# Introduction to Stochastic Thermodynamics: from Fluctuation Theorems to Thermodynamic Trade-off Relations

## Lecture 1

2022 ICTP-KIAS School on Statistical Physics for Life Sciences

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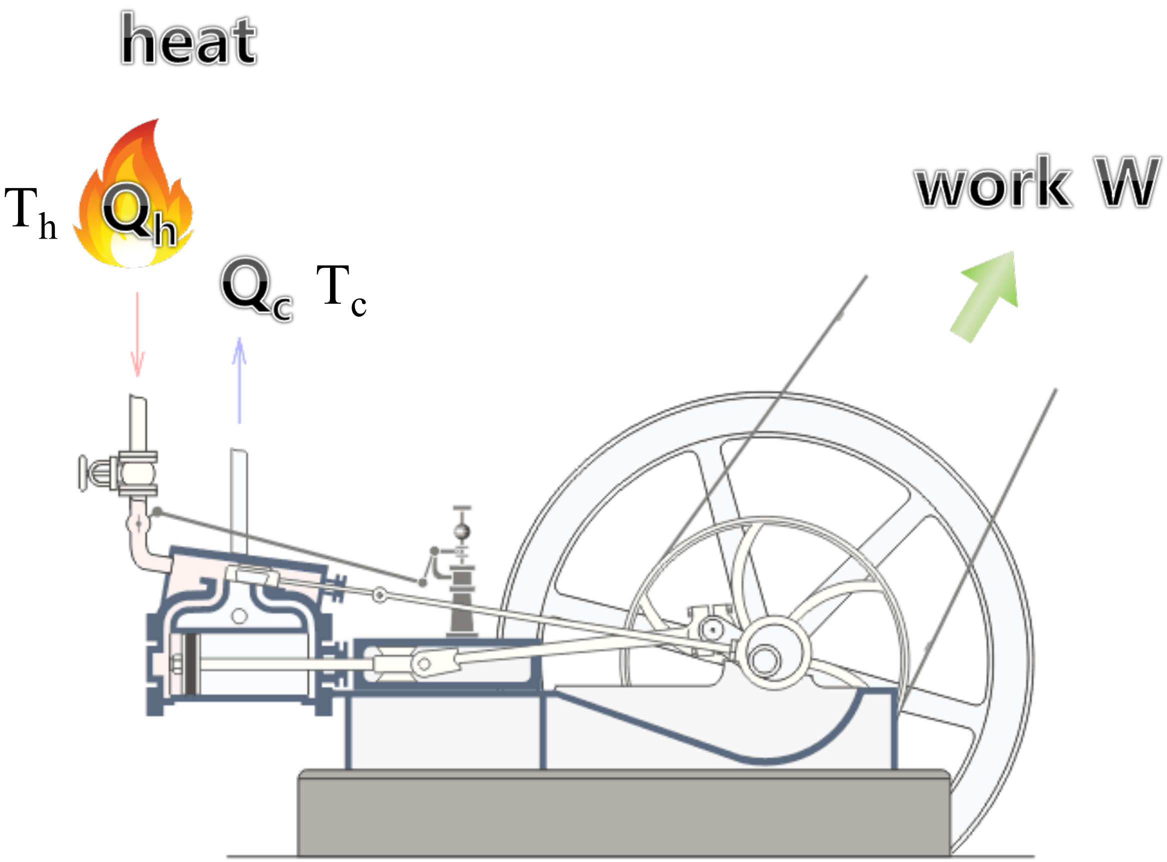
imagine the impossible

KIAS KOREA INSTITUTE FOR ADVANCED STUDY

# What is Stochastic "Thermodynamics"?

a branch of physics that deals with **heat**, **work**, and **temperature**, and their relation to **energy**, **entropy**, and the physical properties of matter and radiation

Wikipedia: Thermodynamics




relations

1st: $\Delta E = Q_h - Q_c - W$

$E$: energy of the engine

$$Q_c = Q_h - W - \Delta E$$

($\Delta E = 0$, one cycle)

2nd: $$\Delta S \equiv -\frac{Q_h}{T_h} + \frac{Q_h}{T_c} - \frac{W}{T_c} \geq 0$$

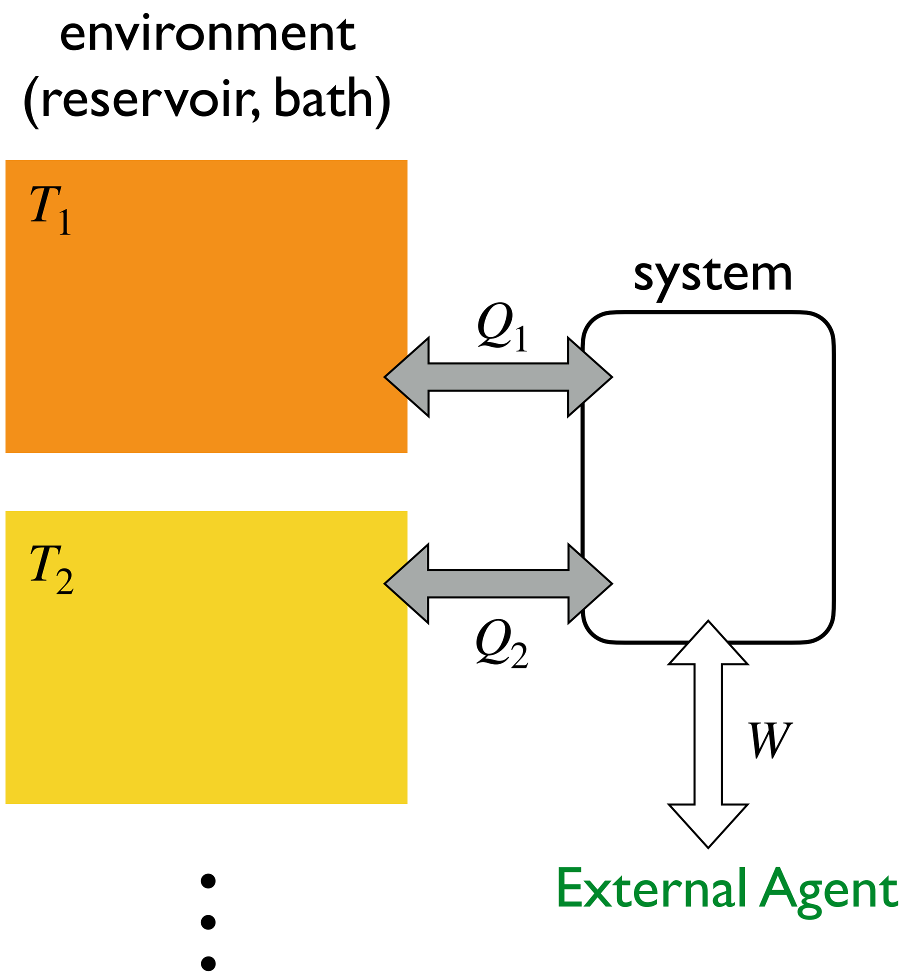
$$\frac{Q_h}{T_c}\left(1 - \frac{T_c}{T_h}\right) - \frac{W}{T_c} \geq 0$$

$$\rightarrow 1 - \frac{T_c}{T_h} \geq \frac{W}{Q_h} = \eta$$

# What is Stochastic “Thermodynamics”?

a branch of physics that deals with heat, work, and temperature, and their relation to energy, entropy, and the physical properties of matter and radiation

Wikipedia: Thermodynamics




heat: energy transferred from/into bath

work: energy transferred from/into E.A.

→ open system

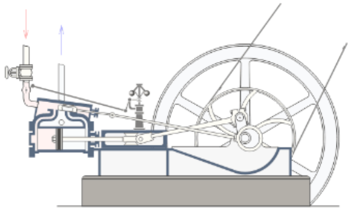
relations: 1st, 2nd laws…

→ thermodynamic properties are determined

# What is “Stochastic” Thermodynamics?

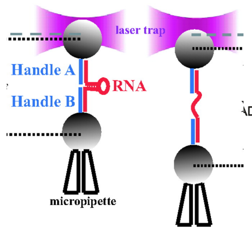
$10^{0}$ m $10^{-3}$ m $10^{-6}$ m $10^{-9}$ m

meso/microscopic system

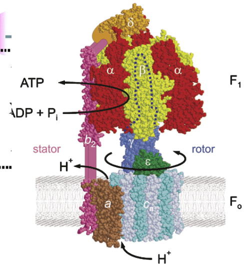


Motion is deterministic.

