MATE 664   Lec 03
Jan 12 – 2026

1. Recap of Irreversible Thermodynamics

① Microscopic ⇌ Macroscopic

microstate
- point in phase space
$$\{ \vec{x}_i, \vec{p}_i \}$$
- Counting function
Ω (of some macroscopic property)

$$\left\{ \begin{array}{l} \text{Intensive } \; T \; P \; \mu_i \\[2mm] \text{Extensive } \; H \; S \; G \; F \; N_i \end{array} \right.$$

$$dS = \frac{1}{T} dU + \frac{P}{T} dV + \frac{\mu_i}{T} \Sigma N_i + \cdots$$

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

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

1° Boltzmann distribution
Cannonical ensemble at eq. :

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

negative sign = decay

prob. at $\bar{E} + \Delta E$ prob. at E

i For system that eq. at U_I°, it is unlikely to find
$$U_I \gg U_I^{\circ}$$

ii If $\langle U_I \rangle \neq U_I^{\circ}$ ⇒ away from eq.
will balance to eq. with $\langle U_I \rangle = U_I^{\circ}$

② How do we know where eq. is?

Maximizing entropy S of the (universe)

Objective: $\max(S_T)$ w.r.t. some thermo. property

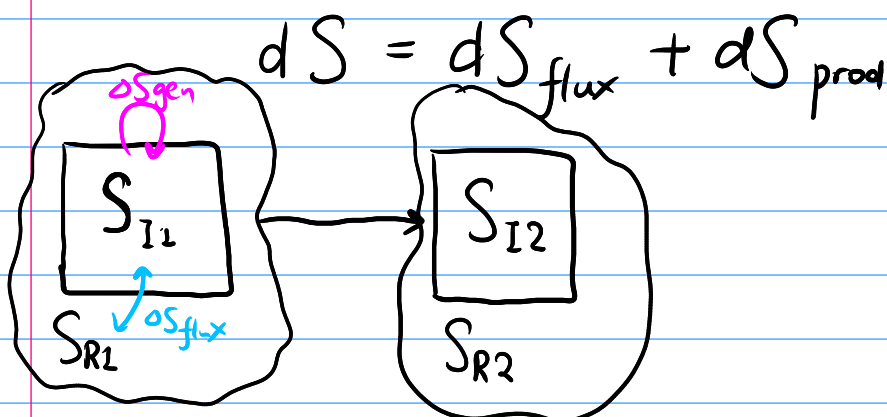$$\Rightarrow \left(\frac{\partial S_T}{\partial X_i}\right)\Big|_{constraints} = 0$$

$$\left(\text{Also } \frac{\partial^2 S_T}{\partial X_i^2} < 0, \text{ will talk later}\right)$$

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

$$\left(\frac{\partial S_T}{\partial X_I}\right)_V = \left(\frac{\partial S_I}{\partial X_I}\right)_V + \left(\frac{\partial S_R}{\partial X_I}\right)_V \Rightarrow \left(\frac{\partial S_I}{\partial X_I}\right)_V = \left(\frac{\partial S_R}{\partial X_R}\right)_V$$

$$\underset{\color{red}{\frac{1}{T_I}}}{} \qquad \underset{\color{magenta}{\frac{1}{T_R}}}{}$$

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

Use entropy production

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

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

2) Be created / produced (∂S_{prod})

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

Local eq.

cell 1   cell 2

S_1 ⇄ S_2 . . . . .

V_1 ↻ V_2 ↻

Local eq.

$\begin{cases} dS = 0 \\ dS_{prod} \end{cases}$ (may be nonzero)
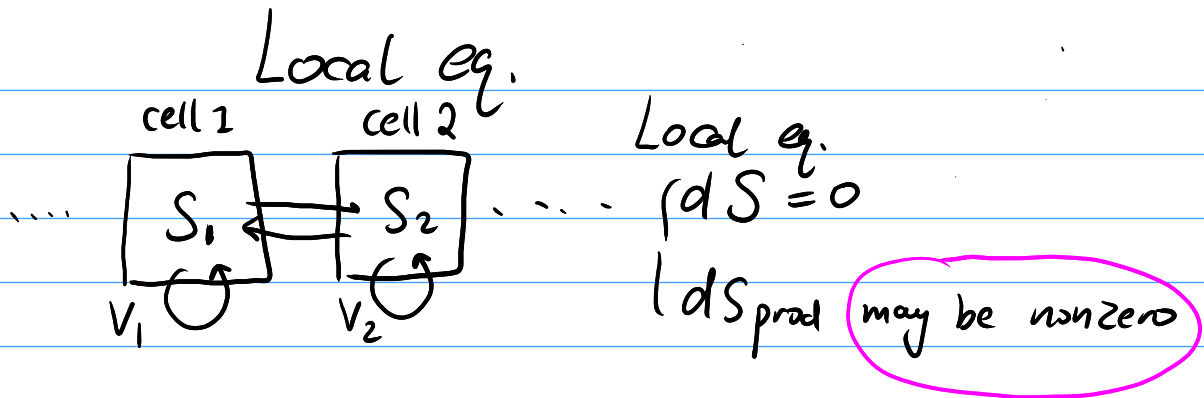
Often in textbooks like Balluffi, we take local density of entropy ⇒ $S = \dfrac{S_i}{V_i}$

