

# Only Old Wine in New Bottles? Thermodynamics of Mixtures from a PDE Point of View

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# Overview

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## Nonequilibrium Thermodynamics

Step 1 – The conservation PDEs for mass, charge, and momentum

Step 2 – The energy conservation PDE

Step 3 – The entropy evolution PDE

Step 4 – The constitutive laws

Conclusion

# Nonequilibrium Thermodynamics



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# Nonequilibrium Thermodynamics - Introduction

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## What is Nonequilibrium Thermodynamics

Nonequilibrium Thermodynamics is a macroscopic continuum theory that provides a general framework for the description of the dynamics in multicomponent systems (mixtures).

## Characterizations from the literature

*Nonequilibrium thermodynamics provides us with a general framework for the macroscopic description of irreversible processes.*

(S. De Groot, P. Mazur)

*Nonequilibrium thermodynamics is founded on the explicit expression for the entropy production rate in terms of irreversible processes that we can identify and study experimentally.*

(I. Prigogine)

# Nonequilibrium Thermodynamics - Introduction

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## Characteristic features of Nonequilibrium Thermodynamics

- allows to derive the governing equations for mixtures
- describes the dynamics in mixtures with densities and PDEs
- provides a formula for the entropy production rate
- allows to validate the thermodynamic consistency of constitutive laws

## Conclusion

- Nonequilibrium thermodynamics is a useful framework for the mathematical modeling of mixtures.
- Nonequilibrium Thermodynamics allows to check the thermodynamic consistency of mathematical models of mixtures

# Nonequilibrium Thermodynamics - The Building Blocks

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## **Step 1: The conservation PDEs for mass, charge, and momentum**

- set up the conservation PDEs for each constituent
- derive the conservation PDEs for the mixture from its constituents

## **Step 2: The energy conservation PDE**

- choose an ansatz for the energy densities for the constituents
- set up the energy conservation PDEs for the constituents
- derive the energy conservation PDE for the mixture
- show the 1st law of thermodynamics

# Nonequilibrium Thermodynamics - The Building Blocks

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## Step 3: The entropy evolution PDE

- use a nonequilibrium Gibbs relation
- derive the entropy evolution PDE
- obtain a formula for the entropy production rate
- show the 2nd law of thermodynamics

## Step 4: The constitutive laws

- choose the constitutive laws
- validate the thermodynamic consistency of the constitutive laws

**Result: Obtain a thermodynamically consistent PDE model.**

# Step 1 – The conservation PDEs for mass, charge, and momentum



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## Step 1: The variables

Mixtures are multicomponent systems of  $L$  constituents.

- solutes:  $l = 1, \dots, L - 1$
- solvent:  $l = L$

Constituent variable	corresponding Mixture variable	Units
$\rho_l$ mass density	$\rho = \sum_l \rho_l$ total mass density	$[kg/m^3]$
$y_l = \rho_l/\rho$ mass fraction	$1 = \sum_l y_l$	$[/]$
$\mathbf{u}_l$ velocity field	$\mathbf{u} = \sum_l y_l \mathbf{u}_l$ barycentric velocity field	$[m/s]$
$r_l$ mass production rate	$0 = \sum_l r_l$ mass continuity	$[kg/(m^3s)]$
$\mathbf{j}_l = \rho_l(\mathbf{u} - \mathbf{u}_l)$ drift mass flux	$0 = \sum_l \mathbf{j}_l \implies \mathbf{j}_L = -\sum_{l=1}^{L-1} \mathbf{j}_l$	$[kg/(m^2s)]$
$e_0 z_l m_l^{-1} \rho_l$ charge	$\rho_f = \sum_l e_0 z_l m_l^{-1} \rho_l$ free charge density	$[C/m^3]$

## Step 1: The mass balance equations

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### 1. Mass continuity for the $l$ th constituent :

$$\partial_t \rho_l + \nabla \cdot (\rho_l \mathbf{u} + \mathbf{j}_l) = r_l$$

### 2. Sum over $l$ and involve $\sum_l r_l = 0$ (mass continuity w.r.t. to reactions)

### 3. Mass continuity for the mixture:

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

#### Crucial observation

$f$  scalar function,  $\mathbf{v}$  vector field,  $\frac{D}{Dt}$  material derivative w.r.t. to  $\mathbf{u}$

$$\partial_t(\rho f) + \nabla \cdot (\rho f \mathbf{u}) = \rho [\partial_t f + \mathbf{u} \cdot \nabla f] + f [\partial_t \rho + \nabla \cdot (\rho \mathbf{u})] = \rho \frac{D}{Dt} f ,$$

$$\partial_t(\rho \mathbf{v}) + \nabla \cdot (\rho \mathbf{u} \otimes \mathbf{v}) = \rho [\partial_t \mathbf{v} + \nabla \mathbf{v} \mathbf{u}] + \mathbf{v} [\partial_t \rho + \nabla \cdot (\rho \mathbf{u})] = \rho \frac{D}{Dt} \mathbf{v}$$

