid phase moving in the fluid in the pores is negligible and we can even set $\alpha_3 = 0$. Let us now completely ignore the second momentum balance, which is possible, if the solid phase fraction and volume fraction is definitely much more complicated and depends in general on the detailed structure of the pores, their shape, etc.). So under these assumptions, the partial Cauchy stress of the fluid reads

$$\tau_f = -\phi_f p \mathbf{I}.$$  \hspace{1cm} (7.46)

If we use $\rho_f = \rho_f^m \phi_f$, the momentum balance for the fluid has reduced to

$$\mathbf{0} = -\nabla (\phi_f p) + \rho_f^m \phi_f \mathbf{g} + \mathbf{I}_f,$$  \hspace{1cm} (7.47)

if we now keep in the interaction force only the drag term and the equilibrium term, i.e. if we consider

$$\mathbf{I} = -\alpha_1 (\mathbf{v}_f - \mathbf{v}) + p \nabla \phi_f,$$  \hspace{1cm} (7.48)

Based on the extensions and generalizations of the above drag and lift contributions to the interaction force, the following ansatz can be found in the literature for interaction force between solid phase moving with velocity $\mathbf{v}_s$ dispersed in liquid moving with velocity $\mathbf{v}_f$:

$$\mathbf{I} = \alpha_1 (\mathbf{v}_s - \mathbf{v}_f) + \alpha_2 D_f (\mathbf{v}_s - \mathbf{v}_s) + \alpha_3 (\mathbf{W}_s - \mathbf{W}_f) (\mathbf{v}_s - \mathbf{v}_f) + \alpha_4 \left( \frac{D_f \mathbf{v}_s}{Dt} - \frac{D_s \mathbf{v}_f}{Dt} \right) + \alpha_5 \nabla \phi + p \nabla \phi,$$  \hspace{1cm} (7.44)

where $D_f = \frac{1}{2} (\nabla \mathbf{v}_f + \nabla^T \mathbf{v}_f)$, $\mathbf{W}_f = \frac{1}{2} (\nabla \mathbf{v}_f - \nabla^T \mathbf{v}_f)$, $D_s = \frac{1}{2} (\nabla \mathbf{v}_s + \nabla^T \mathbf{v}_s)$, $\mathbf{W}_s = \frac{1}{2} (\nabla \mathbf{v}_s - \nabla^T \mathbf{v}_s)$. Note that the expression does not contain the buoyancy force, which enters the momentum balance through the partial Cauchy stress, and it contains non-classical diffusion term $\alpha_5 \nabla \phi$ and also the last term $-p \nabla \phi$, which corresponds to the equilibrium remainder derived in the last section (only with concentration replaced by volume fraction).

### 7.4 Darcy’s law

Darcy’s law is a law describing the flow of fluids through porous media. Formulated by Henry Darcy in 1856, based on experiments of flow of water through beds of sand, it is commonly viewed as a relationship between the fluid mass flux and pressure gradient in the medium. We will show three ways how to infer the form of this law, which will also give us some insight into possible generalizations of this law.

#### 7.4.1 Reduction of two-component momentum balance

Consider a two-component medium composed of solid porous matrix and a fluid. Let the two components not interact chemically (i.e. no mass transfer between the components). In the context of class-II mixture theory, we have the following generic form of the partial momentum balances for the components:

$$\frac{\partial (\rho_f \mathbf{v}_f)}{\partial t} + \text{div} (\rho_f \mathbf{v}_f \otimes \mathbf{v}_f) = \text{div} \mathbf{T}_f + \rho_f \mathbf{g} + \mathbf{I}_f,$$  \hspace{1cm} (7.45a)

$$\frac{\partial (\rho_s \mathbf{v}_s)}{\partial t} + \text{div} (\rho_s \mathbf{v}_s \otimes \mathbf{v}_s) = \text{div} \mathbf{T}_s + \rho_s \mathbf{g} - \mathbf{I}_f,$$  \hspace{1cm} (7.45b)

where $\mathbf{I}_f = -\mathbf{I}_s$. Let us now completely ignore the second momentum balance, which is possible, if the solid matrix is for example some rock, in such case the deformation of the rock resulting from the flow of the fluid through the pores is negligible and we can even set $\mathbf{v}_s = \mathbf{0}$. Let us, moreover, neglect the inertial forces on the left-hand side of momentum balance for the fluid (this is possible for small enough Reynolds numbers) and let us, in addition, keep only the isotropic part of the partial Cauchy stress $\mathbf{T}_f$. If the (real measurable) pressure in the fluid in the pores is $p$, then the effective partial pressure exerted by the fluid on some surface of the porous medium would be $p$ times fraction of the surface exposed to the fluid. Often a good approximation is to consider average volume fraction of the fluid $\phi_f$ at the given point (though the relation between surface fraction and volume fraction is definitely much more complicated and depends in general on the detailed structure of the pores, their shape, etc.,). So under these assumptions, the partial Cauchy stress of the fluid reads

$$\mathbf{T}_f \approx -\phi_f p \mathbf{I}.$$  \hspace{1cm} (7.46)

If we use $\rho_f = \rho_f^m \phi_f$, the momentum balance for the fluid has reduced to

$$\mathbf{0} = -\nabla (\phi_f p) + \rho_f^m \phi_f \mathbf{g} + \mathbf{I}_f,$$  \hspace{1cm} (7.47)

if we now keep in the interaction force only the drag term and the equilibrium term, i.e. if we consider

$$\mathbf{I} \approx -\alpha_1 (\mathbf{v}_f - \mathbf{v}) + p \nabla \phi_f,$$  \hspace{1cm} (7.48)
we obtain Darcy's law in the form

\[
\alpha_1 \mathbf{v}_f = -\phi_f (\nabla p - \rho_f g^m). \tag{7.49}
\]

### 7.4.2 Derivation from macroscopic analogy

Let's consider a porous material and a fluid (water flowing through a bed of sand). Let us simplify the pores as channels with circular cross-section. Let us consider stationary laminar Poiseuille flow through a straight segment of a pore. Under an imposed pressure gradient in the pore, the flow - the volume of water expelled from the segment per second - would be

\[
h = \frac{\pi a^4}{8 \mu_f} |\nabla p|, \tag{7.50}
\]

where \(a\) is the radius of the pore and \(\mu_f\) is the dynamic viscosity of the fluid. A vectorial generalization, which takes into account that the pore is not straight reads

\[
h = -\frac{\pi a^4}{8 \mu_f X} \nabla p, \tag{7.51}
\]

FIXME - add figure

where \(X\) is so-called tortuosity, which is essentially a geometric factor only. Let us now move back from this idealized pore to the sand bed and consider some particular channel (pore). Let us denote \(d\) the characteristic dimension of the sand grains, and \(\phi_f \sim a^2 d^2\) the fluid volume fraction, the flux through the channel becomes

\[
h = -\frac{\phi_f^2 d^2}{\mu_f X} \nabla p, \tag{7.52}
\]

Let us denote \(\tilde{h}\) the flux of liquid per unit surface, then

\[
\tilde{h} = -\frac{k(\phi)}{\mu_f} \nabla p, \tag{7.53}
\]

where the permeability \(k(\phi) = k_0 \phi^2\), (typically in applications \(k(\phi) = k_0 \phi^n\) with \(n = 2 \ldots 3\)), and where \(k_0 := \frac{a^2}{X}\). From the definition of the volume flux (assuming the porous matrix static)

\[
\tilde{h} = \phi_f \mathbf{v}_f ,
\]

we obtain

\[
\mathbf{v}_f = -\frac{k(\phi)}{\phi_f \mu_f} \nabla p = -\frac{k_0}{\mu_f} \phi_f \nabla p. \tag{7.54}
\]

To include gravity, we only replace the pressure \(p\) with the so-called hydraulic head:

\[
p \rightarrow \underbrace{p + \rho_f^m g z}_{\text{hydraulic head}},
\]

then Darcy's law becomes

\[
\mathbf{v}_f = -\frac{k_0}{\mu_f} \phi_f (\nabla p - \rho_f^m g), \tag{7.55}
\]

compare with (7.49) and observe that we have identified the drag coefficient

\[
\alpha_1 = \frac{\mu_f}{k_0}. \tag{7.56}
\]

The assumption of laminarity of the flow can be translated into an assumption on the associated Reynolds’ number:

\[
Re = \frac{2 \rho_f v_r a}{\mu_f} \sim \frac{2 \rho_f \tilde{h} d}{\mu_f \phi_f} \sim \frac{2 \rho_f k |\nabla p| d}{\mu_f^2 \sqrt{\phi_f}} \frac{\phi_f^{3/2}}{X} \left( \frac{\rho_f \sqrt{g d^3}}{\mu_f} \right)^2,
\]

where in the last equality, we took the scale of the pressure gradient \(|\nabla p| \sim \rho_f g\), i.e. hydrostatic. For water, \((\mu_f \sim 10^{-3} \text{ Pa s}, \rho_f \sim 10^3 \text{ kg m}^{-3})\), taking we obtain \(Re \sim \frac{10^3}{1000} (100 \phi_f)^{3/2} \times (d \text{ [in mm]})^3\). For porosities of the order of units of percent, and for critical Reynolds number \(Re_{\text{crit}} \sim 10^3\) we obtain the critical pore size \(d_{\text{crit}}\) of the order of milimeters.
7.4.3 Derivation through homogenization

