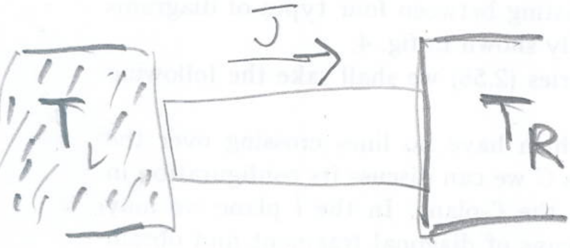
# Lecture 2 (Steady state $\tau \to \infty$) 1

So far we have discussed transient Fluctuation theorems which are true for systems which are prepared in equilibrium and then driven by time-dependent forces for a finite time $\tau$.

A different type of F.T. is the Steady State F.T. which we now discuss.

Consider a system in contact with two heat baths at temperatures $T_L$ and $T_R$.

Clearly it is in a nonequilibrium steady state carrying heat current.



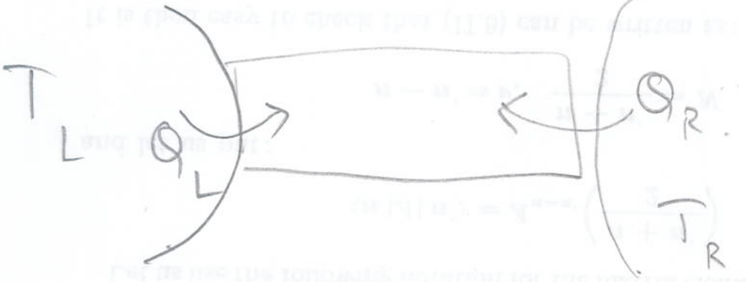

$T_L > T_R$.

Suppose in time $\tau$ heat $Q_L$, $Q_R$ flows from left reservoir into system

From thermodynamics we would say that in time $\tau$, the entropy generated is $S = Q_L\left(\frac{1}{T_R} - \frac{1}{T_L}\right) \geq 0$

Heat always flows from Hot to Cold.

However in small systems we will see that $Q_L$ is a fluctuating variable which can even be negative once in a while ("transient violation" of 2nd Law)




~~We~~ We can measure:

In time $\tau$: $Q_L$ heat enters system from left reservoir

$Q_R$ heat " " " right "

Energy changes by $\Delta H = Q_L + Q_R$

On average $\langle Q_L \rangle = -\langle Q_R \rangle$, $\langle \Delta H \rangle = 0$.

Entropy generated $\frac{S}{k_B} = Q_L (\beta_R - \beta_L)$ has a distribution

S.S.F.T $\lim_{\tau \to \infty} \frac{P(S)}{P(-S)} = e^{S/k_B}$ | Precise statement on the probability of rare fluctuations.

Gallavotti - Cohen.

S grows with $\tau$ and system size and so -ve entropy events become very rare.

# Other forms of stating the S.S.F.T

For large $\tau$, $P(s)$ has the scaling form $P(s) \sim e^{f\left(\frac{s}{\tau}\right)\tau}$

$f(s)$ is the $\boxed{\text{large-deviation function}}$

$s/\tau$

describes the distribution beyond $O(\sqrt{\tau})$ deviations around the mean

S.S.F.T then implies the following symmetry for the LDF

$$f(s) - f(-s) = \frac{s}{k_B}$$

or $P(Q) \sim e^{f(q)\tau}$ $\quad q = \frac{Q}{\tau}$

$$\boxed{f(q) - f(-q) = \Delta\beta q}$$

## Cumulant generating function

$$Z(\lambda) = \int dQ\, e^{-\lambda Q}\, P(Q) = \langle e^{-\lambda Q} \rangle.$$