**Conservative formulation**  $\iff$  **Non-conservative formulation**

## Step 1: The mass balance equations

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1. Mass continuity for the  $l$ th constituent ( $\rho_l = \rho y_l$ ):

$$\partial_t \rho_l + \nabla \cdot (\rho_l \mathbf{u} + \mathbf{j}_l) = r_l \quad \iff \quad \rho \frac{D}{Dt} y_l + \nabla \cdot \mathbf{j}_l = r_l$$

2. Sum over  $l$  and involve  $\sum_l r_l = 0$  (mass continuity w.r.t. to reactions)

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$$\partial_t(\rho \mathbf{v}) + \nabla \cdot (\rho \mathbf{u} \otimes \mathbf{v}) = \rho [\partial_t \mathbf{v} + \nabla \mathbf{v} \mathbf{u}] + \mathbf{v} [\partial_t \rho + \nabla \cdot (\rho \mathbf{u})] = \rho \frac{D}{Dt} \mathbf{v}$$

**Conservative formulation**  $\iff$  **Non-conservative formulation**

## Step 1: The momentum balance equations

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### 1. Momentum continuity for the $l$ th constituent:

$$\partial_t(\rho \mathbf{u}_l) + \nabla \cdot (\rho_l \mathbf{u}_l \otimes \mathbf{u}_l) = \nabla \cdot \mathbf{T}_l + e_0 z_l m_l^{-1} \rho_l \mathbf{E} + \mathbf{F}_l^{int} + r_l \mathbf{u}_l$$

2. Sum over  $l$  and involve  $\sum_l \mathbf{F}_l^{int} + r_l \mathbf{u}_l = 0$  (no internal momentum production)

### 3. Momentum continuity for the mixture:

$$\partial_t(\rho \mathbf{u}) + \nabla \cdot (\rho \mathbf{u} \otimes \mathbf{u}) = \nabla \cdot \mathbf{T} + \rho_f \mathbf{E}$$

#### The stress tensors

- The mixture stress tensor  $\mathbf{T}$  is given by

$$\mathbf{T} := \sum_l \mathbf{T}_l - \rho_l (\mathbf{u}_l - \mathbf{u}) \otimes (\mathbf{u}_l - \mathbf{u}) = \sum_l \mathbf{T}_l - \mathbf{j}_l \otimes (\mathbf{u}_l - \mathbf{u})$$

- For the conservation of the angular momentum, we have

$$\mathbf{T} = \mathbf{T}^\top \quad (\text{Cauchy's 2nd law of motion})$$

- The  $\mathbf{T}_l$  can be non-symmetric as long as  $\mathbf{T}$  remains symmetric

## Step 2 – The energy conservation PDE



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## STEP 2: The first law of thermodynamics

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**Ansatz for the evolution PDE for the total energy density  $\rho e^{tot}$ :**

$$\partial_t (\rho e^{tot}) + \nabla \cdot (\rho e^{tot} \mathbf{u} + \mathbf{j}_e) = r_e \quad (1)$$

**The first law of thermodynamics**

$$r_e = 0$$

## STEP 2: The first law of thermodynamics

---

**Ansatz for the evolution PDE for the total energy density  $\rho e^{tot}$ :**

$$\partial_t (\rho e^{tot}) + \nabla \cdot (\rho e^{tot} \mathbf{u} + \mathbf{j}_e) = r_e \quad (1)$$

### The first law of thermodynamics

$$r_e = 0 \quad \implies \quad \partial_t (\rho e^{tot}) + \nabla \cdot (\rho e^{tot} \mathbf{u} + \mathbf{j}_e) = 0$$

## STEP 2: The first law of thermodynamics

Ansatz for the evolution PDE for the total energy density  $\rho e^{tot}$ :

$$\partial_t (\rho e^{tot}) + \nabla \cdot (\rho e^{tot} \mathbf{u} + \mathbf{j}_e) = r_e \quad (1)$$

### The first law of thermodynamics

$$r_e = 0 \quad \implies \quad \partial_t (\rho e^{tot}) + \nabla \cdot (\rho e^{tot} \mathbf{u} + \mathbf{j}_e) = 0$$

### Fundamental ansatz for the energy densities

$$\begin{aligned} \rho e_l^{tot} &:= \frac{1}{2} \rho_l |\mathbf{u}_l|^2 + e_0 z_l m_l^{-1} \rho_l \Phi + \rho_l e_l^{int} \\ \implies \rho e^{tot} &:= \rho \sum_l y_l e_l^{tot} = \frac{1}{2} \rho |\mathbf{u}|^2 + \rho_f \Phi + \rho e^{int} \end{aligned} \quad (2)$$

Here, the internal energy density  $\rho e^{int}$  of the mixture given by

$$\rho e^{int} := \rho \sum_l y_l e_l^{int} + \frac{1}{2} \rho_l \sum_l |\mathbf{u}_l - \mathbf{u}|^2$$



## STEP 2: The energy evolution equations

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### The procedure:

