§8. Link to statistical physics.

- Boltzmann distribution
- link to statistical physics

Q: What distinguishes

- equilibrium from
- non-equilibrium systems.

A: FDT.

Detailed balance

time cont. | time discrete

$\frac{d}{dt} p(x,t) = \mathcal{L} p(x,t)$

$\equiv$ Fokker-Planck eqn.

$\frac{d}{dt} P_j(t) = P_i(t) L_{ij}$

$\equiv$ Master eqn.

We say the dynamics obeys detailed balance if

(i) there exists an equilibrium distrib.

$p^*(x)$ $\qquad$ P^*_j

(ii) the joint probability is symmetric

$p^*(x',T; x,0) = p^*(x,T; x',0)$ $\qquad$ $P^*(i,T; j,0) = P^*(j,T; i,0)$

$L_{ji} P^*_j = L_{ij} P^*_i$.

Zero net current at equilibrium. $i \longrightarrow j$

$\boxed{\text{Detailed balance}}$ continued

Example: Boltzmann distribution for canonical ensemble.

- states $0, 1, 2, \ldots$
  with energies $E_0, E_1, E_2, \ldots$
  and probabilities $p_i^* = \frac{1}{Z} \exp(-\beta E_i)$
- $$\frac{L_{ji}}{L_{ij}} = \exp[-\beta(E_i - E_j)]$$

Counterexample: Circular current.

$$1 \xrightarrow{r} 2 \xrightarrow{r} 3 \xrightarrow{r} 1 \qquad \underline{\underline{L}} = \begin{pmatrix} -r & r & 0 \\ 0 & -r & r \\ r & 0 & -r \end{pmatrix}$$

$\lambda_1 = 0. \qquad e_1 = (1/3, 1/3, 1/3)^T$

$\lambda_2 = \lambda_3^* = \left(-\frac{3}{2} + i\frac{\sqrt{3}}{2}\right) r$ complex

$\Rightarrow$ net current at equilibrium.

Example: 2-state Telegraph process: $1 \underset{q_1}{\overset{q_2}{\rightleftarrows}} 2$

Detailed balance for Hamiltonian Systems

- Hamiltonian H

$$\dot p_i = -\frac{\partial H}{\partial q_i}, \quad \dot q_i = \frac{\partial H}{\partial p_i}$$

- Macroscopic observable $y = Y(q,p)$.
- Detailed balance

If (i) H even in p_i

(no magnet. field, no ext. rotation
$\longrightarrow$ can be relaxed)

(ii) Y even in p_i

then

$$\bar{T}_T(y'|y) \cdot P^*(y) = \bar{T}_T(y|y')\, P^*(y').$$

N.B. We always have $T_T(y'|y)P^*(y) = T_{-T}(y|y')P^*(y')$.

Proof:

- time reversal

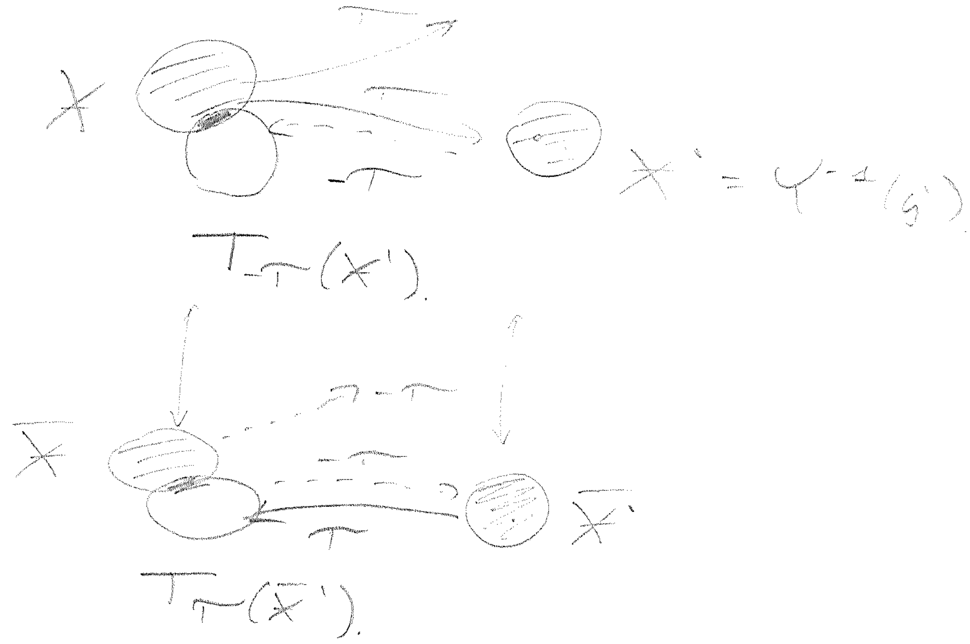
$$\bar t = -t, \quad \bar q_i = +q_i, \quad \bar p_i = -p_i$$

