Fluctuations and Responses in Stochastic Processes

Joonhyun Yeo

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Microscopic description of dynamics

- Classical mechanics
  - Hamilton eps. of motion:

$$\dot{\mathbf{q}}_i = \frac{\partial H}{\partial \mathbf{p}_i} = -\{H, \mathbf{q}_i\}_{PB}, \quad \dot{\mathbf{p}}_i = -\frac{\partial H}{\partial \mathbf{q}_i} = -\{H, \mathbf{p}_i\}_{PB}$$

  - Liouville eq. for phase space distribution $\rho(\{\mathbf{q}_i\}, \{\mathbf{p}_i\}, t)$: $\langle A(\{\mathbf{q}\}, \{\mathbf{p}\})\rangle_t = \int d^N\mathbf{q} d^N\mathbf{p}\, \rho A$.

$$\frac{\partial \rho}{\partial t} = \left[\frac{\partial H}{\partial \mathbf{q}} \cdot \frac{\partial}{\partial \mathbf{p}} - \frac{\partial H}{\partial \mathbf{p}} \cdot \frac{\partial}{\partial \mathbf{q}}\right] \rho = \{H, \rho\}_{PB}$$

- Quantum mechanics
  - Heisenberg eqs. of motion:

$$\dot{\mathbf{q}}_i = \frac{i}{\hbar}[H, \mathbf{q}_i], \quad \dot{\mathbf{p}}_i = \frac{i}{\hbar}[H, \mathbf{p}_i]$$

  - von Neumann eq. for density operator ρ: $\langle A(\{\mathbf{q}\}, \{\mathbf{p}\})\rangle_t = \mathsf{Tr}[\rho A]$.

$$\frac{\partial \rho}{\partial t} = -\frac{i}{\hbar}[H, \rho]$$

Macroscopic description

- Equilibrium: Thermodynamic laws for state variables
- Nonequilibrium: Near (not far from) equilibrium
  - Hydrodynamic description using transport coefficients
  - Onsager reciprocal relations ← time-reversal symmetry
  - Green-Kubo relations ← fluctuation-response relations

Mesoscopic description

- Effective theory obtained by separating System and Bath (Reservoir)
- Bath degrees of freedom give *stochastic* elements
- The time evolution of $\rho(t)$ for (System)+(Bath) is unitary: $d\rho/dt = (-i/\hbar)[H, \rho]$

- Observable A in System: $\langle A \rangle = \mathsf{Tr}_S[\rho_S A]$, where

$$\rho_S(t) = \mathsf{Tr}_B \rho(t)$$

- So formally,

$$\frac{\partial \rho_S}{\partial t} = -\frac{i}{\hbar} \mathsf{Tr}_B [H(t), \rho(t)]$$

- **Langevin**: Effective dynamic equation including stochastic elements
- **Fokker-Planck**: Corresponding probability conservation equation
- Formalisms: Langevin (Stochastic DE), Fokker-Planck (PDE), Path Integrals (Martin-Siggia-Rose: Classical; Schwinger-Keldysh: Quantum)

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Outline

Contents

1 Macroscopic Theory

1.1 Transport Coefficients

Contents

Macroscopic Theory of Irreversible Processes

- Consider the case where a local equilibrium is achieved at some cell a within time scale τ_{micro}. (*NOT* far from equilibrium situation)
- Global equilibrium is achieved at $\tau_{\text{macro}} \gg \tau_{\text{micro}} \Leftarrow$ Conservation Laws
- length scale ℓ_{micro} over which local eq. is established $\ll \ell_{\text{macro}}$: length scale of variation of thermodynamic quantities
- Hydrodynamic Regime: Consider system with local equilibrium subject to perturbation of long wavelength $\lambda \gg \ell_{\text{micro}}$ and low frequency $\omega \ll 1/\tau_{\text{micro}}$. (Focus on excitation modes with $\omega \to 0$ as $q \to 0$)
- $A_i(a,t)$: Extensive variable in a at time t
- $\Phi_i(a \to b)$: Flux (amount of A_i transferred from a to b per unit time)
- Clearly $\Phi_i(a \to b) = -\Phi_i(b \to a)$.
- Conservation laws:
$$\frac{dA_i(a,t)}{dt} = -\sum_{b \neq a} \Phi_i(a \to b)$$
- Local form: Introduce density $\rho_i(\boldsymbol{r},t)$ for $A_i(a,t)$
$$A_i(a,t) = \int_{V(a)} d\boldsymbol{r}\ \rho_i(\boldsymbol{r},t)$$
- Current $\boldsymbol{j}_i$ for flux:
$$\sum_{b \neq a} \Phi_i(a \to b) = \int_{S(a)} d\boldsymbol{S} \cdot \boldsymbol{j}_i = \int_{V(a)} d\boldsymbol{r}\ \boldsymbol{\nabla} \cdot \boldsymbol{j}_i$$
- Conservation Law:
$$\frac{\partial \rho_i}{\partial t} + \boldsymbol{\nabla} \cdot \boldsymbol{j}_i = 0$$
- Attribute an entropy $S(a)$ to each cell (Remember we are in local equilibrium in a cell): $S_{\text{tot}} = \sum_a S(a)$.
- Define a conjugate intensive variable
$$\gamma_i(a) \equiv \frac{\partial S_{\text{tot}}}{\partial A_i(a)} = \frac{\partial S(a)}{\partial A_i(a)}, \quad \gamma_i(\boldsymbol{r},t) \equiv \frac{\partial S_{\text{tot}}}{\partial \rho_i(\boldsymbol{r},t)}$$
- Examples: $A_i = N$, $\gamma_N = -\mu/T$; $A_i = E$, $\gamma_E = 1/T$
- Affinity $\Gamma_i(a,b) \equiv \gamma_i(b) - \gamma_i(a)$ for neighbouring cells a and b measures the force imbalance thus the deviation from global equilibrium

- Local form: $\Gamma_i(\boldsymbol{r},t) = d\boldsymbol{r} \cdot \boldsymbol{\nabla}\gamma_i(\boldsymbol{r},t)$
- Transport Coefficient $L_{ij}(a,b)$: For sufficiently small Γ_i, flux depends linearly on affinity

$$\Phi_i(a \to b) = \sum_j L_{ij}(a,b)\Gamma_j(a,b)$$

$$\Phi_i(b \to a) = -\Phi_i(a \to b) = \sum_j L_{ij}(b,a)\Gamma_j(b,a) = -\sum_j L_{ij}(b,a)\Gamma_j(a,b)$$

$$\Rightarrow L_{ij}(a,b) = L_{ij}(b,a)$$

- Local form:

$$j_i^\alpha(\boldsymbol{r},t) = \sum_{j,\beta} L_{ij}^{\alpha\beta}\partial_\beta\gamma_j(\boldsymbol{r},t)$$

- Heat diffusion
  - Thermal conductivity κ: $\boldsymbol{j}_E = -\kappa\boldsymbol{\nabla}T$
  - Note that $\gamma_E = 1/T$

$$j_E^\alpha = \sum_\beta L_{EE}^{\alpha\beta}\partial_\beta(\frac{1}{T}) = -(\frac{1}{T^2})\sum_\beta L_{EE}^{\alpha\beta}\partial_\beta T \Rightarrow L_{EE}^{\alpha\beta} = \delta^{\alpha\beta}T^2\kappa$$

  - Continuity eq.:

$$\frac{\partial\rho_E}{\partial t} = -\boldsymbol{\nabla}\cdot\boldsymbol{j}_E = \kappa\nabla^2 T$$

  - If we write $\rho_E = CT$ (C=specific heat), then we have diffusion eq. $\frac{\partial T}{\partial t} = \frac{\kappa}{C}\nabla^2 T$.
- Particle diffusion
  - Fick's law with diffusion constant D: $\boldsymbol{j}_N = -D\boldsymbol{\nabla}n$
  - Note that $\gamma_N = -\mu/T$:

$$\boldsymbol{\nabla}\gamma_N = -\boldsymbol{\nabla}(\frac{\mu}{T}) = -\frac{1}{T}\left(\frac{\partial\mu}{\partial n}\right)_T\boldsymbol{\nabla}n = -\frac{1}{T}\frac{1}{\kappa_T n^2}\boldsymbol{\nabla}n$$

  - We therefore have

$$L_{NN}^{\alpha\beta} = \delta^{\alpha\beta}DT\kappa_T n^2$$

- Entropy production

$$\begin{aligned}\frac{dS_{\text{tot}}}{dt} &= \sum_i\int d\boldsymbol{r}\,\frac{\delta S_{\text{tot}}}{\delta\rho_i(\boldsymbol{r},t)}\frac{\partial\rho_i(\boldsymbol{r},t)}{\partial t} = -\sum_i\int d\boldsymbol{r}\;\gamma_i(\boldsymbol{r},t)\boldsymbol{\nabla}\cdot\boldsymbol{j}_i(\boldsymbol{r},t)\\ &= -\sum_i\int d\boldsymbol{r}\;\boldsymbol{\nabla}\cdot\{\gamma_i(\boldsymbol{r},t)\boldsymbol{j}_i(\boldsymbol{r},t))\} + \sum_i\int d\boldsymbol{r}\;\boldsymbol{j}_i(\boldsymbol{r},t)\cdot\boldsymbol{\nabla}\gamma_i(\boldsymbol{r},t)\\ &= \sum_{i,j}\sum_{\alpha,\beta}(\partial_\alpha\gamma_i(\boldsymbol{r},t))\,L_{ij}^{\alpha\beta}\,(\partial_\beta\gamma_j(\boldsymbol{r},t))\end{aligned}$$

- This quantity should be positive definite (≥ 0)
- We will show below that (Onsager reciprocal relations)

$$L_{ij}^{\alpha\beta}(\{\gamma_k\}) = \varepsilon_i\varepsilon_j L_{ji}^{\beta\alpha}(\{\varepsilon_k\gamma_k\}),$$

  where ε_i is the parity of A_i under time reversal.

1.2 Onsager Reciprocal Relations

Contents

Onsager Reciprocal Relations

- Extensive variables: $\{A_i\}$, $\{B_i\}$; Under time reversal $A_i \to A_i$, $B_i \to -B_i$
- Equilibrium values:$\{\bar{A}_i\}$, $\{\bar{B}_i\}$; Fluctuations: $a_i \equiv A_i - \bar{A}_i$, $b_i \equiv B_i - \bar{B}_i$
- Departure from equilibrium in entropy

$$\Delta S = -\frac{1}{2}\sum_{i,j}\alpha_{ij}a_i a_j - \frac{1}{2}\sum_{i,j}\beta_{ij}b_i b_j \equiv -\frac{1}{2}\boldsymbol{x}^T \cdot \mathsf{g} \cdot \boldsymbol{x},$$

  where $\boldsymbol{x} = (\boldsymbol{a}, \boldsymbol{b})^{\mathrm{t}}$. (For a closed system $\rho_s(\boldsymbol{a}, \boldsymbol{b}) \sim e^{\Delta S/k_B}$ serves as a pdf for fluctuations. We only consider the parity symmetric pdf.)

