

# Introduction to stochastic thermodynamics

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Naoto Shiraishi (Gakushuin University)

Based on my textbook (Springer, in preparation)



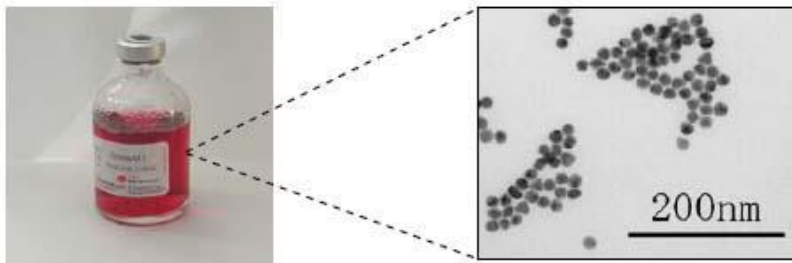
# Subject of stochastic thermodynamics

Conventional thermodynamics

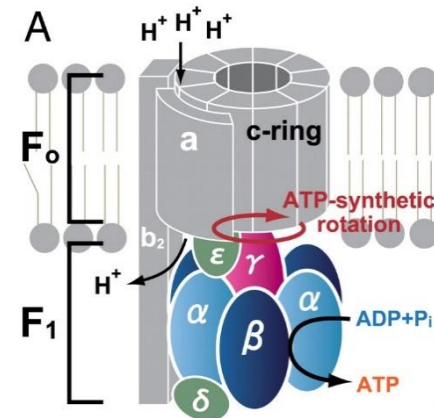
Macroscopic systems. No fluctuation.

Stochastic thermodynamics

We can treat small systems with thermal fluctuation.

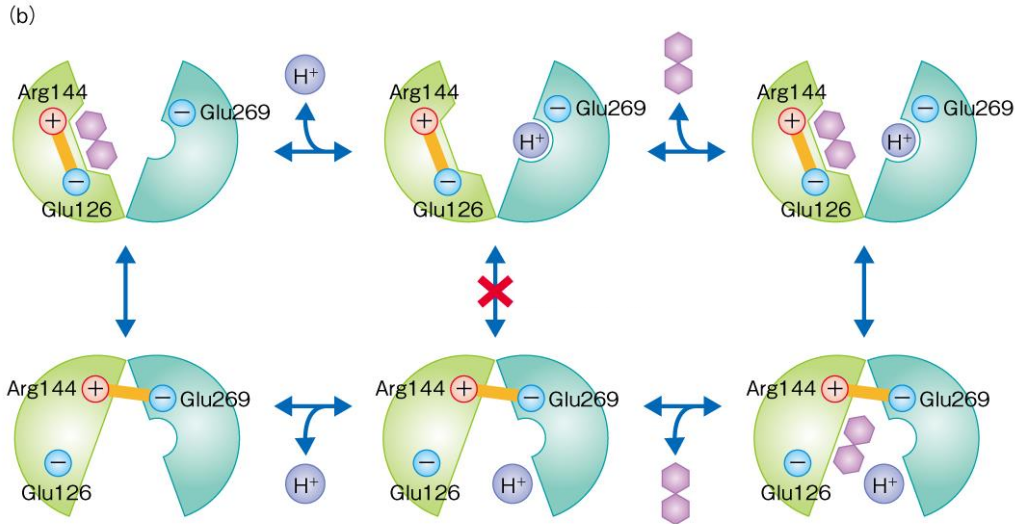


Colloidal particle

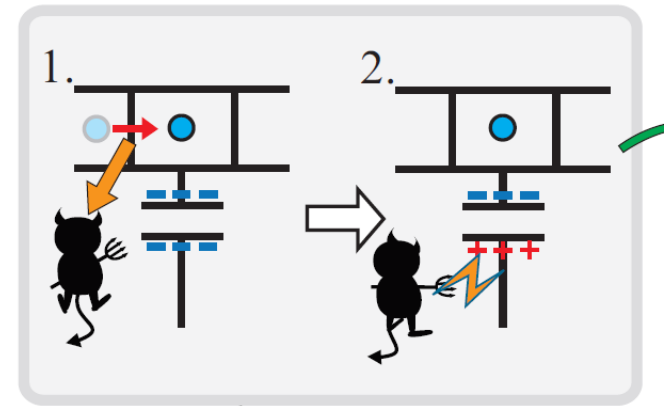


Molecular motors

# State space of system



(<http://leading.lifesciencedb.jp/2-e009>)

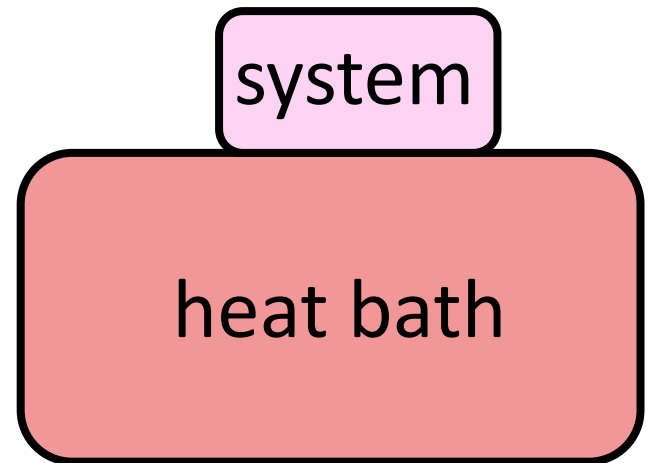


(<https://phys.org/news/2016-01-maxwell-demon-self-contained-information-powered-refrigerator.html>)

In this lecture, state space is **discrete**.  
(For continuous systems, we take proper discretization and continuum limit)

# Role of heat bath

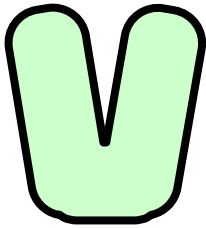
Setup: System is attached to large heat bath(s).



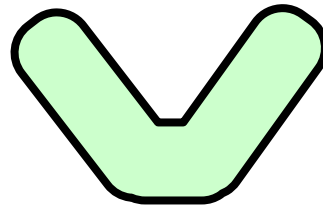
The heat bath induces the stochastic nature of dynamics of the system.

# Stochasticity from heat bath

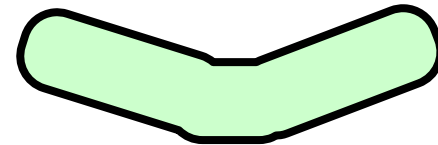
Example: protein with three stable states



