

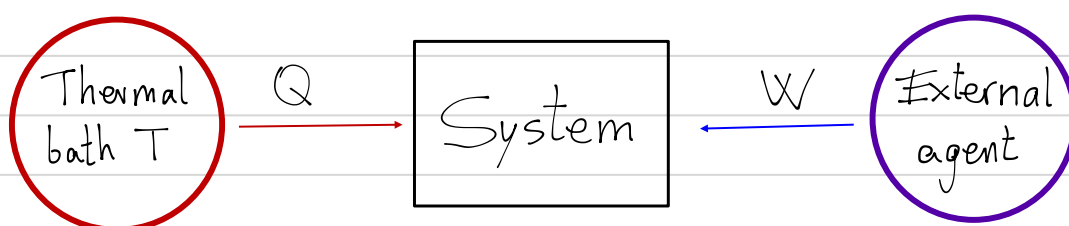
3. Thermodynamics

3.1. Heat and work

We focus on systems in contact with a single thermal bath at temperature T driven by an external agent who changes a parameter λ in the Hamiltonian $H(x; \lambda)$ according to a protocol $\lambda(t)$, $t \in [0, \tau]$.

Work and heat are defined as follows:

$$\frac{d}{dt} \langle H(x; \lambda) \rangle = \underbrace{\int dx \rho(x, t) \frac{dH(x; \lambda)}{d\lambda} \Big|_{\lambda=\lambda(t)} \dot{\lambda}(t)}_{\text{work } \dot{W}} + \underbrace{\int dx \frac{d\rho(x, t)}{dt} H(x; \lambda(t))}_{\text{heat } \dot{Q}}$$



Both are positive if energy enters the system.

$\rho(x, t)$ evolution: Langevin/Fokker-Planck; master equation (for x discrete), Liouville ($Q=0$), Lindblad (quantum), ...

Along the whole process $t \in [0, \tau]$:

$$W = \int_0^\tau \dot{W} dt = \int_{\lambda(0)}^{\lambda(\tau)} \underbrace{\left\langle \frac{\partial H(x; \lambda)}{\partial \lambda} \right\rangle_{\lambda=\lambda(t)}}_{\text{Force}} \underbrace{d\lambda(t)}_{\text{Displacement}} \quad ; \quad Q = \int_0^\tau \dot{Q} dt$$

$$\Delta \langle H \rangle = \langle H(\tau) \rangle - \langle H(0) \rangle = W + Q \quad \leftarrow \text{First Law}$$

For quasi-static processes ($\dot{\lambda}$ small):

$$\rho(x,t) \simeq \rho_{eq}(x;\lambda(t)) = \frac{e^{-\beta H(x;\lambda(t))}}{Z(\lambda(t))}$$

$$\left\langle \frac{\partial H}{\partial \lambda} \right\rangle = \int dx \frac{\partial H}{\partial \lambda} \frac{e^{-\beta H}}{Z(\lambda)} = -\frac{1}{\beta Z(\lambda)} \frac{\partial}{\partial \lambda} \int dx e^{-\beta H}$$

$$= -\frac{kT}{Z} \frac{\partial}{\partial \lambda} Z = \frac{\partial}{\partial \lambda} F_{eq}(\lambda) \quad \text{with} \quad F_{eq}(\lambda) = -kT \ln Z(\lambda)$$

Along a quasi-static process: $W = F_{eq}(\lambda(z)) - F_{eq}(\lambda(0)) = \Delta F_{eq}$

$$\Delta \langle H \rangle = \Delta F_{eq} + Q = \Delta \langle H \rangle - T \Delta S(\rho_{eq}) + Q$$

$$\Rightarrow T \Delta S(\rho_{eq}) = Q = -T \Delta S_{bath} \Rightarrow \Delta S(\rho_{eq}) + \Delta S_{bath} = 0$$

no entropy production

Dissipative work: $W - \Delta F = T \Delta_e S \geq 0$ ($= 0$ for quasi-static reversible processes)
entropy production

