MATE 664 Lecture 03

Driving Forces in Irreversible Thermodynamics

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Recap of Lecture 02

Key ideas from last lecture:

- Crash course on statistical mechanics
    - Microstate in phase space   macroscopic property with probability
    - Measurement of microstate   entropy   Boltzmann formula
    - Explain Boltzmann distribution
    - Explain entropy maximizing principle
- Introduction to irreversible thermodynamics
    - Postulate 1: local equilibrium assumption
    - Postulate 2: rate of entropy production is non-zero
    - Postulate 3: linear coupling between flux and forces
    - Postulate 4: symmetry between coupling coefficients

Learning Outcomes

After today's lecture, you will be able to:

- **Recall** the entropy production equation and link to rate
- **Analyze** the formula for entropy production the driving force expression
- **Derive** general equation for driving forces in system
- **Formulate** relationship between reciprocal driving force situations

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Entropy Balance Equation

General form:

$$\frac{dS}{dt} = \left(\frac{dS}{dt}\right)_{\text{exchange}} + \left(\frac{dS}{dt}\right)_{\text{production}}$$

- Exchange: entropy flow across system boundaries
- Production: entropy generated internally
- Entropy **can flow** and **can be generated**

Entropy Production In Microscopic Cells

When applying local equilibrium, we generally consider **entropy density** $s = S_i/V_i$ for a certain *microscopic cell*.

Using *Balluffi book* notations, entropy balance equation looks like:

$$\frac{\partial s}{\partial t} = -\nabla \cdot \vec{J}_s + \dot{\sigma}$$

- $\vec{J}_s$: flux of entropy (exchange)
- $\dot{\sigma}$: entropy generation rate

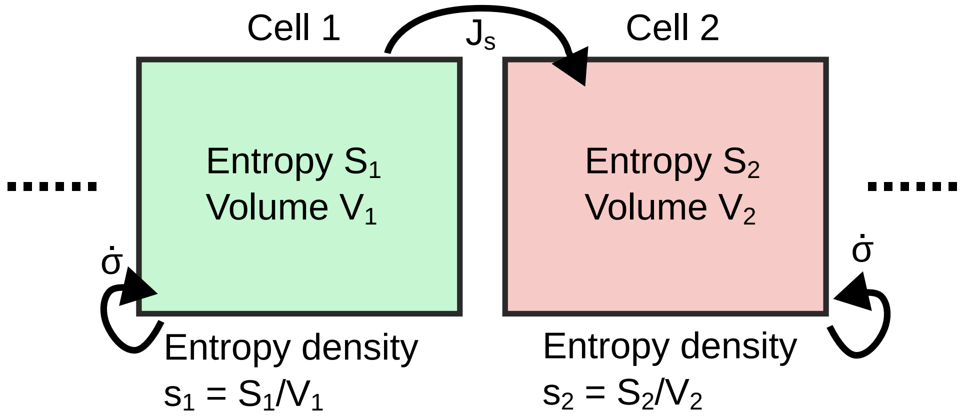

Figure 1: Scheme of microcell and entropy balance

Irreversible Thermodynamics

Central law:

$$\dot{\sigma} = \frac{\partial s}{\partial t} + \nabla \cdot \vec{J}_s \geq 0$$

- This is the local form of the second law.
- Equilibrium $\dot{\sigma} = 0$
- Can we have $\frac{\partial s}{\partial t} = 0$?

Entropy Balance: Solving $\dot{\sigma}$ and $\vec{J}_s$

Chain rule again! For any thermodynamic quantity ξ_i:

$$\begin{aligned} \frac{\partial s}{\partial t} &= \sum_i \frac{\partial s}{\partial \xi_i} \frac{\partial \xi_i}{\partial t} && (1) \\ &= \sum_i \frac{\partial s}{\partial \xi_i} (-\nabla \cdot \vec{J}_{\xi_i}) && (2) \end{aligned}$$

- What quantities ξ_i can be used?
- How do we solve $\frac{\partial s}{\partial \xi_i}$?

Entropy Flux and Production: Results

After arranging the formula for entropy balance and apply laws in vector operations, we get:

$$\begin{aligned} \vec{J}_s &= \sum_i \frac{\partial s}{\partial \xi_i} \vec{J}_{\xi_i} && (3) \\ \dot{\sigma} &= \sum_i \vec{J}_{\xi_i} \cdot \nabla \left(\frac{\partial s}{\partial \xi_i} \right) && (4) \end{aligned}$$

- It seems everything has relation with:
    - A flux $\vec{J}_{\xi_i}$

  - An coefficient $\frac{\partial s}{\partial \xi_i}$ (Onsager's affinity)

- Non-negative entropy production $\vec{J}_{\xi_i}$ and gradient (vector) $\nabla \left(\frac{\partial s}{\partial \xi_i}\right)$ have an angle no more than 90 degrees!