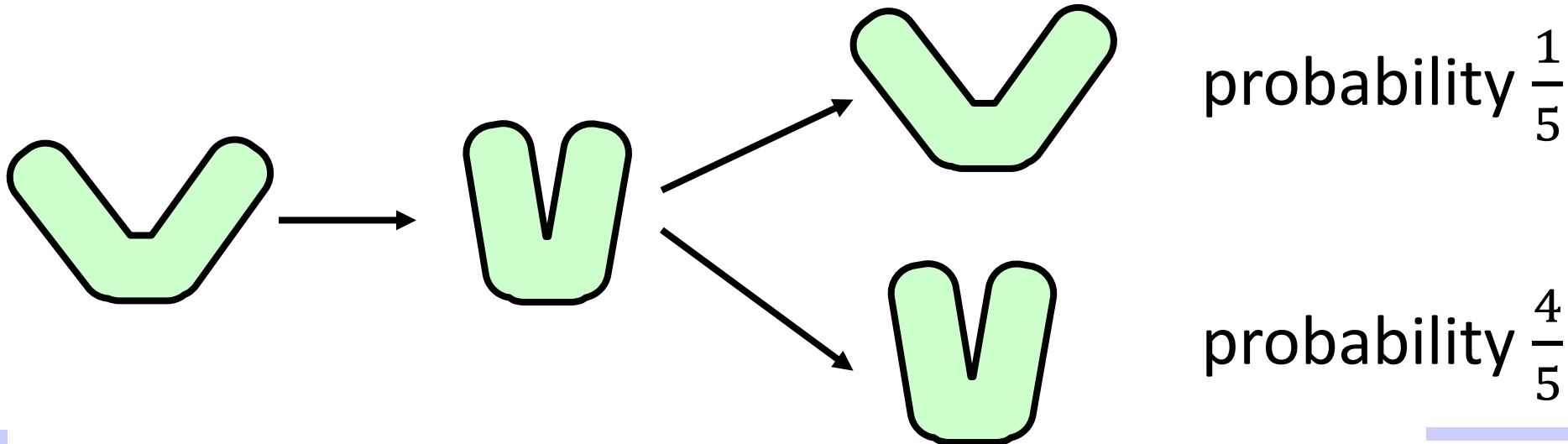
1:Close



2:Middle

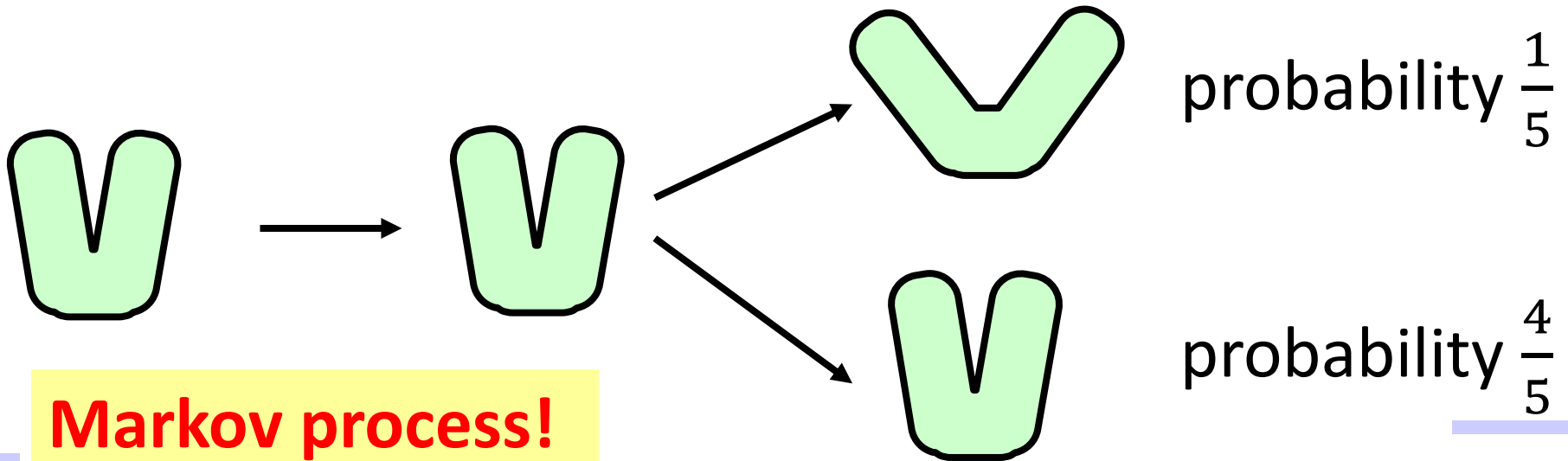
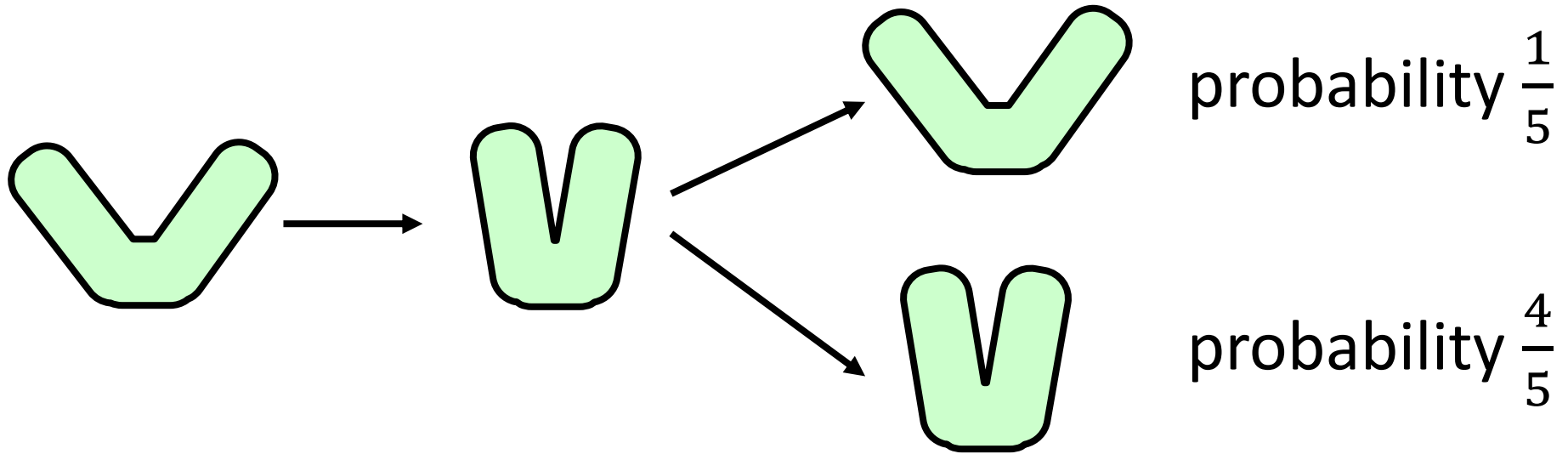