1. Derive a PDE for the kinetic energy density  $\frac{1}{2}\rho|\mathbf{u}|^2$
2. Derive a PDE for the electric potential energy density  $\rho_f\Phi$
3. Ansatz for the internal energy density:  $\partial_t(\rho e^{int}) + \nabla \cdot (\rho e^{int}\mathbf{u} + \mathbf{q}) = h$   
( $\mathbf{q}$  heat flux,  $h$  internal energy production rate)
4. Insert 1. – 3. and (2) into (1)

### The energy evolution PDEs

- Obtain a formula for  $\mathbf{j}_e$ . This yields  $(\mathbf{i}_f := \sum_l e_0 z_l m_l^{-1} \mathbf{j}_l$  free current flux)  
$$\partial_t(\rho e^{tot}) + \nabla \cdot (\rho e^{tot}\mathbf{u} + \mathbf{q} + \Phi\mathbf{i}_f - \mathbf{T}\mathbf{u}) = 0 \quad \text{[energy conservation]}$$
- Obtain a formula for  $h$ . This yields  
$$\partial_t(\rho e^{int}) + \nabla \cdot (\rho e^{int}\mathbf{u} + \mathbf{q}) = \mathbf{i}_f \cdot \mathbf{E} + \mathbf{T} : \nabla\mathbf{u} \quad \text{[“heat equation”]}$$

## Step 3 – The entropy evolution PDE



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## STEP 3: The second law of thermodynamics

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**Ansatz for the evolution PDE for the entropy density  $\rho s$ :**

$$\partial_t(\rho s) + \nabla \cdot (\rho s \mathbf{u} + \mathbf{j}_s) = \sigma \quad \iff \quad \rho \frac{D}{Dt} s = -\nabla \cdot \mathbf{j}_s + \sigma \quad (3)$$

**The second law of thermodynamics**

$$\sigma \geq 0$$

## STEP 3: The second law of thermodynamics

---

**Ansatz for the evolution PDE for the entropy density  $\rho s$ :**

$$\partial_t(\rho s) + \nabla \cdot (\rho s \mathbf{u} + \mathbf{j}_s) = \sigma \quad \Longleftrightarrow \quad \rho \frac{D}{Dt} s = -\nabla \cdot \mathbf{j}_s + \sigma \quad (3)$$

### The second law of thermodynamics

$$\sigma \geq 0 \quad \Longrightarrow \quad \partial_t(\rho s) + \nabla \cdot (\rho s \mathbf{u} + \mathbf{j}_s) \geq 0$$

## STEP 3: The second law of thermodynamics

Ansatz for the evolution PDE for the entropy density  $\rho s$ :

$$\partial_t(\rho s) + \nabla \cdot (\rho s \mathbf{u} + \mathbf{j}_s) = \sigma \quad \Longleftrightarrow \quad \rho \frac{D}{Dt} s = -\nabla \cdot \mathbf{j}_s + \sigma \quad (3)$$

### The second law of thermodynamics

$$\sigma \geq 0 \quad \Longrightarrow \quad \partial_t(\rho s) + \nabla \cdot (\rho s \mathbf{u} + \mathbf{j}_s) \geq 0$$

### Equilibrium Gibbs relation

In equilibrium:  $e^{int} = e^{int}(s, v, y_1, \dots, y_L)$

This yields the equilibrium Gibbs relation

$$de^{int} = \underbrace{\partial_s e^{int}}_{=: T} ds + \underbrace{\partial_v e^{int}}_{=: -p} dv + \sum_I \underbrace{\partial_{y_I} e^{int}}_{=: \mu_I} dy_I = T ds - p dv + \sum_I \mu_I dy_I$$

## STEP 3: The nonequilibrium Gibbs relation

### Nonequilibrium Gibbs relation

In nonequilibrium:  $e^{int}(t, x) = e^{int}(s(t, x), v(t, x), y_1(t, x), \dots, y_L(t, x))$

This yields the nonequilibrium Gibbs relation

$$\begin{aligned}\frac{D}{Dt}e^{int} &= \underbrace{\partial_s e^{int}}_{=:T} \frac{D}{Dt}s + \underbrace{\partial_v e^{int}}_{=: -p} \frac{D}{Dt}v + \sum_l \underbrace{\partial_{y_l} e^{int}}_{=: \mu_l} \frac{D}{Dt}y_l \\ &= T \frac{D}{Dt}s - p \frac{D}{Dt}v + \sum_l \mu_l \frac{D}{Dt}y_l\end{aligned}$$

Combine the nonequilibrium Gibbs relation with equation (3). This yields

$$-\nabla \cdot \mathbf{j}_s + \sigma = \frac{1}{T} \frac{D}{Dt}e^{int} + \frac{p}{T} \frac{D}{Dt}v - \frac{1}{T} \sum_l \mu_l \frac{D}{Dt}y_l$$