3.2. Non-equilibrium free energy

For a physical system in state ρ and Hamiltonian H , we define:

$$\mathcal{F}(\rho; H) \equiv \langle H \rangle_{\rho} - T S(\rho)$$

→ Shannon/von Neumann

$$S(\rho) \equiv -k \int dx p(x) \ln p(x)$$

Properties:

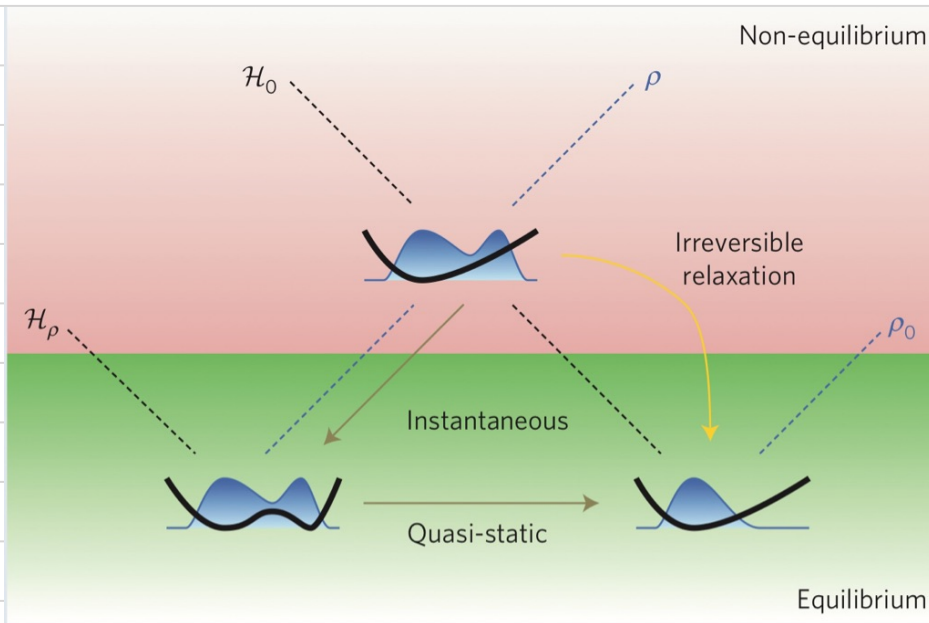
i) $\mathcal{F}(\rho_{\text{eq}}; H) = F_{\text{eq}} = -kT \ln Z$ ← equilibrium free energy

ii) $\mathcal{F}(\rho; H) = \int dx p(x) [H(x) + kT \ln p(x)] \geq \mathcal{F}(\rho_{\text{eq}}; H) = F_{\text{eq}}$

$$\Rightarrow \mathcal{F}(\rho; H) \geq F_{\text{eq}} \quad (= F_{\text{eq}} \Leftrightarrow \rho = \rho_{\text{eq}})$$

iii) The work performed by an external agent to drive a system from state ρ to ρ' and from Hamiltonian H to H' in contact with a thermal bath at temperature T : (Esposito, van den Broeck, 2011) is bound as:

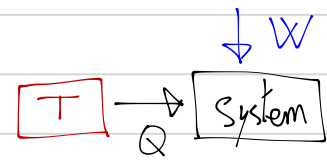
$$W \geq \mathcal{F}(\rho'; H') - \mathcal{F}(\rho; H) = \Delta \mathcal{F}$$



JMRP, Hovovitz,
Sagawa.
Nat. Phys (2015).

iv) The excess work can be related with an entropy production:

$$\begin{aligned} \Delta_e S &= -\frac{Q}{T} + \Delta S = \\ &= -\frac{\Delta \langle H \rangle - W - T \Delta S}{T} \\ &= \frac{W - \Delta \mathcal{F}}{T} \end{aligned}$$



$$\Delta \langle H \rangle = Q + W$$

$$\Rightarrow W - \Delta \mathcal{F} = T \Delta_e S \geq 0$$

Surprisingly we can drive a system from and/or to non-equilibrium states reversibly: i) with zero entropy production $\Delta_e S$; and ii) operationally reversible, i.e., we can invert the process and recover all the work.