3:Open





# Markov process



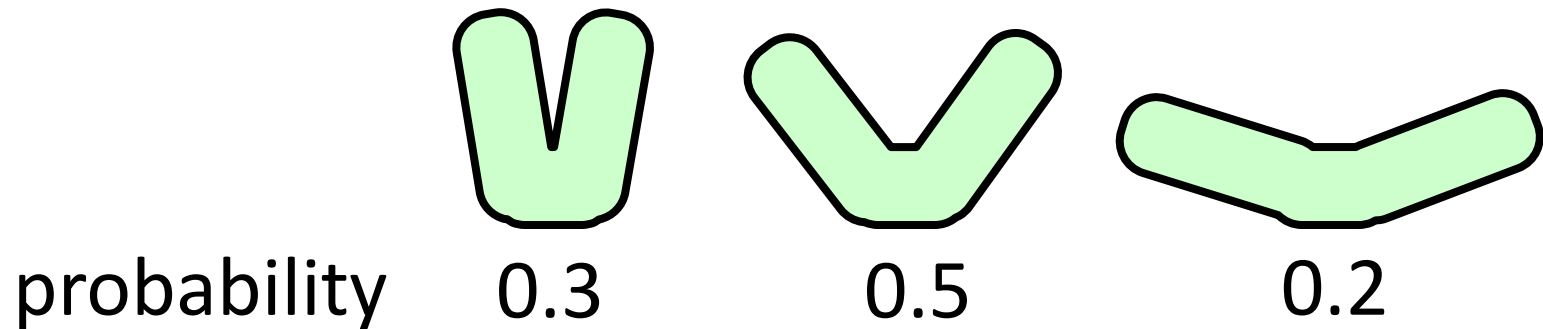
**Markov process!**



# State = Probability distribution

**State of system = Probability distribution on (microscopic) states.**

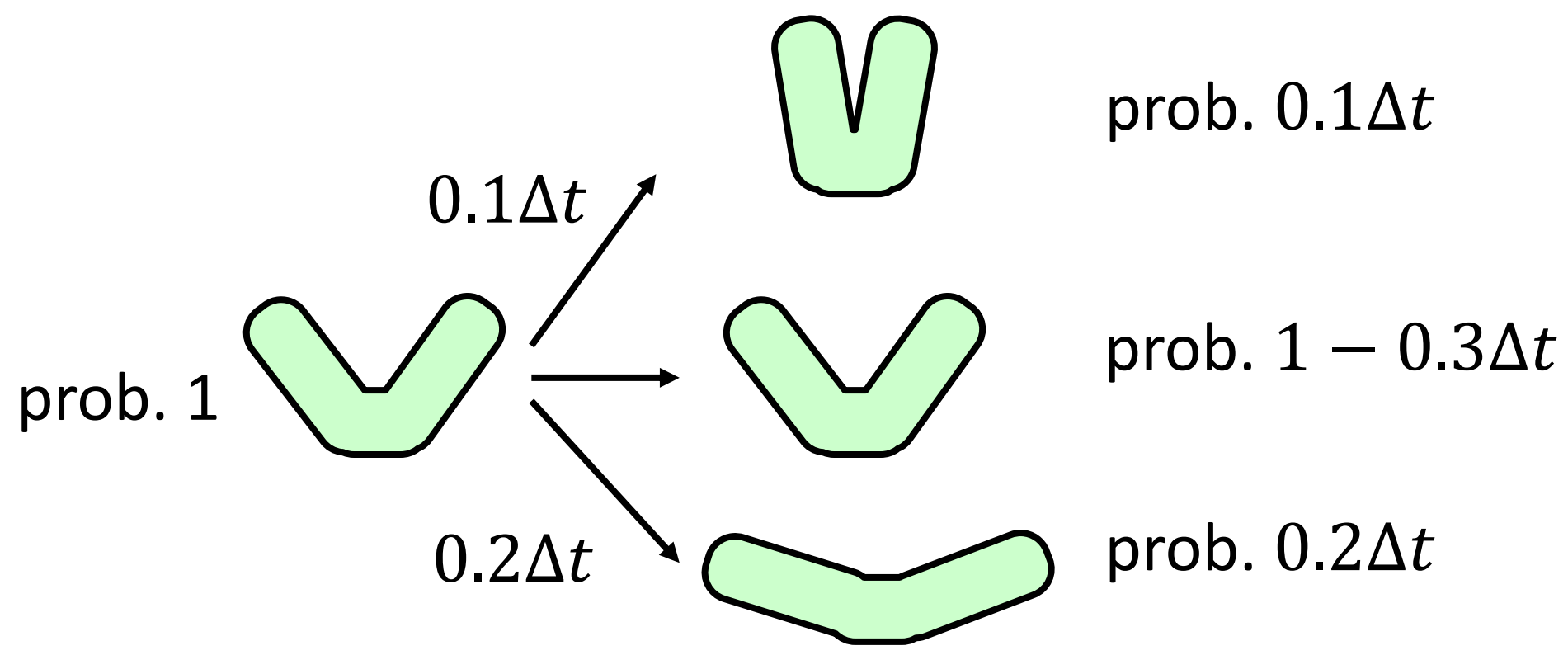
Ex)



→ We describe it as  $p = \begin{pmatrix} p_1 \\ p_2 \\ p_3 \end{pmatrix} = \begin{pmatrix} 0.3 \\ 0.5 \\ 0.2 \end{pmatrix}$



# Stochastic transition in continuous time



$$p(t) = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}$$

$$p(t + \Delta t) = \begin{pmatrix} 0.1\Delta t \\ 1 - 0.3\Delta t \\ 0.2\Delta t \end{pmatrix}$$







# Stochastic transition in continuous time



prob.  $0.1\Delta t$

$$\frac{\Delta p}{\Delta t} = \frac{p(t + \Delta t) - p(t)}{\Delta t} = \begin{pmatrix} 0.1 \\ -0.3 \\ 0.2 \end{pmatrix} \quad (\text{in this case})$$

$$p(t) = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}$$

$$p(t + \Delta t) = \begin{pmatrix} 0.1\Delta t \\ 1 - 0.3\Delta t \\ 0.2\Delta t \end{pmatrix}$$



# Transition matrix and master equation

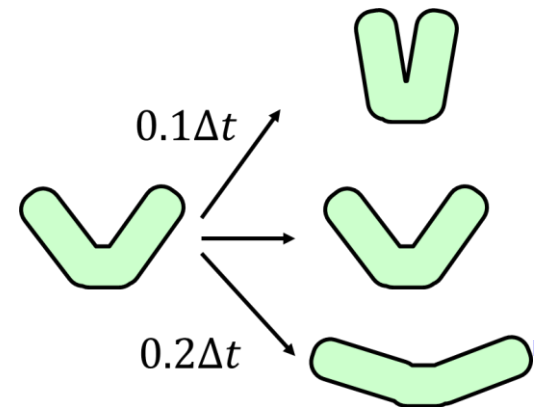
Taking  $\Delta t \rightarrow 0$ ,  $\frac{\Delta p}{\Delta t}$  becomes  $\frac{dp}{dt}$ .

## Master equation

$$\frac{d}{dt} \begin{pmatrix} p_1 \\ p_2 \\ p_3 \end{pmatrix} = \begin{pmatrix} R_{11} & R_{12} & R_{13} \\ R_{21} & R_{22} & R_{23} \\ R_{31} & R_{32} & R_{33} \end{pmatrix} \begin{pmatrix} p_1 \\ p_2 \\ p_3 \end{pmatrix}$$

ex) In the previous slide,

$$R_{12} = 0.1, R_{32} = 0.2, R_{22} = -0.3$$



# Conditions for transition matrix

$$\frac{d}{dt} \begin{pmatrix} p_1 \\ p_2 \\ p_3 \end{pmatrix} = \begin{pmatrix} R_{11} & R_{12} & R_{13} \\ R_{21} & R_{22} & R_{23} \\ R_{31} & R_{32} & R_{33} \end{pmatrix} \begin{pmatrix} p_1 \\ p_2 \\ p_3 \end{pmatrix}$$

Transition matrix  $R$  should satisfy

## 1. Non-negativity


$$R_{ij} \geq 0 \quad (i \neq j)$$

(∵ probability cannot be negative)

## 2. Normalization condition

$$\sum_i R_{ij} = 0 \quad \text{for any } j.$$

(∵  $\sum_j p_j$  should be normalized to 1)



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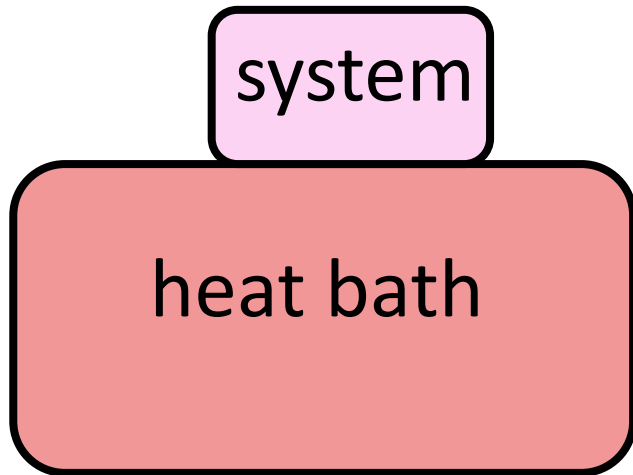
Before here, we provide  
mathematical description of  
stochastic Markov processes.