**Insert the PDEs for  $e^{int}$ ,  $v$ , and  $y_l \implies$  Obtain formulas for  $\mathbf{j}_s$  and  $\sigma$**

## STEP 3: The entropy production rate

### The entropy production rate

$$\underbrace{\sigma}_{\text{entropy production}} = \underbrace{-\frac{1}{T} \nabla T \cdot \mathbf{j}_s}_{\text{entropic part}} + \underbrace{\frac{1}{T} \nabla \mathbf{u} : \boldsymbol{\tau}}_{\text{viscous part}} - \underbrace{\frac{1}{T} \sum_I \nabla \mu_I^{el} \cdot \mathbf{j}_I}_{\text{mixing part}} - \underbrace{\sum_I \frac{\mu_I^{el}}{T} r_I}_{\text{el.chem. part}} \geq 0$$

entropy flux

$$\mathbf{j}_s = \frac{1}{T} \mathbf{q} - \sum_I \frac{\mu_I^{el}}{T} \mathbf{j}_I + \frac{\Phi}{T} \mathbf{i}_f$$

stress tensor

$$\boldsymbol{\tau} = -p \mathbf{1} + \boldsymbol{\tau}$$

electrochemical potential

$$\mu_I^{el} = \frac{e_0 z_I}{m_I} \Phi + \mu_I$$

### Outcome:

- $\sigma$  is expressed in terms of measurable quantities
- contributions to  $\sigma$  are revealed

### Criterion for thermodynamic consistency

Constitutive laws for  $\boldsymbol{\tau}$ ,  $\mathbf{j}_I$ ,  $\mathbf{q}$ ,  $r_I$ ,  $\mu_I^{el}$  must respect  $\sigma > 0$

## Step 4 – The constitutive laws



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## STEP 4: The governing equations

### Poisson's equation:

$$-\nabla \cdot (\epsilon_0 \epsilon_r \nabla \Phi) = \rho_f$$

### Mass conservation: $l \in \{1, \dots, L-1\}$

$$\partial_t \rho_l + \nabla \cdot (\rho_l \mathbf{u} + \mathbf{j}_l) = r_l$$

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

### Momentum conservation:

$$\begin{aligned} \partial_t (\rho \mathbf{u}) + \nabla \cdot (\rho \mathbf{u} \otimes \mathbf{u}) \\ = -\nabla \rho + \nabla \cdot \boldsymbol{\tau} + \rho_f \mathbf{E} \end{aligned}$$

### Internal energy evolution:

$$\begin{aligned} \partial_t (\rho e^{int}) + \nabla \cdot (\rho e^{int} \mathbf{u} + \mathbf{q}) \\ = -\rho \nabla \cdot \mathbf{u} + \boldsymbol{\tau} : \nabla \mathbf{u} + \mathbf{E} \cdot \mathbf{i}_f \end{aligned}$$

### Dependent variables:

$$\rho_L = \rho - \sum_l^{L-1} \rho_l$$

$$\mathbf{j}_L = -\sum_l^{L-1} \mathbf{j}_l$$

### Involved Ansatzes:

$$\mathbf{T} = -\rho \mathbf{1} + \boldsymbol{\tau}$$

$$\rho e^{tot} = \rho e^{int} + \rho_f \Phi + \frac{1}{2} \rho |\mathbf{u}|^2$$

### Dependent equations:

$$\partial_t (\rho e^{tot}) + \nabla \cdot (\rho e^{tot} \mathbf{u} + \mathbf{q} + \Phi \mathbf{i}_f - \mathbf{T} \mathbf{u}) = 0$$

$$\rho \frac{D}{Dt} \mathbf{s} = \frac{\rho}{T} \frac{D}{Dt} e^{int} + \frac{\rho \rho}{T} \frac{D}{Dt} \mathbf{v} - \frac{\rho}{T} \sum_l \mu_l \frac{D}{Dt} \mathbf{y}_l$$

Here, we can insert  $\rho \frac{D}{Dt} \mathbf{v} = \nabla \cdot \mathbf{u}$

## STEP 4: Example 1 – Fluid mechanical equations

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one species ( $L = 1$ ), electrically neutral ( $z_l = 0$ )

### Governing equations

#### Mass conservation:

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

#### Momentum conservation:

$$\partial_t (\rho \mathbf{u}) + \nabla \cdot (\rho \mathbf{u} \otimes \mathbf{u}) = -\nabla p + \nabla \cdot \boldsymbol{\tau}$$

#### Internal energy evolution:

$$\partial_t (\rho e^{int}) + \nabla \cdot (\rho e^{int} \mathbf{u} + \mathbf{q}) = -p \nabla \cdot \mathbf{u} + \boldsymbol{\tau} : \nabla \mathbf{u}$$

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### Constitutive ansatzes ( $\eta$ shear viscosity, $\eta_v$ bulk viscosity, $\kappa$ heat capacity)

$$\boldsymbol{\tau} := \eta [\nabla \mathbf{u} + \nabla \mathbf{u}^\top] + \eta_v (\nabla \cdot \mathbf{u}) \mathbb{1} \quad \text{[Newtonian fluid]}$$

$$\mathbf{q} := -\kappa \nabla T \quad \text{[Fourier's law]}$$

## STEP 4: Example 1 – Fluid mechanical equations

---

one species ( $L = 1$ ), electrically neutral ( $z_l = 0$ )

