

# Extended Forms of the Second Law for General Time-dependent Stochastic Processes

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- 1 Preliminary notions
- 2 Mathematical Constructions
- 3 The Second Laws of Thermodynamics
- 4 Applications to Classical Thermodynamic Processes

# Classical states and Master equation

- Classical states are points in phase space and the evolution of a classical system is the hopping processes between the states.
- The set of equations that describes transitions is:

## Master Equations

$$\frac{dp_i(t)}{dt} = \sum_{j=1}^N [q_{ji}(t)p_j(t) - q_{ij}p_i(t)]$$

where  $p_i$  is a discrete set of probability distribution and  $q_{ij}(t)$  is the transition density matrices collectively denoted as  $Q(t)$ .

# Classical states and Master equation

- *Remarks*

## Master Equations

$$\frac{dp_i(t)}{dt} = \sum_{j=1}^N [q_{ji}(t)p_j(t) - q_{ij}p_i(t)]$$

- Master equations say: probability change rate of one state is the total contribution from all other states, including both the pumping in and leaking out transitions.
- Sum of all the equations gives  $\dot{p}_{\text{total}} = 0$ , therefore, the hopping system can be visualized as an electric circuit where total ‘charge’ is conserved!

# Steady State

- The *steady state* is the case where time derivatives of all individual states vanish.
- Charge on each node stays constant w/r time!
- The master equations, if  $\dot{\pi}_i = 0$  for all  $i$ , then read,

$$0 = \sum_{j=1}^N [q_{ji}(t)\pi_j(t) - q_{ij}\pi_i(t)]$$

in shorthand notation  $\pi Q(t) = 0$ .

# Picture of $\pi Q(t) = 0$

Pumping-in equals leaking-out!

$$\sum_{j=1}^N q_{ji}(t) \pi_j(t) = \left( \sum_{j=1}^N q_{ij} \right) \pi_i(t)$$

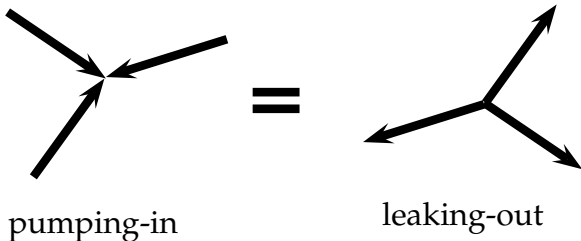
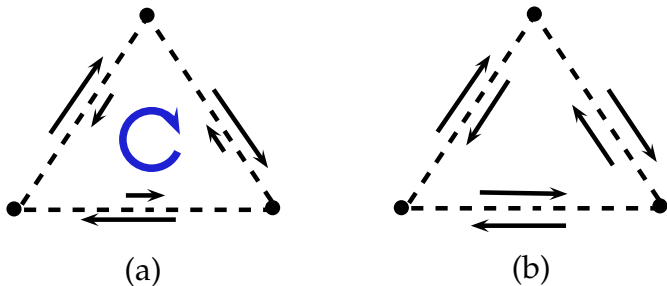


Figure: Pumping-in equals leaking-out for each node!

# Detailed Balance

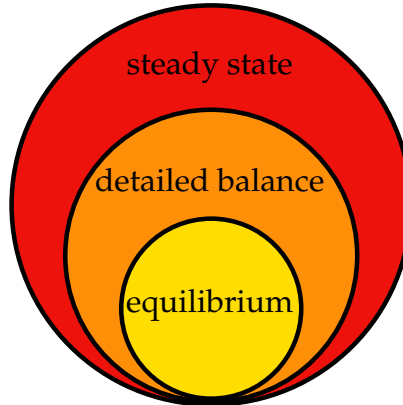
- What is a detailed balance?
- For state  $i$  and each  $j$ ,  $q_{ji}p_j = q_{ij}p_i$ ,
- There is no current between any two nodes and hence, no net current in the whole circuit!



**Figure:** (a) A general steady state; (b) a state in detailed balance.

# Thermodynamic equilibrium

- What is a thermodynamic equilibrium?



**Figure:** Venn diagram of ‘steady state’, ‘detailed balance’ and ‘thermodynamic equilibrium’.



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# Entropy and its time derivative

- Time dependent entropy is the

## General Entropy

$$S [\{p_i(t)\}] = -k_B \sum_i p_i(t) \log p_i(t)$$

- Take time derivative!
- Split the derivative into two parts

## The Interior and Exterior Parts

$$\frac{dS(t)}{dt} = d_i S + d_e S = e_p(t) - h_d(t)$$

# Instantaneous entropy production rate and heat dissipation rate

- Where ...