We now put **physics** into it.

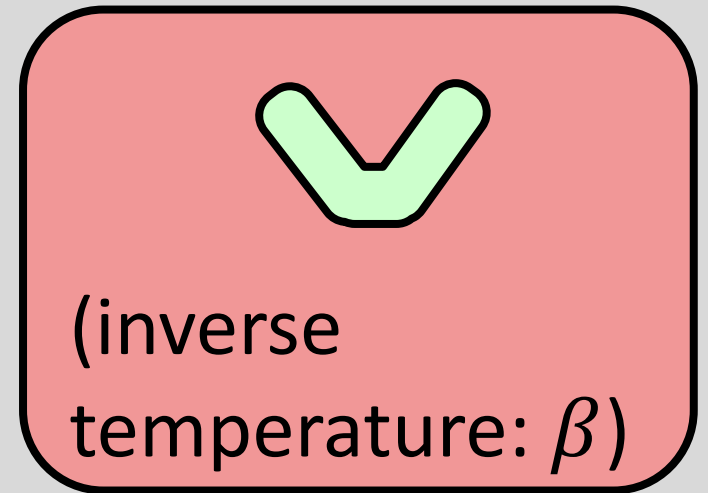


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# Situation (re-show)



Ex)



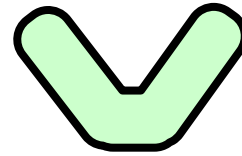
For simplicity, we consider case of a single heat bath for a while.

# Equilibrium distribution is invariant

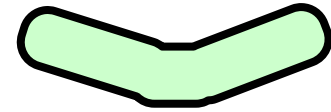
energy of states



$E_1$



$E_2$



$E_3$

Then, equilibrium (Gibbs / canonical) distribution

$$p^G = \frac{1}{Z} \begin{pmatrix} e^{-\beta E_1} \\ e^{-\beta E_2} \\ e^{-\beta E_3} \end{pmatrix}$$

should be invariant:

$$\frac{d}{dt} p^G = R p^G = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}$$

# Equilibrium distribution is invariant

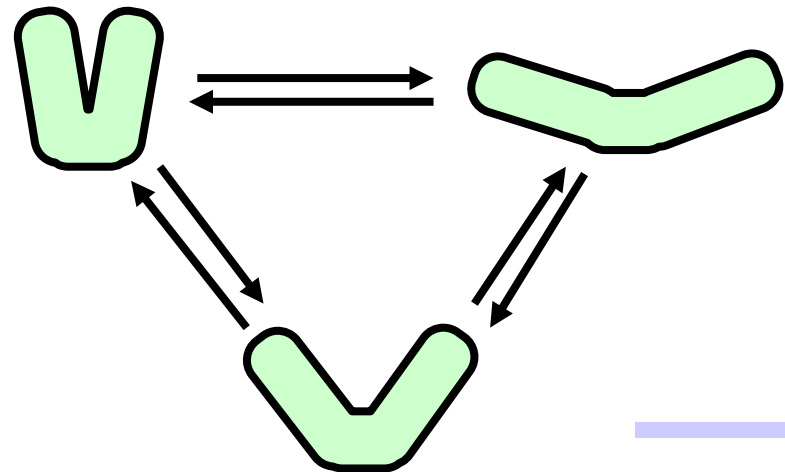
## Invariant condition

$p^G$  does not change in time.

$$\sum_i R_{ij} p_j^G = 0 \text{ for any } j$$

All physical systems satisfy this condition.

Moreover, various systems satisfy a stronger condition!



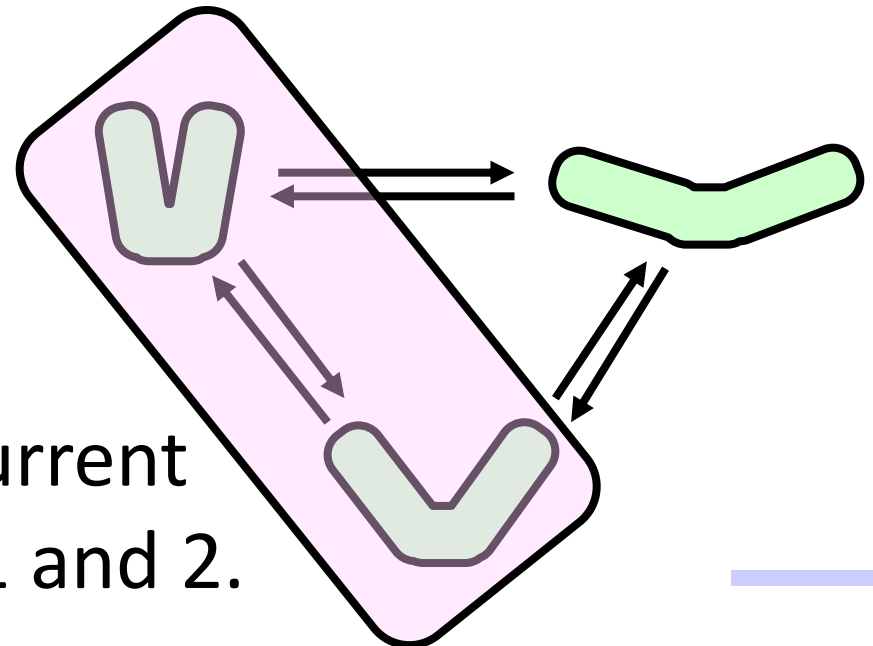
# Detailed-balance condition

## Detailed-balance condition

In equilibrium, no probability current between any two states.

$$R_{ij}p_j^G = R_{ji}p_i^G$$

No probability current  
between states 1 and 2.

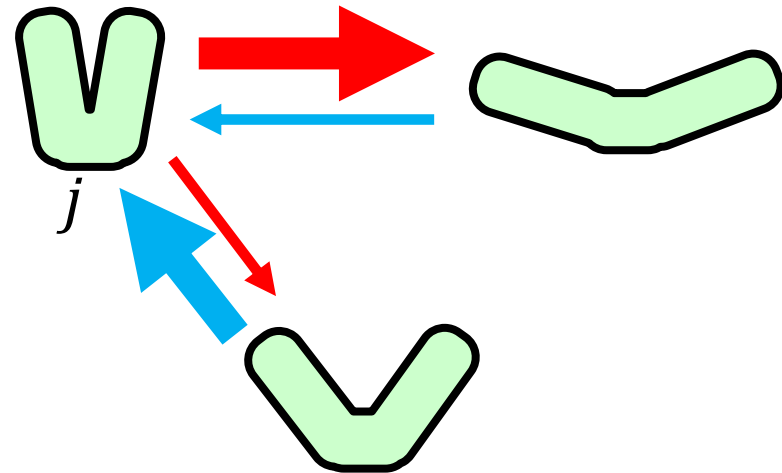




# Tentative summary

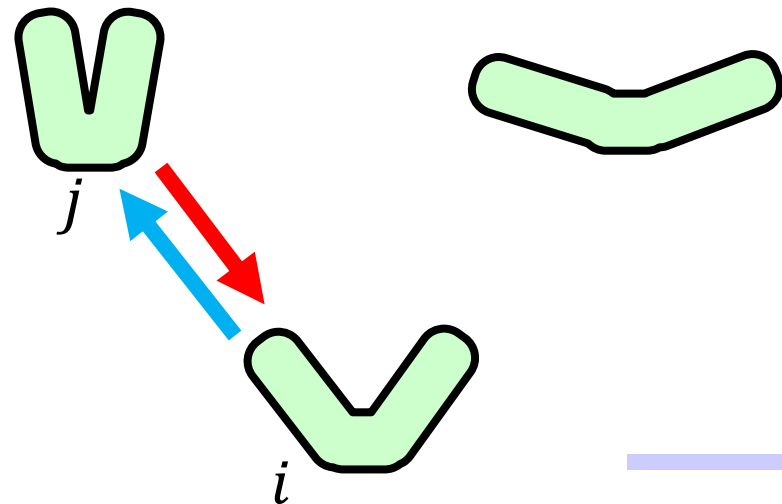
## Invariant condition

$$\boxed{\sum_{i(\neq j)} R_{ij} p_j^G} = \boxed{\sum_{i(\neq j)} R_{ji} p_i^G}$$