Let us consider a Stokes flow of a viscous incompressible fluid through channels in a porous medium with a characteristic dimension \(l\), onto which is imposed a pressure gradient of the order \(\delta p/l\), and which has porous micro-structure at scale \(d\), as in Figure 7. Let us assume a periodic structure as in Fig.7, i.e. \(\Omega\) being viewed as a union of cells \(\Omega_i^{\text{cell}}\), i.e. \(\Omega = \cup_i \Omega_i^{\text{cell}}\), and each cell \(\Omega_i^{\text{cell}}\) is composed of a fluid part \(\Omega_i^f\) and solid part \(\Omega_i^s\), such that \(\Omega_i^{\text{cell}} = \Omega_i^f \cup \Omega_i^s\), \(\forall i\). Let us define the fluid and solid parts of \(\Omega\) by

\[
\Omega^f \overset{\text{def}}{=} \cup_i \Omega_i^f, \quad \Omega^s \overset{\text{def}}{=} \cup_i \Omega_i^s.
\]

(7.57)

Then we can formulate the Stokes flow problem in the fluid part of the domain \(\Omega^f\) as follows

\[
\text{div} \, \mathbf{v} = 0 \quad \text{in} \, \Omega^f, \quad (7.58a)
\]

\[
0 = -\nabla p + \mu_f \Delta \mathbf{v} \quad \text{in} \, \Omega^f, \quad (7.58b)
\]

supplemented with boundary conditions, e.g.

\[
\mathbf{v} = 0, \quad \text{at} \, \partial \Omega^f. \quad (7.58c)
\]

Let us first rewrite the above system in a dimensionless form. Let us introduce the following scale for the flow velocity:

\[
[\mathbf{v}] = \frac{d^2 [\delta p]}{l \mu_f}, \quad (7.59)
\]

the motivation here being naturally the Darcy’s law, which we want to derive. Note that this is a typical scenario with homogenization - by the “right” choice of scales, you obtain the “right” results. Let us write down the Stokes problem in a dimensionless form, assuming the scaling of the spatial gradient with the macroscopic scale \(l\) (i.e. taking \(\nabla = \frac{1}{l} \tilde{\nabla}\)):

\[
\text{div} \tilde{\mathbf{v}} = 0 \quad \text{in} \, \tilde{\Omega}^f, \quad (7.60a)
\]

\[
0 = -\tilde{\nabla} \tilde{p} + \frac{d^2 \delta p}{l^3} \tilde{\Delta} \tilde{\mathbf{v}} \quad \text{in} \, \tilde{\Omega}^f, \quad (7.60b)
\]

\[
\tilde{\mathbf{v}} = 0, \quad \text{at} \, \partial \tilde{\Omega}^f, \quad (7.60c)
\]

where the tildes denote the dimensionless counterparts of dimensional quantities (i.e. for each quantity \(\psi\) we consider its scale \([\psi]\) and a dimensionless \(\tilde{\psi}\) such that \(\psi = [\psi] \tilde{\psi}\)). Introducing a small parameter \(\varepsilon := d/l\), and omitting the tilde symbol for brevity, we obtain

\[
\text{div} \mathbf{v}_\varepsilon = 0 \quad \text{in} \, \Omega^f, \quad (7.61a)
\]

\[
0 = -\nabla p_\varepsilon + \varepsilon^2 \Delta \mathbf{v}_\varepsilon \quad \text{in} \, \Omega^f, \quad (7.61b)
\]

\[
\mathbf{v}_\varepsilon = 0, \quad \text{at} \, \partial \Omega^f, \quad (7.61c)
\]

Figure 7: A porous medium (left) with a spatial scale \(l\), which is assumed to possess an internal structure occurring at a scale \(d\).
where we explicitly added the subscript $\varepsilon$ to the unknowns $v_\varepsilon$, $p_\varepsilon$ in order to underline the dependence of these fields on the considered micro-structure.

Now we want to employ the technique of asymptotic expansions. Consider for a given $\varepsilon$ any field variable associated with the problem, denoted $\psi_\varepsilon(x, t)$. Now the basic idea of formal asymptotic expansion is to express the quantity $\psi_\varepsilon$ as a series in powers of $\varepsilon$:

$$\psi_\varepsilon = \sum_{i=0}^{\infty} \varepsilon^i \psi^{(i)}_\varepsilon,$$

(7.62)

where $\psi^{(i)}_\varepsilon$ are yet to be specified. Since the problem is characterized by two structures: macro-structure $\Omega$ and micro-structure $\Omega_{cell}$, it seems reasonable to introduce

$$\psi^{(i)} : \Omega \times \Omega_{cell} \to \mathbb{R}^k,$$

(7.63)

with

$$\psi^{(i)}_\varepsilon(x, t) \overset{\text{def}}{=} \psi^{(i)}(x, \frac{x}{\varepsilon}, t)$$

(7.64)

such that $\psi^{(i)}$ is periodic in the second variable $\xi \overset{\text{def}}{=} \frac{x}{\varepsilon}$.

**Remark 29.** How should one understand this? Think of $\psi$ being the density, for instance. It is clear, that the density can exhibit very strong oscillations (density of the fluid inside the channel can be very different from the density of the surrounding rock), but at the same time, when “averaged” over the characteristic small-scale $d$, it may be only a mildly spatially varying function, or even a constant. So it makes sense to try to separate the behavior at the two spatial scales from each other by defining $\rho_\varepsilon(x, t) \overset{\text{def}}{=} \rho(x, \xi, t)$. For a given $x$ and $t$, the function $\rho(x, \xi, t)$ describes the variation of density within the cell (micro-structure), this corresponding to density variations due to the fact that the cell is composed of two materials - say water and rock. The small-scale variable $\xi$ therefore cares for the description of density variations on the fine scale.

What about the dependence of the two-scale function $\psi(x, \xi, t)$ on $x$? If we take the original (and possibly very fast varying density field $\rho_\varepsilon(x, t)$) and define an average value over the cell centered at $x$ by

$$\langle \rho \rangle(x, t) \overset{\text{def}}{=} \frac{1}{|\Omega_{cell}|} \int_{\Omega_{cell}(x)} \rho_\varepsilon(x', t) \, dx',$$

(7.65)

we get

$$\langle \rho \rangle(x, t) = \frac{1}{|\Omega_{cell}|} \int_{\Omega_{cell}(x)} \rho(x, \xi, t) \, d\xi,$$

(7.66)

which is the sought interpretation - as expected the dependence of $\rho(x, \xi, t)$ on $x$ captures the “slow” (averaged) spatial dependence of the density.

So adopting the two-scale separation (7.63), the asymptotic expansion (7.62) takes the form

$$\psi_\varepsilon(x, t) = \sum_{i=0}^{\infty} \varepsilon^i \psi^{(i)}_\varepsilon(x, \xi, t).$$

(7.67)

In view of (7.63), we thus obtain the following identity:

$$\nabla_x \psi_\varepsilon(x, t) = \left( \nabla_x + \frac{1}{\varepsilon} \nabla_\xi \right) \psi(x, \xi, t),$$

(7.68)

the first part of the operator measuring the changes in the macroscopic coordinate $x$, the second measuring variations at the microscopic coordinate $\xi$.

Coming back to our Stokes flow problem, the two-scale asymptotic expansions of velocity $v_\varepsilon$ and pressure $p_\varepsilon$ read

$$v_\varepsilon(x, t) = v^{(0)}(x, \xi, t) + \varepsilon v^{(1)}(x, \xi, t) + \varepsilon^2 v^{(2)}(x, \xi, t) + \ldots$$

(7.69)

$$p_\varepsilon(x, t) = p^{(0)}(x, \xi, t) + \varepsilon p^{(1)}(x, \xi, t) + \varepsilon^2 p^{(2)}(x, \xi, t) + \ldots$$

(7.70)

Plugging these expansions into the mass balance (7.61a) yields

$$\text{div}_x \left( v^{(0)} + \varepsilon v^{(1)} + \varepsilon^2 v^{(2)} + \ldots \right) + \frac{1}{\varepsilon} \text{div}_\xi \left( v^{(0)} + \varepsilon v^{(1)} + \varepsilon^2 v^{(2)} + \ldots \right) = 0,$$

(7.71a)
and, similarly, the balance of linear momentum (7.71b) becomes

$$0 = -\left( \nabla_x + \frac{1}{\varepsilon} \nabla_\xi \right) (p^{(0)} + \varepsilon p^{(1)} + \varepsilon^2 p^{(2)} + ...) + \varepsilon^2 \left( \nabla_x + \frac{1}{\varepsilon} \nabla_\xi \right) \left( v^{(0)} + \varepsilon v^{(1)} + \varepsilon^2 v^{(2)} + ... \right) .$$  (7.71b)

Both the above equations were formulated in $\Omega^f$, so now in terms of the two-scale expansion, they hold in $\Omega \times \Omega^f_{cell}$. The boundary condition (7.61c) becomes

$$0 = v^{(0)}(x, \xi, t) + \varepsilon v^{(1)}(x, \xi, t) + \varepsilon^2 v^{(2)}(x, \xi, t) + ... \quad \text{in } \Omega \times \partial \Omega^f_{cell} .$$  (7.71c)

The idea of formal asymptotic expansion is now to gather in each balance equation the terms multiplied by the same power of $\varepsilon$ and write down a hierarchy of corresponding sub-problems. The justification of such a hierarchy is within homogenization technique ensured by a (here strictly formal) limit procedure $\lim_{\varepsilon \to 0^+}$.