- Thermodynamic Forces

$$F_i^a \equiv \frac{\partial \Delta S}{\partial a_i}, \quad F_i^b \equiv \frac{\partial \Delta S}{\partial b_i}, \quad \to \quad \boldsymbol{F}^{\boldsymbol{x}} \equiv \frac{\partial \Delta S}{\partial \boldsymbol{x}} = -\mathsf{g} \cdot \boldsymbol{x}$$

- Macroscopic description of the approach to equilibrium $\to$ Transport Coefficients: $\dot{x} = J = \mathsf{L} \cdot \mathsf{F}^x$

$$\frac{\partial a_i}{\partial t} = \sum_j L_{ij}F_j^a + \sum_j M_{ij}F_j^b, \qquad \frac{\partial b_i}{\partial t} = \sum_j M'_{ij}F_j^a + \sum_j N_{ij}F_j^b$$

- We can write

$$\frac{\partial \boldsymbol{x}}{\partial t} = \mathcal{L} \cdot \boldsymbol{F}^{\boldsymbol{x}} = -\Gamma \cdot \boldsymbol{x},$$

  where $\Gamma = \mathcal{L} \cdot \mathsf{g}$ or $\mathcal{L} = \Gamma \cdot \mathsf{g}^{-1}$.

- Given $\boldsymbol{x}(t=0) = \boldsymbol{x}_0$, the solution is

$$\boldsymbol{x}(t; \boldsymbol{x}_0) = e^{-t\Gamma} \cdot \boldsymbol{x}_0 \equiv \int d\boldsymbol{x}\, \boldsymbol{x} P_t(\boldsymbol{x}|\boldsymbol{x}_0).$$

- Time correlation function $C_{kl}(t) \equiv \langle x_k(t) x_l(0)\rangle$

$$\begin{aligned} C_{kl}(t) &= \int d\boldsymbol{x}_0\; x_k(t; \boldsymbol{x}_0) x_{0l}\; \rho_s(\boldsymbol{x}_0) = \int d\boldsymbol{x}_0\; (e^{-t\Gamma} \cdot \boldsymbol{x}_0)_k x_{0l}\; \rho_s(\boldsymbol{x}_0) \\ &= \int d\boldsymbol{x}_0 \int d\boldsymbol{x}\; x_k x_{0l} P_t(\boldsymbol{x}|\boldsymbol{x}_0)\rho_s(\boldsymbol{x}_0) = \int d\boldsymbol{x} \int d\boldsymbol{x}_0\; x_{0k} x_l P_t(\boldsymbol{x}_0|\boldsymbol{x})\rho_s(\boldsymbol{x}) \end{aligned}$$

- Microscopic reversibility: Detailed Balance

$$P_t(\boldsymbol{x}|\boldsymbol{x}')\rho_s(\boldsymbol{x}') = P_t(\tilde{\boldsymbol{x}'}|\tilde{\boldsymbol{x}})\rho_s(\tilde{\boldsymbol{x}}),$$

  where $\tilde{\boldsymbol{x}} = (\boldsymbol{a}, -\boldsymbol{b})^{\mathrm{t}}$.

- Invoke the DB

$$C_{kl}(t) = \int d\boldsymbol{x} \int d\boldsymbol{x}_0\; x_{0k} x_l P_t(\tilde{\boldsymbol{x}}|\tilde{\boldsymbol{x}}_0)\rho_s(\tilde{\boldsymbol{x}}_0) = \int d\boldsymbol{x} \int d\boldsymbol{x}_0\; \tilde{x}_{0k}\tilde{x}_l P_t(\boldsymbol{x}|\boldsymbol{x}_0)\rho_s(\boldsymbol{x}_0)$$

- Note that
$$\int d\boldsymbol{x}\ \tilde{x}_l P_t(\boldsymbol{x}|\boldsymbol{x}_0) = \tilde{x}_l(t;\boldsymbol{x}_0).$$

- But $\tilde{\boldsymbol{x}}$ also satisfies
$$\frac{\partial \tilde{\boldsymbol{x}}}{\partial t} = \tilde{\mathcal{L}}\cdot\tilde{\boldsymbol{F}}^{\boldsymbol{x}} = -\tilde{\Gamma}\cdot\tilde{\boldsymbol{x}}, \qquad \tilde{\boldsymbol{x}}(t;\boldsymbol{x}_0) = \widetilde{e^{-t\Gamma}\cdot\boldsymbol{x}_0} = e^{-t\tilde{\Gamma}}\cdot\tilde{\boldsymbol{x}}_0$$
where
$$\mathcal{L} = \begin{pmatrix} \mathtt{L} & \mathtt{M} \\ \mathtt{M}' & \mathtt{N} \end{pmatrix}, \qquad \tilde{\mathcal{L}} = \begin{pmatrix} \mathtt{L} & -\mathtt{M} \\ -\mathtt{M}' & \mathtt{N} \end{pmatrix}, \qquad \tilde{\Gamma} = \tilde{\mathcal{L}}\cdot\mathtt{g}$$

- We therefore have
$$C_{kl}(t) = \int d\boldsymbol{x}_0\ \tilde{x}_{0k}(e^{-t\tilde{\Gamma}}\cdot\tilde{\boldsymbol{x}}_0)_l\rho_s(\boldsymbol{x}_0) = \langle\tilde{x}_k(0)\tilde{x}_l(t)\rangle$$
$\rightarrow$ Time reversal symmetry + Time translational symmetry

- Note that
$$\int d\boldsymbol{x}_0\ x_{0i}x_{0j}\rho_s(\boldsymbol{x}_0) = \int d\boldsymbol{x}_0\ \tilde{x}_{0i}\tilde{x}_{0j}\rho_s(\boldsymbol{x}_0) = k_B(\mathtt{g}^{-1})_{ij}$$

- It follows that
$$\sum_m (e^{-t\Gamma})_{km}(\mathtt{g}^{-1})_{ml} = \sum_m (\mathtt{g}^{-1})_{km}(e^{-t\tilde{\Gamma}})_{lm} = \sum_m (\mathtt{g}^{-1})_{km}(e^{-t\tilde{\Gamma}})^{\mathrm{t}}_{ml}$$
$$e^{-t\tilde{\Gamma}^{\mathrm{t}}} = \mathtt{g}\cdot e^{-t\Gamma}\cdot\mathtt{g}^{-1}, \qquad \tilde{\Gamma}^{\mathrm{t}} = \mathtt{g}\cdot\Gamma\cdot\mathtt{g}^{-1}$$

- Since $\mathtt{g}$ is symmetric,
$$(\tilde{\mathcal{L}}\cdot\mathtt{g})^{\mathrm{t}} = \mathtt{g}\cdot\tilde{\mathcal{L}}^{\mathrm{t}} = \mathtt{g}\cdot\mathcal{L}\cdot\mathtt{g}\cdot\mathtt{g}^{-1}$$
$$\boxed{\tilde{\mathcal{L}}^{\mathrm{t}} = \mathcal{L}}$$
$$\boxed{\mathtt{L}^{\mathrm{t}} = \mathtt{L}, \quad \mathtt{M}^{\mathrm{t}} = -\mathtt{M}', \quad \mathtt{N}^{\mathrm{t}} = \mathtt{N}}$$

- Example: Coupling between thermal and particle diffusion
  - Gas of light particles scattering elastically
  - Temperature gradient can produce particle flux; Density gradient can produce heat flow
  - Currents
$$\boldsymbol{j}_E = L_{EE}\boldsymbol{\nabla}\frac{1}{T} + L_{EN}\boldsymbol{\nabla}(\frac{-\mu}{T}), \qquad \boldsymbol{j}_N = L_{NE}\boldsymbol{\nabla}\frac{1}{T} + L_{NN}\boldsymbol{\nabla}(\frac{-\mu}{T})$$
  - Onsager relation: $L_{EN} = L_{NE}$
  - In the absence of particle current $\boldsymbol{j}_N = 0$,
$$L_{NE}\boldsymbol{\nabla}\frac{1}{T} + L_{NN}\boldsymbol{\nabla}(\frac{-\mu}{T}) = 0, \qquad \boldsymbol{\nabla}(\frac{-\mu}{T}) = \frac{L_{NE}}{L_{NN}}\boldsymbol{\nabla}\frac{1}{T}$$
$$\boldsymbol{j}_E = \frac{1}{L_{NN}}(L_{EE}L_{NN} - L_{EN}^2)\boldsymbol{\nabla}\frac{1}{T}$$
  - Thermal conductivity in this case is
$$\kappa = \frac{1}{T^2 L_{NN}}(L_{EE}L_{NN} - L_{EN}^2) \geq 0$$

2 Mesoscopic Theories

2.1 Langevin Equation

Contents

Langevin equation

Brownian motion

$$m\frac{dv}{dt} = F(t)$$

What to include in $F(t)$?

- frictional force $-\gamma v$: $v(t) = e^{-\gamma t/m}v(0) \to 0$ as $t \to \infty$. Inconsistent with $\langle v^2 \rangle = k_B T/m$ at thermal equilibrium
- Need fluctuating (random) force $\xi(t)$ to keep it alive
  - Simplest form of random force: Gaussian white noise

$$\langle \xi(t) \rangle = 0, \quad \langle \xi(t)\xi(t') \rangle = 2B\delta(t - t')$$

$$\boxed{m\frac{dv}{dt} = -\gamma v + \xi(t)} \tag{1}$$

- Effect of environment ("heat bath"): systematic part $(-\gamma v)$ + fluctuating part (ξ)
- There is a relationship between the two: Fluctuation-Dissipation Relation

Let $v(t) = e^{-\gamma t/m}w(t)$, then $dw/dt = e^{\gamma t/m}\xi(t)/m$. Therefore

$$v(t) = e^{-\gamma t/m}v(0) + \int_0^t dt' e^{-\gamma(t-t')/m}\xi(t')/m \tag{2}$$

Let us calculate $\langle v(t_1)v(t_2) \rangle$. The cross term is zero. We have to evaluate

$$\begin{aligned}
&\int_0^{t_1} dt' e^{-\gamma(t_1-t')/m} \int_0^{t_2} dt'' e^{-\gamma(t_2-t'')/m} \langle \xi(t')\xi(t'') \rangle/m^2 \\
=&e^{-\gamma(t_1+t_2)/m} \int_0^{t_1} dt' \int_0^{t_2} dt'' e^{\gamma(t'+t'')/m}\, 2B\delta(t'-t'')/m^2 \\
=&\frac{B}{\gamma m}e^{-\gamma(t_1+t_2)/m}\left[e^{2\gamma \min(t_1,t_2)/m} - 1\right] = \frac{B}{\gamma m}(e^{-\gamma|t_1-t_2|/m} - e^{-\gamma(t_1+t_2)/m})
\end{aligned}$$

We have

$$\langle v(t_1)v(t_2) \rangle = \left(v^2(0) - \frac{B}{\gamma m}\right)e^{-\gamma(t_1+t_2)/m} + \frac{B}{\gamma m}e^{-\gamma|t_1-t_2|/m}$$

$$\langle v^2(t) \rangle = e^{-2\gamma t/m}\left(v^2(0) - \frac{B}{\gamma m}\right) + \frac{B}{\gamma m} \to \frac{B}{\gamma m} \quad \text{as} \quad t \to \infty$$

Comparing with $\langle v^2 \rangle_{\rm eq} = k_B T/m$, we have

$$\boxed{\gamma = \frac{B}{k_B T} = \frac{1}{k_B T}\int_0^\infty dt \langle \xi(t)\xi(0) \rangle} \qquad \texttt{FDR of 2nd kind}$$

Balance between dissipation (driving to "dead" state) and fluctuation (driving to "alive" state) to maintain thermal equilibrium.

