

MATE 664 Lec 03

Jan 12 - 2025

1. Recap of Irreversible Thermodynamics

① Microscopic \rightleftharpoons Macroscopic

microstate
• point in phase space
 $\{\vec{x}_i, \vec{p}_i\}$

• Counting function

Ω (of some
macroscopic property)

Intensive $T P \mu_i$
Extensive $H S G F N_i$

$$dS = \frac{1}{T} dU + \frac{P}{T} dV + \frac{\mu_i}{T} \sum N_i + \dots$$

Boltzmann Eq $S = k_B T \ln \Omega$

② Getting out-of-eq from eq. thermodyn.

1. Boltzmann distribution

Canonical ensemble at eq.:

$$P(E + \Delta E) = P(E) e^{-\frac{\Delta E}{k_B T}}$$

negative sign = decay

↑ prob. at $E + \Delta E$ ↑ prob. at E

i For system that eq. at U_I^0 , it is unlikely to find $U_I \gg U_I^0$

ii If $\langle U_I \rangle \neq U_I^0 \Rightarrow$ away from eq.
will balance to eq. with $\langle U_I \rangle = U_I^0$

② How do we know where eq. is ?

Maximizing entropy S of the universe

Objective = $\max(S_T)$ w.r.t. same thermo. property

$$\Rightarrow \left(\frac{\partial S_I}{\partial X_i} \right) \Big|_{\text{constraints}} = 0$$

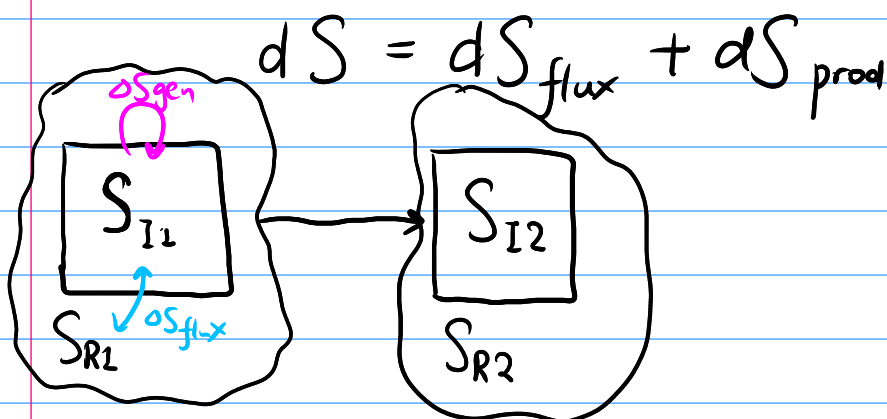
(Also $\frac{\partial^2 S_I}{\partial X_i^2} < 0$, will talk later)

Example $X = T$, for I & R systems,

$$\left(\frac{\partial S_T}{\partial X_I} \right)_V = \left(\frac{\partial S_I}{\partial X_I} \right)_V + \left(\frac{\partial S_R}{\partial X_I} \right)_V \Rightarrow \underbrace{\left(\frac{\partial S_T}{\partial X_I} \right)_V}_{\frac{1}{T_I}} = \underbrace{\left(\frac{\partial S_R}{\partial X_R} \right)_V}_{\frac{1}{T_R}}$$

③ How to characterize "rate" of out-of-eq ?