Looking at the leading-order terms standing at $\varepsilon^{-1}$ in the mass balance (7.71a), we obtain:

$$\text{div}_\xi v^{(0)} = 0 .$$  (7.72)

In the momentum balance (7.71b) the leading order term ($\varepsilon^{-1}$) yields

$$\nabla_\xi p^{(0)} = 0 ,$$  (7.73)

which only tells us that $p^{(0)}(x, \xi, t) = p^{(0)}(x, t)$ which is valuable but not sufficient information. Let us inspect the terms at $\varepsilon^0$:

$$-\nabla_x p^{(0)} - \nabla_\xi p^{(1)} + \Delta_\xi v^{(0)} = 0 , \quad \text{in } \Omega \times \Omega^f_{cell} .$$  (7.74)

We observe that we can rewrite the problem at this level for each fixed $x$ as a Stokes system (in variables $\xi, t$) on the given cell $\Omega^f_{cell}(x)$ for $(p^{(1)}, v^{(0)})$ under known $p^{(0)}(x, t)$.

$$\text{div}_\xi v^{(0)} = 0 \quad \text{in } \Omega^f_{cell} \quad \text{(7.75a)}$$

$$-\nabla_\xi p^{(1)} + \Delta_\xi v^{(0)} + \nabla_x p^{(0)} = 0 \quad \text{in } \Omega^f_{cell} \quad \text{(7.75b)}$$

and the boundary condition (7.61c) becomes

$$v^{(0)} = 0 \quad \text{at } \partial \Omega^f_{cell} . \quad \text{(7.75c)}$$

Note that the term $\nabla_x p^0$ is a constant vector in the system thanks to independence on $\xi$, see (7.73). The solution of the so-called cell problem (7.75) can thus be found by solving three auxiliary cell sub-problems

$$\text{div}_\xi v^{(0)}_a = 0 \quad \text{in } \Omega^f_{cell} \quad \text{(7.76a)}$$

$$-\nabla_\xi p^{(1)}_a + \Delta_\xi v^{(0)}_a + e_a = 0 \quad \text{in } \Omega^f_{cell} \quad \text{(7.76b)}$$

$$v^{(0)} = 0 \quad \text{at } \partial \Omega^f_{cell} . \quad \text{(7.76c)}$$

for $a = 1, 2, 3$, since then by linearity, we get the sought solution of (7.75) in the form

$$v^{(0)}(x, \xi, t) = -\sum_{a=1}^3 \frac{\partial p^{(0)}(x, t)}{\partial x_a} v^{(0)}_a(x, \xi, t) .$$  (7.77)

Denoting the volume average over the cell centered at $x$ by $\langle v^{(0)}(x, t) \rangle$:

$$\langle v^{(0)}(x, t) \rangle \overset{\text{def}}{=} \frac{1}{\Omega_{cell}} \int_{\Omega_{cell}(x)} v^{(0)}(x, \xi, t) \, d\xi ,$$  (7.78)

we get

$$\langle v^{(0)}(x, t) \rangle = -\sum_{a=1}^3 (v^{(0)}_a(x, t)) \frac{\partial p^{(0)}}{\partial x_a}(x, t) .$$  (7.79)
We obtained Darcy’s law as a relation between the leading-order terms of the two-scale asymptotic expansions of velocity and pressure:

\[\left\langle v^{(0)}(x,t)\right\rangle(x,t) = -\frac{k(\phi,x,t)}{\mu_f \phi} \nabla_x p^{(0)}(x,t)\,\text{.}\]  

(7.80)

where the (in general) tensorial permeability \(k\) is defined as

\[k(\phi,x,t) \overset{\text{def}}{=} \frac{3}{\mu_f \phi} \sum_{\alpha=1}^{3} \left\langle v^{(0)}_\alpha(x,t)\right\rangle (x,t) \otimes e_\alpha\,\text{.}\]  

(7.81)

Note that we obtained characterization of the permeability in terms of (averaged) solution of the cell-problem, which is computable (e.g by numerical simulation), provided that we explicitly describe the geometry of the cell problem. This is the strongest point of the homogenization technique - the possibility to evaluate the “upscaled” material parameters (such as permeability) by solving some associated cell problem and analysing its solution.

**Remark 30.** The physically weak point of the homogenization procedure is the limit procedure \(\lim_{\epsilon \to 0^+}\) which we used to “justify” the validity of the hierarchy of subproblems at different orders of \(\epsilon\). In reality, the microscale \(\epsilon\) may be small, but it is certainly fixed and does not converge to zero.

### 7.5 Generalizations of Darcy’s law: models of Brinkman and Forchheimer

**Brinkmann’s model** is the following extension of Darcy’s law:

\[\alpha v_f = -\phi(\nabla p - p^m \mathbf{g}) + \mu_f \phi \Delta v_f\,\text{.}\]  

(7.82)

which can be viewed as an extension of the derivation described in Section 7.4.1 where we would keep also the deviatoric part of the partial Cauchy stress tensor, i.e. if we included the effect of internal friction in the fluid itself.

**Darcy-Forchheimer** extension of Darcy’s law represents a whole class of models in which the friction coefficient \(\alpha\) in Darcy’s law depends explicitly on the velocity \(|v_f|\):

\[\alpha(|v_f|)v_f = -\phi(\nabla p - p^m \mathbf{g}) + \mu_f \phi \Delta v_f\,\text{.}\]  

(7.83)

This makes the relationship between the pressure gradient in the medium and the flux non-linear.

### 7.6 A thermodynamic framework for a mixture of two liquids

In this section we provide a derivation of constitutive closures for a binary two-fluid system through the procedure of maximization of rate of entropy production.

Let us start from complete mixture description, i.e. let us consider the following system of balance equations

\[
\frac{\partial \rho_a}{\partial t} + \text{div}(\rho_a \mathbf{v}_a) = m_a, \quad \alpha = 1,\ldots,N, \\
\frac{\partial (\rho_a \mathbf{v}_a)}{\partial t} + \text{div}(\rho_a \mathbf{v}_a \otimes \mathbf{v}_a) = \text{div} \mathbf{T}_a + \rho_a \mathbf{b}_a + \mathbf{I}_a + m_a \mathbf{v}_a, \quad \alpha = 1,\ldots,N, \\
\frac{\partial (\rho_a E_a)}{\partial t} + \text{div}(\rho_a E_a \mathbf{v}_a) = \text{div} \left[ \mathbf{T}_a \mathbf{v}_a - \mathbf{q}_a \right] + \rho_a \mathbf{b}_a \cdot \mathbf{v}_a + \rho_a r_a + \epsilon_a + \mathbf{I}_a \cdot \mathbf{v}_a + m_a E_a, \quad \alpha = 1,\ldots,N,
\]

(7.84a-d)

where \(E_a = e_a + \frac{1}{2} |\mathbf{v}_a|^2\), and the above relations are supplemented with the constraints on the interaction terms

\[
\sum_{a=1}^{N} m_a = 0, \\
\sum_{a=1}^{N} (\mathbf{I}_a + m_a \mathbf{v}_a) = 0, \\
\sum_{a=1}^{N} (\epsilon_a + \mathbf{I}_a \cdot \mathbf{v}_a + m_a E_a) = 0.
\]