Note that

- If $v^2(0) = B/(\gamma m) = k_B T/m$, then $\langle v^2(t)\rangle = \langle v^2\rangle_{\rm eq}$
- If $v^2(0) = B/(\gamma m) = k_B T/m$, then $\langle v(t_1)v(t_2)\rangle = \langle v(t_1 - t_2)v(0)\rangle$

Mean Squared Displacement, $\langle(\Delta x(t))^2\rangle$, where $\Delta x(t) \equiv x(t) - x(0)$.

$$\langle(\Delta x(t))^2\rangle = \int_0^t dt' \int_0^t dt'' \, \langle v(t')v(t'')\rangle.$$

Consider

$$\frac{\partial\langle(\Delta x(t))^2\rangle}{\partial t} = 2\int_0^t dt''\langle v(t)v(t'')\rangle = 2\int_0^t dt''\langle v(t-t'')v(0)\rangle = 2\int_0^t ds\langle v(s)v(0)\rangle$$

We expect $\langle(\Delta x(t))^2\rangle \sim 2Dt$ as $t \to \infty$ with diffusion constant D. We have

$$\boxed{D = \int_0^\infty ds\langle v(s)v(0)\rangle} \quad \texttt{Green-Kubo formula}$$

Explicit calculation shows that ($*$ Exercise)

$$\begin{aligned}\langle(\Delta x(t))^2\rangle &= \frac{2B}{\gamma^2}\left[t - \frac{m}{\gamma} + \frac{m}{\gamma}e^{-\gamma t/m}\right] + \left(v_0^2 - \frac{B}{\gamma m}\right)\left(\frac{1 - e^{-\gamma t/m}}{\gamma/m}\right)^2 \\ &\sim \frac{2B}{\gamma^2}t \qquad \text{as } t \to \infty\end{aligned}$$

We can identify

$$\boxed{D = \frac{B}{\gamma^2} = \frac{k_B T}{\gamma}} \quad \texttt{Einstein relation}$$

We can write for mobility μ as

$$\boxed{\mu \equiv \frac{1}{\gamma} = \frac{1}{k_B T}\int_0^\infty dt\langle v(t)v(0)\rangle} \quad \texttt{FDR of 1st kind}$$

Suppose there is an uniform external driving force f so that

$$m\frac{dv}{dt} = -\frac{v}{\mu} + f + \xi(t)$$

As $t \to \infty$, the average velocity approaches

$$\langle v\rangle \to \mu f$$

Therefore we can regard μ as a response of the velocity to the external driving. So the above FDR is a relationship between the response and the correlation or fluctuation. $\Rightarrow$ $\boxed{\textit{Fluctuation} - \textit{Response Relation}}$

2.2 Generalized Langevin Equations

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Generalized Langevin equations

The reservoir may produce a generalized friction term which includes memory effect

$$m\frac{dv}{dt} = -\int_0^t dt'\ \gamma(t-t')v(t') + \xi(t)$$

Laplace transform

$$\mathcal{L}\{v\} = \hat{v}(\omega) \equiv \int_0^\infty dt\ e^{i\omega t}v(t), \quad \mathrm{Im}(\omega) > 0,$$

$$\mathcal{L}\{\dot{v}\} = -v(0) - i\omega\hat{v}(\omega), \quad \mathcal{L}\{\int_0^t dt'\gamma(t-t')v(t')\} = \hat{\gamma}(\omega)\hat{v}(\omega)$$

Multiply by $v(0)$ and take the average remembering $\langle\xi(t)v(0)\rangle = 0$ for $t > 0$.

$$\frac{dC(t)}{dt} = -\int_0^t dt'\ \gamma(t-t')C(t') \ \ \textsf{with} \ \ C(t) \equiv \langle v(t)v(0)\rangle, \quad \textsf{or}$$

$$\hat{C}(\omega) = \frac{\langle v^2(0)\rangle}{\hat{\gamma}(\omega)/m - i\omega}$$

Suppose adding a time-dependent external driving force $f(t)$. Taking the average and Laplace transform,

$$-i\omega\langle\hat{v}(\omega)\rangle - v(0) = -\frac{1}{m}\hat{\gamma}(\omega)\langle\hat{v}(\omega)\rangle + \frac{1}{m}\hat{f}(\omega),$$

We introduce the response function $\mu(t)$ as

$$\langle v(t)\rangle = \int_0^t dt'\mu(t-t')f(t'), \qquad \hat{\mu}(\omega) = \frac{1}{m}\frac{1}{\hat{\gamma}(\omega)/m - i\omega}$$

We therefore have

$$\hat{\mu}(\omega) = \frac{1}{m\langle v^2(0)\rangle}\hat{C}(\omega), \quad \mu(t) = \frac{1}{m\langle v^2(0)\rangle}\langle v(t)v(0)\rangle$$

If $\langle v^2(0)\rangle = k_BT/m$, then

$$\boxed{\hat{\mu}(\omega) = \frac{1}{k_BT}\int_0^\infty dt\ e^{i\omega t}\langle v(t)v(0)\rangle} \qquad \texttt{FDR of 1st kind}$$

To show FDR of 2nd kind, consider

$$\begin{aligned}\frac{1}{m^2}\int_0^\infty dt\ e^{i\omega t}\langle\xi(0)\xi(t)\rangle &= \int_0^\infty dt\ e^{i\omega t}\left\langle \dot{v}(0)\left[\dot{v}(t) + \frac{1}{m}\int_0^t dt'\ \gamma(t-t')v(t')\right]\right\rangle \\ &= \int_0^\infty dt\ e^{i\omega t}\langle\dot{v}(0)\dot{v}(t)\rangle + \frac{\hat{\gamma}(\omega)}{m}\int_0^\infty dt\ e^{i\omega t}\langle\dot{v}(0)v(t)\rangle\end{aligned}$$

Time-translational invariance:

$$\frac{d}{dt_0}\langle v(t_0)v(t_0+t)\rangle = 0, \quad \langle\dot{v}(t_0)v(t_0+t)\rangle = -\langle v(t_0)\dot{v}(t_0+t)\rangle, \quad \langle\dot{v}(t_0)v(t_0)\rangle = 0$$

Integrating by parts the first term, we have

$$\begin{aligned}\frac{1}{m^2}\int_0^\infty dt\ e^{i\omega t}\langle\xi(0)\xi(t)\rangle &= -i\omega\int_0^\infty dt\ e^{i\omega t}\langle\dot{v}(0)v(t)\rangle + \frac{\hat{\gamma}(\omega)}{m}\int_0^\infty dt\ e^{i\omega t}\langle\dot{v}(0)v(t)\rangle \\ &= \left(i\omega - \frac{\hat{\gamma}(\omega)}{m}\right)\int_0^\infty dt\ e^{i\omega t}\langle v(0)\dot{v}(t)\rangle \\ &= \left(i\omega - \frac{\hat{\gamma}(\omega)}{m}\right)\left(-\langle v^2(0)\rangle - i\omega\int_0^\infty dt\ e^{i\omega t}\langle v(0)v(t)\rangle\right) \\ &= \left(i\omega - \frac{\hat{\gamma}(\omega)}{m}\right)\left(-\langle v^2(0)\rangle - i\omega\frac{\langle v^2(0)\rangle}{\hat{\gamma}(\omega)/m - i\omega}\right)\end{aligned}$$

- We therefore have

$$\frac{1}{m^2}\int_0^\infty dt\, e^{i\omega t}\langle\xi(0)\xi(t)\rangle = \frac{\langle v^2(0)\rangle}{m}\hat{\gamma}(\omega)$$

  or

$$\hat{\gamma}(\omega) = \frac{1}{m\langle v^2(0)\rangle}\int_0^\infty dt\, e^{i\omega t}\langle\xi(0)\xi(t)\rangle$$

- If $\langle v^2(0)\rangle = k_B T/m$, then

$$\boxed{\hat{\gamma}(\omega) = \frac{1}{k_B T}\int_0^\infty dt\, e^{i\omega t}\langle\xi(0)\xi(t)\rangle} \quad \texttt{FDR of 2nd kind}$$

  We have a colored noise: non-Markovian dynamics

- For $\gamma(t) = 2\gamma\delta(t)$, we recover the white noise limit.

2.3 Quantum Brownian Motion: Caldeira-Leggett Model

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Quantum Brownian Motion: Caldeira-Leggett Model

Treat a heat bath as a collection of harmonic oscillators:

- System

$$H_S = \frac{p^2}{2m} + U(x)$$

- Bath

$$H_B = \sum_j \left(\frac{p_j^2}{2m_j} + \frac{1}{2}m_j\omega_j^2 q_j^2\right) = \sum_j \hbar\omega_j(b_j^\dagger b_j + \frac{1}{2})$$

- Interaction: $H_I = -x\sum_j \kappa_j q_j \equiv -xB$.

- The interaction renormalises the potential, so we need counter term: $H_C = x^2\sum_j \kappa_j^2/(2m_j\omega_j^2)$ that can be absorbed into $U(x)$. (In this way, the minimum potential energy is given by $\partial H/\partial x = \partial U/\partial x = 0$.)

- Total Hamiltonian $H = H_S + H_B + H_I + H_C$

$$H = \frac{p^2}{2m} + U(x) + \sum_j \left(\frac{p_j^2}{2m_j} + \frac{m_j\omega_j^2}{2}(q_j - \frac{\kappa_j}{m_j\omega_j^2}x)^2\right) \tag{3}$$

- Heisenberg Eqs. of motion: For Heisenberg operators $x(t) = e^{iHt/\hbar}xe^{-iHt/\hbar}$ etc.,

  - System

$$\dot{x}(t) = \frac{i}{\hbar}[H, x(t)] = \frac{p(t)}{m},$$

$$\dot{p}(t) = \frac{i}{\hbar}[H, p(t)] = -U'(x) + \sum_j \kappa_j q_j(t) - \sum_j \frac{\kappa_j^2}{m_j\omega_j^2}x(t)$$

– Bath

$$\dot{q}_j(t) = \frac{i}{\hbar}[H, q_j(t)] = \frac{p_j(t)}{m_j}$$

$$\dot{p_j}(t) = \frac{i}{\hbar}[H, p_j(t)] = -m_j\omega_j^2 q_j(t) + \kappa_j x(t)$$

- Bath eqs. of motion are linear, so we can solve them. Rewrite the eqs. for $\{q_j, p_j\}$ as

$$\dot{\mathtt{Q}}(t) = \mathtt{A} \cdot \mathtt{Q}(t) + \mathtt{C}(t)$$

where

$$\mathtt{Q}(t) = \begin{pmatrix} q_j(t) \\ p_j(t) \end{pmatrix}, \quad \mathtt{A} = \begin{pmatrix} 0 & 1/m_j \\ -m_j\omega_j^2 & 0 \end{pmatrix}, \quad \mathtt{C}(t) = \begin{pmatrix} 0 \\ \kappa_j x(t) \end{pmatrix}$$