## Detailed-balance condition

$$\boxed{R_{ij} p_j^G} = \boxed{R_{ji} p_i^G}$$

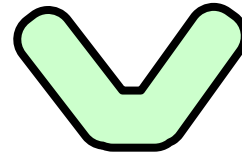


# Definition of internal energy

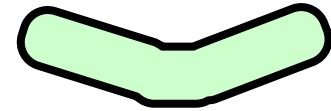
energy of states



$E_1$



$E_2$

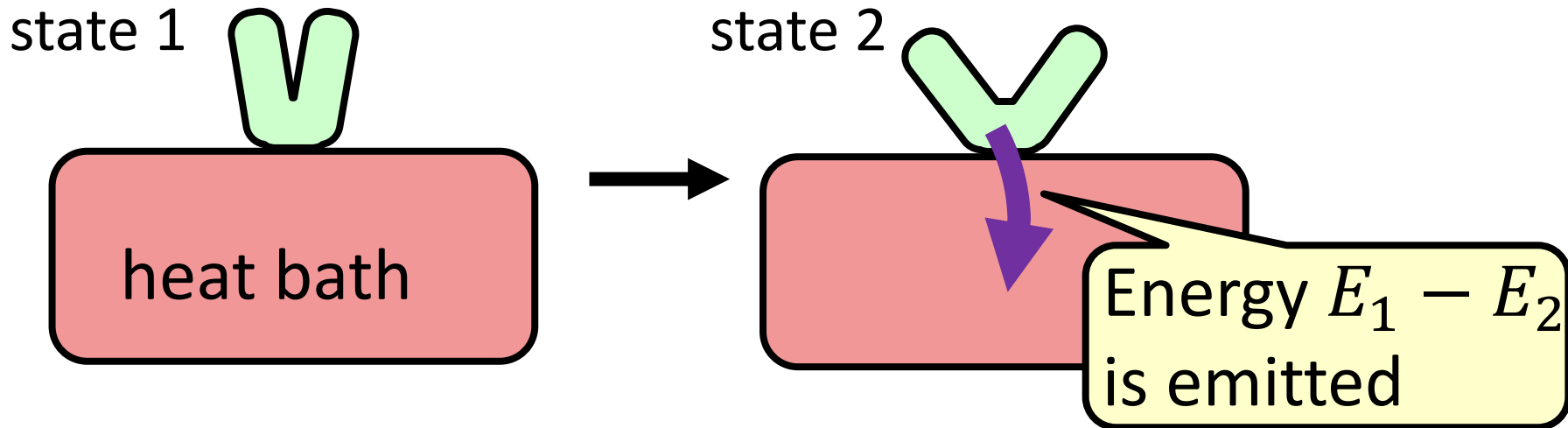


$E_3$

**Internal energy = Average of energy**

$$E = \langle E \rangle = \sum_i E_i p_i$$

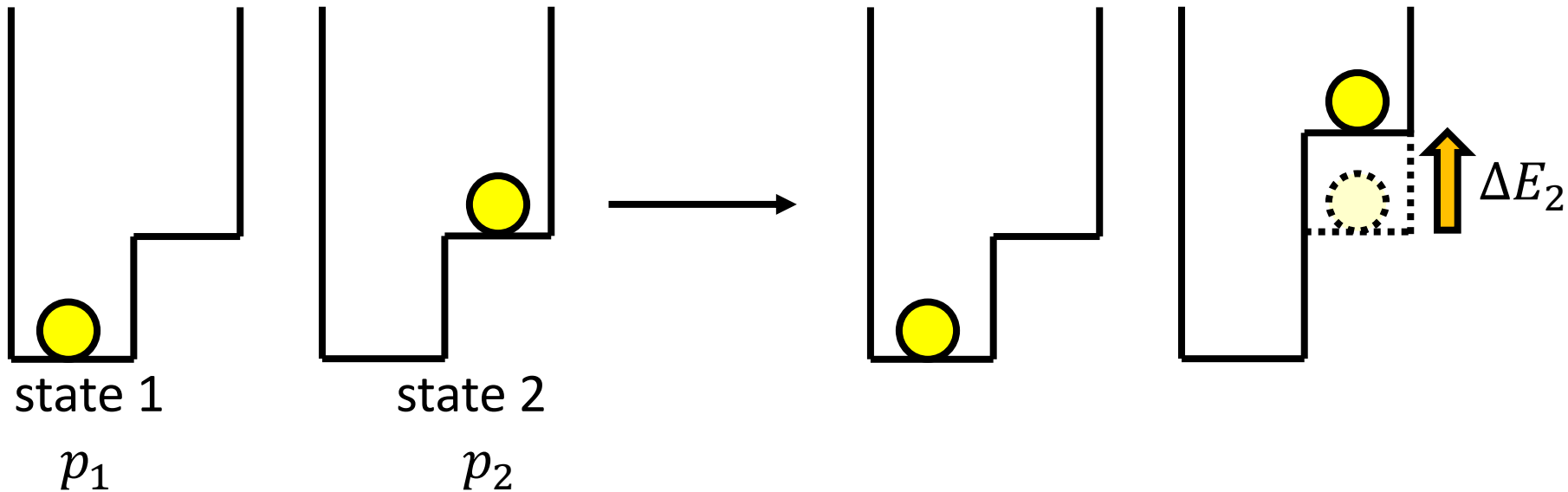
# Definition of heat



**Heat = Energy emission due to transition**

$$\begin{aligned}\text{Heat rate: } \dot{Q} &:= \sum_{i,j} (E_j - E_i) R_{ij} p_j \\ &= - \sum_{i,j} E_i R_{ij} p_j \quad (\text{We used } \sum_i R_{ij} = 0)\end{aligned}$$

# Definition of work



This process requires average energy  $p_2 \Delta E_2$ .

**Work = Energy change due to change of state energy**

$$\text{Work rate: } \dot{W} = \sum_i \frac{dE_i}{dt} p_i$$

# First law of thermodynamics

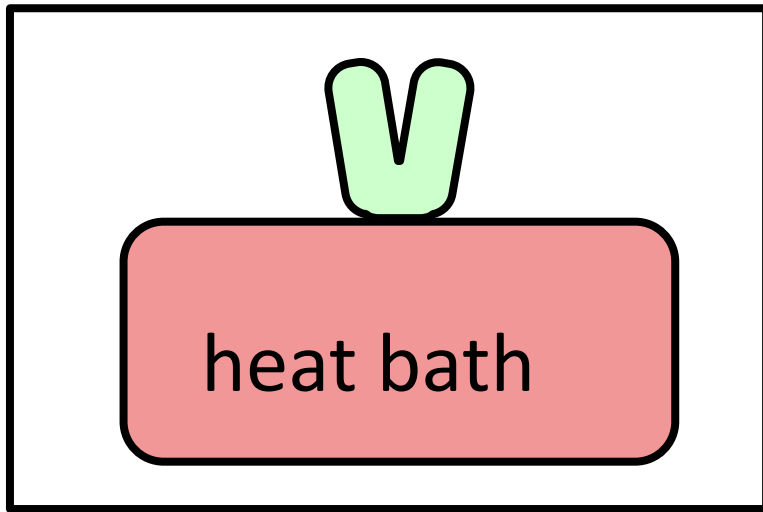
Employing these definitions, the first law of thermodynamics (energy conservation) is satisfied:

$$\dot{E} = \dot{W} - \dot{Q}$$

Derivation:

$$\begin{aligned} \frac{d}{dt} \langle E \rangle &= \sum_i \frac{d}{dt} (E_i p_i) = \sum_i p_i \frac{dE_i}{dt} + \sum_i E_i \frac{dp_i}{dt} \\ &= \sum_i p_i \frac{dE_i}{dt} + \sum_i E_i \sum_j R_{ij} p_j \end{aligned}$$

# Entropy



System + bath is **isolated!**

We want to define  $S_{system}$  and  $S_{bath}$  such that  $\Delta S_{system} + \Delta S_{bath}$  is always nonnegative (law of entropy increase).