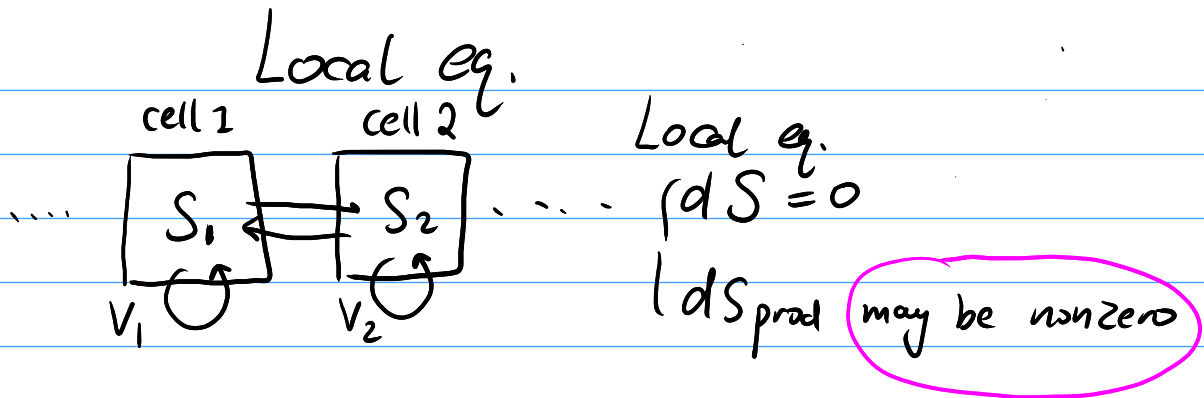
Use entropy production



Entropy can = 1) Flow / redistribute (dS_{flux})

2) Be created / produced (dS_{prod})

Irreversible process : $dS_{\text{prod}} \geq 0$



Often in textbooks like Balluffi, we take local density of entropy $\Rightarrow s = \frac{S_i}{V_i}$

$$\frac{\partial S}{\partial t} = - \underbrace{\nabla \cdot \vec{J}_S}_{\text{Divergence of entropy flux}} + \underbrace{\dot{\sigma}}_{\text{entropy production}}$$

$$\left(\nabla \cdot (J_x, J_y, J_z) \right) = \frac{\partial J_x}{\partial x} + \frac{\partial J_y}{\partial y} + \frac{\partial J_z}{\partial z}$$

OR $\dot{\sigma} = \frac{\partial S}{\partial t} + \nabla \cdot \vec{J}_S \geq 0$

We want to derive both
 what is \vec{J}_S & what is $\dot{\sigma}$

General continuity eq

$$\frac{da}{dt} + \nabla \cdot b = s$$

$s > 0 \Rightarrow \text{source}$

$s < 0 \Rightarrow \text{sink}$

Entropy production is a source term to flux eq

$$\frac{\partial S}{\partial t} = - \nabla \cdot \vec{J}_S + \boxed{\dot{\sigma}} \rightarrow \text{Source term}$$

S is not conserved

Balluffi

\Uparrow

Let's assume a general thermodynamic quantity ξ_i

$$\left(\xi_i = \frac{x_i}{V_i} \right)$$

Chain rule

$$\frac{\partial S}{\partial t} = \sum_i \frac{\partial S}{\partial \xi_i} \boxed{\frac{\partial \xi_i}{\partial t}} = \sum_i \frac{\partial S}{\partial \xi_i} \left(- \nabla \cdot \vec{J}_{\xi_i} \right)$$

\Uparrow
Maxwell

For any conserved quantity (cannot be created/destroyed)

$$x_i \Rightarrow \frac{\partial x_i}{\partial t} = - \nabla \cdot \vec{J}_{x_i}$$

$\nabla \cdot \vec{v}$ divergence $\nabla[\text{scalar}]$ gradient

Chain rule for ∇ : $\nabla \cdot (\vec{A} \vec{B}) = \vec{B} \cdot \nabla \vec{A} + \vec{A} \nabla \cdot \vec{B}$

Annotations: ∇ is a vector, \vec{A} and \vec{B} are vectors. $\nabla \cdot \vec{A}$ is a scalar, $\vec{B} \cdot \nabla \vec{A}$ is a scalar.

$$\vec{A} \nabla \cdot \vec{B} = -\vec{B} \cdot \nabla \vec{A} + \nabla \cdot (\vec{A} \vec{B})$$

$$\frac{\partial S}{\partial t} = \sum_i \frac{\partial S}{\partial \xi_i} (-\nabla \cdot \vec{J}_{\xi_i}) = - \sum_i \frac{\partial S}{\partial \xi_i} \underbrace{\nabla \cdot \vec{J}_{\xi_i}}_{\vec{A} \cdot \vec{B}}$$

(Need form
 $\frac{\partial S}{\partial t} = -\nabla \cdot \vec{J}_S + \dot{\sigma}$)

$$= - \sum_i \left[-\vec{J}_{\xi_i} \cdot \nabla \frac{\partial S}{\partial \xi_i} + \nabla \cdot \left(\frac{\partial S}{\partial \xi_i} \vec{J}_{\xi_i} \right) \right]$$