- The solution to this equation is

$$\mathtt{Q}(t) = e^{\mathtt{A}t} \cdot \mathtt{Q}(0) + \int_0^t ds\; e^{\mathtt{A}(t-s)} \cdot \mathtt{C}(s)$$

- We can easily show that

$$e^{\mathtt{A}t} = \cos(\omega_j t)\mathtt{1} + \frac{1}{\omega_j}\sin(\omega_j t)\mathtt{A} = \begin{pmatrix} \cos(\omega_j t) & \frac{1}{m_j\omega_j}\sin(\omega_j t) \\ -m_j\omega_j\sin(\omega_j t) & \cos(\omega_j t) \end{pmatrix}.$$

- We have

$$q_j(t) = q_j(0)\cos(\omega_j t) + p_j(0)\frac{1}{m_j\omega_j}\sin(\omega_j t) + \frac{\kappa_j}{m_j\omega_j}\int_0^t ds\;\sin(\omega_j(t-s))x(s)$$

- Recall that

$$q_j(0) = \sqrt{\frac{\hbar}{2m_j\omega_j}}(b_j + b_j^\dagger), \qquad p_j(0) = -i\sqrt{\frac{\hbar m_j\omega_j}{2}}(b_j - b_j^\dagger)$$

- Therefore

$$q_j(t) = \sqrt{\frac{\hbar}{2m_j\omega_j}}(e^{-i\omega_j t}b_j + e^{i\omega_j t}b_j^\dagger) + \frac{\kappa_j}{m_j\omega_j}\int_0^t ds\;\sin(\omega_j(t-s))x(s)$$

- Inserting this into eq. for $p(t)$

$$\begin{aligned}\dot{p}(t) = -U'(x) &+ \sum_j \kappa_j\sqrt{\frac{\hbar}{2m_j\omega_j}}(e^{-i\omega_j t}b_j + e^{i\omega_j t}b_j^\dagger) \\ &- \sum_j \frac{\kappa_j^2}{m_j\omega_j^2}x(t) + \sum_j \frac{\kappa_j^2}{m_j\omega_j}\int_0^t ds\;\sin(\omega_j(t-s))x(s)\end{aligned}$$

- Recall that

$$B = B(0) \equiv \sum_j \kappa_j q_j = \sum_j \kappa_j\sqrt{\frac{\hbar}{2m_j\omega_j}}(b_j + b_j^\dagger)$$

- Time evolution (in the interaction picture) of this is denoted by

$$B(t) \equiv e^{iH_Bt/\hbar}Be^{-iH_Bt/\hbar} = \sum_j \kappa_j\sqrt{\frac{\hbar}{2m_j\omega_j}}(e^{-i\omega_j t}b_j + e^{i\omega_j t}b_j^\dagger) \tag{4}$$

- Integrating by parts,

$$\begin{aligned}\dot{p}(t) &= -U'(x) - \sum_j \frac{\kappa_j^2}{m_j\omega_j^2} x(t) + \sum_j \frac{\kappa_j^2}{m_j\omega_j} \int_0^t ds\ \sin(\omega_j(t-s))x(s) + B(t) \\ &= -U'(x) - \frac{d}{dt}\int_0^t ds\ \gamma(t-s)x(s) + B(t) \\ &= -U'(x) - \int_0^t ds\ \gamma(t-s)\dot{x}(s) + \xi(t), \end{aligned} \tag{5}$$

where $\xi(t) = B(t) - \gamma(t)x(0)$. Note that the counter term is cancelled.

- Here, the dissipation kernel is

$$\boxed{\gamma(t) \equiv \sum_j \frac{\kappa_j^2}{m_j\omega_j^2}\cos(\omega_j t)}, \quad t > 0$$

- The above is in standard form of the generalized (quantum) Langevin Eq.

- Properties of the bath are described by the spectral density of the oscillator frequencies:

$$J(\omega) \equiv \frac{\pi}{2}\sum_j \frac{\kappa_j^2}{m_j\omega_j}\delta(\omega - \omega_j)$$

- We can rewrite

$$\boxed{\gamma(t) = \frac{2}{\pi}\int_0^\infty d\omega\ \frac{J(\omega)}{\omega}\cos(\omega t)}, \qquad t > 0$$

  - Ohmic bath: $J(\omega) \sim \omega$ or $J(\omega) = \gamma\omega$. Then $\gamma(t) = 2\gamma\delta(t)$, and $\int_0^t ds\gamma(t-s)\dot{x}(s) = \gamma\dot{x}(t)$; Markov limit.
  - High-frequency cutoff - Drude form: $J(\omega) = \gamma\omega\Omega^2/(\omega^2+\Omega^2)$. Then $\gamma(t) = \gamma\Omega\exp(-\Omega t)$. Memory effect for the time scale $\tau \sim \Omega^{-1}$.

- $B(t)$ (or $\xi(t)$) plays a role of stochastic force from the bath.

- One can show that (left as Problem)

$$\langle B(t)\rangle = 0$$

$$\langle [B(t), B]\rangle = [B(t), B] = -\frac{2i\hbar}{\pi}\int_0^\infty d\omega\ J(\omega)\sin(\omega t)$$

$$\langle \{B(t), B\}\rangle = \frac{2\hbar}{\pi}\int_0^\infty d\omega\ J(\omega)\coth(\frac{1}{2}\beta\hbar\omega)\cos(\omega t),$$

where the average is evaluated with respect to the bath Hamiltonian, i.e. $\langle\cdots\rangle = \mathsf{Tr}[\rho_B(\cdots)]$ where $\rho_B = (1/Z)e^{-\beta H_B}$ with $Z = \mathsf{Tr}e^{-\beta H_B}$.

- In the classical limit $\beta\hbar\omega \ll 1$,

$$\frac{1}{2}\langle\{B(t), B\}\rangle = k_B T\gamma(t)$$

- Recall that

$$B(t) = \sum_j \kappa_j\left\{q_j(0)\cos(\omega_j t) + p_j(0)\frac{1}{m_j\omega_j}\sin(\omega_j t)\right\}$$

- Therefore the shifted stochastic force is

$$\begin{aligned}\xi(t) &\equiv B(t) - \gamma(t)x(0) \\ &= \sum_j \kappa_j \left\{ \left(q_j(0) - \frac{\kappa_j}{m_j\omega_j^2} x(0) \right) \cos(\omega_j t) + p_j(0) \frac{1}{m_j\omega_j} \sin(\omega_j t) \right\}.\end{aligned}$$

- Noting that q_j, p_i and x operator on different Hilbert space, we see that $\xi(t)$ satisfies the exactly same statistics as $B(t)$ when we use the shifted bath Hamiltonian, i.e. $\rho'_B = (1/Z')e^{-\beta H'_B}$, where

$$H'_B = \sum_j \left[\frac{p_j^2(0)}{2m_j} + \frac{1}{2} m_j\omega_j^2 \left(q_j(0) - \frac{\kappa_j}{m_j\omega_j^2} x(0) \right)^2 \right]$$

2.4 Fokker-Planck Equation

Contents

Fokker-Planck Equation

- Sometimes we face nonlinear problems like Brownian particle in a potential

$$\begin{aligned}\frac{dx}{dt} &= \frac{p}{m} \\ \frac{dp}{dt} &= -\gamma \frac{p}{m} - \nabla U(x) + \xi(t), \qquad \langle \xi(t)\xi(t') \rangle = 2B\delta(t-t')\end{aligned}$$

- Let us consider a general form, for $i = 1, 2, \ldots, N$,

$$\boxed{\frac{dx_i}{dt} = f_i(\boldsymbol{x}(t)) + \xi_i(t)},$$

where $\langle \xi_i(t) \rangle = 0$ and $\langle \xi_i(t)\xi_j(t') \rangle = 2D_{ij}\delta(t-t')$.

- Convenient to work with the Fokker-Planck equation for the probability density at time t

$$P(\mathbf{x}, t) = \langle \delta(\mathbf{x} - \mathbf{x}(t)) \rangle,$$

where the average is with respect to noise and $\mathbf{x}(t)$ is the solution of the above Langevin eq. with some initial condition $\mathbf{x}(0) = \mathbf{x}_0$

- $P(\mathbf{x}, t)$ satisfies the Fokker-Planck eq., which is a deterministic p.d.e.

$$\boxed{\frac{\partial}{\partial t} P(\mathbf{x}, t) = -\sum_i \frac{\partial}{\partial x_i} \left(f_i(\mathbf{x}) P(\mathbf{x}, t) \right) + \sum_{i,j} \frac{\partial^2}{\partial x_i \partial x_j} D_{ij} P(\mathbf{x}, t)}$$

- The derivation can be found in many textbooks. (See also my lecture note for PSI 2014)
- The F-P equation is of the form

$$\partial_t P(\mathbf{x}, t) = -\mathtt{L}(\boldsymbol{x}) P = -\boldsymbol{\nabla} \cdot \mathbf{J},$$

where

$$\mathtt{L}(\boldsymbol{x}) = \sum_i \frac{\partial}{\partial x_i} f_i(\mathbf{x}) - \sum_{i,j} \frac{\partial^2}{\partial x_i \partial x_j} D_{ij}$$

is the F-P differential operator and

$$J_i = f_i P - \sum_j \partial_j D_{ij} P$$

is the probability current.

- Stationary solution: $P^{\rm s}(x)$ satisfies $\partial_t P^{\rm s} = -\mathtt{L}P^{\rm s} = 0$ or $\boldsymbol{\nabla} \cdot \mathbf{J}^{\rm s} = 0$.

Examples

① <u>Brownian motion</u>

$$\dot{p} = -\gamma \frac{p}{m} + \xi, \qquad \langle \xi(t)\xi(t')\rangle = 2B\delta(t-t')$$

$$\boxed{\partial_t P(p,t) = \partial_p(\frac{\gamma}{m}p + B\partial_p)P(p,t)}$$

Maxwell-Boltzmann dist.

$$P_{\rm eq} \sim \exp(-p^2/(2mk_BT))$$

becomes the stationary solution if $\gamma = B/(k_BT)$. [FDR of 2nd kind].

In this case $J^{\rm s} = 0$.

② <u>Brownian particle in a potential</u> (Kramer's equation)

$$\frac{dx}{dt} = \frac{p}{m}$$
$$\frac{dp}{dt} = -\gamma\frac{p}{m} - \nabla U(x) + \xi(t), \qquad \langle \xi(t)\xi(t')\rangle = 2B\delta(t-t')$$

$$\boxed{\partial_t P(x,p,t) = -\partial_x \frac{p}{m} P(x,p,t) - \partial_p(-\frac{\gamma}{m}p - (\partial_x U(x)) - B\partial_p)P(x,p,t)}$$

Again equilibrium dist.

$$P_{\rm eq} \sim \exp\left[-\frac{p^2}{2mk_BT} - \frac{U(x)}{k_BT}\right]$$

becomes the stationary solution $P^{\rm s}$ if $\gamma = B/(k_BT)$. In this case, stationary currents

$$J^{\rm s}_x(x,p) = \frac{p}{m}P^{\rm s}(x,p), \quad J^{\rm s}_p(x,p) = (-\frac{\gamma}{m}p - (\partial_x U(x)) - B\partial_p)P^{\rm s}(x,p)$$

do <u>not</u> vanish. But the "irreversible" part

$$J^{\rm s,ir}_p(x,p) \equiv (-\frac{\gamma}{m}p - B\partial_p)P^{\rm s}(x,p) = 0$$

does vanish. The "reversible" part $J^{\rm s,rev}_p(x,p) \equiv -(\partial_x U(x))P^{\rm s}(x,p)$ satisfies

$$\partial_x J^{\rm s}_x + \partial_p J^{\rm s,rev}_p = 0$$

③ <u>Driven colloidal particle in a periodic potential</u>

- Overdamped limit: Friction is so large that inertia term can be negelcted. In 1d,

$$\dot{x} = \gamma^{-1}f(x) + \eta(t), \quad \langle \eta(t)\eta(t')\rangle = 2D\delta(t-t'),$$

  where $D = B\gamma^{-2}$.