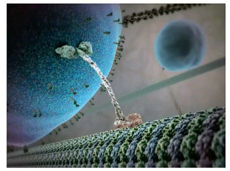
Brownian particle,
many biological systems




RNA folding
/unfolding




F1-motor



kinesin

In microscopic scale, motion is not deterministic,
but random or stochastic.

YouTube: Myosin V molecular motor

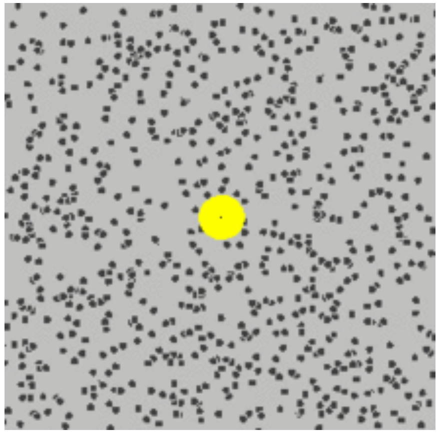
# What is "Stochastic" Thermodynamics?

Source of stochasticity - environment

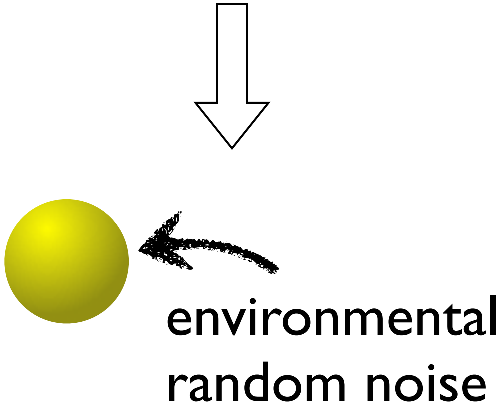
: interaction between a system and environmental particles

→ In principle, the motion is deterministic.

→ But, practically infeasible to keep track of all degrees of freedom of environmental particles.



Wikipedia: Brownian motion




→ treat the environmental interaction as a simple random noise

- Langevin equation (continuous state)
- master equation (discrete state)

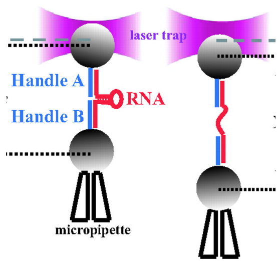
# What is "Stochastic Thermodynamics"?

: thermodynamics for stochastic systems (small & open)

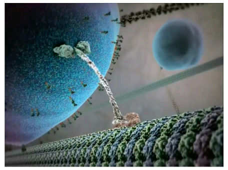
What are

heat, work, stochastic trajectory?

Lecture 1




RNA folding/unfolding



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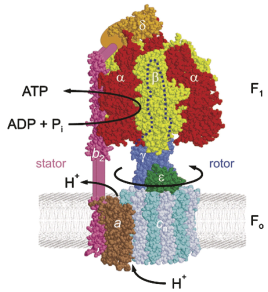



F1-motor

What are

the thermodynamic laws and relations?

Entropy production and Fluctuation Theorems (FT) Lecture 2

Thermodynamic Uncertainty Relations (TUR)

Lecture 3

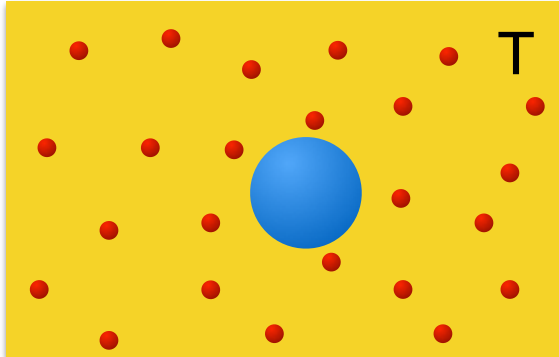
Thermodynamic speed limit

Lecture 4

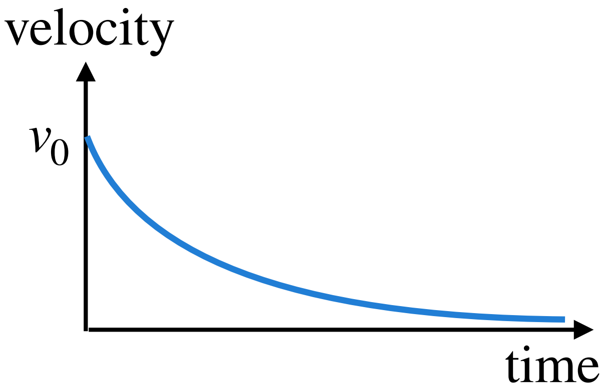
# Thermodynamics for Langevin Dynamics

## 1. Description of Langevin equation

phenomenological description of interaction of environmental particles




1) dissipation

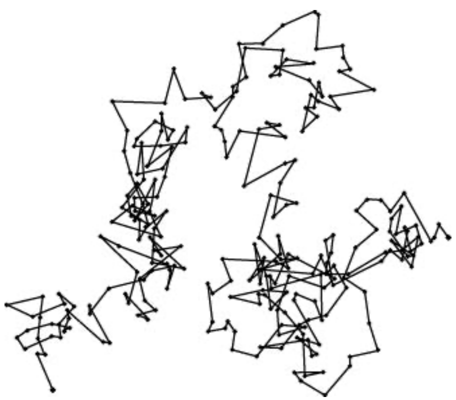



$$m\dot{v} = -\gamma v$$

$(m$ : mass, $\gamma$ : dissipation coefficient$)$

$$\therefore \quad v(t) = v(0)e^{-\gamma t/m} \quad \rightarrow \quad v = 0 \text{ in the long time limit?}$$

2) random motion



$$m\dot{v} = -\gamma v + \xi \qquad (\xi : \text{white} - \text{Gaussian random noise})$$

i) $\langle \xi \rangle = 0 \quad \Rightarrow \quad m\langle \dot{v} \rangle = -\gamma \langle v \rangle$

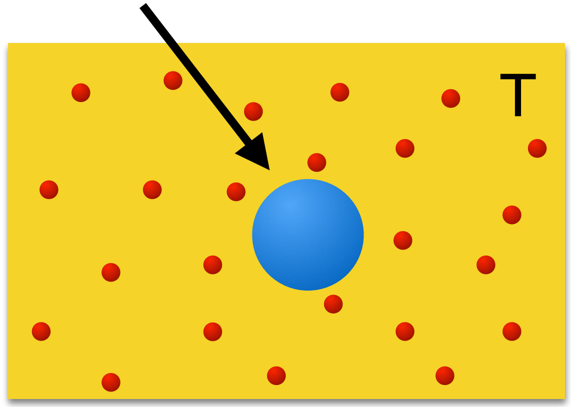
ii) $\langle \xi(t)\xi(t') \rangle = 2B\delta(t - t')$ (Markovian noise)

$$\therefore \quad v(t) = v(0)e^{-\gamma t/m} + \int_0^t dt' e^{-\gamma(t-t')/m}\xi(t')/m$$

$$\rightarrow \lim_{t\to\infty} \langle v^2(t) \rangle = \frac{B}{\gamma m} = \frac{k_B T}{m} \text{ (equipartition)} \quad \Rightarrow B = \gamma k_B T \text{ (Einstein)}$$

# Thermodynamics for Langevin Dynamics

## I. Description of Langevin equation




$$x(t+dt) - x(t) = v(t)dt$$

$$m\left(v(t+dt) - v(t)\right) = -\,\partial_x U(\lambda(t), x(t))dt + f_{\rm nc}(t)dt - \gamma v(t)dt + \xi(t)dt$$

$$\langle \xi(t) \rangle = 0, \;\; \langle \xi(t)\xi(t') \rangle = 2\gamma k_{\rm B} T \delta(t - t')$$