What Are The Affinities, Anyway?

Consider generalized 1st law of thermodynamics:

$$ds = \frac{1}{T}du - \sum_i \frac{\psi_i}{T} d\xi_i \tag{5}$$

It requires:

- ξ_i is an **extensive property**
- ψ_i in an **intensitve property** often called **potential**
- ξ_i is **conjugate** to ψ_i

What are ψ and ξ?

- General entropy differential (extended variables):

$$ds = \frac{1}{T}du - \frac{p}{T}dv - \sum_i \frac{\psi_i}{T} d\xi_i$$

- ξ_i: **extensive variables**
  - volume v
  - charge q
  - concentration c
  - surface area A
  - dipole moment $\mathbf{p}$
  - magnetic moment $\mathbf{b}$

- ψ_i: **conjugate intensive variables**
  - pressure p
  - electric potential ϕ

  - chemical potential μ
  - surface energy γ
  - external electric field $\mathbf{E}$
  - magnetic field $\mathbf{H}$

Each (ψ_i, ξ_i) pair contributes to entropy change.

Entropy Flux and Production In Driving Force Terms

We can rewrite the entropy balance equation using individual fluxes:

$$\vec{J}_s = -\sum_i \frac{\psi_i}{T}\vec{J}_{\xi_i} = \frac{1}{T}\vec{J}_u - \sum_i \frac{\psi_i}{T}\vec{J}_{\xi_i} \tag{6}$$

$$\dot{\sigma} = -\sum_i \vec{J}_{\xi_i}\cdot\nabla\left(\frac{\psi_i}{T}\right) = \vec{J}_u\cdot\nabla\left(\frac{1}{T}\right) - \sum_i \vec{J}_{\xi_i}\cdot\nabla\left(\frac{\psi_i}{T}\right) \tag{7}$$

- If u also have an corresponding potential, what will it be?

Entropy Production: With Flux of Heat Term

Often we wanted to write entropy generation using flux of heat $\vec{J}_Q = T\vec{J}_s$:

$$T\dot{\sigma} = -\frac{\vec{J}_Q}{T}\cdot\nabla T - \sum_i \vec{J}_{\xi_i}\cdot\nabla\psi_i \tag{8}$$

- Why is there a negative sign before each term?
- Can you generalize this term?

General Formula for Entropy Production

$$\boxed{\dot{\sigma} = -\sum_i [\text{flux of } \xi_i] \cdot [\nabla(\text{conjugate potential } \psi_i)]} \tag{9}$$

- ξ_i must be **extensive** ⇒ scales with system size V_i
- ψ_i is the **conjugate intensive potential**
  - does *not* scale with V_i
- $\nabla\psi_i$ acts as the **thermodynamic driving force**

This compact form unifies all irreversible transport processes.

What Are The Driving Forces (From Irreversible Thermodynamics)?

Some quantities and their driving forces, see *Balluffi Table 2.1*

Extensive quantity ξ_i	Flux $\vec{J}_{\xi_i}$	Conjugate force	Potential ψ_i
Heat Q	$\vec{J}_Q$	$-\frac{1}{T}\nabla T$	$\dfrac{1}{T}$
Chemical component i	$\vec{J}_i$	$-\nabla\mu_i$	μ_i
Electric charge q	$\vec{J}_q$	$-\nabla\phi$	ϕ

- Each row represents one irreversible transport process
- Force = gradient of the conjugate intensive potential
- Flux · Force contributes to entropy production

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Empirical Laws of Fluxes

We also know that fluxes are having empirical relation to the driving force (in a gradient form):

$$\text{Flux} = (\text{transport coefficient}) \times (\text{driving force})$$

Fourier's law (heat conduction)

$$\vec{J}_Q = -k\nabla T = -kT^2\nabla\left(\frac{1}{T}\right)$$

Fick's law (mass diffusion)

$$\vec{J}_i = -D_i\nabla c_i = -\mu_i c_i \nabla \mu_i$$

Ohm's law (electrical conduction)

$$\vec{J}_q = -\rho\nabla\phi$$

Entropy Production in the Uncoupled Case

If each flux is influenced by only **one dominant driving force (D.F.)**:

$$\text{entropy production} = (\text{flux}) \cdot (\text{driving force})$$

Using linear response:

$$\vec{J} = (\text{coefficient}) \times (\text{D.F.})$$

we obtain

$$\boxed{T\dot{\sigma} = (\text{coefficient})\, \|\text{D.F.}\|^2}$$

Consequences of Irreversible Dynamics (Uncoupled Driving Force)