- In equilibrium Einstein relation holds; $B = \gamma(k_BT)$ or $D = (k_BT)/\gamma$.

- Stationary state satisfies
$$\frac{d}{dx}\left(-\gamma^{-1}f(x)+D\frac{d}{dx}\right)P^{\rm s}(x)=0$$
- If $f(x)=-V'(x)+F$ where $V(x)$ is a periodic potential and F is a uniform drive, one can have Nonequilibrium steady state (NESS) described by $P^{\rm s}$
- Nonzero stationary current
$$J^{\rm s}=\gamma^{-1}f(x)P^{\rm s}(x)-DP^{\rm s\prime}(x)\neq 0.$$
- Detailed Balance is broken

Detailed Balance

The Fokker-Planck equation can be written as

$$\frac{\partial}{\partial t}P(\boldsymbol{x},t)=\int d\boldsymbol{x}'\ \left[W_{\boldsymbol{x},\boldsymbol{x}'}\ P(\boldsymbol{x}',t)-W_{\boldsymbol{x}',\boldsymbol{x}}P(\boldsymbol{x},t)\right],$$

where $W_{\boldsymbol{x},\boldsymbol{x}'}$ is the transition rate from $\boldsymbol{x}'$ to $\boldsymbol{x}$ given by

$$W_{\boldsymbol{x},\boldsymbol{x}'}=-\mathtt{L}(\boldsymbol{x})\delta(\boldsymbol{x}-\boldsymbol{x}')=\left[-\sum_i\partial_i f_i(\mathrm{x})+\sum_{i,j}D_{ij}\partial_i\partial_j\right]\delta(\boldsymbol{x}-\boldsymbol{x}')$$

The Detailed Balance condition for the stationary state distribution is defined by

$$\boxed{W_{\boldsymbol{x},\boldsymbol{x}'}P^{\rm s}(\boldsymbol{x}')=W_{\boldsymbol{\epsilon x}',\boldsymbol{\epsilon x}}P^{\rm s}(\boldsymbol{\epsilon x})},$$

where $\epsilon_i=+1$ if x_i is even (e.g. position) and $\epsilon_i=-1$ if x_i is odd (e.g. momentum).

$$\begin{aligned}
(\text{l.h.s.})=&-\mathtt{L}(\boldsymbol{x})\delta(\boldsymbol{x}-\boldsymbol{x}')P^{\rm s}(\boldsymbol{x}')=-\mathtt{L}(\boldsymbol{x})P^{\rm s}(\boldsymbol{x})\delta(\boldsymbol{x}-\boldsymbol{x}')\\
=&-\left(\mathtt{L}(\boldsymbol{x})P^{\rm s}(\boldsymbol{x})\right)\delta(\boldsymbol{x}-\boldsymbol{x}')+\sum_i\left(-f_i(\boldsymbol{x})P^{\rm s}(\boldsymbol{x})+2\sum_j D_{ij}\left(\partial_j P^{\rm s}(\boldsymbol{x})\right)\right)\partial_i\delta(\boldsymbol{x}-\boldsymbol{x}')\\
&+\sum_{i,j}D_{ij}\partial_i\partial_j\delta(\boldsymbol{x}-\boldsymbol{x}')
\end{aligned}$$

$$\begin{aligned}
(\text{r.h.s.})=&\left[-\sum_i\epsilon_i\partial'_i f_i(\boldsymbol{\epsilon x}')+\sum_{i,j}\epsilon_i\epsilon_j D_{ij}\partial'_i\partial'_j\right]\delta(\boldsymbol{x}'-\boldsymbol{x})P^{\rm s}(\boldsymbol{\epsilon x})\\
=&P^{\rm s}(\boldsymbol{\epsilon x})\left[-\sum_i\epsilon_i\partial'_i f_i(\boldsymbol{\epsilon x}')+\sum_{i,j}\epsilon_i\epsilon_j D_{ij}\partial'_i\partial'_j\right]\delta(\boldsymbol{x}'-\boldsymbol{x})\\
=&P^{\rm s}(\boldsymbol{\epsilon x})\left[\sum_i\epsilon_i f_i(\boldsymbol{\epsilon x})\partial_i+\sum_{i,j}\epsilon_i\epsilon_j D_{ij}\partial_i\partial_j\right]\delta(\boldsymbol{x}-\boldsymbol{x}')\equiv-P^{\rm s}(\boldsymbol{\epsilon x})\mathtt{L}^\dagger(\boldsymbol{\epsilon x})\delta(\boldsymbol{x}-\boldsymbol{x}')
\end{aligned}$$

- Coefficient of $\delta(\boldsymbol{x}-\boldsymbol{x}')$: $\boxed{\mathtt{L}(\boldsymbol{x})P^{\rm s}(\boldsymbol{x})=0}$ (Stationarity)
- Coefficient of $\partial_i\delta(\boldsymbol{x}-\boldsymbol{x}')$:
$$-f_i(\boldsymbol{x})P^{\rm s}(\boldsymbol{x})+2\sum_j D_{ij}\left(\partial_j P^{\rm s}(\boldsymbol{x})\right)=\epsilon_i f_i(\boldsymbol{\epsilon x})P^{\rm s}(\boldsymbol{\epsilon x})$$

- Coefficient of $\partial_i \partial_j \delta(\boldsymbol{x}-\boldsymbol{x}')$: $\boxed{D_{ij} P^{\rm s}(\boldsymbol{x}) = \epsilon_i \epsilon_j D_{ij} P^{\rm s}(\boldsymbol{\epsilon x})} \rightarrow \boxed{P^{\rm s}(\boldsymbol{x}) = P^{\rm s}(\boldsymbol{\epsilon x})}$

  The second condition for DB becomes

$$\boxed{f_i^{\rm ir}(\boldsymbol{x}) P^{\rm s}(\boldsymbol{x}) - \sum_j D_{ij} \partial_j P^{\rm s}(\boldsymbol{x}) \equiv J_i^{\rm s,ir}(\boldsymbol{x}) = 0}$$

or

$$f_i^{\rm ir}(\boldsymbol{x}) = -\sum_j D_{ij} \partial_j \phi(\boldsymbol{x}), \quad \text{where} \;\; P^{\rm s}(\boldsymbol{x}) = e^{-\phi(\boldsymbol{x})}$$

The total stationary current $J_i^{\rm s} = J_i^{\rm s,rev} + J_i^{\rm s,ir}$: The first condition becomes

$$\boxed{\sum_i \partial_i J_i^{\rm s,rev}(\boldsymbol{x}) = \sum_i \partial_i (f_i^{\rm rev}(\boldsymbol{x}) P^{\rm s}(\boldsymbol{x})) = 0}$$

- Define $\boldsymbol{f} \equiv \boldsymbol{f}^{\rm rev} + \boldsymbol{f}^{\rm ir}$:

$$f_i^{\rm rev}(\boldsymbol{x}) \equiv \frac{1}{2}[f_i(\boldsymbol{x}) - \epsilon_i f_i(\boldsymbol{\epsilon x})], \quad f_i^{\rm ir}(\boldsymbol{x}) \equiv \frac{1}{2}[f_i(\boldsymbol{x}) + \epsilon_i f_i(\boldsymbol{\epsilon x})]$$

- $f_i^{\rm rev}(\boldsymbol{\epsilon x}) = -\epsilon_i f_i^{\rm rev}(\boldsymbol{x})$ behaves like $\dot{x}_i$ and $f_i^{\rm ir}(\boldsymbol{\epsilon x}) = \epsilon_i f_i^{\rm ir}(\boldsymbol{x})$ behaves opposite to $\dot{x}_i$ under time reversal.
- For example,

$$\dot{x} = \underbrace{p/m}_{f_x^{rev}}, \qquad \dot{p} = \underbrace{-(\gamma/m)p}_{f_p^{ir}} \underbrace{-U'(x)}_{f_p^{rev}} + \xi$$

- For an overdamped case,

$$\gamma \dot{x} = \underbrace{f(x)}_{f_x^{ir}} + \xi$$

3 Fluctuation-Response Relations

3.1 Microscopic Level: Linear Response Theory

Contents

Linear Response Theory

- The von Neumann eq. for the density operator

$$\frac{\partial \rho}{\partial t} = -\frac{i}{\hbar}[H, \rho] \equiv -\mathcal{L}\rho$$

- Add to a stationary Hamiltonian H_0 a small time-dep. perturbation

$$H = H_0 - \lambda(t) B, \qquad B^\dagger = B$$

- Then $\mathcal{L}(t) = \mathcal{L}_0 + \mathcal{L}_1(t)$, where

$$\mathcal{L}_1(\cdot) = -\frac{i}{\hbar}[B, \cdot]\lambda(t)$$

- Write $\rho = \rho_0 + \rho_1$ with $\dot{\rho}_0 = -\mathcal{L}_0 \rho_0$. Then

$$\partial_t \rho_1 = -\mathcal{L}_0 \rho_1 - \mathcal{L}_1 \rho_0 + O(\lambda^2)$$

- The solution with initial condition $\rho_1(-\infty) = 0$ is

$$\rho_1(t) = -\int_{-\infty}^{t} dt' \; e^{-\mathcal{L}_0(t-t')} \mathcal{L}_1(t') \rho_0$$

- Suppose initially $\rho(-\infty) = \rho_0(-\infty) = (1/Z) \exp[-\beta H_0] = \rho_{\text{eq}}$, the equilibrium distribution. Then

$$\rho(t) = \rho_{\text{eq}} - \int_{-\infty}^{t} dt' \; e^{-\mathcal{L}_0(t-t')} \mathcal{L}_1(t') \rho_{\text{eq}}$$

- The expectation value of an observable A is given by

$$\langle A \rangle_t = \mathsf{Tr}[A\rho(t)] = \langle A \rangle_0 + \frac{i}{\hbar} \int_{-\infty}^{t} dt' \; \mathsf{Tr}\left(A e^{-\mathcal{L}_0(t-t')} [B, \rho_{\text{eq}}] \right) \lambda(t')$$

- Note that for any operator X satisfying $\dot{X} = -\mathcal{L}_0 X = -(i/\hbar)[H_0, X]$, the solution can be expressed in two different ways as

$$e^{-\mathcal{L}_0 t} X = e^{-iH_0 t/\hbar} \; X \; e^{iH_0 t/\hbar}$$

- Therefore, we have

$$\begin{aligned}
\langle A \rangle_t =& \langle A \rangle_0 + \frac{i}{\hbar} \int_{-\infty}^{t} dt' \; \mathsf{Tr}\left(A e^{-iH_0(t-t')/\hbar} [B, \rho_{\text{eq}}] e^{iH_0(t-t')/\hbar} \right) \lambda(t') \\
=& \langle A \rangle_0 + \frac{i}{\hbar} \int_{-\infty}^{t} dt' \; \mathsf{Tr}\left([A(t), B(t')] \rho_{\text{eq}} \right) \lambda(t') \\
\equiv& \langle A \rangle_0 + \int_{-\infty}^{\infty} dt' \; \chi_{AB}(t-t') \lambda(t')
\end{aligned}$$

  where $A(t) \equiv \exp(iH_0 t/\hbar) A \exp(-iH_0 t/\hbar)$ and similarly defined $B(t')$ are Heisenberg operator w.r.t. H_0 (interaction picture).