But, is this possible with non-equilibrium states? Is not there a continuous relaxation producing entropy and dissipating an energy that cannot be recovered?

This is true except if there is a huge separation of time scales:

process time \gg relaxation time.

This is the case for phase coexistence (magnetic memories) high energy barriers (DNA).

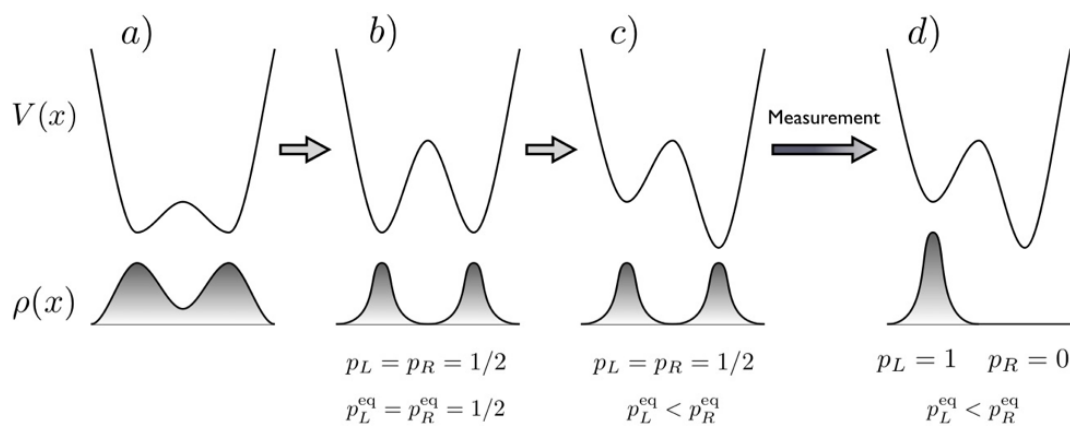


Fig. 1. An illustration of non-equilibrium states arising from ergodicity breaking and measurement. A Brownian particle at temperature T moves in a double-well potential $V(x)$ which is modified by an external agent. The potential and the probability density $\rho(x)$ of the position x of the particle are both depicted in the figure. (a) Initially the barrier is low enough for the particle to jump from one well to the other. (b) The potential barrier is raised up to some value far above kT and an effective ergodicity breaking occurs if we consider a time scale much shorter than the jump rate. The probability that the particle is in the left or the right region is $p_l = 1/2$, with $l = L, R$, because ergodicity is broken in a symmetric way. (c) After the transition has occurred, the left well is raised and the right one is lowered. The probability p_l remains $1/2$ for $l = L, R$, since jumps do not occur in the time scale of the process, whereas the equilibrium probability, p_l^{eq} in Eq. (10), changes. (d) After an error-free measurement that finds the particle in the left well, this post-measurement non-equilibrium state is now a probability density with support in the left well, yielding $p_L = 1$.

3.3. Stochastic thermodynamics.

Energy transfers, entropy and information can be defined as per trajectory (usually stochastic) $x(t)$:

• Energy: $\dot{u} = \frac{d}{dt} H(x(t); \lambda(t)) dt$

• Work: $\dot{w} = \left. \frac{\partial H(x(t); \lambda)}{\partial \lambda} \right|_{\lambda=\lambda(t)} \dot{\lambda}(t)$

• Heat: $\dot{q} = \dot{u} - \dot{w}$

• Entropy: $s = -k \ln p(x(t), t)$

Here $x(t)$ is the trajectory of the system (Langevin, random walk, Markov chain, ...). $p(x, t)$ is the probability distribution of $x(t)$. $y(t)$ is the trajectory of another system or the measurement outcome.