- Empirically, all transport coefficients are **positive** from irreversible thermodynamics
- Therefore:

$$\sigma \geq 0$$

- Entropy production vanishes only when:

$$\vec{\sigma} = 0 \quad \Longleftrightarrow \quad \|\text{D.F.}\| = 0$$

- The second law constrains transport coefficients

- Positivity of entropy production ⇒ positivity of coefficients
- This reasoning will be generalized when **fluxes are coupled**

Linear Irreversible Thermodynamics: Coupled Fluxes

- Extensive quantities: ξ_i
- Conjugate driving forces:

$$\vec{F}_i \equiv -\nabla \psi_i$$

- Associated fluxes: $\vec{J}_i$

We write them in a matrix form as shown in Lecture 2

$$\vec{J} = \mathbf{L}\,\vec{F}$$

or, component-wise,

$$\vec{J}_i = \sum_j L_{ij}\,\vec{F}_j$$

Entropy Production with Coupling

$$\dot{sigma} = \sum_i \vec{J}_i \cdot \vec{F}_i = \sum_{i,j} L_{ij}\,\vec{F}_i \cdot \vec{F}_j$$

- Second law requires:

$$\dot{sigma} \geq 0$$

- $\mathbf{L}$ must be **positive semi-definite**

Onsager Reciprocity (Again!)

Under microscopic reversibility:

$$\boxed{L_{ij} = L_{ji}}$$

- Symmetry of **L** reduces number of independent coefficients
- Fundamental constraint linking kinetics and thermodynamics

Physical Examples of Coupling

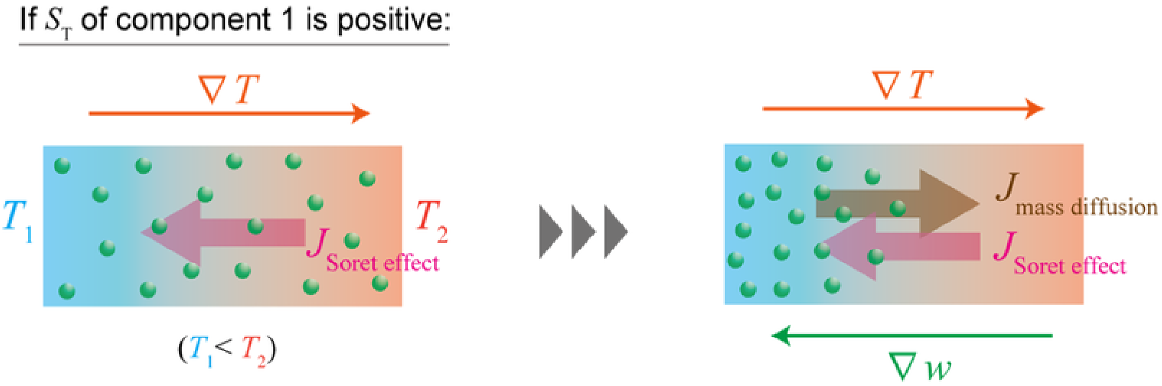
- Thermoelectric effects (Seebeck / Peltier)
- Thermodiffusion (Soret / Dufour)
- Electrokinetic transport