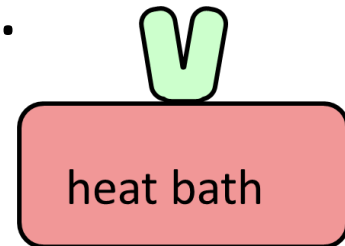
# Entropy in conventional thermodynamics

In conventional thermodynamics, entropy is

- defined for **equilibrium** states.
- given by  $dS = \beta dQ$  (Clausius relation).

Entropy of bath:  $\dot{S}_{bath} := \beta \dot{Q}$  indeed works.

**How to define entropy of system?**





We introduce entropy  
in information theory!





# Example: weather



Sunny days: very usual  
→ Little surprise



Snowy days: very rare  
→ Big surprise!

(photo: 2016/1)

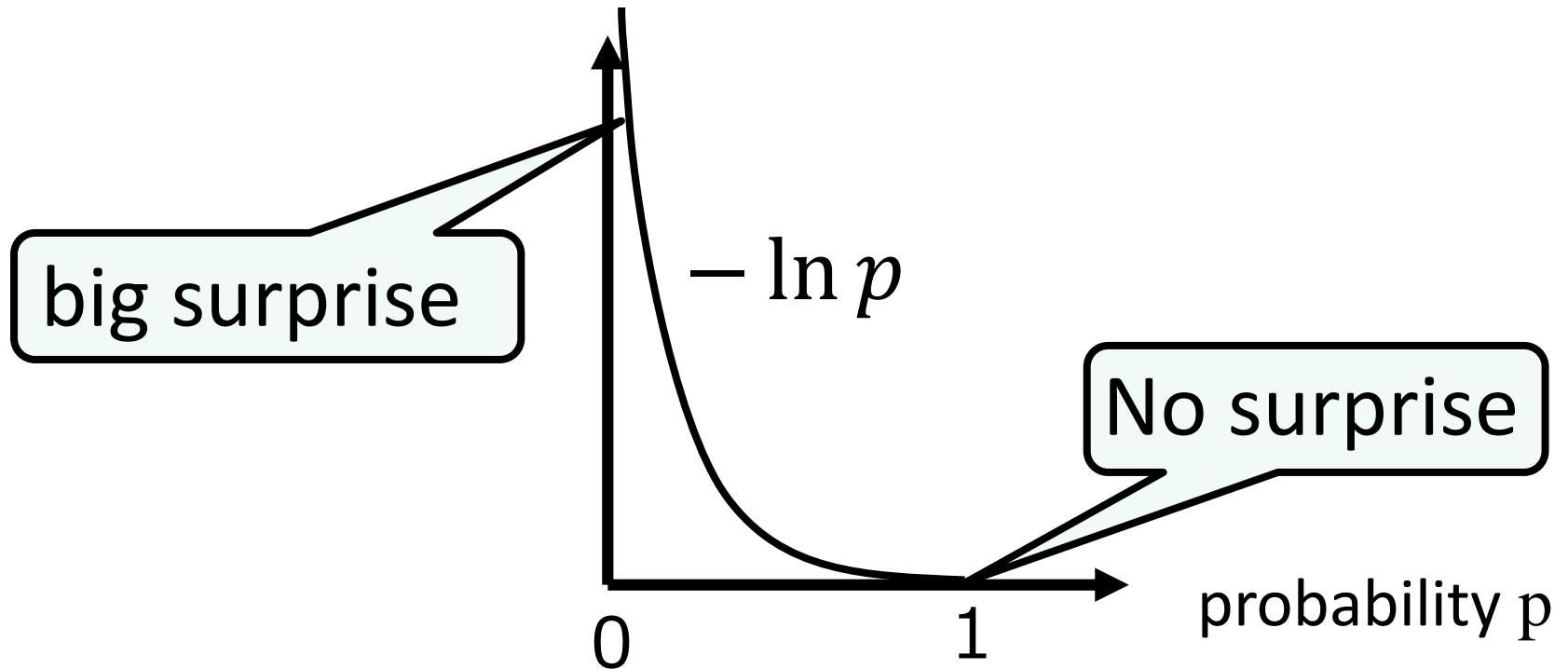
# Quantizing degree of surprise

## Axiom of surprisal

- Non-negative continuous function (w.r.t. probability of event)
- If A and B are independent events with each other, then surprisal for “A and B” is sum of surprisal for A and that for B.

Then, surprisal is uniquely determined as  $-C \cdot \ln p$   
( $C$ : constant,  $p$ : probability for event)

# Shannon entropy



Average of surprisal:  $\mathbf{H(p) = -\sum_i p_i \ln p_i}$

→ This is **Shannon entropy!**



# Properties of Shannon entropy

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Events occur very randomly (high stochasticity).

→ Degree of surprise is large.

→ Shannon entropy is large.




Events occur almost deterministically.

→ Degree of surprise is small.

→ Shannon entropy is small.