### Note on stochastic calculus

regular function product

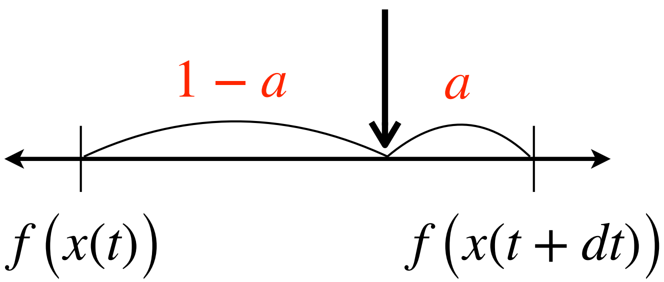
$$\left\langle f\left(x(t)\right) x(t) \right\rangle \underset{?}{=} \left\langle f\left(\underline{x(t+dt)}\right) x(t) \right\rangle = \left\langle \left[ f\left(x(t)\right) + \partial_x f\left(x(t)\right) v(t)dt \right] x(t) \right\rangle$$

$$= x(t) + v(t)dt$$

$$= \left\langle f\left(x(t)\right) x(t) \right\rangle + \underline{\left\langle \partial_x f\left(x(t)\right) v(t) x(t) \right\rangle dt}$$

$$= 0 \quad (dt \to 0 \text{ limit})$$

$$f^a(t) \equiv (1-a) f\left(x(t+dt)\right) + a f\left(x(t)\right)$$




$$(0 \le a \le 1)$$

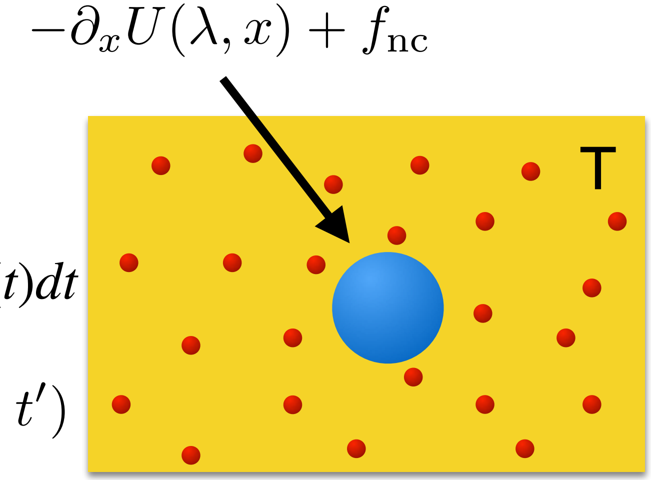
$$\left\langle f\left(x(t)\right) \odot_a x(t) \right\rangle \equiv \langle f^a(t) x(t) \rangle$$

$$= (1-a) \left\langle f\left(x(t+dt)\right) x(t) \right\rangle + a \left\langle f\left(x(t)\right) x(t) \right\rangle$$

$$= \left\langle f\left(x(t)\right) x(t) \right\rangle$$

# Thermodynamics for Langevin Dynamics

## I. Description of Langevin equation




$$x(t+dt) - x(t) = v(t)dt$$

$$m\left(v(t+dt) - v(t)\right) = -\partial_x U(\lambda(t), x(t))dt + f_{\rm nc}(t)dt - \gamma v(t)dt + \xi(t)dt$$

$$\langle \xi(t) \rangle = 0, \ \ \langle \xi(t)\xi(t') \rangle = 2\gamma k_{\rm B} T \delta(t-t')$$

### Note on stochastic calculus

**function & noise product**

$$\langle v(t)\xi(t) \rangle \underset{?}{=} \langle v(t+dt)\xi(t) \rangle$$

$$\langle v(t)\xi(t) \rangle = \langle v(t) \rangle \langle \xi(t) \rangle = 0$$

$$\langle v(t+dt)\xi(t) \rangle = \underbrace{\langle v(t)\xi(t) \rangle}_{=0} + \frac{1}{m}\underbrace{\left\langle \left(-\partial_x U(t) + f_{\rm nc}(t) - \gamma v(t)\right)\xi(t) \right\rangle}_{=0} dt + \underbrace{\frac{1}{m}\langle \xi(t)\xi(t) \rangle dt}_{=\frac{2\gamma k_B T}{m}}$$

$$\langle v(t) \odot_a \xi(t) \rangle = (1-a)\langle v(t+dt)\xi(t) \rangle + a\langle v(t)\xi(t) \rangle = \frac{2\gamma k_B T}{m}(1-a)$$

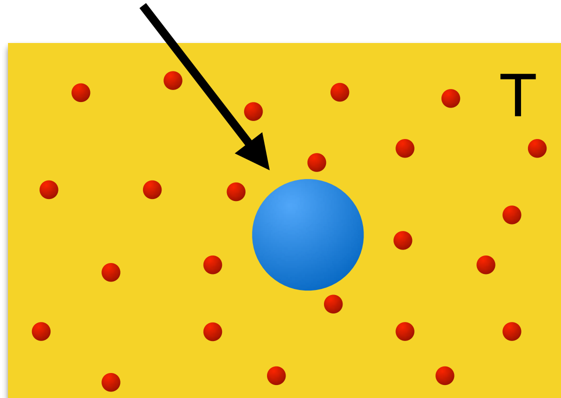
Stratonovich : $a = 1/2$ $\ (\circ \equiv \odot_{1/2})$ e.g. $v(t) \circ \xi(t)$

Ito : $a = 1$ $\ (\bullet \equiv \odot_1)$ e.g. $v(t) \bullet \xi(t)$

# Thermodynamics for Langevin Dynamics

## 2. Definitions of heat and work

Sekimoto, Prog. Theo. Phys. 130, 17 (1998)




$$x(t+dt) - x(t) = v(t)dt$$

$$m\left(v(t+dt) - v(t)\right) = -\,\partial_x U(\lambda(t), x(t))dt + f_{\rm nc}(t)dt - \gamma v(t)dt + \xi(t)dt$$

$$\langle \xi(t) \rangle = 0, \ \ \langle \xi(t)\xi(t') \rangle = 2\gamma k_{\rm B} T \delta(t-t')$$

$$\underbrace{v(t) \circ m\left(v(t+dt) - v(t)\right)}_{= dK} = \underbrace{-v(t) \circ \partial_x U(\lambda(t), x(t))dt}_{= -\,dU + \partial_\lambda U \dot{\lambda} dt} + \underbrace{v(t) \circ f_{\rm nc}(t)dt}_{= f_{\rm nc}(t) v(t) dt} + v(t) \circ \left(-\gamma v(t) + \xi(t)\right) dt$$

$$\underbrace{dK + dU}_{= dE} = \underbrace{\partial_\lambda U \dot{\lambda} dt + f_{\rm nc}(t) v(t) dt}_{= dW} + \underbrace{v(t) \circ \left(-\gamma v(t) + \xi(t)\right) dt}_{= dQ} \quad \text{: 1st law}$$

Work : $dW_{\rm c} = \partial_\lambda U \dot{\lambda} dt$ : work done by conservative force or Jarzynski work

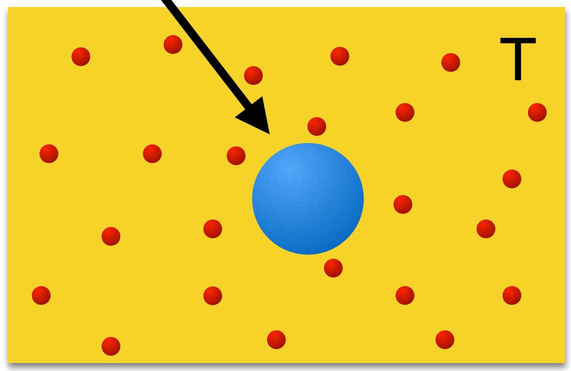
$dW_{\rm nc} = f_{\rm nc} v dt$ : work done by nonconservative force

$dW = dW_{\rm c} + dW_{\rm nc}$ : work done by external force

Heat : $dQ = v(t) \circ \left(-\gamma v(t) + \xi(t)\right) dt$ : work done by heat-bath force (must be Stratonovich)

# Thermodynamics for Langevin Dynamics

2. Definitions of heat and work Sekimoto, Prog. Theo. Phys. 130, 17 (1998)




overdamped limit $(m/\gamma \to 0)$

$$\dot{x} = v, \quad m\dot{v} = -\partial_x U(\lambda, x) + f_{\rm nc} - \gamma v + \xi$$

$$\langle \xi(t) \rangle = 0, \ \langle \xi(t)\xi(t') \rangle = 2\gamma k_{\rm B} T \delta(t - t')$$

Velocity is always equilibrated, integrated out.

$$\Longrightarrow \quad 0 = -\partial_x U(\lambda, x) + f_{\rm nc} - \gamma \dot{x} + \xi$$

$$\gamma \left( x(t+dt) - x(t) \right) = -\partial_x U(\lambda(t), x(t))dt + f_{\rm nc}(t)dt + \xi(t)dt$$