Their averages are the quantities previously introduced:

$$W = \langle w \rangle, \Delta \langle H \rangle = \Delta u \quad Q = \langle q \rangle \quad S = \langle s \rangle$$

For Langevin dynamics:

• Overdamped: $\gamma \dot{x} = F(x, \lambda) + \xi \quad F = -\partial_x V(x, \lambda)$

$$\dot{w} = \left. \frac{\partial V(x, \lambda)}{\partial \lambda} \right|_{x(t), \lambda(t)} \dot{\lambda}(t)$$

$$\dot{q} = \underbrace{\frac{\partial V(x, \lambda)}{\partial x}}_{\text{Stratonovich}} \dot{x} = -F v \quad \underbrace{\text{dissipated power}}$$

• Underdamped: $m \dot{v} = -\gamma v + F(x, \lambda) + \xi$

$$u = \frac{1}{2} m v^2 + V(x, \lambda) \Rightarrow \dot{u} = m v \dot{v} + \frac{\partial V}{\partial \lambda} \dot{\lambda} + \frac{\partial V}{\partial x} \dot{x} = -\gamma v^2 + v \xi + \frac{\partial V}{\partial \lambda} \dot{\lambda}$$

$$\dot{w} = \left. \frac{\partial V(x, \lambda)}{\partial \lambda} \right|_{x(t), \lambda(t)} \dot{\lambda}(t)$$

$$\dot{q} = -\gamma v^2 + v \xi = -F v$$

3.3.1. Fluctuation theorems.

Consider a system at thermal equilibrium at temperature T and with Hamiltonian $H(x; \lambda(0))$. An external agent drives the system as $\lambda(t)$ with $t \in [0, z]$. Let $P(\omega)$ the probability distribution for the total work along the process.

Now consider the reverse process: the system starts at equilibrium at temperature T and Hamiltonian $H(x; \lambda(z))$. Then the agent carries out the reverse protocol $\lambda(z-t)$. Let $\tilde{P}(\omega)$ the probability distribution for the total work along the reverse process.

One can prove (Crooks) that, if $H(x, \lambda)$ is even in momenta:

$$\frac{P(\omega)}{\tilde{P}(-\omega)} = e^{\beta(\omega - \Delta F)} \quad \Rightarrow \quad \langle e^{-\beta\omega} \rangle = e^{-\beta\Delta F}$$

Jarzynski equality

where $\Delta F = F_{eq}(\lambda(z)) - F_{eq}(\lambda(0))$ is the equilibrium free energy difference between the final and the initial λ .
(recall that the process is non-equilibrium!!)

Proof (sketch):

We first prove the theorem for isolated systems (Hamiltonian dynamics). In that case, the evolution is deterministic and the probability of a trajectory $\gamma = \{x(t)\}_{t=0}^z$ is:

$$p(\gamma) = p(x(0)) = \frac{e^{-\beta H(x(0); \lambda(0))}}{Z(\lambda(0))} = e^{-\beta [H(x(0); \lambda(0)) - F_{eq}(\lambda(0))]}$$

provided that γ is a solution of Hamilton equations with initial condition $x(0)$. In that case, $\tilde{\gamma} = \{\tilde{x}(z-t)\}_{t=0}^z$, where \tilde{x} is obtained from x by reversing momenta, is a solution of the Hamilton equations of the reverse process. Then:

$$\tilde{p}(\tilde{\gamma}) = \tilde{p}(\tilde{x}(z)) = \frac{e^{-\beta H(x(z), \lambda(z))}}{Z(\lambda(z))} = e^{-\beta [H(x(z); \lambda(z)) - F_{\text{eq}}(\lambda(z))]}$$

where we have used $H(x; \lambda) = H(\tilde{x}; \lambda)$ (H even in momenta)

Then:

$$\frac{p(\gamma)}{\tilde{p}(\tilde{\gamma})} = e^{\beta(\omega(\gamma) - \Delta F)} \quad (1)$$

with the work functional $\omega(\gamma) = H(x(z); \lambda(z)) - H(x(0); \lambda(0)) = -\omega(\tilde{\gamma})$
We have:

$$P(\omega) = \langle \delta(\omega(\gamma) - \omega) \rangle \quad \text{and} \quad \tilde{P}(\omega) = \langle \delta(\omega(\tilde{\gamma}) - \omega) \rangle$$

where the averages are over $p(\gamma)$ and $\tilde{p}(\tilde{\gamma})$, respectively.