$\sum \nabla \cdot \vec{v} = \nabla \cdot (\sum \vec{v})$

$$= - \sum_i \nabla \cdot \left(\frac{\partial S}{\partial \xi_i} \vec{J}_{\xi_i} \right) + \sum_i \vec{J}_{\xi_i} \cdot \nabla \frac{\partial S}{\partial \xi_i}$$

$$= - \underbrace{\nabla \cdot \left(\sum_i \frac{\partial S}{\partial \xi_i} \vec{J}_{\xi_i} \right)}_{\nabla \cdot \vec{J}_S} + \underbrace{\sum_i \vec{J}_{\xi_i} \cdot \nabla \frac{\partial S}{\partial \xi_i}}_{\dot{\sigma}}$$

$$\begin{aligned} \vec{J}_S &= \sum_i \frac{\partial S}{\partial \xi_i} \vec{J}_{\xi_i} \\ \dot{\sigma} &= \sum_i \vec{J}_{\xi_i} \cdot \nabla \frac{\partial S}{\partial \xi_i} \end{aligned}$$

What is $\frac{\partial S}{\partial \xi_i}$ (Affinity)?

$$\begin{aligned} \Delta U &= \Delta Q + \Delta W \\ du &= T ds - p dv + \sum_i \mu_i dn_i + \dots \end{aligned}$$

General form thermodyn. eqn

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

→ generalized work

ψ_i = intensive potential
 ξ_i = extensive conjugate quant

What are ψ & ξ ?

From Balluffi,

ψ	ξ
pressure P	V volume
electric pot ϕ	q charge
chem pot μ	c chemical conc
surface energy γ	A surface area
external field \vec{E}	\vec{p} dipole moment
magnetic field \vec{H}	\vec{b} magnetic moment

$$\Rightarrow ds = \frac{1}{T} du - \frac{P}{T} dv - \frac{\phi}{T} dq \dots$$

$$\frac{s}{\partial t} = \frac{1}{T} \frac{\partial u}{\partial t} - \frac{1}{T} \sum_i \psi_i \frac{\partial \xi_i}{\partial t}$$

Each has its own flux conservation expression

If u is also generalized: $ds = - \sum_i \frac{\psi_i}{T} d\xi_i$

We have

$$\frac{\partial s}{\partial u} = \frac{1}{T} \Rightarrow \psi_u = -1 \quad \frac{\partial s}{\partial \xi_i} = -\frac{\psi_i}{T}$$

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

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

Often we're interested in heat flux $\vec{J}_q = T \vec{J}_s$
 $[J \cdot m^{-2} \cdot s^{-1}] \quad [J/K \cdot m^{-2} \cdot s^{-1}]$

$$\vec{J}_u = T \vec{J}_s + \sum_i \psi_i \vec{J}_{\xi_i} = \vec{J}_q + \sum_i \psi_i \vec{J}_{\xi_i}$$

\Rightarrow Replace \vec{J}_u in $\dot{\sigma}$

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

Driving force for entropy prod

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

$$\nabla \left(\frac{1}{T} \right) = -\frac{1}{T^2} \nabla T$$

Let's look at the format of $T\dot{\sigma}$

$$T\dot{\sigma} = - \underbrace{\vec{J}_Q}_{\text{flux}} \cdot \underbrace{\left(\frac{1}{T}\nabla T\right)}_{\text{gradient}} - \sum_i \underbrace{\vec{J}_{\xi_i}}_{\text{flux}} \cdot \underbrace{\nabla \psi_i}_{\text{gradient}}$$

General formula

$$T\dot{\sigma} = - \sum_i [\underbrace{\text{flux quantity}}_{\text{D.F.}}] \cdot [\underbrace{\text{gradient of potential}}_{\text{D.F.}}]$$

$\left\{ \begin{array}{l} \xi_i \text{ must be extensive} \Rightarrow \text{change by } V_i \\ \psi_i \text{ conjugate intensive potential} \Rightarrow \text{doesn't change by } V_i \\ \quad \hookrightarrow \text{gradient} = \text{driving force} \end{array} \right.$

Table 2.1 of Balluffi

Extensive	Flux	Conjugate Force	potential
Heat Q	\vec{J}_Q	$-\frac{1}{T} \nabla T$?
Chemical component i	\vec{J}_i	$-\nabla \mu_i$	μ_i
charge q	\vec{J}_q	$-\nabla \phi$	ϕ