## Note on stochastic calculus

underdamped sytem

$$\langle v(t) \odot_a \xi(t) \rangle = (1-a)\langle v(t+dt)\xi(t) \rangle + a\langle v(t)\xi(t) \rangle = \frac{2\gamma k_B T}{m}(1-a)$$

overdamped limit

$$\langle x(t) \odot_a \xi(t) \rangle = (1-a)\underline{\langle x(t+dt)\xi(t) \rangle} + a\underline{\langle x(t)\xi(t) \rangle} = 2k_B T(1-a)$$

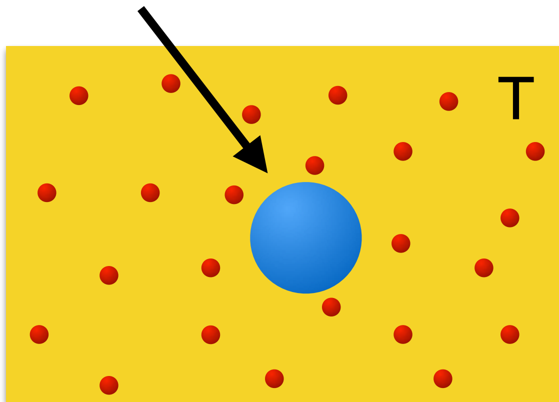
$$= \langle (\xi(t)dt/\gamma)\xi(t) \rangle \qquad = 0$$

$$= 2k_B T$$

# Thermodynamics for Langevin Dynamics

## 2. Definitions of heat and work

Sekimoto, Prog. Theo. Phys. 130, 17 (1998)




overdamped limit $(m/\gamma \to 0)$

$$\gamma\left(x(t+dt)-x(t)\right) = -\partial_x U(\lambda(t), x(t))dt + f_{\rm nc}(t)dt + \xi(t)dt$$

$$\langle \xi(t) \rangle = 0, \quad \langle \xi(t)\xi(t') \rangle = 2\gamma k_{\rm B} T \delta(t-t')$$

$$\dot{x}(t) \circ \gamma\left(x(t+dt)-x(t)\right) = -\dot{x}(t) \circ \partial_x U(\lambda(t), x(t))dt + \dot{x}(t) \circ f_{\rm nc}(t)dt + \dot{x}(t) \circ \xi(t)dt$$

$$= -\partial_x U(\lambda(t), x(t)) \circ dx(t)$$

### Note on stochastic calculus

$$U\left(\lambda(t+dt), x(t+dt)\right) = U\left(\lambda(t)+d\lambda(t), x(t)+dx(t)\right)$$

$dx^2$ contains $\xi(t)\xi(t)dt^2 \sim O(dt)$

$$\approx U\left(\lambda(t), x(t)\right) + \frac{\partial U}{\partial \lambda}d\lambda + \frac{\partial U}{\partial x}dx + \frac{1}{2}\frac{\partial^2 U}{\partial x^2}dx^2$$

**expansion w.r.t $x$ should be Stratonovich!**

$$= \left(\frac{\partial U}{\partial x} + \frac{1}{2}\frac{\partial^2 U}{\partial x^2}dx\right)dx = \frac{\partial U}{\partial x} \circ dx$$

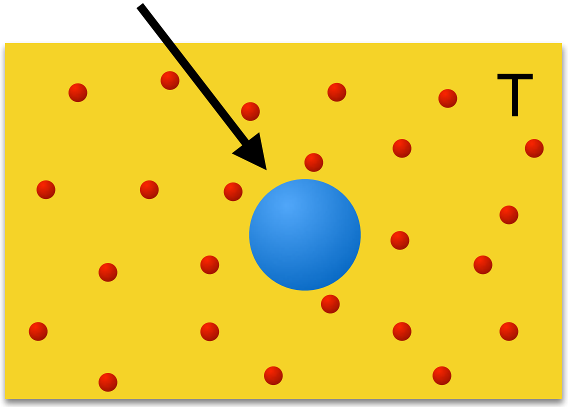
$$dU = U\left(\lambda(t+dt), x(t+dt)\right) - U\left(\lambda(t), x(t)\right) = \partial_\lambda U d\lambda + \partial_x U \circ dx$$

$$\Rightarrow -\partial_x U \circ dx = -dU + \partial_\lambda U d\lambda$$

# Thermodynamics for Langevin Dynamics

## 2. Definitions of heat and work

Sekimoto, Prog. Theo. Phys. 130, 17 (1998)




overdamped limit $(m/\gamma \to 0)$

$$\gamma\left(x(t+dt)-x(t)\right) = -\,\partial_x U(\lambda(t), x(t))dt + f_{\rm nc}(t)dt + \xi(t)dt$$

$$\langle \xi(t)\rangle = 0,\ \ \langle \xi(t)\xi(t')\rangle = 2\gamma k_{\rm B} T\delta(t-t')$$

$$\dot{x}(t)\circ\gamma\left(x(t+dt)-x(t)\right) = -\dot{x}(t)\circ\partial_x U(\lambda(t), x(t))dt + \dot{x}(t)\circ f_{\rm nc}(t)dt + \dot{x}(t)\circ\xi(t)dt$$

$$= -\,dU + \partial_\lambda U\dot{\lambda}dt$$

$$dU = \partial_\lambda U\dot{\lambda}dt + f_{\rm nc}(t)\circ\dot{x}(t)dt + \left(-\gamma\dot{x}(t)+\xi(t)\right)\circ\dot{x}(t)dt$$ : 1st law

$= dE$ $\quad$ $= dW$ $\quad$ $= dQ$

Work : $dW_{\rm c} = \partial_\lambda U\dot{\lambda}dt$ : work done by conservative force or Jarzynski work

$dW_{\rm nc} = f_{\rm nc}\circ\dot{x}dt$ : work done by nonconservative force (must be Stratonovich)

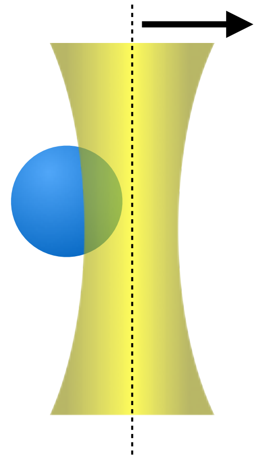
$dW = dW_{\rm c} + dW_{\rm nc}$ : work done by external force

Heat : $dQ = \left(-\gamma\dot{x}(t)+\xi(t)\right)\circ\dot{x}(t)dt$ : work done by heat-bath force (must be Stratonovich)

# Thermodynamics for Langevin Dynamics

## 3. Examples of heat and work calculation

### 1) optical tweezers experiment (overdamped)




$$\gamma \dot{x} = -k(x - \lambda(t)) + \xi, \qquad U\left(\lambda(t), x(t)\right) = \frac{k}{2}\left(x(t) - \lambda(t)\right)^2$$

work (Jarzynski work)

$$dW_c = \frac{\partial U}{\partial \lambda}\dot{\lambda}dt = -k\left(x(t) - \lambda(t)\right) a dt$$

$$\Rightarrow W_c = -ka\int_0^\tau \left(x(t) - at\right) dt = -kadt\sum_{i=0}^{N}\left(x(t_i) - at_i\right) \quad \text{experiment (or simulation)}$$

heat

$$dQ = \left(-\gamma \dot{x}(t) + \xi(t)\right) \circ \dot{x}(t)dt = k\left(x(t) - \lambda(t)\right) \circ dx(t)$$

$$= kx(t) \circ dx(t) - \lambda(t) \circ dx(t) = \frac{k}{2}\left[x(t+dt)^2 - x(t)^2\right] - \lambda(t)\left[x(t+dt) - x(t)\right]$$

$$\Rightarrow Q = \frac{k}{2}\sum_{i=0}^{N}\left[\left(x(t_{i+1})^2 - x(t_i)^2\right) - \lambda(t_i)\left(x(t_{i+1}) - x(t_i)\right)\right]$$

$$= \frac{k}{2}\left(x(t_N)^2 - x(t_0)^2\right) - \frac{k}{2}\sum_{i=0}^{N}\lambda(t_i)\left(x(t_{i+1}) - x(t_i)\right) \quad \text{experiment (or simulation)}$$