From the above equation (1):

$$\delta(\omega(\gamma) - \omega) p(\gamma) e^{-\beta(\omega(\gamma) - \Delta F)} = \delta(-\omega(\tilde{\gamma}) - \omega) p(\tilde{\gamma})$$

and summing over trajectories γ :

$$P(\omega) e^{-\beta(\omega - \Delta F)} = \tilde{P}(-\omega)$$

For systems in contact with a bath, we have:

$$H(x, x_{\text{bath}}, \lambda) = H_S(x, \lambda) + H_{\text{bath}}(x_{\text{bath}}) + H_{\text{int}}(x, x_{\text{bath}})$$

We apply the theorem to the whole system+bath. Since the work is:

$$\omega = \frac{\partial H_S(x, \lambda)}{\partial \lambda} \dot{\lambda} \quad \text{the theorem still holds for open systems.}$$

q.e.d.

A corollary of Crook's theorem is Jarzynski equality:

$$\langle e^{-\beta(\omega - \Delta F)} \rangle = 1$$

from which the second law follows ($\langle e^x \rangle \geq e^{\langle x \rangle}$):

$$1 \geq e^{-\beta(\langle \omega \rangle - \Delta F)} \Rightarrow \langle \omega \rangle - \Delta F \geq 0.$$

where we have used $\langle \omega \rangle = W$. Notice however that (1) is more general than Crook's theorem.

Another interesting result is given by the relative entropy.

For two probability distributions $p(x)$, $q(x)$ we define:

$$D(p(x) \| q(x)) = \sum_x p(x) \ln \frac{p(x)}{q(x)}$$

Relative entropy, Kullback-Leibler distance.

$D(p(x)||q(x))$ measures the distinguishability between $p(x)$ and $q(x)$

From (1) we get:

$$D(p(x)||\tilde{p}(\tilde{x})) = \beta (W - \Delta F)$$

From Crook's theorem:

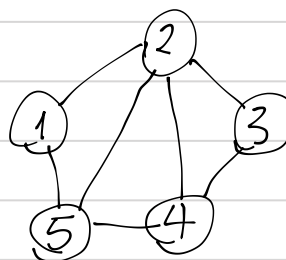
$$D(P(W)||\tilde{P}(-W)) = \beta (W - \Delta F)$$

Therefore: $D(p(x)||\tilde{p}(\tilde{x})) = D(P(W)||\tilde{P}(-W))$

All irreversibility is accounted by the work.

3.4. Discrete systems.

$p(i,t)$ = probability that the system is in state i at time t .



Master equation ($\Gamma_{i \rightarrow j}$ = transition rate)

$$\frac{dp(i,t)}{dt} = \sum_{j \neq i} \underbrace{\left[\underbrace{\Gamma_{j \rightarrow i}}_{\text{Incoming flow}} p(j,t) - \underbrace{\Gamma_{i \rightarrow j}}_{\text{Outgoing flow}} p(i,t) \right]}_{J_{j \rightarrow i}(t)} = \sum_{j \neq i} J_{j \rightarrow i}(t)$$

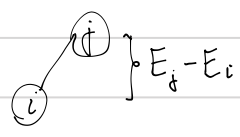
Stationary distribution: $p_{st}(i) \Rightarrow \sum_{j \neq i} J_{j \rightarrow i}^{st} = 0 \quad \forall i$