# Example of Shannon entropy

			<u>Surprisal</u>
	Sunny	70%	0.357
	Cloudy	29%	1.238
	Snowy	1%	4.605

$$H(p) = 0.250 + 0.359 + 0.046 = 0.655$$



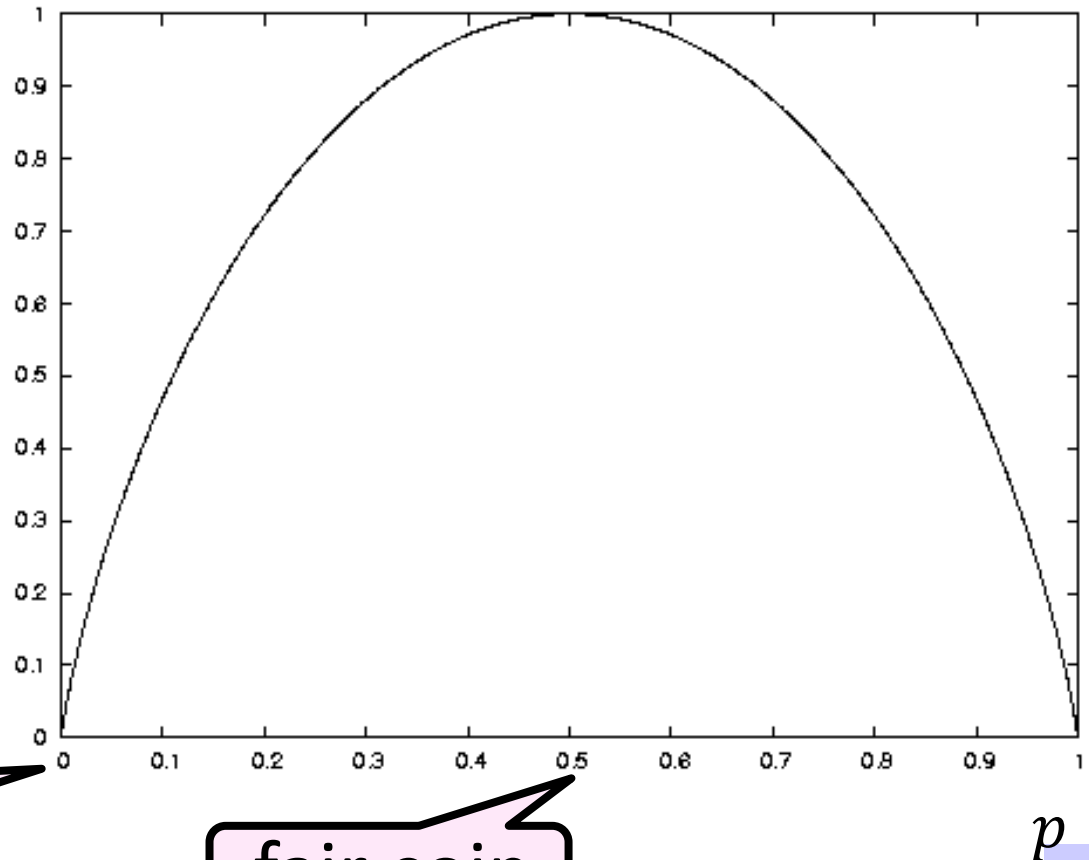
# Example of Shannon entropy (2)

## head/tail of coin

Plot of  $H(p) = -p \ln p - (1 - p) \ln(1 - p)$

$p$ : prob. of head

$$\frac{H(p)}{\ln 2}$$



biased coin  
(always tail)

fair coin

$p$



# Shannon entropy and Boltzmann entropy in statistical mechanics

In equilibrium (Gibbs) distribution, Shannon entropy coincides with Boltzmann entropy.

Ex) Microcanonical ensemble

$$p_i = \frac{1}{\Omega} \quad (\Omega: \text{number of states}).$$

$$H(p) = -\Omega \cdot \frac{1}{\Omega} \ln \frac{1}{\Omega} = \ln \Omega = S \quad (\text{We set } k_B = 1)$$

Ex) Canonical ensemble

$$p_i = \frac{e^{-\beta E_i}}{Z}, \quad H(p) = -\sum_i p_i \ln \frac{e^{-\beta E_i}}{Z} = \beta \langle E \rangle - \beta F = S$$

# Shannon entropy as entropy of stochastic system

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Shannon entropy = A kind of **generalization of equilibrium entropy**.

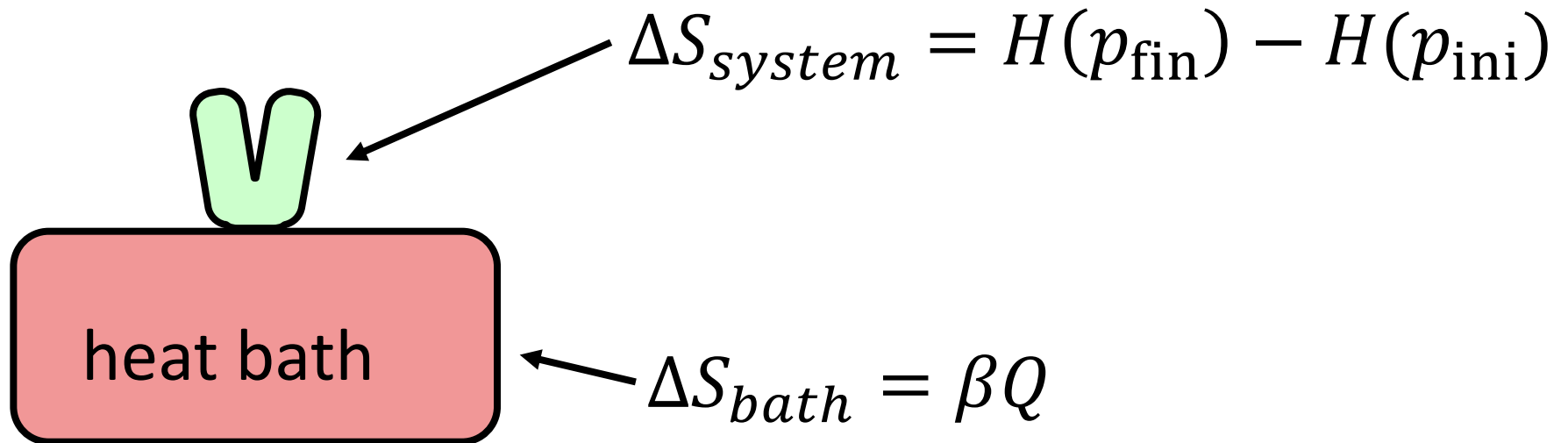
We **define** entropy of fluctuating system by its Shannon entropy.

(As seen later, this definition indeed reproduces thermodynamics if system is attached to baths.)

Information entropy always appears in stochastic thermodynamics (not only in Maxwell's demon).



# Entropy production



**Entropy production (total entropy increase)**

$$\sigma := \Delta S_{system} + \Delta S_{bath}$$

# Entropy production rate

Entropy production rate:  $(\int dt \dot{\sigma} = \sigma)$

$$\dot{\sigma} := \dot{S}_{system} + \dot{S}_{bath}$$

$$= \frac{d}{dt} \left( - \sum_i p_i \ln p_i \right) - \sum_i \beta E_i \frac{dp_i}{dt}$$

$$= - \sum_{i,j} R_{ij} p_j \ln p_i - \beta \sum_{i,j} E_i R_{ij} p_j$$

master equation:  $\frac{dp_i}{dt} = \sum_j R_{ij} p_j$

# Entropy production rate in systems with detailed-balance

If system satisfies detailed-balance condition,

$$\dot{\sigma} = \sum_{i,j} R_{ij} p_j \ln \frac{R_{ij} p_j}{R_{ji} p_i}$$

∴ Using  $\ln \frac{R_{ij}}{R_{ji}} = \beta(E_j - E_i)$  and  $\sum_i R_{ij} = 0$ , we have

$$\sum_{i,j} R_{ij} p_j [\beta(E_j - E_i) + \ln p_j - \ln p_i] = \sum_{i,j} R_{ij} p_j [-\beta E_i - \ln p_i] = \dot{\sigma}$$

# Second law of thermodynamics

## Theorem: Second law in stochastic thermodynamics

For any systems, we have

$$\dot{\sigma} \geq 0$$

(which directly implies  $\sigma \geq 0$ )

In conventional thermodynamics, second law is an empirical law (axiom).

In stochastic thermodynamics, **second law is a proved theorem.**


(Remark: This is not derivation of second law of thermodynamics, since our definition employs results in thermodynamics;  $S_{bath} = \beta Q$ )

# Proof (case with detailed balance)

We use relation  $(a - b) \ln \frac{a}{b} \geq 0$

( $\because \ln \frac{a}{b} \geq 0$  if and only if  $(a - b) \geq 0$ )

$$\begin{aligned}\dot{\sigma} &= \sum_{i,j} R_{ij} p_j \ln \frac{R_{ij} p_j}{R_{ji} p_i} \\ &= \frac{1}{2} \sum_{i,j} (R_{ij} p_j - R_{ji} p_i) \ln \frac{R_{ij} p_j}{R_{ji} p_i} \\ &\geq 0\end{aligned}$$



Before going to the proof for general cases, we introduce Kullback-Leibler divergence (relative entropy).