The driving forces are surprisingly close to empirical forms

Fourier's law $\vec{J}_Q = - \underset{\substack{\uparrow \\ \text{thermal conductivity}}}{k} \nabla T = -k T^2 \nabla \left(\frac{1}{T} \right)$

Fick's law $\vec{J}_i = -D_i \nabla C_i$
 $= - \underset{\substack{\uparrow \\ \text{mobility}}}{\mu_i} C_i \nabla \mu_i$

Ohm's law $\vec{J}_q = - \underset{\substack{\uparrow \\ \text{conductivity}}}{\rho} \nabla \phi$
 \swarrow scalar prod

OR $[\text{Flux}] = [\text{coeff}] \times [\text{Driving force}]$

If Each flux is only influenced by 1 major D.F.

$$\begin{aligned} \Rightarrow [\text{Entropy production}] &= [\text{Flux}] \cdot [\text{Driving Force}] \\ &= ([\text{coeff}] \times [\text{D.F.}]) \cdot [\text{D.F.}] \\ &= [\text{coeff}] \times \|\text{D.F.}\|^2 \end{aligned}$$

In empirical forms, all coeff are positive

$$\Leftrightarrow [\text{Entropy production}] \geq 0$$

$$\Downarrow \sigma = 0 \text{ when } \|\text{D.F.}\| = 0$$

(In reality we go from $\sigma \geq 0 \Rightarrow$ each coeff must be positive)

Linear Irreversible Thermodyn

Extensive quantities ξ_i
 ↳ Driving force \vec{F}_i
 ↳ Flux \vec{J}_i

Matrix form

$$\vec{J} = \mathbb{L} \cdot \vec{F}$$

$$J_{ij} = \sum_j L_{ij} F_j$$

Driving force of ξ_j (usually $\nabla \psi_j$)
 Not ξ_j Not ψ_j

$$\vec{F} = -\frac{1}{T} \nabla T - \nabla \phi - \nabla \mu_i$$

$$\xi_i: Q \quad q \quad N_i \quad \dots$$

$$\mathbb{L} = \begin{pmatrix} L_{QQ} & L_{Qq} & L_{QN} & \dots \\ L_{qQ} & L_{qq} & L_{qn} & \dots \\ L_{nQ} & L_{nq} & L_{nn} & \dots \end{pmatrix}$$

coupling coeff

Direct (kinetic) coeff

$$T \dot{\sigma} = \sum_j \sum_i L_{ij} \vec{F}_i \cdot \vec{F}_j$$

Fourier's law $\vec{J}_Q = -k \nabla T$

$$= L_{QQ} \left(-\frac{1}{T} \nabla T \right)$$

$$\therefore k = \frac{L_{QQ}}{T}$$

↑
thermal conductivity

Fick's first law

$$\begin{aligned}\vec{J}_m &= -D_i \nabla C_i \\ &= -L_{mm} \nabla \mu_i\end{aligned}$$

Ideal solution

$$\mu_i = \mu_i^0 + k_B T \ln C_i$$

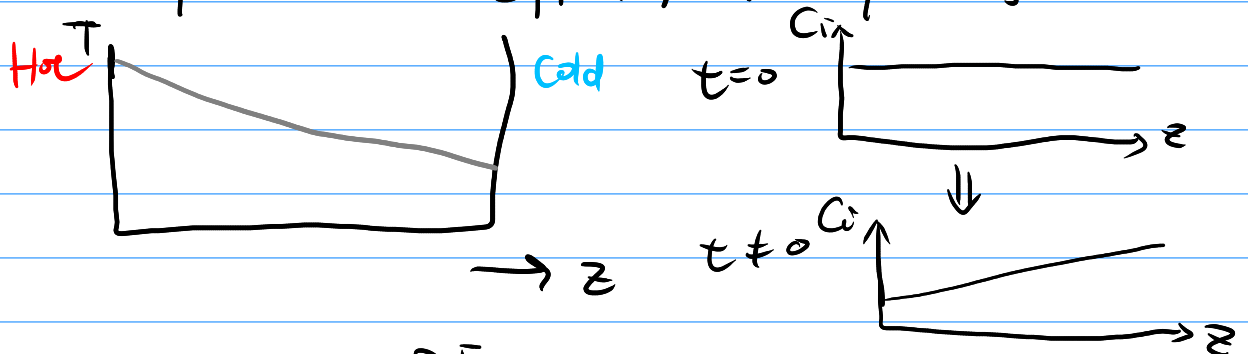
Boltzmann dist again!

$$\nabla \mu_i = k_B T \frac{1}{C_i} \nabla C_i \Rightarrow k_B T \frac{1}{C_i} L_{mm} = D_i$$

$$L_{mm} = \frac{C_i D_i}{k_B T}$$

What about non-zero coupling coeff?