# Thermodynamics for Langevin Dynamics

## 3. Examples of heat and work calculation

### 2) 2-dimensional Brownian gyrator (overdamped)

$$\gamma \dot{x} = \boxed{-kx} \boxed{+\epsilon y} + \xi_x$$

$$\gamma \dot{y} = \boxed{-ky} \boxed{-\epsilon x} + \xi_y$$

conservative non-conservative

$$\langle \xi_a(t) \xi_b(t') \rangle = 2\gamma k_\mathrm{B} T_a \delta_{ab} \delta(t - t')$$

work

$$dW_\mathrm{c} = \frac{\partial U}{\partial \lambda} \dot{\lambda} dt = 0$$

$$dW_{\mathrm{nc},x} = \epsilon y(t) \circ dx(t) = \epsilon y(t) \big( x(t+dt) - x(t) \big)$$

$$dW_{\mathrm{nc},y} = -\epsilon x(t) \circ dy(t) = \epsilon x(t) \big( y(t+dt) - y(t) \big)$$

heat

$$dQ_x = \big( -\gamma \dot{x}(t) + \xi_x(t) \big) \circ dx(t) = \big( kx(t) - \epsilon y(t) \big) \circ dx(t)$$

$$= \frac{k}{2} \left( x(t+dt)^2 - x(t)^2 \right) - \epsilon y(t) \big( x(t+dt) - x(t) \big)$$

$$dQ_y = \Big( -\gamma \dot{y}(t) + \xi_y(t) \Big) \circ dy(t) = \big( ky(t) + \epsilon x(t) \big) \circ dy(t)$$

$$= \frac{k}{2} \left( y(t+dt)^2 - y(t)^2 \right) + \epsilon x(t) \big( y(t+dt) - y(t) \big)$$

# Thermodynamics for Langevin Dynamics

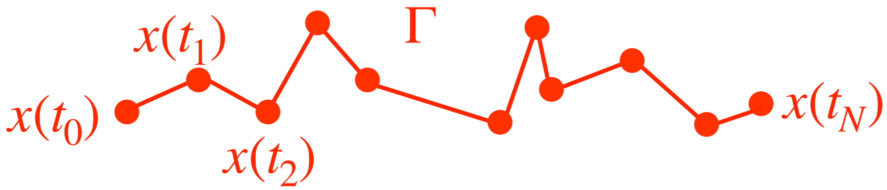
4. Stochastic trajectory

$$\gamma\left(x(t+dt)-x(t)\right)=f(x(t))dt+dW(t)$$

$$\langle dW(t)\rangle = 0,\ \ \langle dW(t)dW(t')\rangle = \begin{cases} 0 & (t\neq t') \\ 2\gamma k_B T dt & (t=t') \end{cases}$$

Schematic of a stochastic system

$$t_n \equiv ndt \quad (t_N=\tau)$$




1) Probability for observing the transition $x(t_n)\rightarrow x(t_n{+}dt)$

probability for observing Gaussian random variable $z$: $P(z)dz=\dfrac{1}{\sqrt{2\sigma\pi}}e^{-\frac{z^2}{2\sigma}}dz$

probability for observing Gaussian noise $dW(t_n)$:

$$d(dW(t_n)) = \gamma dx(t_n+dt)$$

$$P(dW(t_n))d(dW(t_n)) = \frac{1}{\sqrt{2\sigma\pi}}e^{-\frac{dW(t_n)^2}{2\sigma}}d(dW(t_n)) \qquad (\sigma = 2\gamma k_B T dt)$$

$$= \frac{1}{\sqrt{4\pi\gamma k_B T}}\exp\left[-\frac{1}{4\gamma k_B T dt}\left\{\gamma\left(x(t_n+dt)-x(t_n)\right)-f(x(t_n))dt\right\}^2_{\bullet}\right]\gamma dx(t_n+dt)$$

$$x(t_n+dt)-x(t_n)=\dot{x}(t_n)dt$$

Ito

$$= \frac{1}{\sqrt{4\pi k_B T/\gamma}}\exp\left[-\frac{dt}{4k_B T/\gamma}\left\{\dot{x}(t_n)-f(x(t_n))/\gamma\right\}^2_{\bullet}\right]dx(t_n+dt)$$

$$= P\left(x(t_n+dt)\,|\,x(t_n)\right)dx(t_n+dt)$$

# Thermodynamics for Langevin Dynamics

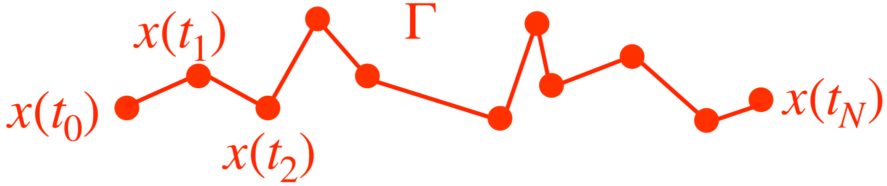
4. Stochastic trajectory

$$\gamma\left(x(t+dt)-x(t)\right)=f(x(t))dt+dW(t)$$

$$\langle dW(t)\rangle=0,\ \ \langle dW(t)dW(t')\rangle=\begin{pmatrix}0 & (t\neq t')\\ 2\gamma k_{\rm B}Tdt & (t=t')\end{pmatrix}$$

Schematic of a stochastic system

$t_n \equiv n dt \quad (t_N=\tau)$




2) Conditional probability for observing $\Gamma$ starting from $x(t_0)$

$$\mathscr{P}\left(\Gamma\,|\,x(t_0)\right)=\prod_{n=1}^{N}P\left(x(t_n)\,|\,x(t_{n-1})\right)dx(t_n)$$

$$=\prod_{n=1}^{N}\left(\frac{dx(t_n)}{\sqrt{4\pi k_{\rm B}T/\gamma}}\right)\exp\left[-\frac{dt}{4k_{\rm B}T/\gamma}\sum_{n=0}^{N-1}\left\{\dot{x}(t_n)-f(x(t_n))/\gamma\right\}^2.\right]$$

3) probability for observing $\Gamma$

$$\mathscr{P}(\Gamma)=\mathscr{P}\left(\Gamma\,|\,x(t_0)\right)p_0(x(t_0))dx(t_0)$$

initial distribution

$$=\prod_{n=0}^{N}\left(\frac{dx(t_n)}{\sqrt{4\pi k_{\rm B}T/\gamma}}\right)\exp\left[-\frac{1}{4k_{\rm B}T/\gamma}\int_0^{\tau}dt\left\{\dot{x}(t)-f(x(t))/\gamma\right\}^2.\right]p_0(x(t_0))$$

# Thermodynamics for Langevin Dynamics

## 4. Stochastic trajectory

$$\gamma\left(x(t+dt)-x(t)\right)=f(x(t))dt+dW(t)$$

$$\langle dW(t)\rangle=0,\ \ \langle dW(t)dW(t')\rangle=\begin{cases}0 & (t\neq t')\\ 2\gamma k_{\mathrm{B}}Tdt & (t=t')\end{cases}$$

Schematic of a stochastic system

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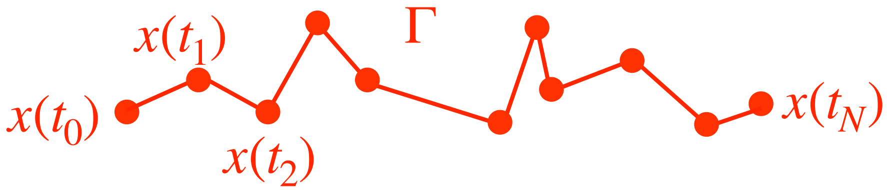



3) probability for observing $\Gamma$

$$\mathscr{P}(\Gamma)=\prod_{n=0}^{N}\left(\frac{dx(t_n)}{\sqrt{4\pi k_{\mathrm{B}}T/\gamma}}\right)\exp\left[-\frac{1}{4k_{\mathrm{B}}T/\gamma}\int_0^\tau dt\left\{\dot{x}(t)-f(x(t))/\gamma\right\}_{\bullet}^2\right]p_0(x(t_0))$$