(7.85a-c)
Let us define
\[ N \alpha = \sum_{a=1}^{N} \alpha^a \]
which implies
\[ \alpha = \bar{\alpha} \] and so we can write
\[ N \alpha = \sum_{a=1}^{N} \alpha^a \]
Multiplying (7.84b) by \( v \), we obtain after some manipulation (cf Sec. 5.6) the balance of kinetic energy:
\[
\frac{\partial}{\partial t} \left( \frac{\rho_a |v_a|^2}{2} \right) + \text{div} \left( \frac{\rho_a |v_a|^2}{2} v_a \right) = \text{div}(\tau_a v_a) - \tau_a : \nabla v_a + \rho_a b_a \cdot v_a + I_a \cdot v_a + m_a \frac{|v_a|^2}{2},
\]
(7.86)
Subtracting this balance from (7.84c), we get reduced balance of energy in the form of internal energy balance
\[
\frac{\partial (\rho_a e_a)}{\partial t} + \text{div}(\rho_a e_a v_a) = - \text{div} q_a + \rho_a r_a + \tau_a : \nabla v_a + \varepsilon_a + m_a e_a,
\]
(7.87)
summing over \( a \) and using constraints (7.85), we arrive at
\[
\frac{\partial}{\partial t} \left( \sum_{a=1}^{N} \rho_a e_a \right) + \text{div} \left( \sum_{a=1}^{N} \rho_a e_a v_a \right) = - \text{div} \left( \sum_{a=1}^{N} q_a \right) + \sum_{a=1}^{N} \rho_a r_a + \sum_{a=1}^{N} \tau_a : \nabla v_a + \sum_{a=1}^{N} (\varepsilon_a + m_a e_a),
\]
(7.88)
which can be recast to the form (cf. eq. 5.88)
\[
\frac{\partial}{\partial t} \left( \sum_{a=1}^{N} \rho_a e_a \right) + \text{div} \left( \sum_{a=1}^{N} \rho_a e_a v_a \right) + \text{div} \left( \sum_{a=1}^{N} \rho_a e_a u_a \right) = - \text{div} \left( \sum_{a=1}^{N} q_a \right) + \sum_{a=1}^{N} \rho_a r_a + \sum_{a=1}^{N} \tau_a : \nabla v_a
\]
\[ - \sum_{a=1}^{N} I_a \cdot u_a - \sum_{a=1}^{N} m_a \frac{|u_a|^2}{2},\]
(7.89)
Let us now consider a binary mixture, i.e. take \( N = 2 \). Since by definition of the diffusive velocities \( u_a \) it holds
\[
\rho_1 u_1 + \rho_2 u_2 = 0,
\]
(7.90)
we have
\[
v_1 - v_2 = u_1 - u_2 = - \left( \frac{\rho_2}{\rho_1} + 1 \right) u_2 = \left( 1 + \frac{\rho_1}{\rho_2} \right) u_1,
\]
(7.91)
which implies
\[
u_1 = \frac{\rho_2}{\rho}(v_1 - v_2) = (1 - c)(v_1 - v_2), \quad \] (7.92)
\[
u_2 = - \frac{\rho_1}{\rho}(v_1 - v_2) = -c(v_1 - v_2), \quad \] (7.93)
where \( c := c_1 \). Consequently, it holds
\[
\sum_{a=1}^{N} \rho_a e_a u_a = \rho c(1-c)(e_1 - e_2)(v_1 - v_2).
\]
(7.94)
Let us define
\[
q_I := \sum_{a=1}^{N} q_a, \quad \rho r_I := \sum_{a=1}^{N} \rho_r a, \quad \rho e_I := \sum_{a=1}^{N} \rho e_a,
\]
(7.95)
we can rewrite the internal energy balance as follows
\[
\frac{\partial}{\partial t}(\rho e_I) + \text{div}(\rho e_I v) = - \text{div} q_I + \rho r_I + m_1 \text{div} v_1 + m_2 \text{div} v_2 + \tau_1 : D_I^1 + \tau_2 : D_I^2 - \nabla E_{12} \cdot (v_1 - v_2)
\]
\[ = \left( m_1 \right)^2 (1-c)^2 + \left( 1 - c \right)^2 \left( v_1 - v_2 \right)^2,\]
(7.96)
and so we can write
\[
\rho e_I = - \text{div} q_I + \rho r_I + \left( m_1 - E_{12} \right) \text{div} v_1 + \left( m_2 + E_{12} \right) \text{div} v_2 + \tau_1 : D_I^1 + \tau_2 : D_I^2
\]
\[ - \left( 1 - c \right) I_1 - c I_2 + \text{\nabla} E_{12} + \frac{m_2}{2} (1-2c)(v_1 - v_2) \cdot (v_1 - v_2),\]
(7.97)
where \( m := m_1 \). Let us assume that both components have the same temperature \( \theta = \theta_1 = \theta_2 \). Let us distinguish the compressible and incompressible cases.
7.6.1 **Compressible case**

Let us assume that the (internal) Helmholtz free energy of the mixture is simply

\[ \Psi_I = \Psi_1(\theta, \rho, c) + c \Psi_2(\theta, \rho, c), \]  

(7.98)

where \( \Psi_1, \Psi_2 \) are the partial Helmholtz free energies (Legendre transforms of \( e_1, e_2 \), respectively). Let us define

\[ \eta_I := - \frac{\partial \Psi_I}{\partial \theta}, \]  

(7.99)

and let us assume \( \eta = \eta_I \). Then we get

\[ \rho \Psi_I = \rho(e_I - \theta \eta) = \rho \dot{e}_I - \rho \eta \dot{\theta} - \rho \theta \dot{\eta}, \]  

(7.100)

and also, by definition,

\[ \rho \dot{\Psi}_I = \rho \left( \frac{\partial \Psi_I}{\partial \theta} \dot{\theta} + \frac{\partial \Psi_I}{\partial \rho} \dot{\rho} + \frac{\partial \Psi_I}{\partial c} \dot{c} \right), \]  

(7.101)

comparing these two relations, and using (7.99) together with mass balances in the \( \rho \cdot c \) form (cf. FIXME)

\[ \rho \theta \dot{\eta} = \rho \dot{e}_I + p \text{div} \mathbf{v} - \mu (m - \text{div} \mathbf{j}), \]  

(7.102)

where we defined as usually the thermodynamic pressure \( p \) and the chemical potential \( \mu \) as

\[ p := \rho^2 \frac{\partial \Psi_I}{\partial \rho}, \quad \mu := \frac{\partial \Psi_I}{\partial c}, \]  

(7.103)

and where the diffusive flux \( \mathbf{j} \) can be written as

\[ \mathbf{j} = \rho c u_1 = \rho c (1-c) \mathbf{v}_1 - \mathbf{v}_2. \]  

(7.104)

Let us plug-in the internal energy balance (7.96), and the identity

\[ \text{div} \mathbf{v} = \text{div}(c \mathbf{v}_1 + (1-c) \mathbf{v}_2) = c \text{div} \mathbf{v}_1 + (1-c) \text{div} \mathbf{v}_2 + \nabla c \cdot (\mathbf{v}_1 - \mathbf{v}_2), \]  

(7.105)

we obtain

\[ \rho \theta \dot{\eta} = - \text{div} \mathbf{q}_I + \rho r_1 + (m_1 - E_{12} + c p) \text{div} \mathbf{v}_1 + (m_2 + E_{12} + (1-c)p) \text{div} \mathbf{v}_2 + \tau_1 : D_1^d + \tau_2 : D_2^d + \text{div}(\mathbf{j}) - \mu m \]
\[ - \left( (1-c) \mathbf{I}_1 - c \mathbf{I}_2 + \nabla E_{12} + \frac{m}{2} (1-2c)(\mathbf{v}_1 - \mathbf{v}_2) - p \nabla c + \rho c (1-c) \nabla \mu \right) \cdot (\mathbf{v}_1 - \mathbf{v}_2). \]

(7.106)

Dividing by \( \theta \), we recast the above equation into the form of entropy balance:

\[ \rho \dot{\eta} + \text{div} \left( \frac{\mathbf{q}_I - \mu \mathbf{j}}{\theta} \right) + \frac{\rho r_1}{\theta} \]
\[ = \frac{1}{\theta} \left\{ (m_1 - E_{12} + c p) \text{div} \mathbf{v}_1 + (m_2 + E_{12} + (1-c)p) \text{div} \mathbf{v}_2 + \tau_1 : D_1^d + \tau_2 : D_2^d + \text{div}(\mathbf{j}) - \mu m - \frac{\mathbf{q} - \mu \mathbf{j}}{\theta} \]
\[ - \left( (1-c) \mathbf{I}_1 - c \mathbf{I}_2 + \nabla E_{12} + \frac{m}{2} (1-2c)(\mathbf{v}_1 - \mathbf{v}_2) - p \nabla c + \rho c (1-c) \nabla \mu \right) \cdot (\mathbf{v}_1 - \mathbf{v}_2) \right\}, \]

(7.107)

from where we interpret the terms contributing to entropy change as entropy flux, entropy supply and the term in \( \frac{\mathbf{q}}{\theta} \) as entropy production \( \xi \). Let us now assume slight extension of the class-I formula for entropy production in a binary mixture of heat conducting and chemically-reacting linear fluids, the extension being inclusion of one more term corresponding to class-II feature – dissipation due to drag force between the two fluids, i.e. let us postulate

\[ \xi = \dot{\xi} = \frac{3\lambda + 2\nu}{3} (\text{div} \mathbf{v})^2 + 2\nu ||D||^2 + \kappa ||\nabla \theta||^2 + \beta \mu^2 + \alpha ||v_1 - v_2||^2, \]

(7.108)

where

\[ 3\lambda + 2\nu \geq 0, \nu \geq 0, \kappa \geq 0, \beta \geq 0, \alpha \geq 0, \]

(7.109)
which ensure non-negativity of the entropy production in accord with the second law of thermodynamics. Note that we consider the very simplest setting, piece-wise quadratic form (even for the chemical reaction), which as we know corresponds to piece-wise linear closure relations between the associated thermodynamic fluxes and affinities in the classical case. Let us now identify the closure relations by employing the principle of maximization of entropy production (PMEP), i.e. let us define the Lagrange function and let us now maximize with respect to the “class-II” affinities, i.e. let us solve

\[
\mathcal{L} := \hat{\xi} + I_1(\tilde{\xi} - \ldots) .
\]  