**Entropy production rate** ( Symmetric gradient:  $\nabla^s \mathbf{u} := \frac{1}{2} (\nabla \mathbf{u} + \nabla \mathbf{u}^\top)$  )

$$\begin{aligned} T\sigma &= -T^{-1} \nabla T \cdot \mathbf{q} + \nabla \mathbf{u} : \boldsymbol{\tau} \\ &= \kappa T^{-1} |\nabla T|^2 + 2\eta \nabla^s \mathbf{u} : \nabla^s \mathbf{u} + \eta_V |\nabla \cdot \mathbf{u}|^2 \\ &\geq (2\eta n^{-1} + \eta_V) |\nabla \cdot \mathbf{u}|^2 \\ &\geq 0, \quad \text{if } 2\eta \geq n \eta_V \end{aligned}$$

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**Thermodynamically consistent ansatzes for  $\boldsymbol{\tau}$  and  $\mathbf{q}$**

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**Thermodynamically consistent ansatzes for  $\boldsymbol{\tau}$  and  $\mathbf{q}$**

**Solution vector:**  $(\rho, T, \mathbf{u})$

**Dependent variables:**  $e^{int} = e^{int}(\rho, T)$ ,  $p = p(\rho, T)$ ,  $\eta = \eta(\rho, T)$ .

The ansatzes for these dependencies can not be verified by  $\sigma \geq 0$

## STEP 4: Example 2 – The diffusion equation

Isothermal ( $T \equiv \text{const}$ ), electrically neutral ( $z_l = 0$ ), incompressible ( $\rho \equiv \text{const}$ ), no flow ( $\mathbf{u} \equiv 0$ )

### Governing equations

**Mass conservation:**  $l \in \{1, \dots, L-1\}$

$$\partial_t \rho_l + \nabla \cdot \mathbf{j}_l = r_l$$

**Momentum conservation:**

$$-\nabla p = 0$$

**Dependent variables:**

$$\rho_L = \rho - \sum_l^{L-1} \rho_l$$

$$\mathbf{j}_L = -\sum_l^{L-1} \mathbf{j}_l$$

## STEP 4: Example 2 – The diffusion equation

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## STEP 4: Example 2 – The diffusion equation

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### Constitutive ansatzes (mobility $\omega_l$ , stoich. coeff. $s_{ij}$ , constants $\beta_l, k_j^f, k_j^b$ )

$$\mu_l := \mu^0(p, T) + \frac{k_b T}{m_l} (\beta_l + \ln y_l) \quad [\text{chemical potential}]$$

$$\mathbf{j}_l := -m_l \omega_l \rho_l \nabla (\mu_l - \mu_L) \quad [\text{diffusion flux}]$$

$$r_l := m_l \sum_j s_{lj} R_j \quad [\text{mass production rate}]$$

$$R_j := k_j^f \prod_{s_{ij} < 0} y_i^{-s_{ij}} - k_j^b \prod_{s_{ij} > 0} y_i^{s_{ij}} \quad [\text{reaction rate}]$$

## STEP 4: Example 2 – The diffusion equation

Isothermal ( $T \equiv \text{const}$ ), electrically neutral ( $z_l = 0$ ), incompressible ( $\rho \equiv \text{const}$ ), no flow ( $u \equiv 0$ )

### Entropy production rate

$$\sigma = -\frac{1}{T} \sum_{l=1}^L \nabla \mu_l \cdot \mathbf{j}_l - \sum_{l=1}^L \frac{\mu_l}{T} r_l \geq 0$$

### Diffusive entropy production

$$\begin{aligned} -\frac{1}{T} \sum_{l=1}^L \nabla \mu_l \cdot \mathbf{j}_l &= -\frac{1}{T} \left( \sum_{l=1}^{L-1} \nabla \mu_l \cdot \mathbf{j}_l + \nabla \mu_L \cdot \mathbf{j}_L \right) \\ &= -\frac{1}{T} \left( \sum_{l=1}^{L-1} \nabla \mu_l \cdot \mathbf{j}_l - \sum_{l=1}^{L-1} \nabla \mu_L \cdot \mathbf{j}_l \right) \end{aligned}$$

## STEP 4: Example 2 – The diffusion equation

Isothermal ( $T \equiv \text{const}$ ), electrically neutral ( $z_l = 0$ ), incompressible ( $\rho \equiv \text{const}$ ), no flow ( $\mathbf{u} \equiv 0$ )

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$$\sigma = -\frac{1}{T} \sum_{l=1}^L \nabla \mu_l \cdot \mathbf{j}_l - \sum_{l=1}^L \frac{\mu_l}{T} r_l \geq 0$$

### Diffusive entropy production

$$\begin{aligned} -\frac{1}{T} \sum_{l=1}^L \nabla \mu_l \cdot \mathbf{j}_l &= -\frac{1}{T} \left( \sum_{l=1}^{L-1} \nabla \mu_l \cdot \mathbf{j}_l + \nabla \mu_L \cdot \mathbf{j}_L \right) \\ &= -\frac{1}{T} \sum_{l=1}^{L-1} \nabla (\mu_l - \mu_L) \cdot \mathbf{j}_l \end{aligned}$$