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$Z(\lambda)$ can be evaluated using saddle-point approach

$$Z(\lambda) = \int dq\, e^{-\lambda q} e^{F(q) r}$$

$$= \int dq\, e^{(F(q) - \lambda q) r}$$

$$\sim e^{[F(q^*) - \lambda q^*] r} \sim e^{\mu(\lambda) r}$$

$$F'(q^*) = \lambda$$

Alternatively $F(q) = \mu(\lambda^*) + \lambda^* q$

$$\mu'(\lambda^*) = -q$$

$$\mu(\lambda) = \max_q [F(q) - \lambda q]$$

$$= \max_q [F(-q) + (\Delta\beta - \lambda) q]$$

$$= \max_q [F(q) - (\Delta\beta - \lambda) q] = \mu(\Delta\beta - \lambda)$$

Thus the S.S.F.T can be stated in ? the following 3 "equivalent forms".
[Sometimes the equivalence of ensembles $\mu(\lambda)$ and $f(q)$ can break down]

$$\lim_{\tau\to\infty} \frac{P(Q)}{P(-Q)} \sim e^{\Delta\beta q \tau} \quad -(1) \qquad q = \frac{Q}{\tau}$$

$$f(q) - f(-q) = \Delta\beta q \quad -(2)$$

$$\mu(\lambda) = \mu(\Delta\beta - \lambda) \quad -(3)$$

Note that $\mu(\lambda) = \frac{1}{\tau}\ln Z(\lambda)$ is the cumulant generating function.

$$\mu(\lambda) = \sum_{n=1}^{\infty} \frac{\langle Q^n\rangle_c}{\tau}\frac{(-\lambda)^n}{n!}$$

$\mu(0) = 0 \quad -\mu'(0) = J$ average current.

$$\mu''(0) \underset{\tau\to\infty}{\overset{Lt}{=}} \frac{\langle Q^2\rangle_c}{\tau}.$$

$$\boxed{\text{The Fluctuation symmetry implies linear-response theory.}}$$

$$\mu(\lambda;\Delta\beta) = \mu(\Delta\beta-\lambda;\Delta\beta)$$

$$\mu'(0;\Delta\beta)\lambda + \mu''(0;\Delta\beta)\frac{\lambda^2}{2} + \cdots$$

$$= \mu'(0;\Delta\beta)(\Delta\beta-\lambda) + \mu''(0;\Delta\beta)\frac{(\Delta\beta-\lambda)^2}{2} + \cdots$$

Equating coefficient of $\lambda$ on both sides, we get;

$$2\mu'(0;\Delta\beta) = -\mu''(0;\Delta\beta)\Delta\beta + O(\Delta\beta^2)$$

$$\Rightarrow \frac{\langle J\rangle_{\Delta\beta}}{\Delta\beta} = \lim_{\tau\to\infty}\frac{\langle Q^2\rangle_{\Delta\beta=0}}{2\tau}$$

$$\Rightarrow \boxed{\frac{\langle J\rangle_{\Delta T}}{\Delta T} = \frac{1}{2k_B T^2}\int_0^\infty dt\,\langle J(0)J(t)\rangle}$$

using $Q = \int_0^\tau J(t)\,dt$

Green-Kubo-Like relation for thermal conductance of an open system.

Onsager relations also follow.

NOTE

Usual Green-Kubo relations relate response functions (e.g transport coefficients) to equilibrium time-correlation functions.

These correlation functions are evaluated for Hamiltonian dynamics.

This is different from the Green-Kubo-like relations that we derived from the fluctuation theorems. Here the dynamics is that of an open system (for example driven by heat baths in the boundaries)

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# Systems in Contact with heat baths

The interaction of a system with baths can be modeled in various ways e.g Langevin dynamics for a Brownian particle

$$m\frac{dv}{dt} = -\frac{\partial H(x_t)}{\partial q} + \left[-\gamma\frac{dq}{dt} + (2\gamma k_B T)^{1/2}\eta(t)\right]$$

Delta-correlated Gaussian noise with $\langle \eta \rangle = 0$

$\langle \eta^2 \rangle = 1$

Energetics.