Coupling: Mass Thermal – Soret / Dufour Effects

Coupled flux–force relations

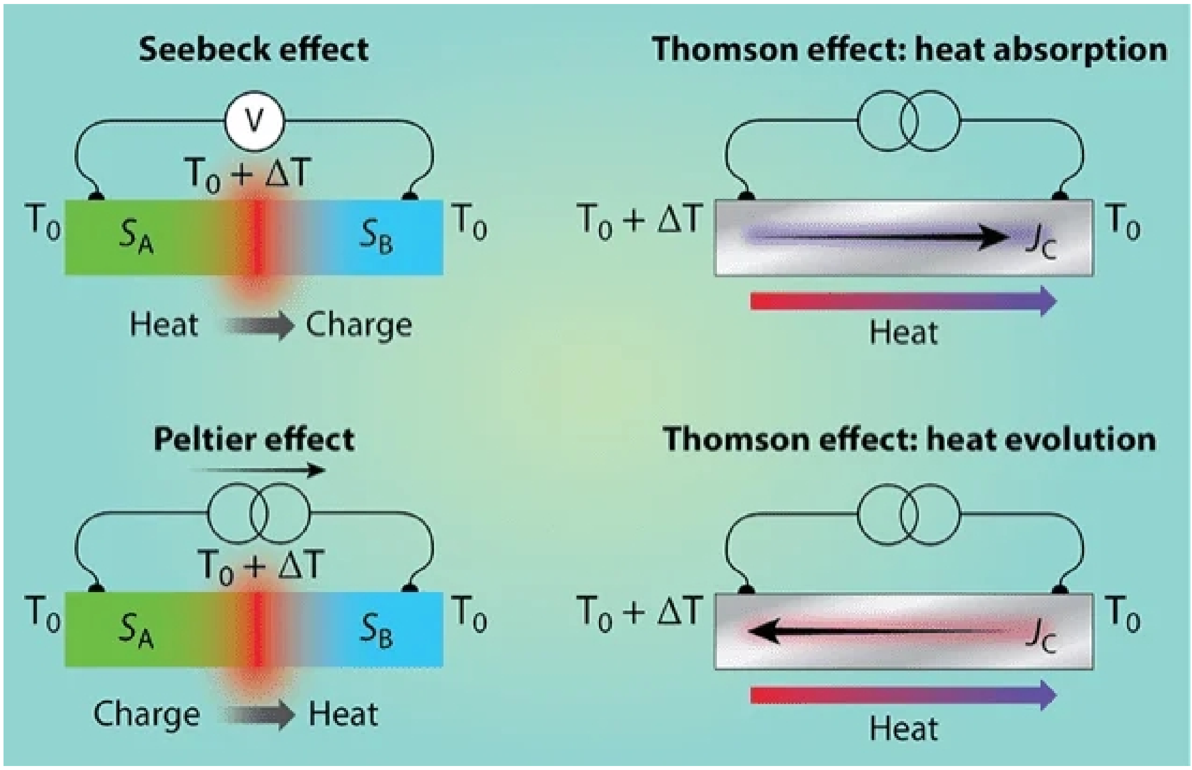
- Mass flux driven by temperature gradient (Soret effect)
- Heat flux driven by concentration gradient (Dufour effect)

Derivation of Sorret thermal conductivity please see lecture handwritten notes



Coupling: Charge Thermal – Seebeck / Peltier Effects

Coupled flux–force relations - Electric current driven by temperature gradient (Seebeck effect) - Heat flux driven by electric field (Peltier effect)



Coupling: Charge Mass – Electrokinetic Phenomena

Coupled flux–force relations - Charge and mass transport are interdependent in ionic systems

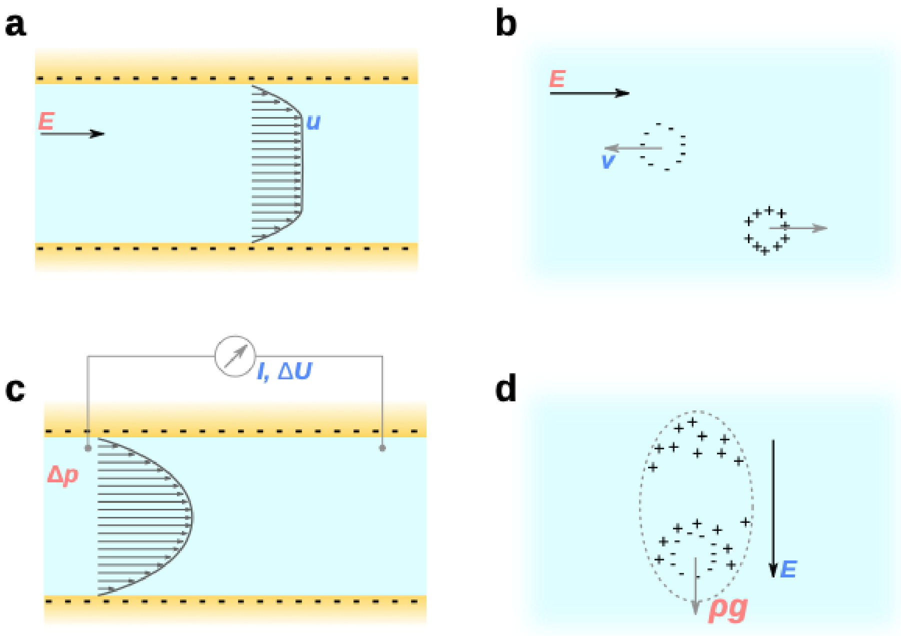
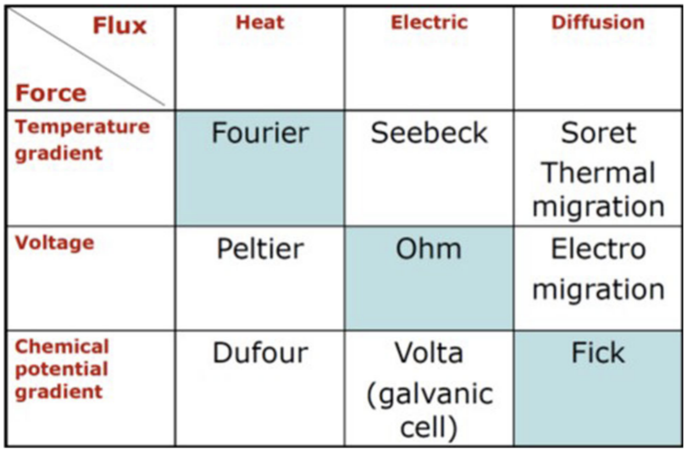