## STEP 4: Example 2 – The diffusion equation

Isothermal ( $T \equiv \text{const}$ ), electrically neutral ( $z_l = 0$ ), incompressible ( $\rho \equiv \text{const}$ ), no flow ( $u \equiv 0$ )

### Entropy production rate

$$\sigma = -\frac{1}{T} \sum_{l=1}^L \nabla \mu_l \cdot \mathbf{j}_l - \sum_{l=1}^L \frac{\mu_l}{T} r_l \geq 0$$

### Diffusive entropy production

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Thermodynamically consistent ansatzes for  $\mathbf{j}_l$

## STEP 4: Example 2 – The diffusion equation

Isothermal ( $T \equiv \text{const}$ ), electrically neutral ( $z_i = 0$ ), incompressible ( $\rho \equiv \text{const}$ ), no flow ( $\mathbf{u} \equiv 0$ )

- reaction rate vector  $\mathbf{R} = (R_1, \dots, R_J)^\top \in \mathbb{R}^J$
- equilibrium constant vector  $\mathbf{K} := (K^1, \dots, K^J)^\top := (k_1^f/k_1^b, \dots, k_J^f/k_J^b)^\top \in \mathbb{R}^J$
- mass fraction vector  $\mathbf{y} = (y_1, \dots, y_L)^\top \in \mathbb{R}^L$
- stoichiometric matrix  $S \in \mathbb{Z}^{L \times J}$

- Equilibrium for the  $j$ th reaction rate  $R_j$

$$R_j(\mathbf{y}) = 0 \quad \Longleftrightarrow \quad K^j = \prod_{s_{ij} \neq 0} (y_i)^{s_{ij}} \quad \Longleftrightarrow \quad \ln(K^j) = \sum_i s_{ij} \ln(y_i)$$

- Simultaneous equilibrium for all reaction rates  $R_j$

$$\mathbf{R}(\mathbf{y}) = \mathbf{0} \quad \Longleftrightarrow \quad \ln(\mathbf{K}) = S^\top \ln(\mathbf{y})$$

**Wegscheider condition / principle of detailed balance**

$J < L$ : an equilibrium mass fraction vector  $\mathbf{y}^*$  with  $\mathbf{R}(\mathbf{y}^*) = \mathbf{0}$  exists

## STEP 4: Example 2 – The diffusion equation

Isothermal ( $T \equiv \text{const}$ ), electrically neutral ( $z_l = 0$ ), incompressible ( $\rho \equiv \text{const}$ ), no flow ( $u \equiv 0$ )

- Definition: Set  $\beta_l = \ln(y_l^*)$
- Equivalence:  $R_j \begin{matrix} \geq \\ \leq \end{matrix} 0 \iff \dots \iff 0 \begin{matrix} \geq \\ \leq \end{matrix} \sum_l s_{lj} (\beta_l + \ln y_l)$
- Estimate:  $R_j \sum_l s_{lj} (\beta_l + \ln y_l) \leq 0$  for  $j \in \{1, \dots, J\}$

### Reactive entropy production

$$\begin{aligned}
 - \sum_l \frac{\mu_l}{T} r_l &= - \underbrace{\frac{\mu^0}{T} \sum_l r_l}_{=0} - \sum_l \frac{k_b T}{m_l T} (\beta_l + \ln(y_l)) \left[ m_l \sum_j s_{lj} R_j \right] \\
 &= -k_b \sum_j R_j \underbrace{\sum_l s_{lj} (\beta_l + \ln(y_l))}_{\leq 0} \geq 0.
 \end{aligned}$$

Thermodynamically consistent ansatzes for  $\mu_l$  and  $r_l$

## STEP 4: Example 2 – The diffusion equation

Isothermal ( $T \equiv \text{const}$ ), electrically neutral ( $z_l = 0$ ), incompressible ( $\rho \equiv \text{const}$ ), no flow ( $u \equiv 0$ )

### The chemical potentials

$$\mu_l(p, T, y_l) = \mu^0(p, T) + \underbrace{\frac{k_b T}{m_l} (\beta_l + \ln y_l)}_{=:\mu_l^{\text{mix}}(T, y_l)} = \mu^0(p, T) + \mu_l^{\text{mix}}(T, y_l)$$

### Pressure independency of the diffusion fluxes

$$\mathbf{j}_l(t, \mathbf{x}) = -m_l \omega_l \rho_l \nabla (\mu_l - \mu_L) = -m_l \omega_l \rho_l \nabla (\mu_l^{\text{mix}} - \mu_L^{\text{mix}})$$

**WARNING:** The pressure equation decouples due to  $\mu_l^0 := \mu^0$

### Remaining governing equations (Reaction-Diffusion system)

$$\partial_t \rho_l + \nabla \cdot \mathbf{j}_l = r_l, \quad \text{for } l \in \{1, \dots, L-1\}$$

From these equations compute:  $\rho_L = \rho - \sum_{l=1}^{L-1} \rho_l$

## STEP 4: Example 2 – The diffusion equation

Isothermal ( $T \equiv \text{const}$ ), electrically neutral ( $z_i = 0$ ), incompressible ( $\rho \equiv \text{const}$ ), no flow ( $u \equiv 0$ )