### Note on stochastic calculus

$$\left\{\dot{x}(t)-f(x(t))/\gamma\right\}_{\odot_a}^2=\dot{x}(t)^2+\frac{f(x(t))^2}{\gamma^2}-\frac{2}{\gamma}f(x(t))\odot_a\dot{x}(t)$$

$$f(x(t))\odot_a\dot{x}(t)=\left[(1-a)f(x(t+dt))+af(x(t))\right]\dot{x}(t)=\left[f(x(t))+(1-a)\partial_x f(x)\dot{x}(t)dt\right]\dot{x}(t)$$

$$=f(x(t))\dot{x}+(1-a)\partial_x f(x)\dot{x}(t)^2dt=f(x(t))\dot{x}+(1-a)\frac{2k_{\mathrm{B}}T}{\gamma}\partial_x f(x)$$

$$=\dot{x}(t)^2+\frac{f(x(t))^2}{\gamma^2}-\frac{2}{\gamma}f(x(t))\dot{x}(t)-(1-a)\frac{4k_{\mathrm{B}}T}{\gamma^2}\partial_x f(x)$$

$$=\left\{\dot{x}(t)-f(x(t))/\gamma\right\}_{\bullet}^2-(1-a)\frac{4k_{\mathrm{B}}T}{\gamma^2}\partial_x f(x)$$

# Thermodynamics for Langevin Dynamics

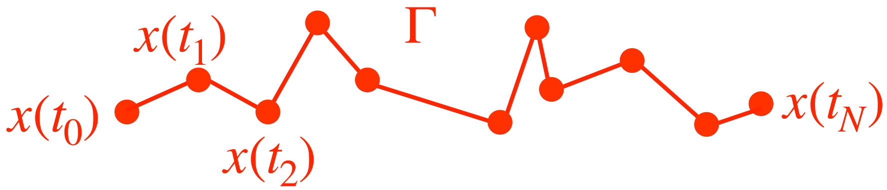
## 4. Stochastic trajectory

$$\gamma\left(x(t+dt)-x(t)\right)=f(x(t))dt+dW(t)$$

$$\langle dW(t)\rangle=0,\ \ \langle dW(t)dW(t')\rangle=\begin{cases}0 & (t\neq t')\\ 2\gamma k_B T dt & (t=t')\end{cases}$$

Schematic of a stochastic system

$t_n \equiv n dt \quad (t_N=\tau)$




3) probability for observing $\Gamma$

$$\mathscr{P}(\Gamma)=\prod_{n=0}^{N}\left(\frac{dx(t_n)}{\sqrt{4\pi k_B T/\gamma}}\right)\exp\left[-\frac{1}{4k_B T/\gamma}\int_0^\tau dt\left\{\dot{x}(t)-f(x(t))/\gamma\right\}_{\bullet}^2\right]p_0(x(t_0))$$

$$\left\{\dot{x}(t)-f(x(t))/\gamma\right\}_{\odot_a}^2=\left\{\dot{x}(t)-f(x(t))/\gamma\right\}_{\bullet}^2-(1-a)\frac{4k_B T}{\gamma^2}\partial_x f(x)$$

$$=\prod_{n=0}^{N}\left(\frac{dx(t_n)}{\sqrt{4\pi k_B T/\gamma}}\right)\exp\left[\int_0^\tau dt\left(-\frac{1}{4k_B T/\gamma}\left\{\dot{x}(t)-f(x(t))/\gamma\right\}_{\odot_a}^2-\frac{(1-a)}{\gamma}\partial_x f(x)\right)\right]p_0(x(0))$$

# Thermodynamics for Langevin Dynamics

## Summary (overdamped Langevin dynamics)

1. work : $dW_{\rm c} = \partial_\lambda U \dot{\lambda} dt \qquad dW_{\rm nc} = f_{\rm nc} \circ \dot{x} dt \qquad dW = dW_{\rm c} + dW_{\rm nc}$

2. heat : $dQ = \left(-\gamma \dot{x}(t) + \xi(t)\right) \circ \dot{x}(t) dt$

3. probability for observing $\Gamma$

$$\mathscr{P}(\Gamma) = \prod_{n=0}^{N} \left( \frac{dx(t_n)}{\sqrt{4\pi k_{\rm B} T/\gamma}} \right) \exp\left[ \int_0^\tau dt \left( -\frac{1}{4k_{\rm B}T/\gamma} \left\{ \dot{x}(t) - f(x(t))/\gamma \right\}^2_{\odot_a} - \frac{(1-a)}{\gamma} \partial_x f(x) \right) \right] p_0(x(0))$$

## Summary (underdamped Langevin dynamics)

1. work : $dW_{\rm c} = \partial_\lambda U \dot{\lambda} dt \qquad dW_{\rm nc} = f_{\rm nc} v dt \qquad dW = dW_{\rm c} + dW_{\rm nc}$

2. heat : $dQ = \left(-\gamma v(t) + \xi(t)\right) \circ v(t) dt$

3. probability for observing $\Gamma$

$$\mathscr{P}(\Gamma) = \prod_{n=0}^{N} \frac{dv(t_n) dx(t_n)}{\sqrt{4\pi k_{\rm B} T/m^2}} \delta\left(\dot{x}(t_n) - v(t_n)\right)$$

$$\times \exp\left[ \int_0^\tau dt \left( -\frac{\left\{ \dot{v}(t) + \gamma v(t)/m - f(t)/m \right\}^2_{\odot_a}}{4k_{\rm B}T/m^2} - \frac{(1-a)}{m} \left\{ \partial_v f(t) - \gamma \right\} \right) \right] p_0(x(0), v(0))$$

# Thermodynamics for Markov Jump Process

## 1. Description of Markov jump process

$$\dot{p}_i = \sum_{j(\neq i)} \left( \underline{R_{ij} p_j} - \underline{R_{ji} p_i} \right)$$

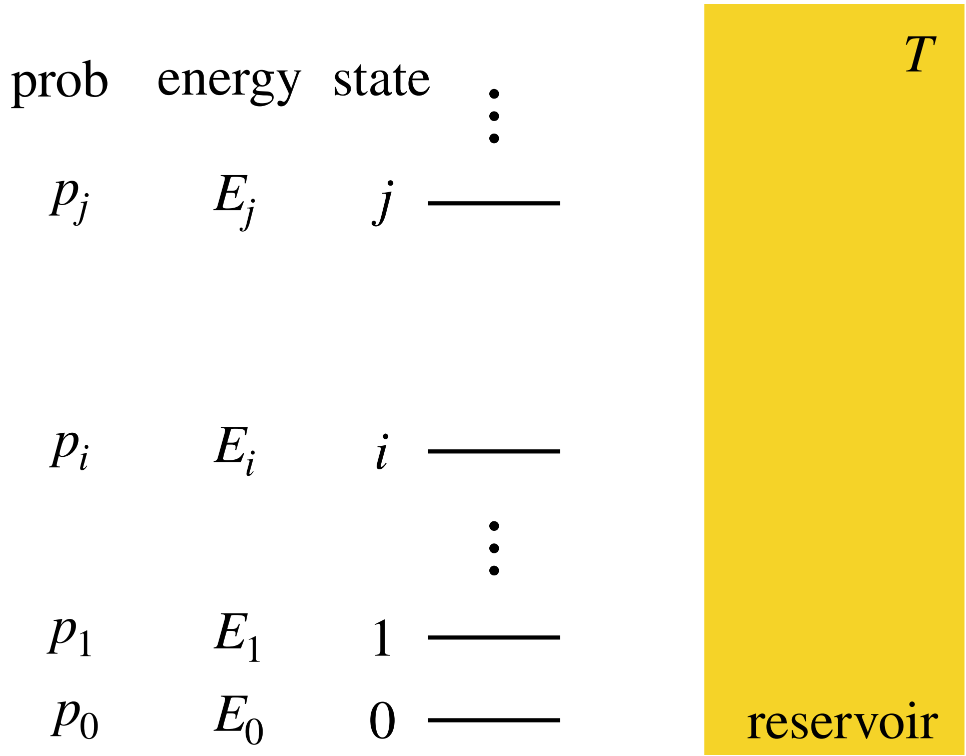
influx into $i$ outflow from $i$

$$= \sum_{j(\neq i)} R_{ij} p_j - \underline{\sum_{j(\neq i)}} R_{ji}\, p_i = \sum_j R_{ij} p_j$$