Figure 14.1: Typical electrokinetic phenomena. (a) electroosmosis. (b) electrophoresis. (c) streaming current / potential. (d) sedimentation potential.

General Matrix for Coupling Effects

Example coupling effect matrix given in *J. Phase Equilib. Diffus.* **2022** 43, 640



Flux Force	Heat	Electric	Diffusion
Temperature gradient	Fourier	Seebeck	Soret Thermal migration
Voltage	Peltier	Ohm	Electro migration
Chemical potential gradient	Dufour	Volta (galvanic cell)	Fick

Fig. 1 Classical cross effects

Some Additional Consequence of Onsager Reciprocity

There are some consequences of Onsager's reciprocity. As Curie's symmetry principle (1894, *Pierre* Curie, *not Marie*) stated, the cause of an effect needs to follow tensor rank selection rule, that:

Flux – Driving Force pair can only be induced when they have the same tensor rank, or differ by 2.

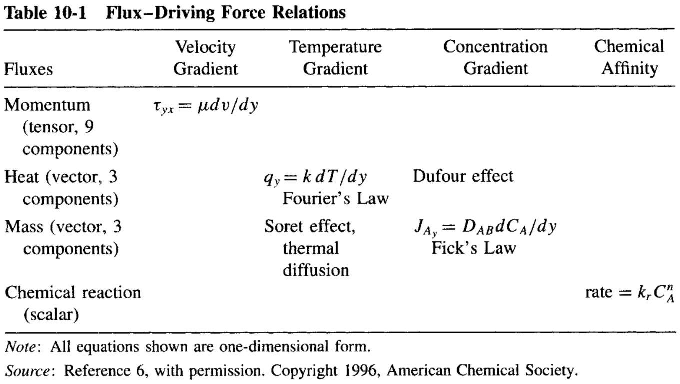


Table 10-1 Flux–Driving Force Relations

Fluxes	Velocity Gradient	Temperature Gradient	Concentration Gradient	Chemical Affinity
Momentum (tensor, 9 components)	$\tau_{yx} = \mu dv/dy$			
Heat (vector, 3 components)		$q_y = k\, dT/dy$ Fourier's Law	Dufour effect	
Mass (vector, 3 components)		Soret effect, thermal diffusion	$J_{A_y} = D_{AB} dC_A/dy$ Fick's Law	
Chemical reaction (scalar)				rate $= k_r C_A^n$

Note: All equations shown are one-dimensional form.

Source: Reference 6, with permission. Copyright 1996, American Chemical Society.

Figure 2: Tensor rank coupling from Griskey Book 2002

The coupling of momentum-transfer (fluid, 2nd-order) and chemical reaction (0th-order) has only been recently proposed! See *J. Chem. Phys.* **2022**, 157, 084901.

Summary

- Entropy balance equation solutions for flux of entropy and entropy production
- Entropy production rate flux of quantity driving force
- Flux of quantity Coefficient Driving Force
- Examples of reciprocal relation in transport phenomena
- Brief introduction of diffusion