- trajectory in (q,p)-phase space

$$x=(q,p) \xrightarrow{T} x'=(q',p').$$

$$\bar x=(\bar q,\bar p) \xleftarrow{T} \bar x'=(\bar q',\bar p').$$

- $P^*(x) = P^*(\bar x)$ by (i).
- $x = \bar x$, $x = Y^{-1}(y)$ by (ii).



$$\overline{T_{-T}(X')} = T_{-T}(\overline{X'})$$

Now

$$\overline{T_T}(y'|y)\cdot P^*(y) = P(y',T;y,0)$$

$$= \int_{X\cap T_{-T}(X')} dx \; P^*(x)$$

$$= \int_{\underbrace{\underbrace{\underbrace{\overline{X\cap T_{-T}(X')}}_{\bar X \cap \overline{T_{-T}(X')}}}_{\bar X \cap T_{-T}(\bar X')}}_{X \cap T_{-T}(X')}} dx \; P^*(x).$$

← because: φ is even in p: $X = \bar X$, $X' = \bar X'$.

$$= \int_{X\cap T_T(X')} dx \; P^*(x) = P(y,T;y',0)$$

$$= \overline{T_T}(y|y')\, P^*(y').$$

q.e.d.

The increase of relative entropy

- Master equation for Markov chain

$$P_j^{n+1} = \sum_i P_i^n T_{ij}$$

$P_i^n \equiv$ probability to be in state i at time $t = t_n$

$T_{ij} \equiv$ matrix of transition probabilities

$\Rightarrow$

$0 \leq T_{ij} \leq 1, \quad \sum_j T_{ij} = 1$

- Stationary distribution

$P_j^* > 0$ st. $\quad P_j^* = \sum_i P_i^* T_{ij} \quad \forall j$

- Rel. entropy (or Kullback-Leibler divergence)

$$D_n = KL(P^n \| P^*) = + \sum_i P_i^n \ln\left(\frac{P_i^n}{P_i^*}\right)$$

<u>Theorem</u> (decrease of rel. entropy)

$$D_{n+1} \leq D_n$$

N.B. $D_n \geq 0$ by Gibbs inequality

Source: Everett, p. 127.

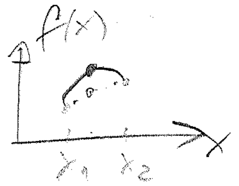
Proof: "direct result of convexity of D_n"

• $\dot{D}_{n+1} = -\sum_j P_j^{n+1} \ln\left(\frac{P_j^{n+1}}{P_j^*}\right)$

expand.

$$= -\sum_j \underbrace{\left(\sum_i P_i^n T_{ij}\right) \ln\left(\frac{\sum_i P_i^n T_{ij}}{\sum_i P_i^* T_{ij}}\right)}_{A_j}$$

• $f(x) = x \ln(x) \Rightarrow$ Convex (i.e. $f'' \geq 0$)



$$\Rightarrow \underbrace{\sum_i \alpha_i f(x_i)}_{LHS} \leq \underbrace{f\left(\sum_i \alpha_i x_i\right)}_{RHS}$$

for $\sum_i \alpha_i = 1$, $\alpha_i \geq 0$.