(7.110)

Let us first perform some auxiliary computations. Since

\[
v = c v_1 + (1-c)v_2 ,
\]  

(7.111)

we have

\[
\nabla v = c \nabla v_1 + (1-c)\nabla v_2 + (v_1-v_2) \otimes \nabla c ,
\]  

(7.112a)

\[
\text{div } v = c \text{div } v_1 + (1-c)\text{div } v_2 + (v_1-v_2) \cdot \nabla c ,
\]  

(7.112b)

\[
D^d = cD^d_1 + (1-c)D^d_2 + \frac{1}{2}((v_1-v_2) \otimes \nabla c + \nabla c \otimes (v_1-v_2)) - \frac{1}{3}(v_1-v_2) \cdot \nabla c I .
\]  

(7.112c)

We get

\[
\frac{\partial \hat{\xi}}{\partial D^d_1} = 4vD^d : \frac{\partial D^d}{\partial D^d_1} = 4v c D^d ,
\]  

(7.113a)

\[
\frac{\partial \hat{\xi}}{\partial D^d_1} = 4vD^d : \frac{\partial D^d}{\partial D^d_2} = 4v(1-c) D^d ,
\]  

(7.113b)

\[
\frac{\partial \hat{\xi}}{\partial \text{div } v_1} = 2\left(\frac{3\lambda + 2\nu}{3}\right) \frac{\partial \text{div } v}{\partial \text{div } v_1} = 2c\left(\frac{3\lambda + 2\nu}{3}\right) \text{div } v ,
\]  

(7.113c)

\[
\frac{\partial \hat{\xi}}{\partial \text{div } v_2} = 2\left(\frac{3\lambda + 2\nu}{3}\right) \frac{\partial \text{div } v}{\partial \text{div } v_2} = 2(1-c)\left(\frac{3\lambda + 2\nu}{3}\right) \text{div } v ,
\]  

(7.113d)

\[
\frac{\partial \hat{\xi}}{\partial (v_1-v_2)} = 4vD^d : \frac{\partial D^d}{\partial (v_1-v_2)} + 2\left(\frac{3\lambda + 2\nu}{3}\right) \text{div } v \cdot \frac{\partial \text{div } v}{\partial (v_1-v_2)} + 2\alpha(v_1-v_2)
\]  

\[= 4vD^d \nabla c + 2\left(\frac{3\lambda + 2\nu}{3}\right) \text{div } v \nabla c + 2\alpha(v_1-v_2) .
\]  

(7.113e)

\[
\frac{\partial \hat{\xi}}{\partial \nabla \vartheta} = 2\kappa \nabla \vartheta ,
\]  

(7.113f)

\[
\frac{\partial \hat{\xi}}{\partial \mu} = 2\beta \mu .
\]  

(7.113g)

Now the necessary conditions for maximum of the Lagrange function are vanishing first derivatives, which
implies
\[ T_1^d = \frac{1+\frac{l_1}{l_1}}{4}\mu D^d, \]  
\[ T_2^d = \frac{1+\frac{l_1}{l_1}}{4(1-c)\mu D^d}, \]  
\[ m_1 - E_{12} + cp = \frac{1+\frac{l_1}{l_1}}{2}c \left( \frac{3\lambda + 2\nu}{3} \right) \text{div}\mathbf{v}, \]  
\[ m_2 + E_{12} + (1-c)p = \frac{1+\frac{l_1}{l_1}}{2} (1-c) \left( \frac{3\lambda + 2\nu}{3} \right) \text{div}\mathbf{v}, \]  
\[ (1-c)\mathbf{I}_1 - c\mathbf{I}_2 + \nabla E_{12} + \frac{m}{2}(1-2c)(\mathbf{v}_1 - \mathbf{v}_2) - p\nabla c + \rho c(1-c)\nabla \mu = -\frac{1+\frac{l_1}{l_1}}{4} \nabla^d \nabla c + 2 \left( \frac{3\lambda + 2\nu}{3} \right) \text{div}\mathbf{v} \nabla c \]  
\[ + 2\alpha(\mathbf{v}_1 - \mathbf{v}_2), \]  
\[ \mathbf{q} - \frac{\mathbf{J}}{\theta} = -\frac{1+\frac{l_1}{l_1}}{2} \kappa \nabla \theta, \]  
\[ m = \frac{1+\frac{l_1}{l_1}}{l_1} 2\beta \mu. \]  

The value of the Lagrange multiplier \( l_1 \) is found by multiplying the above relations by \( D_1, D_2, \text{div}\mathbf{v}_1, \text{div}\mathbf{v}_2, \mathbf{v}_1 - \mathbf{v}_2, \nabla \theta, \) and \( \mu, \) respectively, one arrives at
\[ \frac{1+\frac{l_1}{l_1}}{l_1} 2\hat{\xi} = \hat{\xi} \iff \frac{1+\frac{l_1}{l_1}}{l_1} = \frac{1}{2} \Rightarrow l_1 = -2. \]  

Using the relation
\[ \mathbf{I}_1 + \mathbf{I}_2 + m_1 \mathbf{v}_1 + m_2 \mathbf{v}_2 = \mathbf{0}, \]  
we can rewrite
\[ (1-c)\mathbf{I}_1 - c\mathbf{I}_2 + \frac{m}{2}(1-2c)(\mathbf{v}_1 - \mathbf{v}_2) = \mathbf{I} + \frac{m}{2}(\mathbf{v}_1 - \mathbf{v}_2), \]  
where we denoted \( \mathbf{I} := \mathbf{I}_1. \) So finally, we arrive at the following closure relations
\[ T_1^d = 2\mu D^d, \]  
\[ T_2^d = 2\nu(1-c)\mu D^d, \]  
\[ m_1 = -c\rho + E_{12} + \frac{3\lambda + 2\nu}{3} \text{div}\mathbf{v}, \]  
\[ m_2 = -(1-c)\rho - E_{12} + \frac{3\lambda + 2\nu}{3} (1-c)\text{div}\mathbf{v}, \]  
\[ \mathbf{I} = p\nabla c - \nabla E_{12} - \rho c(1-c)\nabla \mu - 2\nu \nabla^d \nabla c - \left( \frac{3\lambda + 2\nu}{3} \right) \text{div}\mathbf{v} \nabla c - \alpha(\mathbf{v}_1 - \mathbf{v}_2) - \frac{m}{2}(\mathbf{v}_1 - \mathbf{v}_2), \]  
\[ \mathbf{q}_I = -\kappa \nabla \theta + \mu \rho c(1-c)(\mathbf{v}_1 - \mathbf{v}_2), \]  
\[ m = -\beta \mu. \]  

The first four equations imply the following form of the partial Cauchy stresses
\[ \mathcal{T}_1 = (E_{12} - cp)I + \lambda c \text{div}\mathbf{v} I + 2\nu D, \]  
\[ \mathcal{T}_2 = -(E_{12} - (1-c)p)I + \lambda(1-c) \text{div}\mathbf{v} I + 2\nu(1-c)D. \]  

Defining
\[ \mathcal{T}_I := \mathcal{T}_1 + \mathcal{T}_2, \]  
we obtain
\[ \mathcal{T}_I = -pl + \lambda \text{div}\mathbf{v} I + 2\nu D, \]  
and we know, that \( \mathcal{T}_I \) differs from the mixture Cauchy stress only by a quadratic term \( \sum_{\alpha=1}^N \rho_\alpha \mathbf{u}_\alpha \otimes \mathbf{u}_\alpha, \) which can be often ignored. Under such assumptions, we can see that the retrieved mixture Cauchy stress reduced to the classical compressible fluid. Note that in view of \([7.121]\), the formula for the interaction force \([7.122]\) can be rewritten as follows
\[ \mathbf{I} = -\nabla E_{12} - \rho c(1-c)\nabla \mu - \left( \alpha + \frac{m}{2} \right)(\mathbf{v}_1 - \mathbf{v}_2) - \mathcal{T}_I \nabla c. \]
7.6.2 Incompressible case

For an incompressible mixture, we impose additional constraint
\[
\text{div}\, \mathbf{v} = 0, \quad (7.123)
\]
into our thermodynamic framework. Let us impose analogous ansatz for the (internal) Helmholtz free energy \( \Psi_I \), only neglecting the dependence on mixture density (which is now constant provided it was constant at some initial time, which we assume here), i.e. let us assume
\[
\Psi_I = \hat{\Psi}_I(\theta,c) = c\Psi_1(\theta,c) + (1-c)\Psi_2(\theta,c). \quad (7.124)
\]