- Einstein-Smoluchowski relation:  $\omega_i = d_i(k_b T)^{-1}$
- Gradient of the chemical potentials:  $\nabla\mu_i = k_b T m_i^{-1} y_i^{-1} \nabla y_i = k_b T m_i^{-1} \rho_i^{-1} \nabla \rho_i$

### Diffusion fluxes

- Thermodynamically consistent ansatz:

$$\mathbf{j}_i = -m_i \omega_i \rho_i \nabla(\mu_i - \mu_L) = \underbrace{-d_i \nabla \rho_i}_{\text{fickian}} + \underbrace{\frac{m_i \rho_i d_i}{m_L \rho_L} \nabla \rho_L}_{\text{solvent}}$$



## STEP 4: Example 2 – The diffusion equation

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- Approximation in dilute mixtures: ( $y_L \approx \text{const} \implies \nabla\mu_L \approx 0$ )

$$\mathbf{j}_i = -m_i \omega_i \rho_i \nabla(\mu_i - \mu_L) \approx -m_i \omega_i \rho_i \nabla\mu_i = \underbrace{-d_i \nabla \rho_i}_{\text{fickian}}$$

## STEP 4: Example 2 – The diffusion equation

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### Diffusion fluxes

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**WARNING: The Fickian diffusion ansatz is only an approximation of the thermodynamically consistent ansatz**

## STEP 4: Example 3 – The Poisson-Nernst-Planck system

Isothermal ( $T \equiv \text{const}$ ), neutral solvent ( $z_L = 0$ ), incompressible ( $\rho \equiv \text{const}$ ), no flow ( $\mathbf{u} \equiv 0$ )

### Governing equations

#### Poisson's equation:

$$-\nabla \cdot (\epsilon_0 \epsilon_r \nabla \Phi) = \rho_f$$

#### Mass conservation: $l \in \{1, \dots, L-1\}$

$$\partial_t \rho_l + \nabla \cdot \mathbf{j}_l = r_l$$

#### Momentum conservation:

$$-\nabla p = -\rho_f \mathbf{E}$$

#### Dependent variables:

$$\rho_L = \rho - \sum_l^{L-1} \rho_l$$

$$\mathbf{j}_L = -\sum_l^{L-1} \mathbf{j}_l$$

## STEP 4: Example 3 – The Poisson-Nernst-Planck system

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$$-\nabla \cdot (d \nabla p) = -\nabla \cdot (d \rho_f \mathbf{E})$$

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$$-\nabla \cdot (d \nabla \rho) = -\nabla \cdot (d \rho_f \mathbf{E})$$

**Dependent variables:**

$$\rho_L = \rho - \sum_l^{L-1} \rho_l$$

$$\mathbf{j}_L = -\sum_l^{L-1} \mathbf{j}_l$$

### Constitutive ansatzes

$$\mu_l^{el} := \frac{e_0 z_l}{m_l} \Phi + \mu^0(\rho, T) + \frac{k_b T}{m_l} (\beta_l + \ln y_l) \quad [\text{electrochemical potential}]$$

$$\mathbf{j}_l := -m_l \omega_l \rho_l \nabla (\mu_l^{el} - \mu_L^{el}) \quad [\text{diffusion flux}]$$

$$r_l := m_l \sum_j s_{lj} \left[ k_j^f \prod_{s_{ij} < 0} y_i^{-s_{ij}} - k_j^b \prod_{s_{ij} > 0} y_i^{s_{ij}} \right] \quad [\text{mass production rate}]$$

## STEP 4: Example 3 – The Poisson-Nernst-Planck system

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**Isothermal** ( $T \equiv \text{const}$ ), **neutral solvent** ( $z_L = 0$ ), **incompressible** ( $\rho \equiv \text{const}$ ), **no flow** ( $\mathbf{u} \equiv 0$ )

### Entropy production rate

$$\sigma = -\frac{1}{T} \sum_{l=1}^L \nabla \mu_l^{el} \cdot \mathbf{j}_l - \sum_{l=1}^L \frac{\mu_l^{el}}{T} r_l \geq 0$$

**From Example 2: Thermodynamically consistent ansatzes for  $\mu_l^{el}$ ,  $\mathbf{j}_l$ ,  $r_l$**

## STEP 4: Example 3 – The Poisson-Nernst-Planck system

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### Diffusion fluxes

- Thermodynamically consistent ansatz:

$$\mathbf{j}_l = -m_l \omega_l \rho_l \nabla (\mu_l - \mu_L) = \underbrace{-d_l \nabla \rho_l}_{\text{fickian}} + \underbrace{\frac{m_l \rho_l d_l}{m_L \rho_L} \nabla \rho_L}_{\text{solvent}} + \underbrace{\frac{e_0 z_l d_l}{k_b T} \rho_l \mathbf{E}}_{\text{electric}}$$