escape rate $\rightarrow R_{ii} \equiv -\sum_{j(\neq i)} R_{ji}$

$R_{ij}$ : transition rate $j \rightarrow i \quad (i \neq j)$

$R_{ij} p_j$ : mean # of jumps $j \rightarrow i$ per unit time




## 2. Definitions of heat and work

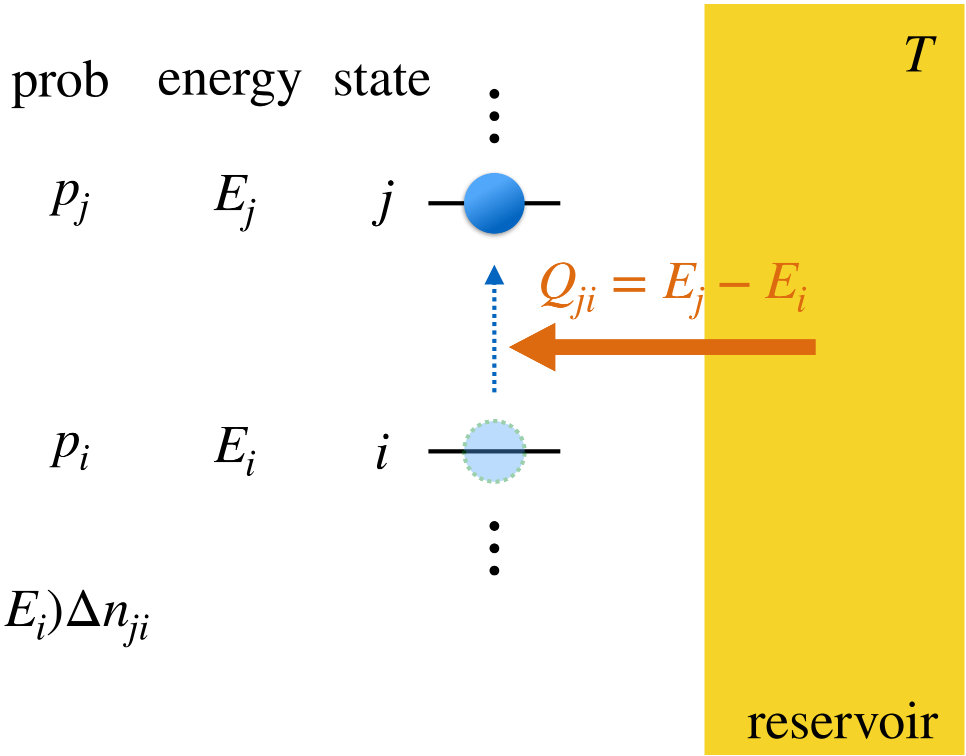
$$\langle E \rangle = \sum_i E_i p_i \longrightarrow \langle \dot{E} \rangle = \underline{\sum_i \dot{E}_i p_i} + \underline{\sum_i E_i \dot{p}_i}$$

power : $\langle \dot{W} \rangle$ heat rate : $\langle \dot{Q} \rangle$

# Thermodynamics for Markov Jump Process

## 2. Definitions of heat and work

transition $i \to j$ induced by $Q_{ji} = E_j - E_i$




$$\langle \dot{E} \rangle = \underbrace{\sum_i \dot{E}_i p_i}_{} + \underbrace{\sum_i E_i \dot{p}_i}_{}$$

power : $\langle \dot{W} \rangle$ heat rate : $\langle \dot{Q} \rangle$

[heat] $\langle \dot{Q} \rangle \equiv \sum_i E_i \dot{p}_i$

$\Delta n_{ji}$ : number of jumps $i \to j$ during $\Delta t$

total heat absorption per Δt : $\Delta E_Q = \sum_{i \neq j} (E_j - E_i) \Delta n_{ji}$

$$\to \langle \Delta E_Q \rangle = \sum_{i \neq j} (E_j - E_i) \langle \Delta n_{ji} \rangle$$

$= R_{ji} p_i \Delta t$ : mean # of jumps $i \to j$ during $\Delta t$

$$\Rightarrow \lim_{\Delta t \to 0} \left\langle \frac{\Delta E_Q}{\Delta t} \right\rangle = \langle \dot{Q} \rangle = \sum_{i \neq j} (E_j - E_i) R_{ji} p_i$$

$$\dot{p}_i = \sum_{j (\neq i)} \left( R_{ij} p_j - R_{ji} p_i \right)$$

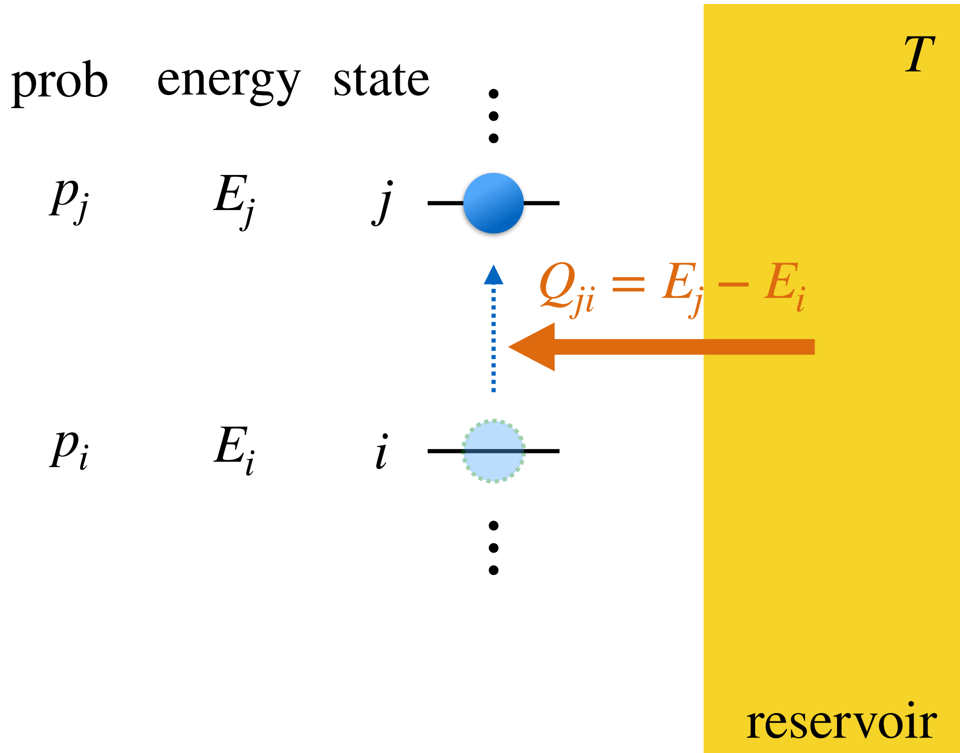
$R_{ij} p_j$ : mean # of jumps $j \to i$ per unit time

# Thermodynamics for Markov Jump Process

## 2. Definitions of heat and work

$$\langle \dot{E} \rangle = \underbrace{\sum_i \dot{E}_i p_i}_{\text{power : } \langle \dot{W} \rangle} + \underbrace{\sum_i E_i \dot{p}_i}_{\text{heat rate : } \langle \dot{Q} \rangle}$$

transition $i \to j$ induced by $Q_{ji} = E_j - E_i$




[heat] $\langle \dot{Q} \rangle \equiv \sum_i E_i \dot{p}_i$

$$\Rightarrow \lim_{\Delta t \to 0} \left\langle \frac{\Delta E_Q}{\Delta t} \right\rangle = \langle \dot{Q} \rangle = \sum_{i \neq j} (E_j - E_i) R_{ji} p_i$$

$$= \sum_{i \neq j} E_j R_{ji} p_i - \sum_{i \neq j} E_i R_{ji} p_i$$

$$= \sum_{j \neq i} E_i R_{ij} p_j - \sum_{i \neq j} E_i R_{ji} p_i = \sum_i E_i \left[ \sum_{j(\neq i)} (R_{ij} p_j - R_{ji} p_i) \right] = \sum_i E_i \dot{p}_i \ : \ \text{heat rate}$$

