

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 $H S G F N_i$

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

$$\text{Boltzmann Eq } S = k_B T \ln \Omega$$

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

i Boltzmann distribution

Canonical ensemble at eq. $= e^{-\frac{\Delta E}{k_B T}}$ negative sign = decay

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

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

ii For system that eq. at U_I^0 , it is unlikely to find $U_I > U_I^0$

iii 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. some thermo. property

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

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

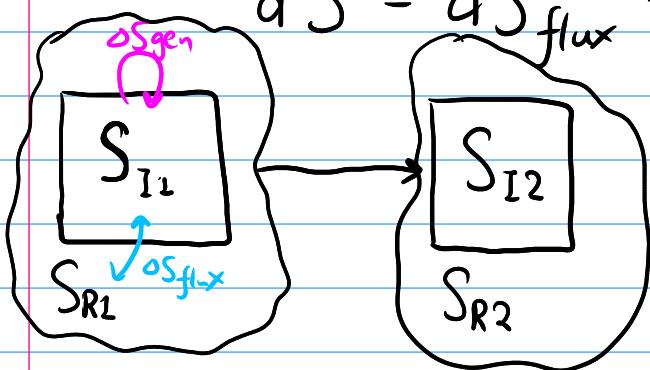
Example $X = T$, for I & R systems,

$$\left(\frac{\partial S_I}{\partial x_I} \right)_V = \left(\frac{\partial S_I}{\partial x_I} \right)_V + \left(\frac{\partial S_R}{\partial x_I} \right)_V \Rightarrow \left(\frac{\partial S_I}{\partial x_I} \right)_V = \left(\frac{\partial S_R}{\partial x_R} \right)_V$$
$$\frac{1}{T_I} \quad \frac{1}{T_R}$$

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

Use entropy production

$$dS = dS_{\text{flux}} + dS_{\text{prod}}$$

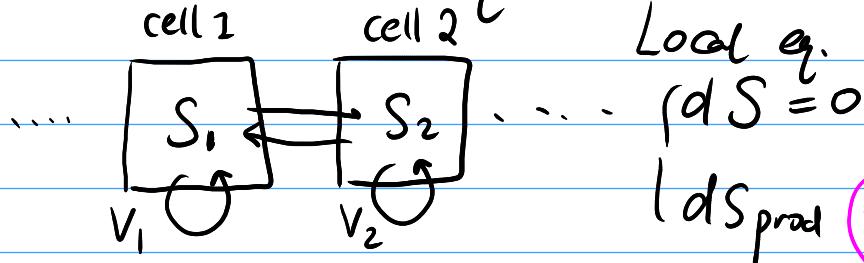


Entropy can = 1) Flow / redistribute (dS_{flux})

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

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

Local eq.



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

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

$\boxed{(\nabla \cdot (J_x, J_y, J_z))}$

$= \frac{\partial J_x}{\partial x} + \frac{\partial J_y}{\partial y} + \frac{\partial J_z}{\partial z}$

Divergence of entropy flux

entropy production

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

We want to derive both
what is 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

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

Source term
 S is not conserved

Balluffi

Let's assume a general thermodynamic quantity ξ_i
($\xi_i = \frac{x_i}{V_i}$)

Chain rule

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

Moving

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 $\nabla[s]$ gradient

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

scalar scalar vector

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

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

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

$$\begin{aligned}
 &= - \sum_i \nabla \cdot \left(\frac{\partial s}{\partial \xi_i} \tilde{J}_{\xi_i} \right) + \sum_i \tilde{J}_{\xi_i} \cdot \nabla \frac{\partial s}{\partial \xi_i} \\
 &= - \nabla \cdot \underbrace{\left(\sum_i \frac{\partial s}{\partial \xi_i} \tilde{J}_{\xi_i} \right)}_{\nabla \cdot J_s} + \underbrace{\sum_i \tilde{J}_{\xi_i} \cdot \nabla \frac{\partial s}{\partial \xi_i}}_{\dot{s}}
 \end{aligned}$$

\leftarrow

$$J_S = \sum_i \frac{\partial S}{\partial \xi_i} \vec{J}_{\xi_i}$$

$$\dot{\sigma} = \sum_i \vec{J}_{\xi_i} \cdot \nabla \frac{\partial S}{\partial \xi_i}$$

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

$$\Delta U = \Delta Q + \Delta W$$

$$dU = Tds - pdV + \sum \mu_i dN_i + \dots$$

General form thermodyn. eqn

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

→ generalized work

$$\left\{ \begin{array}{l} \psi_i = \text{intensive potential} \\ \xi_i = \text{extensive conjugate quantity} \end{array} \right.$$

What are ψ & ξ ?

From Boltzmann,

	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

$$dS = \frac{1}{T} dU - \frac{P}{T} dV - \frac{\phi}{T} dq \dots$$

$$\frac{\partial S}{\partial t} = \frac{1}{T} \left[\frac{\partial U}{\partial t} \right] - \frac{1}{T} \sum_i \psi_i \left[\frac{\partial \xi_i}{\partial t} \right]$$

Each has its own flux

conservation expression

$$\text{If } \kappa \text{ is also generalized: } dS = - \sum_i \frac{\psi_i}{T} d\xi_i$$

We have

$$\frac{\partial S}{\partial U} = \frac{1}{T} \Rightarrow \psi_u = -1 \quad \frac{\partial S}{\partial \xi_i} = - \frac{\psi_i}{T}$$

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

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

$$\text{Often we're interested in heat flux } \vec{J}_Q = T \vec{J}_s$$

$$[\text{J} \cdot \text{m}^{-2} \cdot \text{s}^{-1}] \quad [\text{J} / \text{K m}^{-2} \cdot \text{s}^{-1}]$$