## STEP 4: Example 3 – The Poisson-Nernst-Planck system

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- Approximation in dilute mixtures: ( $y_L \approx \text{const} \implies \nabla \mu_L \approx 0$ )

$$\mathbf{j}_l \approx -m_l \omega_l \rho_l \nabla \mu_l = \underbrace{-d_l \nabla \rho_l}_{\text{fickian}} + \underbrace{\frac{e_0 z_l d_l}{k_b T} \rho_l \mathbf{E}}_{\text{electric}} \quad [\text{Nernst-Planck flux}]$$

## STEP 4: Example 3 – The Poisson-Nernst-Planck system

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The Nernst-Planck flux is only an approximation for dilute solutions

## STEP 4: Example 3 – The Poisson-Nernst-Planck system

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Isothermal ( $T \equiv \text{const}$ ), neutral solvent ( $z_L = 0$ ), incompressible ( $\rho \equiv \text{const}$ ), no flow ( $\mathbf{u} \equiv 0$ )

**Equation for the solvent** (sum over the PDEs for  $\rho_1, \dots, \rho_{L-1}$ )

Use  $\rho_L = \rho - \sum_{l=1}^{L-1} \rho_l$

$$-\partial_t \rho_L + \nabla \cdot \sum_{l=1}^{L-1} \left( -d_l \nabla \rho_l + \frac{e_0 z_l d_l}{k_b T} \rho_l \mathbf{E} \right) = \sum_{l=1}^{L-1} r_l$$

## STEP 4: Example 3 – The Poisson-Nernst-Planck system

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Use  $\rho_L = \rho - \sum_{l=1}^{L-1} \rho_l$ , split  $d_l = (d_l - d) + d$

$$-\partial_t \rho_L + \nabla \cdot (d \nabla \rho_L) + \nabla \cdot \left( \frac{d}{k_b T} \rho_f \mathbf{E} \right) + \dots = \sum_{l=1}^{L-1} r_l$$

## STEP 4: Example 3 – The Poisson-Nernst-Planck system

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$$\partial_t \rho_L - \nabla \cdot (d \nabla \rho_L) - \nabla \cdot \left( \frac{d}{k_b T} \nabla p \right) + \dots = - \sum_{l=1}^{L-1} r_l$$

## STEP 4: Example 3 – The Poisson-Nernst-Planck system

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**The resulting system**

The solution vector  $(\rho_1, \dots, \rho_{L-1}, \mathbf{E}, p)$  consists of

- the electroosmotic pressure  $p$ ,
- the electric field  $\mathbf{E}$ ,
- and the concentrations  $\rho_l$

Here,  $p, \rho_l, \mathbf{E}$  are fully coupled through:

$$p \longrightarrow \rho_L \longrightarrow \rho_l \longleftrightarrow \mathbf{E} \longrightarrow p$$

## STEP 4: Example 3 – The Poisson-Nernst-Planck system

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**Isothermal** ( $T \equiv \text{const}$ ), **neutral solvent** ( $z_L = 0$ ), **incompressible** ( $\rho \equiv \text{const}$ ), **no flow** ( $\mathbf{u} \equiv 0$ )

### Dilute Approximation (Classical Poisson-Nernst-Planck system)

- Solvent PDE remains pressure dependent:

$$\partial_t \rho_L - \nabla \cdot (d \nabla \rho_L) - \nabla \cdot \left( \frac{d}{k_b T} \nabla p \right) + \dots = - \sum_{l=1}^{L-1} r_l$$

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- **WARNING:** Now, the solute PDEs are solvent independent

$$\partial_t \rho_l + \nabla \cdot \left( -d_l \nabla \rho_l + \cancel{\frac{m_l \rho_l d_l}{m_L \rho_L} \nabla \rho_L} + \frac{e_0 z_l d_l}{k_b T} \rho_l \mathbf{E} \right) = r_l$$



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### The resulting system

The solution vector  $(\rho_1, \dots, \rho_{L-1}, \mathbf{E})$  consists of

- the electric field  $\mathbf{E}$ ,
- and the concentrations  $\rho_l$

No coupling from  $p$  to  $\rho_l$ :

$$p \longrightarrow \rho_L \not\longleftrightarrow \rho_l \longleftrightarrow \mathbf{E} \longrightarrow p$$

## STEP 4: Example 3 – The Poisson-Nernst-Planck system

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$$p \longrightarrow \rho_L \quad \rho_l \longleftrightarrow \mathbf{E} \longrightarrow p$$

# Conclusion



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# Conclusion

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## Nonequilibrium thermodynamics

- allows to derive the governing equations for mixtures
- derives a formula for the entropy production rate  $\sigma$  based on Gibbs relation
- allows to validate the constitutive laws

### **Conclusion:**

Nonequilibrium thermodynamics is a framework for the derivation of thermodynamically consistent mathematical models

# Conclusion

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## Presented examples:

- Example 1: The fluid mechanical equations
- Example 2: Reaction–diffusion systems
- Example 3: Poisson-Nernst-Planck systems

### Conclusion:

- Be careful with the pressure ansatz in fluid mechanical systems  
→ Not verifiable through the formula for  $\sigma$
- Be careful with the dilute approximation for charged mixtures  
→ The electroosmotic pressure equation decouples

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**Thank you for your attention**