Example Sorret Effect / Thermophoresis



Heat Q ← $\frac{D.F}{T} \nabla T$
 Mass M ← $-\nabla \mu$

$$\begin{pmatrix} Q \\ M \end{pmatrix} = \begin{pmatrix} L_{QQ} & L_{QM} \\ L_{MQ} & L_{MM} \end{pmatrix} \begin{pmatrix} \frac{D.F}{T} \nabla T \\ -\nabla \mu \end{pmatrix}$$

$L_{MQ} = L_{QM}$

$$\begin{aligned}J_Q &= -L_{QQ} \frac{1}{T} \nabla T - L_{QM} \nabla \mu \\ J_M &= -L_{QM} \frac{1}{T} \nabla T - L_{MM} \nabla \mu\end{aligned}$$

Soret effect : Heat flux $\neq 0$ Mass flux $= 0$
($\nabla C \neq 0$)

$$J_M = -L_{QM} \frac{1}{T} \nabla T - L_{MM} \nabla \mu = 0.$$

$$\nabla \mu = - \frac{L_{QM}}{L_{MM}} \cdot \frac{1}{T} \nabla T \neq 0$$

Similarly $J_Q = -L_{QQ} \frac{1}{T} \nabla T - L_{QM} \nabla \mu$

$$= -L_{QQ} \frac{1}{T} \nabla T + \frac{L_{QM}^2}{L_{MM}} \cdot \frac{1}{T} \nabla T$$

$$= - \left(L_{QQ} - \frac{L_{QM}^2}{L_{MM}} \right) \frac{1}{T} \nabla T$$

\Downarrow
 \tilde{L}_Q

(Although driving force may be written in various ways,
the form for \tilde{L}_Q is the same)

Onsager's another prediction

Coupling \rightarrow 0-order flux (scalar) chem reaction
 1-order flux (vector) heat, mass, electric Coupling
 2-order flux (tensor) momentum

\rightarrow If chemical reaction drives fluid motion

\Downarrow

Fluid velocity field can induce reaction

See Corato et al. JCP 2022
157, 084901

Other examples of linear coupling

$q \rightleftharpoons Q$ Seebeck effect $\nabla T \rightarrow \nabla \phi$
Peltier effect $\nabla \phi \rightarrow \nabla T$
Thomson effect

$q \rightleftharpoons M$ Electro osmosis / osmosis $\nabla \phi \rightarrow \nabla \mu$
Electrokinetic potential $\left\{ \begin{array}{l} \nabla \mu \rightarrow \nabla \phi \\ \psi_m \end{array} \right.$

$p \rightleftharpoons \phi$ Piezoelectricity Stress \rightarrow Current
Current \rightarrow Strain

Diffusion & Driving Forces

From irreversible thermodynamics

mass transfer of species i

(Flux J_i [mole] / [Area] / [time]

| Driving force $-\nabla \mu_i$

$$J_i = -L_{mm} \nabla \mu_i$$

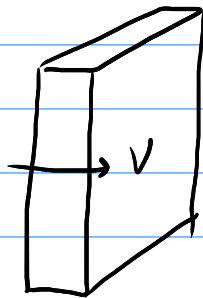
① Fick's 1st law

$$J = -D \nabla C$$

- if ideal solution

- not correct otherwise

② Reference frame



molecules move at \bar{v}

$$\bar{v}_i = -M_i \cdot \nabla \mu$$

\Rightarrow Revised Fick

$$J_i = c_i \bar{v}_i = M_i c_i \nabla \mu$$

$$\text{Flux} = D.F \times \text{Conc} \times \text{Mobility}$$

$$= \text{Diffusivity} \times \text{Gradient of D.F.}$$