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

$\underbrace{\qquad}$ Divergence of entropy flux

$\underbrace{\qquad}$ → entropy production

$$\boxed{\begin{array}{l} \nabla \cdot (J_x, J_y, J_z) \\ = \\ \dfrac{\partial J_x}{\partial x} + \dfrac{\partial J_y}{\partial y} + \dfrac{\partial J_z}{\partial z} \end{array}}$$

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

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

$\boxed{\begin{array}{l} \text{General continuity eq} \\ \dfrac{da}{dt} + \nabla \cdot b = s \\ s > 0 \Rightarrow \text{source} \\ s < 0 \Rightarrow \text{sink} \\ \text{Entropy production is a} \\ \text{source term to flux eq} \end{array}}$

$$\frac{\partial S}{\partial t} = -\nabla \cdot \vec{J}_S \boxed{+ \dot{\sigma}}$$ ⇒ Source term
S is not conserved

Balluffi
⇑

Let's assume a general thermodynamic quantity ξ_i

$\left(\xi_i = \dfrac{X_i}{V_i} \right)$

⇑
Moww

Chain rule

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

For any conserved quantity (cannot be created / destroyed)
$X_i \Rightarrow \dfrac{\partial X_i}{\partial t} = -\nabla \cdot \vec{J}_{X_i}$

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

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

(scalar) (vector) (v) (s) (s)

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

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

$\left(\begin{array}{c} \text{Need form} \\ \frac{\partial S}{\partial t} = -\nabla \cdot J_s \\ + \dot{\sigma} \end{array} \right)$ $\qquad = - \sum_i \left[- \vec{J}_{\xi_i} \cdot \nabla \frac{\partial S}{\partial \xi_i} + \nabla \cdot \left(\frac{\partial S}{\partial \xi_i} \vec{J}_{\xi_i} \right) \right]$

$\left(\begin{array}{c} \sum \nabla \cdot \vec{vec} \\ = \nabla \cdot (\sum \vec{vec}) \end{array} \right)$ $\qquad = - \sum_i \nabla \cdot \left(\frac{\partial S}{\partial \xi_i} \vec{J}_{\xi_i} \right) + \sum_i \vec{J}_{\xi_i} \cdot \nabla \frac{\partial S}{\partial \xi_i}$

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

$$\boxed{\begin{array}{l} J_s = \sum_i \frac{\partial S}{\partial \xi_i} \vec{J}_{\xi_i} \\[2mm] \dot{\sigma} = \sum_i \vec{J}_{\xi_i} \cdot \nabla \frac{\partial S}{\partial \xi_i} \end{array}}$$

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

$\left(\begin{array}{l} \Delta U = \Delta Q + \Delta W \\ dU = T ds - p dv + \sum \mu_i dN_i \\ + \cdots \end{array} \right)$

General form thermodyn. eqn

$$dS = \frac{1}{T} dU - \boxed{\sum_i \frac{\psi_i}{T} \xi_i} \quad \rightarrow \text{generalized work}$$

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

What are ψ & ξ ?

From Ballufft,

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

$$\Rightarrow dS = \frac{1}{T} du - \frac{P}{T} dv - \frac{\phi}{T} dq \quad \cdots$$

$$\frac{S}{\partial t} = \frac{1}{T} \boxed{\frac{\partial u}{\partial t}} - \frac{1}{T} \sum_i \psi_i \cdot \boxed{\frac{\partial \xi_i}{\partial t}}$$

Each has its own flux conservation expression

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

We have

$$\frac{\partial S}{\partial u} = \frac{1}{T} \Rightarrow \psi_u = -1 \qquad \frac{\partial S}{\partial \xi_i} = -\frac{\psi_i}{T}$$

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

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

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

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

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

$\Rightarrow$ 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

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

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

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

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

$\underbrace{}_{flux}$ $\underbrace{}_{gradient}$ $\underbrace{}_{flux}$ $\underbrace{}_{gradient}$

General formula

D.F.

$$T\dot{\sigma} = - \sum_i \left[flux\ quantity_i \right] \cdot \left[\begin{array}{c} gradient\ of \\ potential\ i \end{array} \right]$$

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

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
change q	$\vec{J}_q$	$-\nabla \phi$	ϕ

The driving forces are surprisingly close to empirical forms

Fourier's law $\quad \vec{J}_Q = -\underset{\uparrow}{k} \nabla T = -kT^2 \nabla(\frac{1}{T})$