- Linear susceptibility (Response function) χ is obtained as

$$\boxed{\chi_{AB}(t-t') = \frac{i}{\hbar} \langle [A(t), B(t')] \rangle_0 \Theta(t-t')}$$

- $\Theta(t-t')$ signifies the causality.

- Dropping Θ function, define another function

$$\chi''_{AB}(t) \equiv \frac{1}{2\hbar} \langle [A(t), B(0)] \rangle_0 = \frac{1}{2\hbar} [C_{AB}(t) - C_{BA}(-t)],$$

  where $C_{AB}(t-t') \equiv \langle A(t) B(t') \rangle_0$ is the equilibrium correlation function.

- The Fourier transform satisfies

$$\tilde{\chi}''_{AB}(\omega) = \frac{1}{2\hbar} [\tilde{C}_{AB}(\omega) - \tilde{C}_{BA}(-\omega)]$$

- Using $\tilde{C}_{BA}(-\omega) = e^{-\beta\hbar\omega}\tilde{C}_{AB}(\omega)$ (proved in the next slide), we have the Fluctuation-Dissipation Theorem

$$\boxed{\tilde{\chi}''_{AB}(\omega) = \frac{1}{2\hbar}[1 - e^{-\beta\hbar\omega}]\tilde{C}_{AB}(\omega)}$$

- In the classical limit, $\tilde{\chi}''_{AB}(\omega) = \frac{1}{2}\beta\omega\tilde{C}_{AB}(\omega)$, or $\chi''_{AB}(t) = \frac{i}{2}\beta\frac{d}{dt}C_{AB}(t)$

$$\begin{aligned}\chi_{AB}(t-t') &= 2i\Theta(t-t')\chi''_{AB}(t-t') \\ &= -\Theta(t-t')\beta\frac{d}{dt}C_{AB}(t-t') = \Theta(t-t')\beta\frac{d}{dt'}C_{AB}(t-t').\end{aligned}$$

$$\begin{aligned}C_{AB}(t) &= \frac{1}{Z}\mathsf{Tr}[e^{-\beta H_0}e^{iH_0t/\hbar}Ae^{-iH_0t/\hbar}B] \\ &= \frac{1}{Z}\sum_{n,m} e^{-\beta E_n}e^{i(E_n-E_m)t/\hbar}\langle n|A|m\rangle\langle m|B|n\rangle\end{aligned}$$

$$\tilde{C}_{AB}(\omega) = \frac{2\pi\hbar}{Z}\sum_{n,m} e^{-\beta E_n}\langle n|A|m\rangle\langle m|B|n\rangle\delta(E_n - E_m + \hbar\omega)$$

$$\begin{aligned}\tilde{C}_{BA}(-\omega) &= \frac{2\pi\hbar}{Z}\sum_{n,m} e^{-\beta E_n}\langle n|B|m\rangle\langle m|A|n\rangle\delta(E_n - E_m - \hbar\omega) \\ &= \frac{2\pi\hbar}{Z}\sum_{n,m} e^{-\beta E_m}\langle m|B|n\rangle\langle n|A|m\rangle\delta(E_m - E_n - \hbar\omega) \\ &= e^{-\beta\hbar\omega}\frac{2\pi\hbar}{Z}\sum_{n,m} e^{-\beta E_n}\langle n|A|m\rangle\langle m|B|n\rangle\delta(E_n - E_m + \hbar\omega) \\ &= e^{-\beta\hbar\omega}\tilde{C}_{AB}(\omega)\end{aligned}$$

Example: Electrical Conductivity

- Classical treatment
- Consider a set of N particles of charge q_i located at $\boldsymbol{x}_i$.
- Apply a uniform time-varying electric field $\boldsymbol{E}(t)$.
- Interaction Hamiltonian is

  $$H_I = \sum_i q_i\Phi(\boldsymbol{x}_i),$$

  where $\Phi(\boldsymbol{x})$ is the elctrostatic potential for $\boldsymbol{E}(t) = -\boldsymbol{\nabla}\Phi(\boldsymbol{x})$. We can easily see that $\Phi(\boldsymbol{x}) = -\boldsymbol{x}\cdot\boldsymbol{E}(t)$. We have

  $$H_I = -\sum_i q_i\boldsymbol{x}_i\cdot\boldsymbol{E}(t) = -\boldsymbol{P}\cdot\boldsymbol{E}(t),$$

  where $\boldsymbol{P} \equiv \sum_i q_i\boldsymbol{x}_i$ is the total dipole moment.

- For the conductivity we have correspondences:

  $$A \Leftrightarrow \boldsymbol{J}, \quad \lambda(t) \Leftrightarrow \boldsymbol{E}(t), \quad B \Leftrightarrow \boldsymbol{P}$$

Without perturbing $\boldsymbol{E}$, we expect $\langle J_\alpha \rangle = 0$. In the presence of $\boldsymbol{E}$, we expect

$$\langle J_\alpha(t) \rangle = \int_{-\infty}^{\infty} dt' \, \chi_{\alpha\beta}(t-t') E_\beta(t').$$

We can identify that the response function is the conductivity

$$\chi_{\alpha\beta}(t-t') = \sigma_{\alpha\beta}(t-t')$$

Using the fact that $\dot{\boldsymbol{P}} = \sum_i q_i \dot{\boldsymbol{x}}_i = V\boldsymbol{J}$ in the FDR, we have

$$\boxed{\sigma_{\alpha\beta}(t) = \theta(t)\beta\langle J_\alpha(t)\dot{P}_\beta(0)\rangle = \theta(t)\beta V\langle J_\alpha(t) J_\beta(0)\rangle \equiv \theta(t)\beta V C_{\alpha\beta}(t)}$$

The Fourier-Laplace transform

$$\tilde{\sigma}_{\alpha\beta}(\omega) = \int_{-\infty}^{\infty} dt \, e^{i\omega t}\sigma_{\alpha\beta}(t) = \int_0^\infty dt \, e^{i\omega t}\sigma_{\alpha\beta}(t)$$

Using the integral representation of the theta function,

$$\theta(t) = i\int_{-\infty}^{\infty} \frac{d\omega'}{2\pi}\frac{e^{-i\omega' t}}{\omega' + i\epsilon}, \quad \epsilon = 0^+$$

we have

$$\begin{aligned}
\tilde{\sigma}_{\alpha\beta}(\omega) =& i\beta V \int_{-\infty}^{\infty} dt \, e^{i\omega t} \int_{-\infty}^{\infty} \frac{d\omega'}{2\pi}\frac{e^{-i\omega' t}}{\omega' + i\epsilon}\int_{-\infty}^{\infty}\frac{d\bar{\omega}}{2\pi}e^{-i\bar{\omega}t}\tilde{C}_{\alpha\beta}(\bar{\omega}) \\
=& i\beta V \int_{-\infty}^{\infty}\frac{d\omega'}{2\pi}\int_{-\infty}^{\infty}\frac{d\bar{\omega}}{2\pi}\frac{\tilde{C}_{\alpha\beta}(\bar{\omega})}{\omega' + i\epsilon}(2\pi)\delta(\omega - \omega' - \bar{\omega}) \\
=& -i\beta V \int_{-\infty}^{\infty}\frac{d\bar{\omega}}{2\pi}\frac{\tilde{C}_{\alpha\beta}(\bar{\omega})}{\bar{\omega} - \omega - i\epsilon} \\
=& -i\beta V \mathcal{P}\int_{-\infty}^{\infty}\frac{d\bar{\omega}}{2\pi}\frac{\tilde{C}_{\alpha\beta}(\bar{\omega})}{\bar{\omega} - \omega} + \frac{1}{2}\beta V\tilde{C}_{\alpha\beta}(\omega)
\end{aligned}$$

Longitudinal DC conductivity:

$$\begin{aligned}
\sigma_L \equiv& \frac{1}{3}\sum_\alpha \tilde{\sigma}_{\alpha\alpha}(0) \\
=& \frac{1}{3}\sum_\alpha \left[-i\beta V\mathcal{P}\int_{-\infty}^{\infty}\frac{d\bar{\omega}}{2\pi}\frac{\tilde{C}_{\alpha\alpha}(\bar{\omega})}{\bar{\omega}} + \frac{1}{2}\beta V\tilde{C}_{\alpha\alpha}(0)\right] \\
=& \frac{\beta V}{6}\sum_\alpha \tilde{C}_{\alpha\alpha}(0),
\end{aligned}$$

where we have used the fact that $C_{\alpha\alpha}(t) = C_{\alpha\alpha}(-t)$, and $\tilde{C}_{\alpha\alpha}(\omega) = \tilde{C}_{\alpha\alpha}(-\omega)$.