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

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

$$\dot{\sigma} = \vec{J}_Q \cdot \nabla \left(\frac{1}{T} \right) - \sum_i \frac{\vec{J}_{\xi_i}}{T} \cdot \nabla \psi_i \quad \begin{matrix} \text{Driving force} \\ \text{for entropy} \\ \text{proof} \end{matrix}$$

$$\left(\frac{\partial T}{\partial S} \right)_{\text{constant}} = - \frac{1}{T^2} \frac{\partial T}{\partial S}$$

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

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

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

General formula

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

ξ_i must be extensive \Rightarrow change by V_i

ψ_i conjugate intensive potential \Rightarrow doesn't change by V_i
 ↳ gradient = driving force

Table 2.1 of Bellaffi

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

Fick's law $\vec{J}_i = -D_i \nabla c_i = -M_i c_i \nabla \mu_i$
↑ mobility

Ohm's law $\vec{J}_q = -\rho \nabla \phi$
↑ conductivity

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

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

$$\Downarrow \dot{\sigma} = 0 \text{ when } \| \text{D.F.} \|^2 = 0$$

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

Linear Irreversible Thermodyn

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

Matrix form

$$J = L \cdot F$$

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

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

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

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

$$L = \begin{pmatrix} L_{QQ} & L_{Q1} & L_{Qm} & \dots \\ L_{1Q} & L_{11} & L_{1m} & \dots \\ L_{mQ} & L_{m1} & L_{mm} & \dots \end{pmatrix}$$

Coupling coeff

Direct (kinetic) coeff

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

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

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

↑ thermal conductivity

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

Fick's first law

$$\vec{J}_M = -D_i \nabla C_i \quad ; \text{ Ideal solution}$$

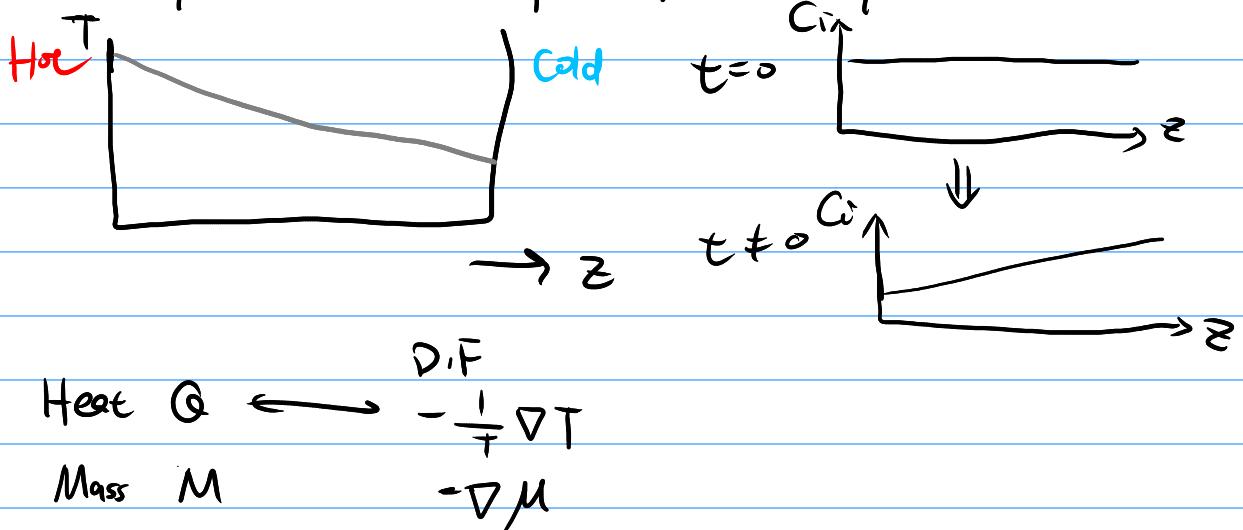
$$= -L_{MM} \nabla \mu_i \quad ; \begin{array}{l} \mu_i = \mu_i^0 + k_B T \ln C_i \\ \text{Boltzmann dist again?} \end{array}$$

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

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

What about non-zero coupling coeff?

Example Soret Effect / Thermophoresis



$$Q \begin{pmatrix} Q & M \\ L_{QQ} & L_{QM} \end{pmatrix}$$

$$M \begin{pmatrix} L_{MQ} \\ \tilde{L}_{QM} \end{pmatrix}$$

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

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

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

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

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

\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

- 0-order flux (scalar) chem reaction
 - 1-order flux (vector) heat, mass, electric
 - 2-order flux (tensor) momentum
- If chemical reaction drives fluid motion

Fluid velocity field can induce reaction

See Corato et al. JCP 2022
157, 084901

Other examples of linear coupling

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

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

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

Diffusion & Driving Forces

From irreversible thermodynamics

mass transfer of species i

$$\begin{cases} \text{Flux } J_i \text{ [mole] / [Area] / [time]} \\ \text{Driving force } -\nabla \mu_i \end{cases}$$

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

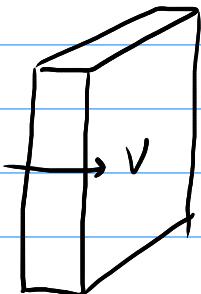
① Fick's 1st law

$$J = -D \nabla C$$

-if ideal solution

- not correct otherwise

② Reference frame



molecules move at \bar{v}_i

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

\Rightarrow Revised fick

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

Flux = D.F. \times Conc \times Mobility

= Diffusivity \times Gradient of D.F.