Let us define as in the compressible case
\[
\eta_I := -\frac{\partial \Psi_I}{\partial \theta}, \quad (7.125)
\]
and let us assume \( \eta = \eta_I \). Then we get
\[
\rho \dot{\Psi}_I = \rho \left( e_I - \theta \eta \right) = \rho \dot{e}_I - \rho \dot{\theta} - \rho \theta \dot{\eta}, \quad (7.126)
\]
and also, by definition,
\[
\rho \dot{\Psi}_I = \rho \left( \frac{\partial \hat{\Psi}_I}{\partial \theta} + \frac{\partial \hat{\Psi}_I}{\partial c} \right), \quad (7.127)
\]
comparing these two relations, and using \( \Phi_9 \) together with mass balances in the \( \rho\cdot c \) form (cf. \( \Phi_{10} \))
\[
\rho \theta \dot{\eta} = \rho \dot{e}_I - \mu (\nabla \dot{c}), \quad (7.128)
\]
where we defined the chemical potential \( \mu \) as before
\[
\mu := \frac{\partial \hat{\Psi}_I}{\partial c}, \quad (7.129)
\]
and where the diffusive flux \( j \) can be written as
\[
j = \rho c \mathbf{u}_1 = \rho c (1-c)(\mathbf{v}_1 - \mathbf{v}_2). \quad (7.130)
\]

Let us plug-in the internal energy balance \( \Phi_{11} \), we obtain
\[
\rho \dot{\eta} = - \text{div}\, \mathbf{q}_I + \rho r_I + (m_1 - E_{12}) \text{div}\, \mathbf{v}_1 + (m_2 + E_{12}) \text{div}\, \mathbf{v}_2 + \nabla E_{12} + \frac{m}{2}(1-2c)(\mathbf{v}_1 - \mathbf{v}_2) + \rho c(1-c) \nabla \mu \cdot (\mathbf{v}_1 - \mathbf{v}_2). \quad (7.131)
\]

Dividing by \( \theta \), we recast the above equation into the form of entropy balance:
\[
\rho \dot{\eta} + \text{div} \left( \frac{\mathbf{q}_I - \mu \mathbf{j}}{\theta} \right) + \frac{\rho r_I}{\theta}
= \frac{1}{\theta} \left\{ (m_1 - E_{12}) \text{div}\, \mathbf{v}_1 + (m_2 + E_{12}) \text{div}\, \mathbf{v}_2 + \nabla E_{12} + \frac{m}{2}(1-2c)(\mathbf{v}_1 - \mathbf{v}_2) + \rho c(1-c) \nabla \mu \cdot (\mathbf{v}_1 - \mathbf{v}_2) \right\}, \quad (7.132)
\]
from where we interpret the terms contributing to entropy change as entropy flux, entropy supply and the term in \( \frac{\rho r_I}{\theta} \) as entropy production \( \xi \). Let us now assume slight extension of the class-I formula for entropy production in a binary mixture of heat conducting and chemically-reacting linear fluids, which is moreover incompressible, again extended by an inclusion of dissipation due to drag force between the two fluids, i.e. let us postulate
\[
\xi = \xi = 2
\nu \|\mathbf{D}_d\|^2 + \kappa |\nabla \dot{\theta}|^2 + \beta \mu^2 + \alpha |\mathbf{v}_1 - \mathbf{v}_2|^2, \quad (7.133)
\]
where
\[
\nu \geq 0, \kappa \geq 0, \beta \geq 0, \alpha \geq 0, \quad (7.134)
\]
which ensures the non-negativity of entropy production, in accord with the second law of thermodynamics. Let us now identify the closure relations by employing the principle of maximization of entropy production (PMEP), but now with additional constraining due to the incompressibility assumption. Let us perform again maximization with respect to the “class-II” affinities, i.e. let us solve

\[
\max_{\mathcal{D}_1^d, \mathcal{D}_2^d, \text{div} \mathbf{v}_1, \text{div} \mathbf{v}_2, \mathbf{v}_1 - \mathbf{v}_2, \nabla \theta, \mu} \mathcal{L} := \hat{\xi} + l_1 (\hat{\xi} - \{\ldots\}) + l_2 \text{div} \mathbf{v} \ .
\] (7.135)

Employing the identity
\[
\text{div} \mathbf{v} = \text{div}(c \mathbf{v}_1 + (1-c) \mathbf{v}_2) = c \text{div} \mathbf{v}_1 + (1-c) \text{div} \mathbf{v}_2 + \nabla c \cdot (\mathbf{v}_1 - \mathbf{v}_2) ,
\] (7.136)

we can proceed as in the compressible case and write down the set of necessary optimality conditions:

\[
\mathcal{T}_1^d = \frac{1+l_1}{l_1} 4 v c \mathcal{D}_1^d , \quad (7.137a)
\]

\[
\mathcal{T}_2^d = \frac{1+l_1}{l_1} 4 v (1-c) \mathcal{D}_2^d , \quad (7.137b)
\]

\[
m_1 - E_{12} = - \frac{l_2}{l_1} c , \quad (7.137c)
\]

\[
m_2 + E_{12} = - \frac{l_2}{l_1} (1-c) , \quad (7.137d)
\]

\[
(1-c) \mathbf{I}_1 - c \mathbf{I}_2 + V E_{12} + \frac{m}{2} (1-2c)(\mathbf{v}_1 - \mathbf{v}_2) + \rho c (1-c) \nabla \mu = - \frac{1+l_1}{l_1} 4 v \mathcal{D}_1^d \nabla c + 2 \alpha (\mathbf{v}_1 - \mathbf{v}_2) + \frac{l_2}{l_1} \nabla c \quad (7.137e)
\]

\[
\mathbf{q}_j - \mu \frac{\partial \mathbf{v}_j}{\partial \theta} = - \frac{1+l_1}{l_1} 2 \kappa \nabla \theta , \quad (7.137f)
\]

\[
m = - \frac{1+l_1}{l_1} 2 \beta \mu . \quad (7.137g)
\]

The value of the Lagrange multiplier \( l_1 \) is found by multiplying the above relations by \( \mathcal{D}_1^d, \mathcal{D}_2^d, \text{div} \mathbf{v}_1, \text{div} \mathbf{v}_2, \mathbf{v}_1 - \mathbf{v}_2, \nabla \theta, \) and \( \mu, \) respectively, and summing these relations together, one arrives at

\[
\frac{1+l_1}{l_1} 2 \hat{\xi} = \frac{l_2}{l_1} (c \text{div} \mathbf{v}_1 + (1-c) \text{div} \mathbf{v}_2 + (\mathbf{v}_1 - \mathbf{v}_2) \cdot \nabla c) \Longrightarrow \frac{1+l_1}{l_1} = \frac{1}{2} \Longrightarrow l_1 = -2 .
\] (7.138)

Summing (7.137c) and (7.137d) yields

\[
m := m_1 + m_2 = \frac{l_2}{l_1} . \quad (7.139)
\]

Using the relation

\[
\mathbf{I}_1 + \mathbf{I}_2 + m_1 \mathbf{v}_1 + m_2 \mathbf{v}_2 = 0 , \quad (7.140)
\]

we can rewrite

\[
(1-c) \mathbf{I}_1 - c \mathbf{I}_2 + \frac{m}{2} (1-2c)(\mathbf{v}_1 - \mathbf{v}_2) = \mathbf{I} + \frac{m}{2} (\mathbf{v}_1 - \mathbf{v}_2) , \quad (7.141)
\]

where we denoted \( \mathbf{I} := \mathbf{I}_1 \). So finally, we arrive at the following closure relations

\[
\mathcal{T}_1^d = 2 v c \mathcal{D}_1^d , \quad (7.142a)
\]

\[
\mathcal{T}_2^d = 2 v (1-c) \mathcal{D}_2^d , \quad (7.142b)
\]

\[
m_1 = c m + E_{12} , \quad (7.142c)
\]

\[
m_2 = - (1-c) m - E_{12} , \quad (7.142d)
\]

\[
\mathbf{I} = - V E_{12} - \rho c (1-c) \nabla \mu - 2 v \mathcal{D}_1^d \nabla c - \left( \frac{3 \lambda + 2 \nu}{3} \right) \text{div} \mathbf{v} \nabla c - \alpha (\mathbf{v}_1 - \mathbf{v}_2) - \frac{m}{2} (\mathbf{v}_1 - \mathbf{v}_2) , \quad (7.142e)
\]

\[
\mathbf{q}_j = - \kappa \nabla \theta + \mu p c (1-c)(\mathbf{v}_1 - \mathbf{v}_2) , \quad (7.142f)
\]

\[
m = - \beta \mu . \quad (7.142g)
\]
The first four equations imply the following form of the partial Cauchy stresses

\[ T_1 = (E_{12} + cm)I + 2\nu cD, \]  
\[ T_2 = (-E_{12} + (1-c)m)I + 2\nu(1-c)D. \]  

(7.143a)

(7.143b)

Defining as before

\[ \mathbb{T}_I := T_1 + T_2, \]  

(7.144)

we obtain

\[ T_I = mI + 2\nu D, \]  

(7.145)

and we know, that \( \mathbb{T}_I \) differs from the mixture Cauchy stress only by a quadratic term \( \sum_{\alpha=1}^{N} \rho_\alpha u_\alpha \otimes u_\alpha \), which can be often ignored. Under such assumptions, we can see that the retrieved mixture Cauchy stress reduced to the classical incompressible fluid. Note that in view of (7.145), the formula for the interaction force (7.146) can be rewritten as follows

\[ I = -\nabla E_{12} - \rho c(1-c)\nabla u_\alpha - \left( a + \frac{m}{2} \right)(\mathbf{v}_1 - \mathbf{v}_2) - \mathbb{T}_I \nabla c, \]  

(7.146)

which in this form coincides with (7.122).