$$\dot{p}_i = -\frac{\partial H(x_t)}{\partial q_i} + \underbrace{\left[-\gamma \frac{dq_i}{dt} + (2\gamma k_B T)^{1/2} \eta_i\right]}_{\text{Force from heat bath.}}$$

$$\sum_i \times \dot{q}_i$$

$$\sum_i \left( \frac{\partial H}{\partial p_i}\dot{p}_i + \frac{\partial H}{\partial q_i}\dot{q}_i \right) = \dot{Q} \quad \text{(rate of heat flow into system from bath)}$$

$$\Rightarrow \frac{dH}{dt} - \frac{\partial H}{\partial t} = \dot{Q}$$

Integrating from $t=0$ to $\tau$ we get.

$$\Delta H = H_B - H_A = \int_0^\tau dt \, \frac{\partial H}{\partial t} + \Delta Q .$$

$$\boxed{\Delta H = W_J + \Delta Q}$$

Like First Law.

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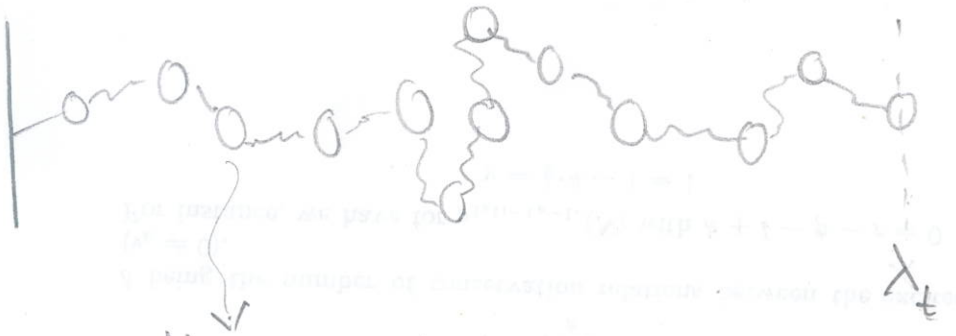
The Langevin equation is an example of a Markov process satisfying the principle of detailed balance.. Instead of proving the FTs' by proceeding as before, we now present a more general approach for Markov processes.

For an RNA polymer




$$\frac{dp_i}{dt} = \underbrace{-\frac{\partial V(q_i;\lambda_t)}{\partial q_i}}_{F_i} + \left[ -\gamma \frac{dq_i}{dt} + (2\gamma k_B T)^{1/2} \eta_i(t) \right]$$

Overdamped dynamics $\Big\}$ $t \gg \frac{m}{\gamma}$

$$\frac{dq_i}{dt} = -\frac{1}{\gamma} \frac{\partial V(\lambda_t)}{\partial q_i} + \left( \frac{2 k_B T}{\gamma} \right)^{1/2} \eta_i(t)$$

Stochastic path $q_i(t+\Delta t) = q_i(t) + p_i(t)\,\Delta t$

$$p_i(t+\Delta t) = p_i(t) + (F_i - \gamma_i p_i)\Delta t + (2\gamma_i k_B T_i \Delta t)^{1/2} \eta_i(t)$$

Since $\eta(t)$ is a stochastic variable the path is also a stochastic variable with a distribution

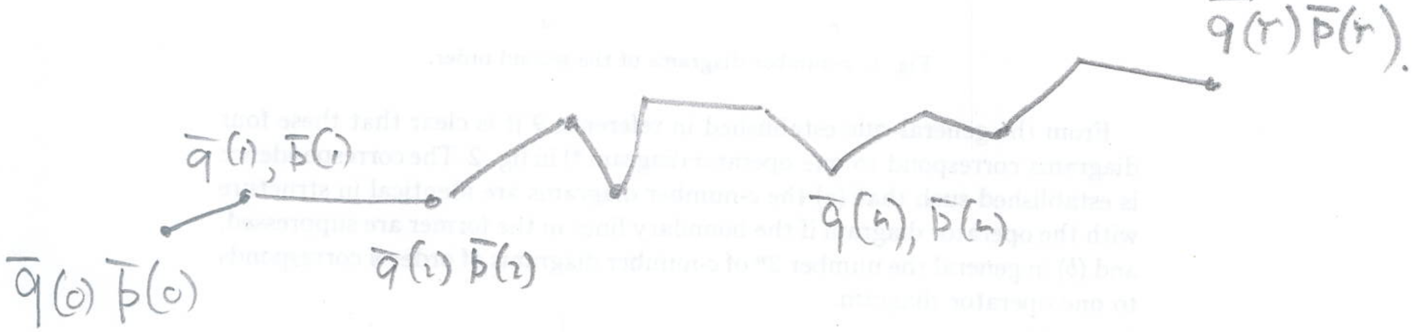
To find the work-distribution we need to sum over the path distribution.