• Choose $\alpha_i = \frac{P_i^* T_{ij}}{C_j}$, $C_j = \sum_i P_i^* T_{ij}$

$x_i = \frac{P_i^n}{P_i^*}$

$$LHS = \sum_i \alpha_i f(x_i) = \frac{1}{C_j} \sum_i P_i^n T_{ij} \ln\left(\frac{P_i^n}{P_i^*}\right)$$

$$RHS = f\left(\sum_i \alpha_i x_i\right) = \frac{1}{C_j} \left(\sum_i P_i^n T_{ij}\right) \cdot \ln\left(\frac{\sum_i P_i^n T_{ij}}{\sum_i P_i^* T_{ij}}\right)$$

$$= A_j / C_j$$

- LHS $\leq$ RHS
  - cancel G_j on both sides
  - sum over j

$\Rightarrow$

$$\underbrace{\sum_j \sum_i P_i^n T_{ij} \ln\left(\frac{P_i^n}{P_i^*}\right)} \leq \sum_j A_j = -D_{n+1}$$

$$\underbrace{\sum_i \underbrace{\left(\sum_j T_{ij}\right)}_{=1} P_i^n \ln\left(\frac{P_i^n}{P_i^*}\right)}_{= -D_n}$$

q.e.d.

N.B. for $P_i^* = \frac{1}{N} \Rightarrow D_n = +\sum_i P_i \ln P_i + \ln N.$

(micro canonical ensemble) $\overset{\text{also}}{\Rightarrow} \sum_i T_{ij} = 1 \equiv T_{ij}$ doubly stochastic

Double-check sign.

Equilibrium vs. Non-equilibrium.

- FDT.
- detailed balance $L_{ji} P_j^* = L_{ij} P_i^*$.
- Equi-partition theorem.

$\underbrace{\qquad\qquad}$
constrains Langevin equation (approach to thermal equilibrium)

- Non-generic steady states possible (circular currents)
- few non-equilibrium fluct. theorems.

Boltzmann distribution
= Maximum-Entropy distribution

macro-state y

$\uparrow \psi$

microstates $x \in \psi^{-1}(y)$

$$S = \int p(x|y) \ln p(x|y)\, dx \quad \text{(natural units, } k_B = 1\text{)}$$

$\equiv$ relative information of x wrt y.

$S/\ln 2$ $\equiv$ average number of yes/no-questions needed to infer x if y known.

[1 nat = ln 2 bits].

Derivation of Boltzmann distribution

System of energy $\langle E \rangle = u$,
in contact with heat bath
of temperature T

$\downarrow$

ensemble of N independent such systems.

- N_i systems in energy state E_i
- Constraints: $\sum N_i = N \quad (1)$

  $\sum Z_i = N \langle E \rangle \quad (2)$

- $W \equiv$ weight function
  (# compatible microstates)

  $$W = \frac{N!}{N_1! \cdot \ldots \cdot N_k!}$$

- $W \to$ max subject to (1), (2)

  $\Rightarrow$ Lagrange multipliers.

  $$0 \overset{!}{=} d\ln W = \sum_i \left(\frac{\partial \ln W}{\partial N_i} \right) dN_i + \alpha \sum dN_i - \beta \sum E_i dN_i$$

  $$\Rightarrow \frac{\partial \ln W}{\partial N_i} + \alpha - \beta E_i = 0 \quad \forall i$$

  $$\Rightarrow \frac{\partial \ln W}{\partial N} \overset{\text{(Stirling)}}{=} \frac{\partial N \ln N}{\partial N_i} - \sum_j \frac{\partial N_j \ln N_j}{\partial N_i} = \ldots = -\ln \frac{N_i}{N}$$

  $$\Rightarrow p_i := \frac{N_i}{N} = \exp(\alpha - \beta E_i)$$

Steady state $\dot{P}^* = 0$:

$P^* \sim \exp(-\beta u)$ = Boltzmann distr.