8 Multiphase continuum thermodynamics

8.1 Introduction

In this chapter we will introduce yet another viewpoint leading to continuum mixture theory, taking a slightly different perspective. Let us consider a situation of a multicomponent material as in Fig.8. Looking at the material from distance, it appears as homogeneous, but inspecting it closer by zooming to a sufficiently fine scale, we find out that it is composed of distinct subregions, each having its own composition and physical properties. These distinguishable states of the material will be denoted as phases in this chapter and such composite material is called a multiphase material. Now each of the phases may be either a single-component material, or it can be a mixture of several components in the sense in which we understood the word mixture until now. So the main difference between a mixture and a multiphase material is in the presence of some (small but still not microscopic) spatial scale, at which, we distinguish different states of the material.

Figure 8: Basic idea behind the concept of multiphase continuum mechanics. We assume that at sufficiently fine scale, we can distinguish individual phases of the material, which themselves on this scale can be described by a single-or-multicomponent mixture theory.

Facing a task of describing the properties of such a composite material, we could either zoom in and formulate on each of the subdomains mixture equations of appropriate type and look for suitable transition conditions between the phases and this is in fact what we will do. But staying at that detailed level of description is often not necessary and mostly even counterproductive and most importantly basically impossible since the information about the internal structure of the material and thus of the geometrical organisation of the various phases of the composite is out of our reach. A natural way to deal with this lack of information is to define some averaging procedure, which will smear out the exact geometrical structure, and will leave
us with balance equations for the smeared out quantities. This way we end up, as we shall see, again with classical mixture balance equations. Since the starting point for the derivation is a finer description of the material (at the mesoscale with distinguishable phases), we expect to obtain some extra information by the end of the day. This is indeed so, in particular, we will gain better insight into the interaction terms between the phases - they will be (averaged) interface interaction mechanisms.

8.2 General balance laws under presence of discontinuities - single continuum

In this chapter, we will first generalize the important analytical tools we have been using in deriving the local form of our balance laws from their integral representations: the Reynolds’ transport theorem and Gauss theorem. So far, we have always tacitly assumed that the balanced quantity is distributed in the bulk continuously or even with higher smoothness so that all the relations written in the form of (strong) PDEs are meaningful. In many situations, it is necessary to relax such assumption and to include material and immaterial interfaces representing discontinuities into the description. Moreover, it may also happen, that the properties of the thin contact zone between two bulk materials are in some sense singular, leading to substantial concentration of some bulk quantities into this zone and consequently, to distinct transport phenomena inside this interfacial zone. In such situations, it is often convenient to represent the zone as a \( n-1 \) dimensional manifold at which we introduce surface counterparts of all considered bulk fields. In such a case, one has to reinspect carefully the formulation of general balance laws, including these new terms, and arrive, as we shall see, to a combination of bulk balance laws in "regular" points outside the discontinuities and surface/interfacial balance laws at the discontinuities/boundaries. Let us immediately note that such a viewpoint gives a nice and natural way of dealing with boundary conditions, since they can be interpreted and treated as (discontinuous) interfaces between the inner bulk of the domain and the "rest of the world".

\[ d \frac{d}{dt} \Psi = -\nabla \cdot \Psi \mathcal{F} + \nabla \cdot \Psi \mathcal{P} + \Psi \mathcal{S} \]  

Figure 9: Control volume \( \Omega \) and discontinuity \( \Gamma \).

Let us consider a single component body in the framework of classical continuum mechanics. Let \( \Psi(\Omega) \) denote a generic additive quantity (such as mass, momentum, energy, etc. contained in a given control material volume \( \Omega \)). Let us consider the general integral balance law for such quantity, i.e. evaluate the rate of change of \( \Psi \), which is considered to result from three generic independent processes (i) the flux through boundaries of the domain \( \Psi \mathcal{F} \), (ii) through internal production \( \Psi \mathcal{P} \) and (iii) as a result of outer supply \( \Psi \mathcal{S} \), i.e. the general balance is postulated in the form

\[ \frac{d}{dt} \Psi = -\nabla \cdot \Psi \mathcal{F} + \nabla \cdot \Psi \mathcal{P} + \Psi \mathcal{S} \]  

Quantity \( \Psi \) is assumed to be composed of a bulk contribution and a surface contribution localized at an internal discontinuity (interface) \( \Gamma \), and both the bulk and the surface contributions are assumed to be representable by corresponding densities. We thus assume to have the following representation:

- Additive quantity \( \Psi \):

\[ \Psi = \int_{\Omega \cup \Omega^-} \psi \Omega \, dx + \int_{\Gamma} \psi \Gamma \, dS \]  

95
• Flux $\mathcal{F}$:

$$\mathcal{F} = \int_{S^+ \cup S^-} \Phi_{\Omega} \cdot n \, dS + \int_{\partial \Gamma} \Phi_{\Gamma} \cdot v \, dl$$  \hspace{1cm} (8.3)

where $n$ is the outer unit boundary to $\partial \Omega$ and $v$ is a outer unit normal to the line $\partial \Gamma$ (lying in $\Gamma$).

• Production $\mathcal{P}$:

$$\mathcal{P} = \int_{\Omega^+ \cup \Omega^-} \xi_{\Omega} \, dx + \int_{\Gamma} \xi_{\Gamma} \, dS$$  \hspace{1cm} (8.4)

• Supply $\mathcal{S}$

$$\mathcal{S} = \int_{\Omega^+ \cup \Omega^-} \Sigma_{\Omega} \, dx + \int_{\Gamma} \Sigma_{\Gamma} \, dS$$  \hspace{1cm} (8.5)

We will distinguish between the bulk contribution $\psi_{\Omega}$ and its surface counterpart $\psi_{\Gamma}$, in the sense that in general $\psi_{\Omega}|_{\Gamma} \neq \psi_{\Gamma}$, that is, the trace of the bulk quantity need not coincide with the corresponding surface quantity. This assumption corresponds to the fact that interfaces are in general zones where material properties may undergo abrupt changes - the transition layers being typically very thin, it is reasonable to treat them as $n-1$ dimensional manifolds, $n$ being the dimension of the “bulk” space, and the corresponding averaged (over the thickness of the layer) bulk quantities are then taken as the independent surface counterparts.

Remark 31. Interpretation of surface quantities - example - surface density $\rho_{\Gamma}$. FIXME-finish - a-la Slattery p.55

In order to obtain the local form of the general integral balance, we will employ the following theorems.

**Theorem 8.1 (Generalized Reynold's transport theorem).** Let $\Omega(t)$ be a material domain composed of two subdomains $\Omega^+(t)$ and $\Omega^-(t)$ separated by a non-material surface (e.g. a phase-change front) $\Gamma(t)$ as in Fig. Then it holds

$$\frac{d}{dt} \int_{\Omega(t)} \psi_{\Omega} \, dx = \int_{\Omega(t)} \frac{\partial \psi_{\Omega}}{\partial t} \, dx + \text{div} \left( \psi_{\Omega} \otimes v \right) \, dx + \int_{\Gamma(t)} [\psi_{\Omega} \otimes (v - v_{\perp}^\Gamma n_{\Gamma})] \cdot n_{\Gamma} \, dS$$  \hspace{1cm} (8.6)

**Proof.** FIXME

**Theorem 8.2 (Surface transport theorem).**

$$\frac{d}{dt} \int_{\Gamma(t)} \psi_{\Gamma} \, dS = \int_{\Gamma(t)} \frac{D_{\Gamma} \psi_{\Gamma}}{Dt} + \psi_{\Gamma} \text{div}_{\Gamma} v_{\Gamma} \, dS$$

$$= \int_{\Gamma(t)} \frac{D_{\Gamma} \psi_{\Gamma}}{Dt} + \psi_{\Gamma} \text{div}_{\Gamma} v_{\Gamma}^\parallel - 2K_M \psi_{\Gamma} \psi_{\Gamma}^\parallel \, dS$$  \hspace{1cm} (8.7)

**Proof.** FIXME

**Theorem 8.3 (Surface Gauss theorem).** Let $t_{\Gamma}$ be a tangent surface vector field. Then it holds

$$\int_{\Gamma(t)} \text{div}_{\Gamma} t_{\Gamma} \, dS = \int_{\partial \Gamma} t_{\Gamma} \cdot n_{\partial \Gamma} \, dl ,$$  \hspace{1cm} (8.9)

where $n_{\partial \Gamma}$ is the outer normal to $\partial \Gamma(t)$ - considered as a tangent vector in $\Gamma(t)$.