↑ thermal conductivity

Fick's law $\quad \vec{J}_i = -D_i \nabla c_i$

$$= -\underset{\uparrow}{\mu_i} c_i \nabla \mu_i$$

↑ mobility

Ohm's law $\quad \vec{J}_q = -\underset{\uparrow}{\rho} \nabla \phi$

↑ conductivity

scalar prod ↙

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

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

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

In empirical forms, all coeff are positive

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

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

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

Linear Irreversible Thermodyn

Extensive quantities ξ_i

$\quad\quad\hookrightarrow$ Driving force $\vec{F}_i$

$\quad\quad\quad\hookrightarrow$ Flux $\vec{J}_i$

Matrix form

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

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

$\Rightarrow$ Driving force of ξ_j (usually $\nabla \psi_j$)

Not ξ_j Not ψ_j

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

$\xi: \quad Q \quad q \quad N_i \quad \cdots\cdots$

Coupling coeff

$$\mathbb{L} = \begin{pmatrix} L_{QQ} & L_{Q2} & L_{QM} \cdots\cdots \\ L_{2Q} & L_{22} & \\ L_{MQ} & & L_{MM} \cdots\cdots \end{pmatrix}$$

$\longrightarrow$ Direct (kinetic) coeff

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

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

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

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

$\uparrow$ thermal conductivity

Fick's first law

$$\vec{J}_M = -D_i \nabla C_i$$

$$= -L_{MM} \nabla \mu_i$$
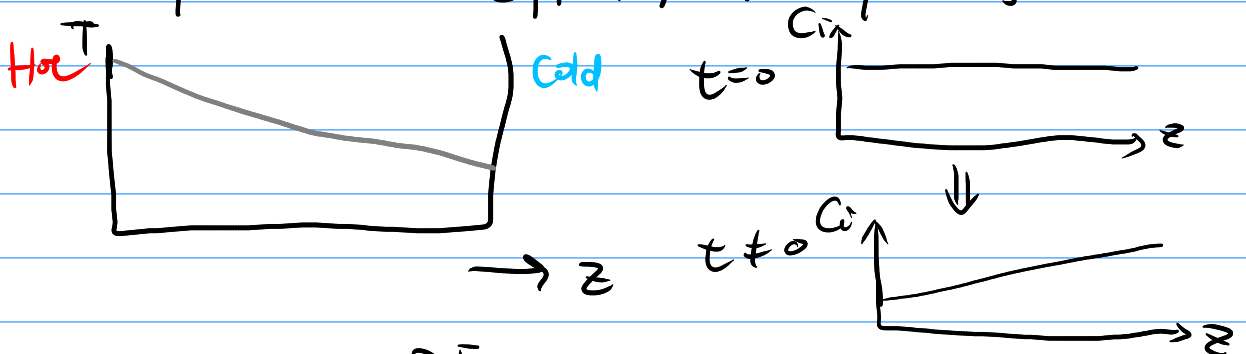
Ideal solution

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

Boltzmann dist again!

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

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

What about non-zero coupling coeff?

Example Sorret Effect / Thermophoresis

Hot T Cold $t=0$ z

$t \neq 0$ z

Heat Q $\longleftrightarrow$ D.F. $-\frac{1}{T} \nabla T$

Mass M $-\nabla \mu$

$$\begin{array}{c|cc} & Q & M \\ \hline Q & L_{QQ} & L_{QM} \\ & & \\ M & \begin{matrix} L_{MQ} \\ = \\ L_{QM} \end{matrix} & L_{MM} \end{array}$$

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

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

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

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

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

$$\tilde{L}_Q$$

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

Onsager's another prediction

Coupling ⟮ 0-order flux (scalar) chem reaction
1-order flux (vector) heat, mass, electric ⟳ Coupling
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

$q \leftrightharpoons Q$ Seebeck effect $\nabla T \longrightarrow \nabla \phi$

           Peltier effect $\nabla \phi \longrightarrow \nabla T$

           Thomson effect

$q \leftrightharpoons M$ Electro phoresis / osmosis $\nabla \phi \longrightarrow \nabla \mu$

           Electrokinetic potential $\begin{cases} \nabla \mu \longrightarrow \nabla \phi \\ \nabla m \end{cases}$

$p \leftrightharpoons \phi$ Piezo electricity   Stress $\longrightarrow$ Current

                               Current $\longrightarrow$ strain

Diffusion & Driving Forces

From irreversible thermodynamics

mass transfer of species i

$\left[\begin{array}{l} \text{Flux } J_i \quad [\text{mole}]/[\text{Area}]/[\text{time}] \\[2mm] \text{Driving force } -\nabla \mu_i \end{array} \right.$
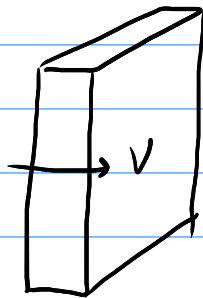
$$J_i = -L_{MM} \nabla \mu_i$$

① Fick's 1st law $\qquad J = -D \nabla C$

- if ideal solution

- not correct otherwise

② Reference frame

molecules move are $\bar{v}$

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

$\Rightarrow$ Revised fick

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

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

$\quad = Diffusivity \times Gradient of D.F.$