Detailed balance: $J_{j \rightarrow i}^{st} = \Gamma_{j \rightarrow i} p_{st}(j) - \Gamma_{i \rightarrow j} p_{st}(i) = 0 \quad \forall i, j$

(DB)

$$\frac{\Gamma_{i \rightarrow j}}{\Gamma_{j \rightarrow i}} = \frac{p_{st}(j)}{p_{st}(i)}$$

For a system in contact with a thermal bath

$$p_{st}(i) = \frac{e^{-\beta E_i}}{Z} \stackrel{\text{DB}}{\Rightarrow} \frac{\Gamma_{i \rightarrow j}}{\Gamma_{j \rightarrow i}} = e^{-\beta(E_j - E_i)}$$


E_i = energy of state i

$Z = \sum_i e^{-\beta E_i}$: partition function

Driving (external agent): $E_i(t)$

$$E(t) = \langle E_i(t) \rangle = \sum_i p(i,t) E_i(t)$$

$$\frac{dE(t)}{dt} = \underbrace{\sum_i E_i(t) \frac{dp(i,t)}{dt}}_{\text{Heat } \dot{Q}} + \underbrace{\sum_i p(i,t) \frac{dE_i(t)}{dt}}_{\text{Work } \dot{W}}$$

$$\dot{Q} = \sum_i E_i(t) \frac{dp(i,t)}{dt} = \sum_i \sum_{j \neq i} E_i(t) J_{j \rightarrow i}(t)$$

$$= \sum_{\substack{j,i \\ j \neq i}} [E_i(t) - E_j(t)] J_{j \rightarrow i}(t) = \sum_{\substack{i,j \\ i \neq j}} kT J_{j \rightarrow i}(t) \ln \frac{\Gamma_{i \rightarrow j}}{\Gamma_{j \rightarrow i}}$$

heat absorbed
in the transition $j \rightarrow i$

$$J_{i \rightarrow j} = -J_{j \rightarrow i}$$

Second law:

$$S(t) = -k \sum_i p(i,t) \ln p(i,t) \quad + \text{Shannon entropy of the system}$$

$$\frac{dS(t)}{dt} = \dot{S}(t) = -k \sum_i \left[\dot{p}(i,t) \ln p(i,t) + \underbrace{\dot{p}(i,t)}_0 \right]$$

(normalization)

$$= -k \sum_i \dot{p}(i,t) \ln p(i,t)$$

$$\Rightarrow \dot{S}(t) = -k \sum_{\substack{i,j \\ i \neq j}} J_{j \rightarrow i}(t) \ln p(i,t)$$

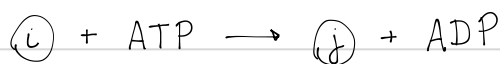
$$= -k \sum_{\substack{i,j \\ i \neq j}} J_{j \rightarrow i}(t) \ln \frac{p(i,t)}{p(j,t)}$$

Total entropy production:

$$\dot{S}_{\text{prod}} = \dot{S} + \dot{S}_{\text{env}} = \dot{S} - \frac{\dot{Q}}{T} = k \sum_{\substack{i,j \\ i \neq j}} J_{j \rightarrow i}(t) \left[-\ln \frac{p(i,t)}{p(j,t)} - \ln \frac{\Gamma_{i \rightarrow j}}{\Gamma_{j \rightarrow i}} \right]$$

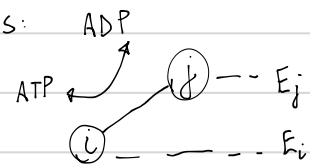
$$\Rightarrow \dot{S}_{\text{prod}}(t) = k \sum_{\substack{i,j \\ i \neq j}} \underbrace{[\Gamma_{j \rightarrow i} p(j,t) - \Gamma_{i \rightarrow j} p(i,t)]}_{\text{same sign}} \ln \frac{\Gamma_{j \rightarrow i} p(j,t)}{\Gamma_{i \rightarrow j} p(i,t)} \geq 0$$