**Proof.** FIXME

In particular, this implies that

$$\int_{\Gamma(t)} \text{div}_{\Gamma} \psi_{\Gamma} v_{\Gamma}^\parallel \, dS = \int_{\partial \Gamma} \psi_{\Gamma} v_{\Gamma}^\parallel \cdot n_{\partial \Gamma} \, dl .$$  \hspace{1cm} (8.10)

By using the generalized Reynolds’ transport theorem, and the surface transport theorem, together with the bulk and surface Gauss’ theorem, under an additional assumption of sufficient smoothness of all the involved quantities, we can derive the following local form of the integral balances [Slattery et al. 2007].

96
• In regular points in the bulk

\[
\frac{\partial \psi^\alpha}{\partial t} + \text{div}(\psi^\alpha \Phi^\alpha t + \psi^\alpha t \mathbf{v} - \psi^\alpha \xi^\alpha t - \psi^\alpha \Sigma^\alpha t - \psi^\alpha \Pi^\alpha t) = 0 ,
\]

where \( \mathbf{v} \) is the material velocity.

• At singular points at discontinuities

\[
\frac{d\psi^\Gamma}{dt} + \psi^\Gamma \text{div} \mathbf{v}^\parallel + 2K_M \psi^\Gamma \mathbf{v}^\parallel - \psi^\Gamma \Phi^\Gamma t + \psi^\Gamma \xi^\Gamma t - \psi^\Gamma \Sigma^\Gamma t - \psi^\Gamma \Pi^\Gamma t = - \left[ \psi^\Gamma \Phi^\Gamma t + \psi^\Gamma t (\mathbf{v} - \mathbf{v}^\parallel t) \cdot \mathbf{n}^\Gamma \right] \cdot \mathbf{n}^\Gamma ,
\]

where \( \mathbf{v}^\Gamma \) is the surface velocity, \( \mathbf{v}^\parallel \) is its projection to the surface \( \Gamma \), and \( \mathbf{v}^\perp \) is its component normal to \( \Gamma \), \( K_M \) is the mean curvature of the surface, and \( \left[ \cdot \right] \) denotes the jump of the bracketed quantity across the surface \( \Gamma \) defined by \( \left[ \cdot \right] \overset{\text{def}}{=} + - - \) where the sign convention is given by the normal vector \( \mathbf{n} \) oriented from - to + side of the surface.

8.3 General balance laws under presence of discontinuities - multicomponent continuum

The above results can be easily extended for multicomponent materials - mixtures. Assuming an \( N \)-component mixture, we introduce index \( \alpha = 1, \ldots, N \) denoting the mixture components, and we can immediately formulate the mixture counterparts to (8.11) and (8.12):

• In regular points in the bulk

\[
\frac{\partial \psi^\alpha_{t}}{\partial t} + \text{div}(\psi^\alpha \Phi^\alpha t + \psi^\alpha t \mathbf{v}_{t}) - \psi^\alpha \xi^\alpha t - \psi^\alpha \Sigma^\alpha t - \psi^\alpha \Pi^\alpha t = 0 ,
\]  

\( \alpha = 1, \ldots, N \),

balancing the quantity \( \psi^\alpha_{t} \) with a corresponding flux \( \psi^\alpha \Phi^\alpha t \), a production \( \psi^\alpha \xi^\alpha t \), an outer supply \( \psi^\alpha \Sigma^\alpha t \) and as expected - a novel term \( \psi^\alpha \Pi^\alpha t \) corresponding to interaction with other components of the mixture. These interaction terms must satisfy the constraint

\[
\sum_{\alpha=1}^{N} \psi^\alpha \Pi^\alpha = 0 ,
\]

expressing the (local) conservation of \( \psi^\alpha_{t} \) during the exchange processes.

• At singular points at discontinuities

\[
\frac{d\psi^\alpha_{t}}{dt} + \psi^\alpha_{t} \text{div} \mathbf{v}^\parallel t - 2K_M \psi^\alpha_{t} \mathbf{v}^\parallel t + \psi^\alpha \Phi^\alpha t - \psi^\alpha \xi^\alpha t - \psi^\alpha \Sigma^\alpha t - \psi^\alpha \Pi^\alpha t = - \left[ \psi^\alpha \Phi^\alpha t + \psi^\alpha_{t} (\mathbf{v} - \mathbf{v}^\parallel t) \cdot \mathbf{n}^\Gamma \right] \cdot \mathbf{n}^\Gamma ,
\]

balancing the surface quantity \( \psi^\alpha_{t} \) with a corresponding surface flux \( \psi^\alpha \Phi^\alpha t \), a surface production \( \psi^\alpha \xi^\alpha t \), an outer surface supply \( \psi^\alpha \Sigma^\alpha t \) and surface interaction terms \( \psi^\alpha \Pi^\alpha t \), which satisfy the constraint

\[
\sum_{\alpha=1}^{N} \psi^\alpha \Pi^\alpha = 0 ,
\]

expressing the (local) conservation of \( \psi^\alpha_{t} \) during the exchange processes.

Remark 32. Note that while we distinguish individual tangential velocities of the components \( \mathbf{v}^\parallel \) \( \alpha = 1, \ldots, N \), we only use one \( \mathbf{v}^\perp \) being the (normal) velocity of the discontinuity \( \Gamma \). The discontinuity is thus not understood as being common to all mixture components. This assumption is without loss of generality in fact, if we adopt the following viewpoint. Whenever any material property of any of the components undergoes a jump or concentration at some surface, we define such a surface as a discontinuity for the whole mixture. The motion of such a surface is then given by the quantity \( \mathbf{v}^\perp \) and we keep in mind, that some quantities (e.g. properties corresponding to several mixture components) can be continuous across the surface.
8.4 Jump conditions

A particular situation arises, if the singular surface does not have any structure, and no accumulation of mass, momentum, energy or entropy occurs there. In such a case the single-component and multi-component general balance laws at singular surfaces (8.12) and (8.15) take the form of so-called jump conditions expressing continuity of the normal component of bulk convective and non-convective fluxes. Since these jump conditions are of particular importance per se, let us write them down explicitly. Recalling the definitions of $\psi_\Omega$ and corresponding non-convective fluxes $\Phi_\Omega$ for the individual balances, we obtain the following set of jump conditions associated to the particular balance laws:

$$\left[ \psi_\Omega + \psi_\Omega (v - v_\Gamma n_\Gamma) \right] \cdot n_\Gamma = 0$$

(8.17)

- **Mass jump condition**

$$\left[ \rho (v - v_\Gamma n_\Gamma) \right] \cdot n_\Gamma = 0$$

(8.18)

This condition expresses the simple fact of continuity of the normal mass flux (i.e. conservation of mass) through the discontinuity of density (e.g. a phase change front). Indeed the quantity $(v - v_\Gamma n_\Gamma) \cdot n_\Gamma$ is the relative motion of the material with respect to the moving discontinuity, multiplied by density, we obtain the mass flux. What mass flows “in”, must flow “out” is what the condition tells us.

- **Momentum jump condition**

$$\left[ T - \rho v \otimes (v - v_\Gamma n_\Gamma) \right] n_\Gamma = 0$$

(8.19)

If the interface is material, i.e. if $v^\pm \cdot n_\Gamma = v_\Gamma^\pm$, one obtains the continuity of traction condition

$$\left[ T \right] n_\Gamma = 0,$$

(8.20)

but not that for non-material surfaces (e.g. phase-change fronts), traction force need not be continuous any more due to the momentum transfer across the interface. Let us inspect one more case, which can often be encountered in practice. This concern a situation, when in the general interfacial balance law (8.15), for linear momentum, we keep the surface stress tensor on the left-hand-side, i.e. we keep $\rho \Phi_\Gamma = - \mathbb{T}_\Gamma$. Moreover, assuming that the interface acts as an isotropic membrane, we assume that the surface Cauchy stress is simply

$$\mathbb{T}_\Gamma = \sigma l_\Gamma,$$

where $\sigma$ is the surface tension and $l_\Gamma$ is the surface projection tensor (surface identity), which is defined as

$$l_\Gamma \overset{\text{def}}{=} 1 - n_\Gamma \otimes n_\Gamma.$$

(8.21)

Then a generalization of (8.19) is obtained:

$$\left[ \mathbb{T} - \rho v \otimes (v - v_\Gamma n_\Gamma) \right] n_\Gamma = \text{div}_\Gamma (\sigma l_\Gamma).$$

(8.22)

The right-hand side can be further expanded into two terms

$$\text{div}_\Gamma (\sigma l_\Gamma) = \nabla_\Gamma \sigma + \sigma \text{div}_\Gamma l_\Gamma = \nabla_\Gamma \sigma - 2K_M n_\Gamma,$$

(8.23)

where $K_M = -\frac{1}{2} \text{div}_\Gamma n_\Gamma$ is the mean curvature.

- **Total energy jump condition**

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

(8.24)

- **Entropy jump condition**

$$\left[ q_\eta + \rho \eta (v - v_\Gamma n_\Gamma) \right] \cdot n_\Gamma = 0.$$

(8.25)
8.5 Framework of the multiphase continuum theory

8.6 Averaging theorems

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