Let $t = n\Delta t$ $\quad \bar{q}_{\phi}(t) \equiv \bar{q}(n)$

$$q_i(n+1) = q_i(n) + p_i(n)\Delta t$$

$$p_i(n+1) \doteq p_i(n) + \left(f_i - \gamma_i \frac{p_i}{m}\right)\Delta t + \left(2\gamma_i k_B T_i \Delta t\right)^{1/2} \xi_i(n)$$

Trajectory in phase-space




$$\text{Prob}\left[\bar{q}(0),\bar{p}(0) \ldots \bar{q}(\tau),\bar{p}(\tau)\right] = p\left[\bar{q}(0),\bar{p}(0)\right] \text{Prob}\left(\text{Path} \mid \bar{q}(0)\bar{p}(0)\right)$$

$$\propto p\left[\bar{q}(0),\bar{p}(0)\right] e^{-\sum_i \frac{1}{4\gamma_i k_B T_i} \int_0^{\tau} \eta_i^2\, dt}$$

Consider also the time-reversed trajectory.

$$\bar{q}'(t) = \bar{q}(\tau - t) \qquad \bar{p}'(t) = -\bar{p}(\tau - t) \qquad \lambda'(t) = \lambda(\tau - t)$$

$$\frac{\mathrm{Prob}_{\lambda}\left[\bar{q}(0)\bar{p}(0)\ldots\bar{q}(\tau)\bar{p}(\tau)\right]}{\mathrm{Prob}_{\lambda'}\left[\bar{q}'(\tau)\bar{p}'(\tau)\ldots\bar{q}'(0)\bar{p}'(0)\right]} = \frac{p\left[\bar{q}(0),\bar{p}(0)\right]}{p\left[\bar{q}(\tau),\bar{p}(\tau)\right]} \cdot$$

$$\times\, e^{-\sum_i \frac{1}{4\gamma_i k_B T_i}\int_0^\tau dt\,(\eta_i^2-\eta_i'^2)}$$

$$\int_0^\tau dt\left[\eta_i^2(t) - \eta_i'^2(t)\right] = \int_0^\tau \left(\dot{p}_i + \frac{\partial H}{\partial q_i} + \frac{\gamma_i}{m}p_i\right)^2 dt - \int_0^\tau \left(\dot{p}_i' + \frac{\partial H}{\partial q_i'} + \frac{\gamma_i}{m}p_i'\right)^2 dt$$

Change $p_i' = -p_i$, $q_i' = q_i$, $s = \tau - t$

$$\int_0^\tau dt\left(\eta_i^2 - \eta_i'^2\right) = \int_0^\tau dt\left[\left(\dot{p}_i + \frac{\partial H}{\partial q_i} + \frac{\gamma_i}{m}p_i\right)^2 - \left(\dot{p}_i + \frac{\partial H}{\partial q_i} - \frac{\gamma_i}{m}p_i\right)^2\right]$$

$$= 4\gamma_i \int_0^\tau dt\left(\dot{p}_i + \frac{\partial H}{\partial q_i}\right)\dot{q}_i$$

$$= 4\gamma_i \int_0^\tau dt\left(-\gamma_i \dot{q}_i + \xi_i\right)\dot{q}_i = 4\gamma_i Q_i$$