Molecular motors use non-equilibrium chemostats as fuel.
For instance, protein motors use ATP to bias transitions



In this case the detailed balance condition reads:

$$\frac{\Gamma_{i \rightarrow j}}{\Gamma_{j \rightarrow i}} = e^{-\beta [E_j - E_i + \mu_{\text{ADP}} - \mu_{\text{ATP}}]}$$



$$= e^{-\beta [\Delta E - \Delta \mu]}$$

$$\Delta \mu = \mu_{\text{ATP}} - \mu_{\text{ADP}} \geq 0$$

ATP bias the transition towards j

In general:

$$\frac{\Gamma_{i \rightarrow j}}{\Gamma_{j \rightarrow i}} = e^{-\beta [E_j - E_i + \Delta F_{i \rightarrow j}^{(env)}]}$$

where $\Delta F_{i \rightarrow j}^{(env)}$ is the change of free energy in the environment due to the transition $i \rightarrow j$.

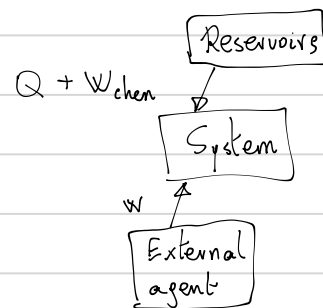
When the free energy of the environment (thermal baths + particle reservoir) changes, the energy flow is not equal to the heat.

Heat is defined as:

$$Q = -T \Delta S_{env}$$

But now:
$$\Delta S_{env} = \frac{\Delta E_{env}}{T} - \sum_{\alpha} \frac{\mu_{\alpha}}{T} \Delta N_{\alpha}$$

↑ chemical species in the reservoirs



or:
$$\Delta F_{env} = \Delta E_{env} - T \Delta S_{env}$$

Consequently:
$$Q = -T \Delta S_{env} = \Delta F_{env} - \Delta E_{env}$$

The energy transferred from the reservoirs to the system is:

$$E_{env \rightarrow sys} = -\Delta E_{env} = Q - \Delta F_{env} = Q + W_{chem}$$

Chemical work $W_{chem} = -\Delta F_{env}$

First law:
$$\Delta E = Q + W_{chem} + W$$

Second law (one temperature T):

$$\Delta S_{\text{total}} = \Delta S_{\text{sys}} + \Delta S_{\text{env}} = \Delta S_{\text{sys}} - \frac{Q}{T}$$

$$= \frac{T\Delta S_{\text{sys}} - \Delta E + W + W_{\text{chem}}}{T} \geq 0$$

$$\Rightarrow -\Delta F + W + W_{\text{chem}} \geq 0 \Rightarrow W + W_{\text{chem}} \geq \Delta F$$

second law for isothermal processes.

The second law is consistent with Shannon entropy and local detailed balance:

$$kT \ln \frac{\Gamma_{i \rightarrow j}}{\Gamma_{j \rightarrow i}} = E_i - E_j - \overbrace{\Delta F_{i \rightarrow j}^{(\text{env})}}^{\Delta E_{i \rightarrow j}^{(\text{env})}} = T \Delta S_{i \rightarrow j}^{(\text{env})} \quad \leftarrow \text{Change of entropy in the environment in a transition } i \rightarrow j.$$

Using the master equation:

$$\dot{S}_{\text{total}} = \dot{S} + \dot{S}_{\text{env}} = \sum_{i,j} J_{i \rightarrow j}(t) \left[k \ln \frac{p(i,t)}{p(j,t)} + k \ln \frac{\Gamma_{i \rightarrow j}}{\Gamma_{j \rightarrow i}} \right]$$

Shannon

$$= k \sum_{i,j} J_{i \rightarrow j}(t) \ln \frac{p(i,t) \Gamma_{i \rightarrow j}}{p(j,t) \Gamma_{j \rightarrow i}} \geq 0$$

Each term is positive