Instantaneous *Entropy Production Rate*

$$d_i S = e_p(t) = \frac{1}{2} k_B \sum_{i,j} [p_i(t) q_{ij}(t) - p_j(t) q_{ji}(t)] \log \frac{p_i(t) q_{ij}(t)}{p_j(t) q_{ji}(t)}$$

Notice,  $e_p(t) \geq 0$ .

- And

*Heat Dissipation Rate*

$$d_e S = h_d(t) = \frac{1}{2} k_B \sum_{i,j} [p_i(t) q_{ij}(t) - p_j(t) q_{ji}(t)] \log \frac{q_{ij}(t)}{q_{ji}(t)}$$

# The heats

- The total heat  $Q_{tot}(t) = h_d(t) T$  further splits into two parts  $Q_{tot} = Q_{hk} + Q_{ex}$  where

## Housekeeping Heat

$$Q_{hk}(t) = \frac{1}{2} k_B T \sum_{i,j} [p_i(t) q_{ij}(t) - p_j(t) q_{ji}(t)] \log \frac{\pi_i(t) q_{ij}(t)}{\pi_j(t) q_{ji}(t)}$$

## Excessive Heat

$$Q_{ex}(t) = \frac{1}{2} k_B T \sum_{i,j} (p_i(t) q_{ij}(t) - p_j(t) q_{ji}(t)) \log \frac{\pi_j(t)}{\pi_i(t)}$$

# Housekeeping heat is positive semi-definite

## Proof for Non-negativity of Housekeeping Heat

$$\begin{aligned}
 Q_{hk}(t) &= k_B T \sum_{i,j} p_i(t) q_{ij}(t) \log \frac{\pi_i(t) q_{ij}(t)}{\pi_j(t) q_{ji}(t)} \\
 &\geq -k_B T \sum_{i,j} p_i(t) q_{ij}(t) \left( \frac{\pi_j(t) q_{ji}(t)}{\pi_i(t) q_{ij}(t)} - 1 \right) \\
 &= -k_B T \sum_i \frac{p_i(t)}{\pi_i(t)} \sum_j \pi_j(t) q_{ji}(t) + k_B T \sum_{i,j} p_i(t) q_{ij}(t) \\
 &= 0
 \end{aligned}$$

- $\log x \leq x - 1$ ,  $\forall x > 0$  and  $\sum_j q_{ij}(t) \equiv 0$ —identity out of nowhere!

# Amendment to the proof

- If  $\sum_j q_{ij}(t) \equiv 0$  is true, master equations have to be amputated!

$$\frac{dp_i(t)}{dt} = \sum_{j=1}^N [q_{ji}(t)p_j(t) - q_{ij}p_i(t)]$$

- Although the proof is blatantly flawed, it is not dead!
- Instead, simply note that  $\pi(t)$  is a steady state, therefore ‘pumping-in equals leaking-out!’

$$\sum_{j=1}^N q_{ji}(t)\pi_j(t) = \left( \sum_{j=1}^N q_{ij} \right) \pi_i(t)$$

# Amendment to the proof

## Proof for Non-negativity of Housekeeping Heat

$$\begin{aligned} Q_{hk}(t) &\geq -k_B T \sum_i \frac{p_i(t)}{\pi_i(t)} \underbrace{\sum_j \pi_j(t) q_{ji}(t)}_{=\left(\sum_{j=1}^N q_{ij}\right) \pi_i(t)} + k_B T \sum_{i,j} p_i(t) q_{ij}(t) \\ &= -k_B T \sum_i \frac{p_i(t)}{\pi_i(t)} \pi_i(t) \left( \sum_{j=1}^N q_{ij} \right) + k_B T \sum_{i,j} p_i(t) q_{ij}(t) \\ &= 0 \end{aligned}$$

- The conclusion is still safe!

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# The Traditional Second Law

- Traditional second law is built on non-negativity of  $e_p$ .

## Clausius Inequality

$$\frac{dS(t)}{dt} + h_d = e_p \geq 0 \Rightarrow T \frac{dS(t)}{dt} + Q_{tot(t)} \geq 0$$

- Let's examine the reversible (quasi-static) process in equilibrium thermodynamics since 'only irreversible processes contribute to entropy production ( $e_p$ ).'

## Lines of Reasoning

Set  $e_p(t) = 0 \Rightarrow$  Detailed balance holds and by examining several time-dependent processes, the author concludes  $\{\pi(t)\} = \{\pi\} \Rightarrow$  the transient states  $\{\pi\}$  are identified with traditional equilibrium states but they are all constant!

# The Extended Second Law

- ‘There is no real reversible process between two different equilibrium states.’
- Strickly speaking, thermodynamic *identities* which rely on reversible paths, are ill-defined.
- To ‘justify’ our sins, we need:

## The Extended Form of the Second Law

$$T \frac{dS}{dt} + Q_{ex}(t) = T e_p - Q_{hk} \geq 0$$

- For equilibrium case,  $Q_{ex} = Q_{tot}$ , it returns to traditional version. The house keeper is our very savior but conventional treatments tend to kill him!

