

irreversibility $I_{nm}(t) = k_B \ln \frac{\Omega_{nm} p_n(t)}{\Omega_{mn} p_m(t)}$

$$\dot{I}(t) = \frac{1}{2} \sum_{nm} J_{nm}(t) I_{nm}(t) \geq 0 \quad \text{always}$$

physical intuition: $\dot{I}(t) = 0$ if and only if

$$I_{nm}(t) = J_{nm}(t) = 0$$

for every n, m trans.

$$\Leftrightarrow \Omega_{mn} p_n(t) = \Omega_{nm} p_m(t)$$

$$\Leftrightarrow \frac{dp_n}{dt} = \sum_m J_{nm}(t) = 0$$

$$\Leftrightarrow \text{stationary state w/ all } J_{nm} = 0$$

$$\dot{I}(t) = 0 \Leftrightarrow \text{ESS}$$

can think of $\dot{I}(t)$ as a "distance" from ESS

$$\dot{I}(t) > 0$$

NESS

$$\frac{dp_n}{dt} = 0 \quad \text{but} \quad J_{nm} \neq 0$$

for some (n, m)

not in a stationary state

$$\frac{dp_n}{dt} \neq 0$$

connect to other physical quantities:

$$I_{nm}(t) = k_B \ln \frac{\Omega_{nm} p_m(t)}{\Omega_{mn} p_n(t)}$$

$$\frac{\Omega_{nm}}{\Omega_{mn}} = e^{-\beta Q_{nm}} \leftarrow \text{heat from env. } m \rightarrow n$$

$$= e^{-\beta (E_n - E_m - W_{nm})} \quad \beta = \frac{1}{k_B T}$$

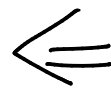
$$\Rightarrow I_{nm}(t) = -\frac{1}{T} Q_{nm} + k_B \ln \frac{p_m(t)}{p_n(t)}$$

$$= -\frac{1}{T} Q_{nm} + (S_n(t) - S_m(t))$$

$$S_n(t) \equiv -k_B \ln p_n(t) \quad \text{new state function "Surprisal"}$$

$$0 \leq p_n(t) \leq 1$$

how
"surprised"
you are to
see state n



$S_n(t)$ is large & positive when
 $p_n(t)$ is close to zero

multiply by $\frac{1}{2} J_{nm}(t)$ and $\sum_{nm}$:

$$\dot{I}(t) = -\frac{\dot{Q}(t)}{T} + \dot{S}(t)$$

$$\dot{Q}(t) = -\frac{1}{2} \sum_{nm} J_{nm} Q_{nm}$$

mean rate of heat
input into system

$$\dot{S}(t) = -\frac{1}{2} \sum_{nm} J_{nm} (S_n - S_m)$$

$$= \frac{d}{dt} S(t)$$

mean
"surprise"
≡ entropy

$$S(t) = \sum_n p_n(t) S_n(t) \\ = -k_B \sum_n p_n(t) \ln p_n(t)$$

Gibbs entropy
formula

Clausius form
of the
2nd law
of thermodyn.

$$dS \geq \frac{\delta Q}{T}$$

$$\frac{dS}{dt} \geq \frac{1}{T} \frac{\delta Q}{dt}$$

⇒

$$\dot{S}(t) = \frac{\dot{Q}(t)}{T} + \underbrace{\dot{I}(t)}_{\geq 0}$$

$$\dot{S}(t) \geq \frac{\dot{Q}(t)}{T} \quad \text{always true}$$

$$\dot{S}(t) = \frac{\dot{Q}(t)}{T} \quad \text{iff ESS}$$

$$\dot{S}(t) = \frac{dS}{dt} = \frac{d}{dt} S(t) \quad \text{true derivative}$$

$$\dot{Q}(t) = \frac{1}{2} \sum_{nm} T_{nm}(t) Q_{nm} \quad \text{not true deriv.}$$

units: entropy $\sim k_B \sim \frac{J}{K}$

$$\dot{S}(t) \sim \frac{\text{entropy}}{\text{time}} \sim \frac{J}{K \cdot s}$$

$$\dot{Q}(t) \sim \frac{\text{energy}}{\text{time}} \sim \frac{J}{s}$$

$$\dot{I}(t) \sim \dot{S}(t) \sim \frac{\text{entropy}}{\text{time}}$$

typical
name:

→ $\dot{I}(t)$ is
"irreversible
entropy prod. rate"

Where is 1st law of thermo?

Start w/ $Q_{nm} = E_n - E_m - W_{nm}$

multiply by $\frac{1}{2} J_{nm}$ + sum $\sum_{n,m}$:

$$\dot{Q}(t) = \underbrace{\dot{E}(t)}_{\frac{d}{dt} E(t)} - \dot{W}(t)$$

first
law of
thermo.

$$\dot{E}(t) = \dot{Q}(t) + \dot{W}(t)$$

rate at
which
system
mean energy
changes

rate
of
heat
input

rate of
work input

energy
cons.

Summary:

1st: $\dot{E}(t) = \dot{Q}(t) + \dot{W}(t)$

2nd: $\dot{S}(t) = \frac{\dot{Q}(t)}{T} + \underbrace{\dot{I}(t)}_{\geq 0}$

combine: $\dot{S} = \frac{\dot{E} - \dot{W}}{T} + \dot{I}$

$$\Rightarrow \dot{E} - T \dot{S} = \dot{W} - T \dot{I}$$

true deriv.

"fake" deriv.

valid at
all t

$$\dot{E} = \frac{d}{dt} E \quad \dot{S} = \frac{d}{dt} S$$

new function $F(t) = E(t) - T S(t)$

Helmholtz
free
energy

$$\dot{F}(t) = \dot{W}(t) - T \dot{I}(t)$$

combo of
1st +
2nd law

Next step: argue that system goes to a stationary state as $t \rightarrow \infty$

prove
this
in general

$$p_n(t) \rightarrow p_n^s \text{ indep. of time}$$

$$\hookrightarrow E(t) = \sum_n p_n(t) E_n$$

$$\rightarrow \sum_n p_n^s E_n \equiv E^s$$

$$S(t) = -k_B \sum_n p_n(t) \ln p_n(t)$$

$$\rightarrow -k_B \sum_n p_n^s \ln p_n^s \equiv S^s$$

$$F(t) \rightarrow F^s \text{ indep. of time}$$

$$\dot{F}(t) \xrightarrow{t \rightarrow \infty} 0 \Rightarrow 0 = \dot{W} - T \dot{I}$$

$$\dot{W} = T \dot{I} \geq 0$$