We finally obtain the Green-Kubo formula as

$$\boxed{\sigma_L = \frac{\beta V}{3}\sum_\alpha \int_0^\infty dt \, \langle J_\alpha(t) J_\alpha(0)\rangle}$$

3.2 Mesoscopic Level: F-P Equation

Contents

FDR / Fokker-Planck Equations

- For the F-P eq., $\partial_t P = -\mathtt{L}P$, consider the case where we apply a small time-dependent perturbation such that

$$\mathtt{L}(\boldsymbol{x},t) = \mathtt{L}_0(\boldsymbol{x}) + \mathtt{L}_1(\boldsymbol{x},t) = \mathtt{L}_0(\boldsymbol{x}) + \lambda(t)\mathtt{L}_1(\boldsymbol{x}), \quad \lambda \text{ small}$$

- Let P^{s} be the stationary solution of $\mathtt{L}_0$: $\mathtt{L}_0(\boldsymbol{x})P^{\mathrm{s}}(\boldsymbol{x}) = 0$.
- Write $P = P^{\mathrm{s}} + P_1$ then the F-P eq. becomes for small λ

$$\partial_t(P^{\mathrm{s}} + P_1) = -(\mathtt{L}_0 + \mathtt{L}_1)(P^{\mathrm{s}} + P_1), \quad \text{or} \quad \partial_t P_1 = -\mathtt{L}_0 P_1 - \mathtt{L}_1 P^{\mathrm{s}} + O(\lambda^2)$$

- The solution with initial condition $P_1(\boldsymbol{x},-\infty) = 0, P(\boldsymbol{x},-\infty) = P^{\mathrm{s}}(\boldsymbol{x})$ is

$$P_1(\boldsymbol{x},t) = -\int_{-\infty}^{t} dt'\, e^{-\mathtt{L}_0(\boldsymbol{x})(t-t')}\mathtt{L}_1(\boldsymbol{x},t')P^{\mathrm{s}}(\boldsymbol{x})$$

- The average of an observable $A(\boldsymbol{x})$ is given by

$$\langle A\rangle_t \equiv \int d\boldsymbol{x}\; P(\boldsymbol{x},t)A(\boldsymbol{x}).$$

- The response to the perturbation is studied using the response function

$$\begin{aligned} R_A(t,t') &\equiv \left.\frac{\delta\langle A\rangle_t}{\delta\lambda(t')}\right|_{\lambda=0} \\ &= -\int d\boldsymbol{x}\; A(\boldsymbol{x})e^{-\mathtt{L}_0(\boldsymbol{x})(t-t')}\mathtt{L}_1(\boldsymbol{x})P^{\mathrm{s}}(\boldsymbol{x}), \quad t > t' \end{aligned}$$

- We define the correlation function $C^0_{AB}(t,t') = \langle A(t)B(t')\rangle_0$ of two observables $A(\boldsymbol{x})$ and $B(\boldsymbol{x})$ at two different times $t > t'$ in the stationary state as

$$C^0_{AB}(t,t') = \int d\boldsymbol{x} \int d\boldsymbol{x'} A(\boldsymbol{x})P(\boldsymbol{x},t|\boldsymbol{x'},t')P^{\mathrm{s}}(\boldsymbol{x'})B(\boldsymbol{x'})$$

- The symbolic solution to the F-P eq. is $P(\boldsymbol{x},t) = \exp[-\mathtt{L}_0(\boldsymbol{x})(t-t_0)]P(\boldsymbol{x},t_0)$, so the conditional probability is $P(\boldsymbol{x},t|\boldsymbol{x'},t') = \exp[-\mathtt{L}_0(\boldsymbol{x})(t-t')]\delta(\boldsymbol{x}-\boldsymbol{x'})$

$$C^0_{AB}(t,t') = \int d\boldsymbol{x} A(\boldsymbol{x})e^{-\mathtt{L}_0(\boldsymbol{x})(t-t')}B(\boldsymbol{x})P^{\mathrm{s}}(\boldsymbol{x}), \quad t > t'$$

  For $t' > t$,

$$C^0_{AB}(t,t') = \int d\boldsymbol{x} B(\boldsymbol{x})e^{-\mathtt{L}_0(\boldsymbol{x})(t'-t)}A(\boldsymbol{x})P^{\mathrm{s}}(\boldsymbol{x}), \quad t' > t$$

- We have the Fluctuation-Response Relation

$$\boxed{R_A(t,t') = \begin{cases} C^0_{AB}(t,t'), & t > t' \\ 0, & t < t' \end{cases}}$$

  where

$$\boxed{B(\boldsymbol{x}) \equiv -\frac{1}{P^{\mathrm{s}}(\boldsymbol{x})}\mathtt{L}_1(\boldsymbol{x})P^{\mathrm{s}}(\boldsymbol{x})}$$

Examples

① Perturbation of the stationary state satisfying DB

Consider for some i

$$\dot{x}_i = f_i(\boldsymbol{x}) + \underbrace{\lambda(t)}_{perturbation} + \xi_i(t)$$

$$\mathtt{L}_1^{\mathtt{i}}(\boldsymbol{x}, t) = \lambda(t)\partial_i, \qquad \mathtt{L}_1^{\mathtt{i}}(\boldsymbol{x}) = \partial_i$$

$$B_i(\boldsymbol{x}) = -\frac{1}{P^{\mathrm{s}}(\boldsymbol{x})}\partial_i P^{\mathrm{s}}(\boldsymbol{x}) = -\sum_j [D^{-1}]_{ij} f_j^{\mathrm{ir}}(\boldsymbol{x}),$$

where we have used the DB condition, $J_i^{\mathrm{s,ir}} = f_i^{\mathrm{ir}} P^{\mathrm{s}} - \sum_j D_{ij}\partial_j P^{\mathrm{s}} = 0$.

$$\boxed{R_A^i(t,t') = -\sum_j [D^{-1}]_{ij} \langle A(t) f_j^{\mathrm{ir}}(t')\rangle_0}, \qquad t > t'$$

② Overdamped system

- In this case, $f = f^{\mathrm{ir}}$.

$$\dot{x} = \gamma^{-1} f(x) + \xi(t), \quad \langle \xi(t)\xi(t')\rangle = 2D\delta(t-t'), \qquad D = k_B T/\gamma$$

- We have

$$R_A(t,t') = -D^{-1}\gamma^{-1}\langle A(t) f(t')\rangle_0 = -\frac{1}{k_B T}\langle A(t) f(t')\rangle_0, \qquad t > t'$$

- In this case, one can show that the (r.h.s) is equal to

$$\boxed{R_A(t,t') = \frac{1}{D}\langle A(t)\dot{x}(t')\rangle_0}, \quad t > t'$$

(See the next slide for the proof.)

△ Special case: $\boxed{f = f^{\mathrm{ir}}}$: Consider (summation convention)

$$\begin{aligned}
\mathtt{L}_0(x_i P^{\mathrm{s}}(\boldsymbol{x})) =& \partial_k(f_k x_i P^{\mathrm{s}}) - \partial_k\partial_l(D_{kl} x_i P^{\mathrm{s}}) \\
=& f_i P^{\mathrm{s}} + \underbrace{x_i\partial_k(f_k P^{\mathrm{s}}) - x_i D_{kl}\partial_k\partial_l P^{\mathrm{s}}}_{x_i \mathtt{L}_0 P^{\mathrm{s}} = 0} - 2D_{ik}\partial_k P^{\mathrm{s}} = -f_i P^{\mathrm{s}}
\end{aligned}$$

For $t > t'$

$$\begin{aligned}
R_A^i(t,t') =& -[D^{-1}]_{ij}\int d\boldsymbol{x} A(\boldsymbol{x}) e^{-\mathtt{L}_0(\boldsymbol{x})(t-t')} f_j(\boldsymbol{x}) P^{\mathrm{s}}(\boldsymbol{x}) \\
=& [D^{-1}]_{ij}\int d\boldsymbol{x} A(\boldsymbol{x}) e^{-\mathtt{L}_0(\boldsymbol{x})(t-t')} \mathtt{L}_0(x_j P^{\mathrm{s}}(\boldsymbol{x})) \\
=& [D^{-1}]_{ij}\frac{d}{dt'}\langle A(t) x_j(t')\rangle_0
\end{aligned}$$

③ Brownian motion with momentum dependent irreversible force

- Consider $\dot{x} = p/m$ and

$$\dot{p} = -\frac{\gamma}{m}p + f(x) + g(p) + \xi(t), \quad \langle \xi(t)\xi(t')\rangle = 2B\delta(t-t'), \quad B = \gamma k_B T$$

- $g(p)$ is irreversible: $g(-p) = -g(p)$. Total irreversible force: $-\gamma p/m + g(p)$.
- Therefore we have

$$\begin{aligned} R_A(t,t') &= -B^{-1}\langle A(t')(-\gamma p(t')/m + g(p(t')))\rangle_0 \\ &= \frac{1}{k_B T}\langle A(t)\frac{p(t')}{m}\rangle_0 - \frac{1}{B}\langle A(t)g(p(t'))\rangle_0 \end{aligned}$$

④ Perturbation of stationary state without DB

- Consider again for some i (We also assume that $f = f^{\mathrm{ir}}$.)

$$\dot{x}_i = f_i(\boldsymbol{x}) + \lambda(t) + \xi_i(t), \quad \mathtt{L}_1^{\mathtt{i}}(\boldsymbol{x},t) = \lambda(t)\partial_i,$$

- Without assuming DB, we have for $P^{\mathrm{s}} = e^{-\phi}$,

$$\frac{J_i^{\mathrm{s}}}{P^{\mathrm{s}}} = f_i(\boldsymbol{x}) + \sum_j D_{ij}\partial_j\phi(\boldsymbol{x}) \equiv \nu_i \neq 0$$

- Then we have

$$B_i(\boldsymbol{x}) = -\frac{1}{P^{\mathrm{s}}(\boldsymbol{x})}\partial_i P^{\mathrm{s}}(\boldsymbol{x}) = \partial_i\phi(\boldsymbol{x}) = \sum_j [D^{-1}]_{ij}(\nu_j - f_j)$$

- Therefore,

$$\boxed{R_A^i(t,t') = \langle A(t)\partial_i\phi(t')\rangle = \sum_j [D^{-1}]_{ij}\langle A(t)(\nu_j(t') - f_j(t'))\rangle}, \quad t > t'$$

- We again have

$$\mathtt{L}_0(x_i P^{\mathrm{s}}(\boldsymbol{x})) = \partial_k(f_k x_i P^{\mathrm{s}}) - \partial_k\partial_l(D_{kl}x_i P^{\mathrm{s}}) = f_i P^{\mathrm{s}} - 2D_{ik}\partial_k P^{\mathrm{s}} = (2\nu_i - f_i)P^{\mathrm{s}}$$

or

$$\mathtt{L}_0(x_i P^{\mathrm{s}}) - \nu_i P^{\mathrm{s}} = (\nu_i - f_i)P^{\mathrm{s}}.$$

- Therefore, we can also write

$$\boxed{R_A^i(t,t') = \sum_j [D^{-1}]_{ij}\langle A(t)(\dot{x}_j(t') - \nu_j(t'))\rangle}, \quad t > t'$$

4 Path integral formalism

4.1 Martin-Siggia-Rose (MSR) Formalism

Contents

MSR Functional-Integral Formalism

Consider again

$$\frac{dx_i}{dt} = f_i(x(t)) + \xi_i(t), \qquad (\star)$$

where $\langle \xi_i(t) \rangle = 0$ and $\langle \xi_i(t)\xi_j(t') \rangle = 2D_{ij}\delta(t-t')$.

Let us use the distribution function $P_\xi[\boldsymbol{\xi}]$ for the Gaussian white noise, which satisfies

$$\int \mathcal{D}\boldsymbol{\xi} P_\xi[\boldsymbol{\xi}]\xi_i(t) = 0, \qquad \int \mathcal{D}\boldsymbol{\xi} P_\xi[\boldsymbol{\xi}]\xi_i(t)\xi_j(t') = 2D_{ij}\delta(t-t')$$

It is given by (summation convention)

$$\begin{aligned} P_\xi[\xi] =& \mathcal{Z}^{-1} \exp(-\frac{1}{4}\int dt\ \xi_i(t) D_{ij}^{-1}\xi_j(t)) \\ =& \mathcal{Z}^{-1} \exp(-\frac{1}{4}\int dt \int dt'\ \xi_i(t) D_{ij}^{-1}\delta(t-t')\xi_j(t')), \end{aligned}$$

where

$$\mathcal{Z} = \int \mathcal{D}\xi\ \exp(-\frac{1}{4}\int dt\ \xi_i(t) D_{ij}^{-1}\xi_j(t)).$$

Gaussian Integrals

Consider (summation convention)

$$P_0(\boldsymbol{x}) = \frac{1}{Z_0}\exp(-\frac{1}{2}x_i A_{ij} x_j),$$

where

$$Z_0 = \int \prod_i dx_i \exp[-\frac{1}{2}x_i A_{ij} x_j] = (2\pi)^{n/2}(\det \mathtt{A})^{-1/2}.$$

From

$$Z_0(b) = \int \prod_i dx_i \exp[-\frac{1}{2}x_i A_{ij} x_j + b_i x_i] = Z_0 \exp[b_i A_{ij}^{-1} b_j]$$

we have

$$\langle x_i x_j \rangle_0 = \int \prod_i dx_i\ x_i x_j P_0(\boldsymbol{x}) = \frac{1}{Z_0}\ \frac{\partial^2}{\partial b_i \partial b_j} Z_0(b)\bigg|_{\boldsymbol{b}=0} = A_{ij}^{-1}$$

$\langle x_i x_j \cdots x_n \rangle_0$ can be expressed in terms of $\langle x_i x_j \rangle_0$.