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$$\therefore \frac{\mathrm{Prob}_{\lambda}[\bar{q}_0\bar{p}_0 \cdots \bar{q}_\tau\bar{p}_\tau]}{\mathrm{Prob}_{\lambda'}[\bar{q}_\tau -\bar{p}_\tau \cdots \bar{q}_0 -\bar{p}_0]} = \frac{p_0[\bar{q}_0\bar{p}_0]}{p_\tau[\bar{q}_\tau -\bar{p}_\tau]}\, e^{-\sum_i \frac{Q_i}{k_B T_i}}$$

$$= e^{S}$$

$$S = -\sum_i \frac{Q_i}{k_B T_i} - \ln P_\tau(\bar{q}_\tau, -\bar{p}_\tau) + \ln p_0(\bar{q}_0, \bar{p}_0)$$

$$P(S) = \int d\bar{q}_0 d\bar{p}_0 \cdots d\bar{q}_\tau d\bar{p}_\tau \; \mathrm{Prob}_{\lambda}[\bar{q}_0 \cdots \bar{p}_\tau]\, \delta(S - S(\Gamma))$$

$$= \int d\bar{q}_0 \cdots d\bar{p}_\tau \; \mathrm{Prob}_{\lambda'}[\bar{q}_\tau -\bar{p}_\tau \cdots \bar{q}_0 -\bar{p}_0]\, e^{S}\, \delta(S - S(\Gamma))$$

$$= e^{S} \int d\bar{q}_0 \cdots d\bar{p}_\tau \; \mathrm{Prob}_{\lambda'}[\bar{q}_\tau -\bar{p}_\tau \cdots \bar{q}_0 \bar{p}_0]\, \delta(S + S(\Gamma_R))$$

$$S(\Gamma_R) = -S(\Gamma)$$

$$= e^{S} P_R(-S)$$

We are free to choose the distributions $p_0, p_r$. If we choose

$$p_0 = \frac{e^{-\beta H(\lambda_A)}}{Z_A}, \quad p_r = \frac{e^{-\beta H(\lambda_B)}}{Z_B}$$

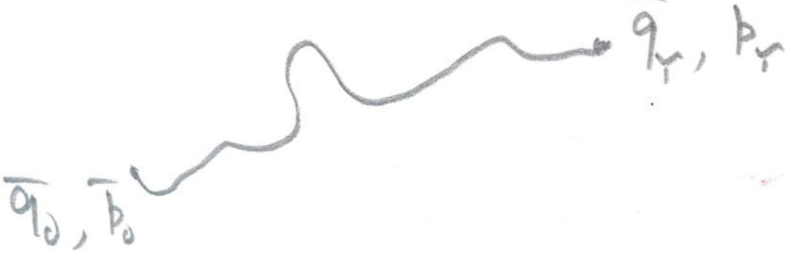
Also assume all $T_i = T$

Then
$$S = -\beta Q + \beta H_B - \beta H_A$$
$$+ \ln Z_B - \ln Z_A$$
$$= \beta\left[\Delta U - Q\right] - \beta\left(F_B - F_A\right)$$

$$\therefore \boxed{S = \beta W - \beta \Delta F}$$

Interpretation of $S = \underbrace{-\beta Q}_{\text{change in entropy of baths}} \underbrace{- \ln p_r + \ln p_0}_{\text{Change in entropy of system.}}$

Depends on the path in phase space



SSFT

Large-deviation functions as smallest eigenvalues of modified Fokker-Planck operators.