# $Te_p(t) - Q_{hk}(t)$ is positive semi-definite

*Proof.*

$$\begin{aligned} Q_f(t) &= Te_p(t) - Q_{hk}(t) \\ &= \sum_{ij} p_i(t) q_{ij}(t) \log \frac{p_i(t) \pi_j(t)}{p_j(t) \pi_i(t)} \\ &\geq \sum_{ij} p_i(t) q_{ij}(t) \left( \frac{p_j(t) \pi_i(t)}{p_i(t) \pi_j(t)} - 1 \right) \\ &= \sum_j \frac{p_j(t)}{\pi_j(t)} \sum_i \pi_i(t) q_{ij}(t) - \sum_i p_i(t) \sum_j q_{ij}(t) \\ &= 0 \end{aligned}$$

# The Extended Second Law

- Then we have:

$$T \frac{dS(t)}{dt} + Q_{ex}(t) = Te_p(t) - Q_{hk}(t) \geq 0$$

- The Corresponding Integral Form:

Extended Form of Clausius Inequality

$$T\Delta S + \int Q_{ex}(t) dt \geq 0$$

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# Applications to Classical Thermodynamic Processes

- Time-independent case
  - Relaxation process toward equilibrium state.
  - Relaxation process toward nonequilibrium steady state.
- Time-dependent case
  - Cyclic process
  - Transitions between equilibrium states
  - Transitions between steady states

# Relaxation process toward equilibrium state

- The free energy, the relative entropy, in the master-equation model reads

$$F(t) = k_B T \sum_i p_i(t) \log \frac{p_i(t)}{\pi_i(t)}$$

- Extended second law predicts

$$\frac{F(t)}{dt} = -Te_p(t) \leq 0$$

- $F(t)$  serves as Lyapunov function for the relaxation process toward equilibrium state.

# Relaxation process toward nonequilibrium steady state

- The extended second law can be reformulated into

$$\frac{dF(t)}{dt} = -Te_p(t) + Q_{hk}(t) \leq 0$$

- $F(t)$  serves as a Lyapunov function for relaxation toward nonequilibrium steady state.
- **Lyapunov property is just a corollary of the the extended second law!**



# Cyclic Processes

- Cyclic means state variables return to their original values after a full cycle.  $\Rightarrow \Delta S = 0$
- Traditional form gives:

$$\int Q_{tot}(t) dt \geq 0$$

- the extended form gives:

$$\int Q_{ex}(t) \geq 0$$

- During a cyclic process, not only the total heat ( $Q_{hk} + Q_{ex}$ ) but also the excess heat could only be from the system into the heat bath rather than follow the opposite direction.

# Transitions between equilibrium states

- The dissipative work is defined as

$$W(t) = -k_B T \sum_i p_i(t) \frac{d \log \pi_i(t)}{dt}$$

- Then author derived

$$\frac{dF(t)}{dt} = W(t) - T e_p$$

- The transition can be decomposed into, first modulation of  $Q(t)$  and second, relaxation toward equilibrium state (with a fixed  $Q(T)$ )
- Then  $\Delta F_1 \leq \int_1 W(t) dt$  and  $\Delta F_2 \leq \int_2 W(t) dt = 0$  for process 1 and 2.
- Hence, in accord with Jarzynski's work, we have

$$\Delta F = \Delta F_1 + \Delta F_2 \leq \int_1 W(t) dt$$

# Transitions between steady states

- Again, split the transition into two process as above, and for each process  $\int_1 Q_{ex}(t) dt \geq -T\Delta S_1$  and  $\int_2 Q_{ex}(t) dt \geq -T\Delta S_2$
- Therefore, with  $\Delta S = \Delta S_1 + \Delta S_2$ , we have

$$\int Q_{ex}(t) dt = \int_1 Q_{ex}(t) dt + \int_2 Q_{ex}(t) dt \geq -T\Delta S$$

- Hatano and Sasa concluded that the equality held for an infinitely slow operation in which the system is in a steady state at each time during a transition ('slow process').

# Summary

Process	1	2	3	4	5	6
$Q_{ex}$	0	0	?	?	?	?
$Q_{hk}$	0	+	0	+	0	+
$e_p$	0	+	+	+	+	+
$Te_p - Q_{hk}$	0	0	+	+	+	+

**Table:** ‘0’=zero ‘+’=positive ‘-’=negative ‘?’=uncertain.

Processes: (1) Equilibrium state; (2) Nonequilibrium steady state; (3) Relaxation process towards equilibrium state; (4) Relaxation process towards nonequilibrium steady state; (5) Transition between equilibrium states; (6) Transition between steady states.

# Questions?