$j \leftrightarrow i$ exchange

$$\dot{p}_i = \sum_{j(\neq i)} \left( R_{ij} p_j - R_{ji} p_i \right)$$

$R_{ij} p_j$ : mean # of jumps $j \to i$ per unit time

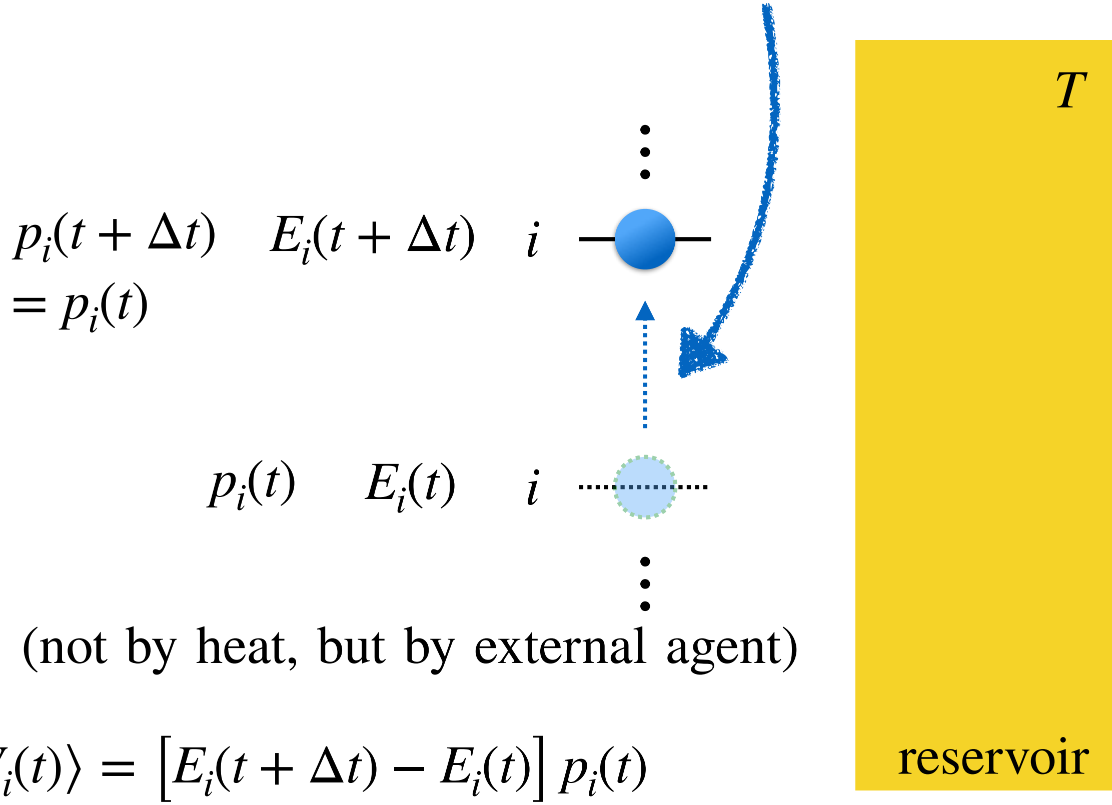
∴ heat is associated with population change.

# Thermodynamics for Markov Jump Process

## 2. Definitions of heat and work

$$\langle \dot{E} \rangle = \underbrace{\sum_i \dot{E}_i p_i}_{\text{power}\,:\,\langle \dot{W} \rangle} + \underbrace{\sum_i E_i \dot{p}_i}_{\text{heat rate}\,:\,\langle \dot{Q} \rangle} \quad : \text{1st law}$$

external agent : $\Delta W_i = E_i(t+\Delta t) - E_i(t)$




[work] $\langle \dot{W} \rangle \equiv \sum_i \dot{E}_i p_i$

System is in state $i$.

Energy of state $i$ is changed during $\Delta t$. (not by heat, but by external agent)

mean work for $E_i(t) \to E_i(t+\Delta t)$ : $\langle \Delta W_i(t) \rangle = \left[E_i(t+\Delta t) - E_i(t)\right] p_i(t)$

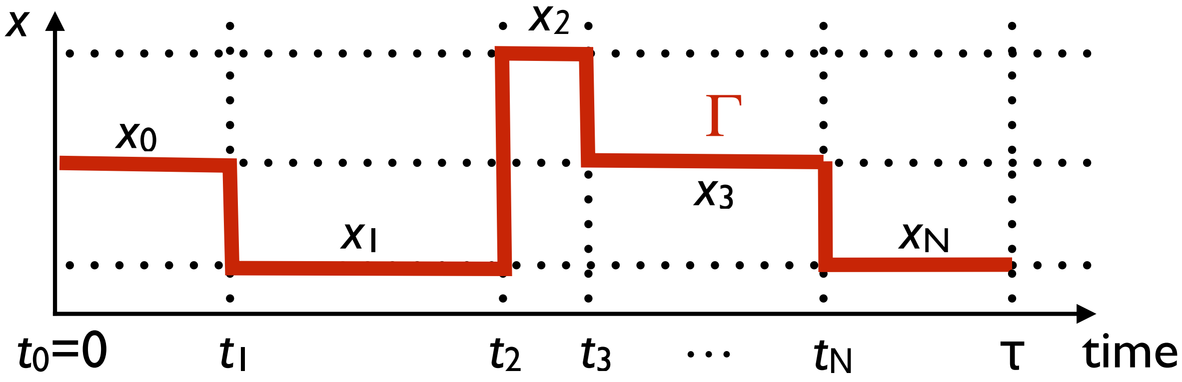
mean work for all changes : $\sum_i \langle \Delta W_i(t) \rangle = \sum_i \left[E_i(t+\Delta t) - E_i(t)\right] p_i(t)$

mean work rate (power) : $\langle \dot{W} \rangle = \lim_{\Delta t \to 0} \sum_i \left\langle \frac{\Delta W_i(t)}{\Delta t} \right\rangle = \sum_i \dot{E}_i(t) p_i(t)$

∴ work is associated with energy level change.

# Thermodynamics for Markov Jump Process

3. Stochastic trajectory




$$\dot{p}_i = \sum_{j(\neq i)} \left( \underbrace{R_{ij} p_j}_{\text{influx into } i} - \underbrace{R_{ji} p_i}_{\text{outflow from } i} \right)$$

influx into $i$ outflow from $i$

Path probability

jump probability $i \to j$ during $\Delta t$ : $R_{ji} \Delta t$

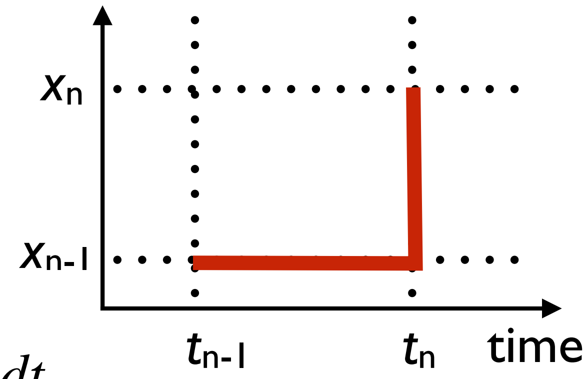
escaping probability from $i$ during $\Delta t$ : $\sum_{j(\neq i)} R_{ji} \Delta t = -R_{ii} \Delta t$

staying probability at $i$ during $\Delta t$ : $1 + R_{ii} \Delta t \approx e^{R_{ii} \Delta t}$

staying probability during $t_{n-1} \sim t_n$ : $e^{\int_{t_{n-1}}^{t_n} R_{x_{n-1}, x_{n-1}}(t) dt}$

probability for the path segment : $\underbrace{e^{\int_{t_{n-1}}^{t_n} R_{x_{n-1}, x_{n-1}}(t) dt}}_{\text{staying}} \cdot \underbrace{R_{x_n, x_{n-1}}}_{\text{jump}}(t_n) dt$

staying jump




path segment

path probability : $\mathscr{P}(\Gamma) = p_{x_0}(0) \prod_{n=1}^{N} \left[ e^{\int_{t_{n-1}}^{t_n} R_{x_{n-1}, x_{n-1}}(t) dt} R_{x_n, x_{n-1}}(t_n) dt \right] e^{\int_{t_N}^{\tau} R_{x_N, x_N}(t) dt}$

# Thermodynamics for Markov Jump Process

## Summary

1. work and heat

$$\langle \dot{E} \rangle = \underbrace{\sum_i \dot{E}_i p_i}_{} + \underbrace{\sum_i E_i \dot{p}_i}_{} \text{ : 1st law}$$

power : $\langle \dot{W} \rangle$ heat rate : $\langle \dot{Q} \rangle$

2. path probability

$$\mathscr{P}(\Gamma) = p_{x_0}(0) \prod_{n=1}^{N} \left[ e^{\int_{t_{n-1}}^{t_n} R_{x_{n-1},x_{n-1}}(t)dt} R_{x_n,x_{n-1}}(t_n)dt \right] \; e^{\int_{t_N}^{\tau} R_{x_N,x_N}(t)dt}$$