Consider a single particle with Langevin dynamics.

$$\dot{x} = p$$
$$\dot{p} = -\frac{\partial H}{\partial x} + \left(-\gamma p + \eta\right)$$

Fokker-Planck equation for the prob. distribution function is given by

$$\frac{\partial P(x,p)}{\partial t} = -\frac{\partial}{\partial x}\left(pP\right) + \frac{\partial}{\partial p}\left(\frac{\partial H}{\partial x}P\right) + \left[\frac{\partial}{\partial p}(\gamma p P) + \gamma k_B T \frac{\partial^2 P}{\partial p^2}\right]$$

or $$\frac{\partial P}{\partial t} = \mathcal{L} P$$

Work done: $$W = \int_0^{\tau} dt \, \frac{\partial H}{\partial t} \qquad \dot{W} = \frac{\partial H}{\partial t}$$

Think of $W$ as another variable so the set $(x, p, W)$ have the equations of motion

$$\dot{x} = p \qquad \dot{p} = -\frac{\partial H}{\partial x} + (-\gamma p + \eta) \qquad \dot{W} = \frac{\partial H}{\partial t}.$$

Then the joint distribution $Q(x, p, W; t)$ satisfies the Fokker-Planck equation

$$\frac{\partial Q}{\partial t} = \mathcal{L} Q - \frac{\partial}{\partial W}\left(\frac{\partial H}{\partial t} Q\right)$$

Define the generating function $Z(x, p, \lambda; t) = \int_{-\infty}^{\infty} dW\, Q\, e^{-\lambda W}$

$$= \left\langle e^{-\lambda W} \right\rangle_{x, p \to \text{specified}}.$$

Then $\underbrace{\frac{\partial Z(x, p, \lambda; t)}{\partial t} = \mathcal{L}_\lambda Z}$ $\quad \mathcal{L}_\lambda = \mathcal{L} - \lambda \frac{\partial H}{\partial t}$

$\hookrightarrow$ Feynman-Kac's equation for distribution of general functionals.

Solution of this equation for the initial condition

$$Z(x, p, \lambda; t=0) = \delta(x - x_0)\, \delta(p - p_0)$$

is given by.

$$|Z_t\rangle = e^{\mathcal{L}_\lambda t} |Z_{t=0}\rangle$$

[Assuming $\mathcal{L}_\lambda$ and hence $\frac{\partial H}{\partial t}$ is time-independent]

$$\therefore Z(x,p,\lambda;t) = \sum_n e^{\varepsilon_n(\lambda)t} \chi_n(x_0,p_0)\,\Psi_n(x,p)$$

where $\mathcal{L}_\lambda |\Psi_n\rangle = \varepsilon_n |\Psi_n\rangle$

$\mathcal{L}_\lambda^{+} |\chi_n\rangle = \varepsilon_n |\Psi_n\rangle$

↳ Adjoint operator.

At large times, the smallest eigenvalue, say $\varepsilon_0$, dominates and we get

$$Z(x,p,\lambda;t) \sim e^{\varepsilon_0(\lambda)t} \chi_n(x_0,p_0)\,\Psi_n(x,p)$$

$$\underbrace{\langle e^{-\lambda W}\rangle}_{\text{average over trajectories and initial conditions}} = \int Z(x,p,\lambda;t\,|\,x_0 p_0 \lambda; t=0)\, \underbrace{\rho(x_0,p_0)}_{\text{Steady state distribution}}\, dx_0\,dp_0\,dx\,dp$$

$$= e^{\mu(\lambda)t}\, g(\lambda)$$

$\boxed{\mu(\lambda) = \varepsilon_0(\lambda)}$ → Cumulant generating function. related to Large Deviation function

$$g(\lambda) = \int dx\,dp\,dx_0\,dp_0\; \chi_n(x_0,p_0)\,\Psi_n(x,p)\,\rho(x_0,p_0)$$

- Sometimes "but not always" the Fokker-Planck (modified) operator $\mathcal{L}_\lambda$ obeys a symmetry e.g. $\mathcal{L}_\lambda = \mathcal{L}^{+}_{1-\lambda}$ and this leads to the fluctuation symmetry

$$\mu(\lambda) = \mu(1-\lambda)$$

- For heat conduction the form of $\mathcal{L}_\lambda$ and the computation of $\mu(\lambda)$, $g(\lambda)$ in harmonic systems can be found in

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