# Kullback-Leibler divergence

## Kullback-Leibler divergence (Relative entropy)

For two distributions  $a_i, b_i$  satisfying  $\sum_i a_i = \sum_i b_i$ ,

$$D(a||b) := \sum_i a_i \ln \frac{a_i}{b_i}$$

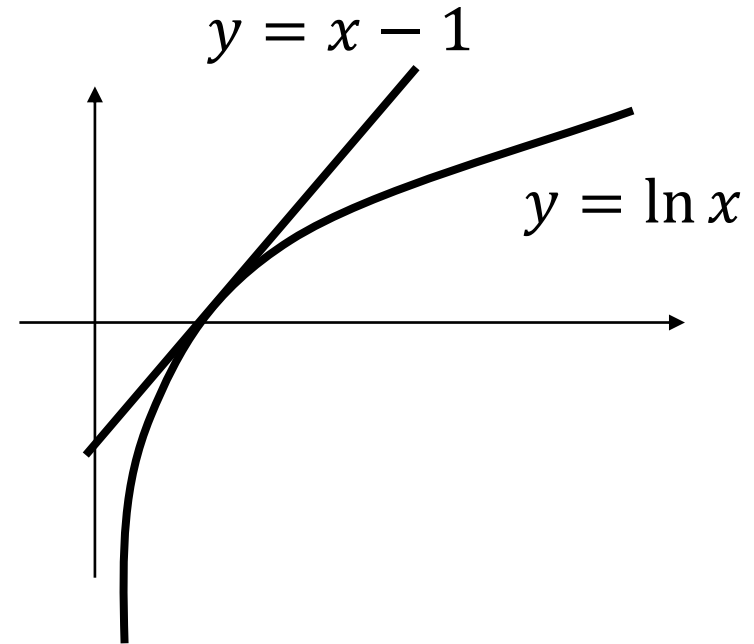
KL-divergence is a kind of (pseudo)-distance between two distributions.

### Theorem:

$$D(a||b) \geq 0$$

# Proof of $D(a||b) \geq 0$

We use  $x - 1 \geq \ln x$



$$\begin{aligned} D(a||b) &= - \sum_i a_i \ln \frac{b_i}{a_i} \geq - \sum_i a_i \left( \frac{b_i}{a_i} - 1 \right) \\ &= - \sum_i (b_i - a_i) = 0 \end{aligned}$$



# Dual transition matrix

We define **dual matrix** as

$$\tilde{R}_{ij} := \frac{R_{ji} e^{-\beta E_i}}{e^{-\beta E_j}}$$

Dual matrix is transition matrix (i.e., satisfying normalization condition) because

$$\sum_i \tilde{R}_{ij} = \frac{\sum_i R_{ji} e^{-\beta E_i}}{e^{-\beta E_j}} = 1$$

Invariance of canonical distribution

# General expression of entropy production rate

$$\begin{aligned}\dot{\sigma} &= - \sum_{i,j} R_{ij} p_j \ln p_i - \beta \sum_{i,j} E_i R_{ij} p_j \\ &= - \sum_{i,j} R_{ij} p_j (\ln p_i - \ln p_j) - \beta \sum_{i,j} (E_i - E_j) R_{ij} p_j \\ &= - \sum_{i \neq j} R_{ij} p_j (\ln p_i - \ln p_j) - \beta \sum_{i \neq j} (E_i - E_j) R_{ij} p_j \\ &= \sum_{i \neq j} R_{ij} p_j \ln \frac{R_{ij} p_j}{\tilde{R}_{ji} p_i}\end{aligned}$$

$\ln \frac{R_{ij}}{\tilde{R}_{ji}} = \beta (E_j - E_i)$

# Entropy production is nonnegative!

$$\sum_{i \neq j} R_{ij} p_j = \sum_j -R_{jj} p_j = \sum_i -\tilde{R}_{ii} p_i = \sum_{i \neq j} \tilde{R}_{ji} p_i$$

Changing dummy index  $j \rightarrow i$  and using

$$\tilde{R}_{ii} = \frac{R_{ii} e^{-\beta E_i}}{e^{-\beta E_i}} = R_{ii}$$

$$\dot{\sigma} = \sum_{i \neq j} R_{ij} p_j \ln \frac{R_{ij} p_j}{\tilde{R}_{ji} p_i} = D(R_{ij} p_j || \tilde{R}_{ji} p_i) \geq 0$$

# Summary

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- We construct the framework of stochastic thermodynamics.
- Heat, work, and entropy production is defined.
- Nonnegativity of entropy production (the second law of thermodynamics)  $\sigma \geq 0$  is proved.

*EVD*



# Remark: time derivative of Shannon entropy

$$-\frac{d}{dt} \sum_i p_i \ln p_i = - \sum_i \left( \frac{dp_i}{dt} \right) \ln p_i - \sum_i p_i \frac{d}{dt} (\ln p_i)$$

$$= \sum_i p_i \left[ \frac{1}{p_i} \frac{d}{dt} p_i \right] = \sum_i \frac{d}{dt} p_i = 0$$

Only the first term remains to be nonzero.

# Shannon entropy does not work in isolated system

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Shannon entropy is invariant under Hamiltonian dynamics (Shannon entropy does not increase).

Shannon entropy is NOT good characterization of entropy of **isolated systems**.

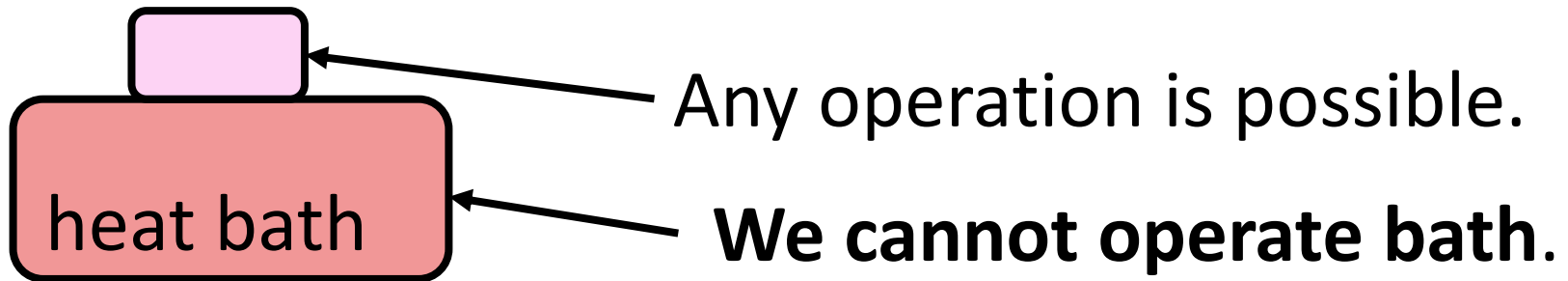
# Why Shannon entropy does not work in isolated systems?

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**Restriction of operation** is inevitable for thermodynamic irreversibility

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## Isothermal system



## Isolated system





# Case of multiple baths



heat bath 2

heat bath 1

$$R_{ij} = R_{ij}^1 + R_{ij}^2$$

Invariant condition

$$\sum_j R_{ij}^1 e^{-\beta^1 E_j} = 0,$$

$$\sum_j R_{ij}^2 e^{-\beta^2 E_j} = 0$$

Detailed-balance condition

$$R_{ij}^1 e^{-\beta^1 E_j} = R_{ji}^1 e^{-\beta^1 E_i}$$

$$R_{ij}^2 e^{-\beta^2 E_j} = R_{ji}^2 e^{-\beta^2 E_i}$$