N.B.

$\alpha = 0$: $\dot{P} = -\nabla(fP) + \nabla^2(D(x)P)$.

<u>Case 2</u>: Thermophoresis.

$$\dot{P} = -\nabla(f - \underbrace{D_T \nabla T}_{\text{thermophoretic drift}})P + \nabla(D \nabla P)$$

$S_T = \frac{D_T}{D} \gtrless 0$ = Soret coefficient

- depends on molecular interaction potentials.

$\Rightarrow$ non-equilibrium phenomenon

Thermal fluctuations: Space-dep. diffusion as case study.

$$\boxed{D = D(x)}$$

$$\gamma \dot{x} = -\frac{\partial u}{\partial x} + \gamma \xi(t) \qquad \dot{x} = -\frac{1}{\gamma}\frac{\partial u}{\partial x} + \xi(t).$$

$$\langle \xi(t)\xi(t')\rangle = 2D(x)\,\delta(t-t').$$

- $D = \frac{k_B T}{\gamma}$ → case 1: $\gamma = \gamma(x)$, $T = T_0$ ⇒ equilibrium
  → case 2: $\gamma = \gamma_0$, $T = T(x)$ ⇒ non-equilib.

Reminder

α-calculus:

(α) $\dot{x}_k = f_k(\underline{x}) + \sum g_{k\ell}(\underline{x})\cdot \xi_\ell$

(α) $\dot{x} = f(x) + g(x)\xi$

$\alpha = 0$ Ito
$\alpha = \frac{1}{2}$ Stratonov.

$$\dot{P} = \frac{\partial}{\partial x_k}\left[-\left(f_k + \alpha \frac{\partial g_{k\ell}}{\partial x_m} g_{m\ell}\right)P + \frac{1}{2}\frac{\partial}{\partial x_m}(g_{k\ell}g_{m\ell}P)\right]$$

$$\dot{P} = \frac{\partial}{\partial x}\left[-\left(f + \frac{\alpha}{2}\frac{\partial g^2}{\partial x}\right)P + \frac{1}{2}\frac{\partial}{\partial x}(g^2 P)\right]$$

Case 1: $\alpha = 1$ (isothermal) correct.
→ Lau & Lubensky PRE

$$\dot{P} = \frac{\partial}{\partial x}\left[-\left(f + \frac{\partial g}{\partial x} g\right)P + \frac{1}{2}\frac{\partial}{\partial x}(g^2 P)\right]$$

$$f = -\frac{1}{\gamma}\frac{\partial u}{\partial x}$$
$$g = \sqrt{2D}$$

$$= -\nabla(fP) + \nabla(D(x)\nabla P).$$

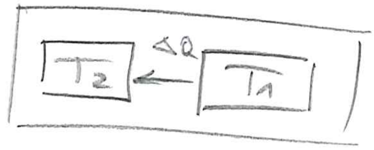
≡ generalization of Fick's law to equilibrium systems

Entropy production

2nd law: $\langle \Delta S \rangle \geq 0.$

Examples

- $$\frac{\Delta S}{k} = \Delta Q \left(\frac{1}{kT_2} - \frac{1}{kT_1} \right)$$



- $$\frac{\Delta S}{k} = - N [x \ln x + (1-x) \ln (1-x)]$$

ideal gas 'a' ideal gas 'b'

$x = \frac{N_a}{N}$

$N = N_a + N_b.$

Fluctuation theorem

$$\frac{P\left(\frac{\Delta S}{k} = I\right)}{P\left(\frac{\Delta S}{k} = -I\right)} = \exp(I)$$

Crooks fluctuation theorem

- microscopic reversibility

$$\frac{P(x(t))}{P(\bar{x}(t))} = \exp \Delta S[x(t)]/k.$$

Jarzynski relation

- isolated systems: $\Delta F \leq W$ adiabatic

$$e^{-\beta \Delta F} = \langle e^{-\beta W} \rangle.$$