Perturbation Expansion (0-dim. field theory)

Consider for example

$$P(\boldsymbol{x}) = \frac{1}{Z}\exp(-\frac{1}{2}x_i A_{ij} x_j + \lambda \sum_i x_i^4),$$

where

$$Z = \int \prod_i dx_i \exp[-\frac{1}{2}x_i A_{ij} x_j + \lambda \sum_i x_i^4)].$$

Expand

$$\exp[\lambda \sum_i x_i^4] = 1 + \lambda \sum_i x_i^4 + \frac{1}{2}\lambda^2 \sum_i x_i^4 \sum_j x_j^4 + O(\lambda^3)$$

Express

$$\langle x_i x_j \rangle = \int \prod_i dx_i\ x_i x_j P(\boldsymbol{x})$$

in terms of $\langle x_i x_j \rangle_0$.

The transition probability is

$$P(\boldsymbol{x}_\tau, \tau | \boldsymbol{x}_0, 0) = \int \mathcal{D}\boldsymbol{\xi} \; P_\xi[\boldsymbol{\xi}] \; \delta(\boldsymbol{x}(\tau) - \boldsymbol{x}_\tau), \qquad (*)$$

where $\boldsymbol{x}(t)$ is the solution to $(\star)$ with the initial condition $\boldsymbol{x}(0) = \boldsymbol{x}_0$.

Now we use the identity

$$1 = \int \mathcal{D}\boldsymbol{x} \; \delta(\dot{\boldsymbol{x}}(t) - \boldsymbol{f}(\boldsymbol{x}(t)) - \boldsymbol{\xi}(t)) \; J[\boldsymbol{x}],$$

where

$$J[\boldsymbol{x}] = \det \left[\frac{\delta G_i[\boldsymbol{x}(t)]}{\delta x_j(t')} \right]$$

is the Jacobian with $G_i[\boldsymbol{x}(t)] \equiv \dot{x}_i(t) - f_i(\boldsymbol{x}(t))$. Using the integral representation of the delta-function,

$$1 = \int \mathcal{D}\boldsymbol{x} \int \mathcal{D}\hat{\boldsymbol{x}} \; J[\boldsymbol{x}] \exp \left[-i \sum_j \int_0^\tau dt \; \hat{x}_j(t) \{ \dot{x}_j(t) - f_j(x(t)) - \xi_j(t) \} \right]$$

Inserting this into $(*)$,

$$\begin{aligned}
&P(\boldsymbol{x}_\tau, \tau | \boldsymbol{x}_0, 0) \\
&= \int \mathcal{D}\xi P_\xi[\xi] \int_{\boldsymbol{x}(0)=\boldsymbol{x}_0}^{\boldsymbol{x}(\tau)=\boldsymbol{x}_\tau} \mathcal{D}\boldsymbol{x} \int \mathcal{D}\hat{\boldsymbol{x}} \; J[\boldsymbol{x}] \; e^{-i \sum_i \int_0^\tau dt \; \hat{x}_i(t) \{ \dot{x}_i(t) - f_i(\boldsymbol{x}(t)) - \xi_i(t) \}} \\
&= \int_{\boldsymbol{x}(0)=\boldsymbol{x}_0}^{\boldsymbol{x}(\tau)=\boldsymbol{x}_\tau} \mathcal{D}\boldsymbol{x} \int \mathcal{D}\hat{\boldsymbol{x}} \; J[\boldsymbol{x}] \exp[-S_0[\boldsymbol{x}, \hat{\boldsymbol{x}}]],
\end{aligned}$$

where

$$S_0[\boldsymbol{x}, \hat{\boldsymbol{x}}] \equiv \int_0^\tau dt \; \left\{ \sum_{i,j} \hat{x}_i(t) D_{ij} \hat{x}_j(t) + i \sum_i \hat{x}_i(t) \{ \dot{x}_i(t) - f_i(\boldsymbol{x}(t)) \} \right\}$$

The average of an observable $A[\boldsymbol{x}(t)]$ which depends on the $\boldsymbol{x}(t)$, $0 \le t \le \tau$ is given by

$$\begin{aligned}
\langle A[\boldsymbol{x}(t)] \rangle &= \int d\boldsymbol{x}_\tau \int d\boldsymbol{x}_0 \; P_i(\boldsymbol{x}_0) \int_{\boldsymbol{x}(0)=\boldsymbol{x}_0}^{\boldsymbol{x}(\tau)=\boldsymbol{x}_\tau} \mathcal{D}\boldsymbol{x} \int \mathcal{D}\hat{\boldsymbol{x}} \; J[\boldsymbol{x}] A[\boldsymbol{x}(t)] e^{-S_0[\boldsymbol{x}, \hat{\boldsymbol{x}}]} \\
&= \int \mathcal{D}\boldsymbol{x} \int \mathcal{D}\hat{\boldsymbol{x}} \; J[\boldsymbol{x}] A[\boldsymbol{x}(t)] e^{-S_0[\boldsymbol{x}, \hat{\boldsymbol{x}}]} P_i(\boldsymbol{x}_0),
\end{aligned}$$

where $P_i(\boldsymbol{x}_0)$ is the initial distribution.

This can be understood from

$$P(\boldsymbol{x}_k, t_k) = \int d\boldsymbol{x}_{\boldsymbol{k-1}} P(\boldsymbol{x}_k, t_k | \boldsymbol{x}_{k-1}, t_{k-1}) P(\boldsymbol{x}_{k-1}, t_{k-1})$$

For a finite time interval $[0, \tau]$, we divide it into M infinitesimal intervals such that $t_0 = 0$ and $t_M = \tau$, $\boldsymbol{x}_M = \boldsymbol{x}_\tau$ and $dt = \tau / M$.

$$P(\boldsymbol{x}_\tau, \tau | \boldsymbol{x}_0, 0) = \int d\boldsymbol{x}_1 \cdots d\boldsymbol{x}_{M-1} \prod_{k=1}^{M} P(\boldsymbol{x}_k, t_k | \boldsymbol{x}_{k-1}, t_{k-1})$$

Evaluation of Jacobian

$$J[\boldsymbol{x}] = \det\left[\frac{\delta G_i(\boldsymbol{x}(t))}{\delta x_j(t')}\right] \equiv \det \mathbb{M}_{ij}(t,t') = \det\left[\delta_{ij}\frac{d}{dt}\delta(t-t') - \frac{\partial f_i}{\partial x_j}\delta(t-t')\right]$$

We can write

$$\mathbb{M}_{ij}(t,t') = \sum_k \int dt'' \mathbb{M}^{(0)}_{ik}(t,t'')\mathbb{M}^{(1)}_{kj}(t'',t'),$$

where

$$\mathbb{M}^{(0)}_{ik}(t,t'') = \delta_{ik}\frac{d}{dt}\delta(t-t'')$$

and

$$\mathbb{M}^{(1)}_{kj}(t'',t') = \delta_{kj}\delta(t''-t') - \theta(t''-t')\frac{\partial f_k}{\partial x_j}$$

Note that $\det\mathbb{M} = \det\mathbb{M}^{(0)}\det\mathbb{M}^{(1)}$ and that $\det\mathbb{M}^{(0)}$ is a constant which can be absorbed into the functional integral measure.

- We therefore have

$$\begin{aligned} J[\boldsymbol{x}] =& \mathcal{N}\det\mathbb{M}^{(1)} = \mathcal{N}\exp[\operatorname{tr}\ln\mathbb{M}^{(1)}] \\ =& \mathcal{N}\exp\Big[-\theta(0)\int dt \sum_i \frac{\partial f_i(\boldsymbol{x}(t))}{\partial x_i} \\ & -\frac{1}{2}\int dt_1\int dt_2\, \theta(t_1-t_2)\theta(t_2-t_1)\sum_{i,j}\frac{\partial f_i(\boldsymbol{x}(t_1))}{\partial x_j}\frac{\partial f_j(\boldsymbol{x}(t_2))}{\partial x_i} - \cdots\Big] \end{aligned}$$

- All but the first term vanish due to the properties of the theta function.
- We therefore have

$$\boxed{J[\boldsymbol{x}] = \mathcal{N}\exp\left[-\theta(0)\int dt\sum_i \frac{\partial f_i(\boldsymbol{x}(t))}{\partial x_i}\right] \equiv \mathcal{N}\exp[-S_J[\boldsymbol{x}]]}$$

- The appearance of $\theta(0)$ is intimately related to the discretization scheme for the stochastic differential equation. (e.g. $\theta(0) = 0 \Leftrightarrow$ Itô, $\theta(0) = 1/2 \Leftrightarrow$ Stratonovich)
- More general average

$$\boxed{\langle\mathcal{O}[\boldsymbol{x},\hat{\boldsymbol{x}}]\rangle = \int\mathcal{D}\boldsymbol{x}\int\mathcal{D}\hat{\boldsymbol{x}}\ \mathcal{O}[\boldsymbol{x},\hat{\boldsymbol{x}}]e^{-S_0[\boldsymbol{x},\hat{\boldsymbol{x}}]-S_J[\boldsymbol{x}]}P_i(\boldsymbol{x}(0))}$$

Onsager-Machlup formula

- Integrating away $\hat{\boldsymbol{x}}$, we have

$$\langle A[\boldsymbol{x}]\rangle \sim \int\mathcal{D}\boldsymbol{x}A[\boldsymbol{x}]\exp[-S_{\text{OM}}[\boldsymbol{x}] - S_J[\boldsymbol{x}]]P_i(\boldsymbol{x}_0),$$

  where

$$S_{\text{OM}}[\boldsymbol{x}] = \frac{1}{4}\int_0^\tau dt\sum_{i,j}\{\dot{x}_i(t) - f_i(\boldsymbol{x}(t))\}D^{-1}_{ij}\{\dot{x}_j(t) - f_j(\boldsymbol{x}(t))\}$$

- $\exp[-S_{\text{OM}}[\boldsymbol{x}] - S_J[\boldsymbol{x}]]$ can be regarded as the probability for the path $\boldsymbol{x}(t)$

4.2 FDR and Time-Reversal Symmetry

Contents

Response functions in the MSR formalism

Consider again for some i

$$\dot{x}_i = f_i(\boldsymbol{x}) + \underbrace{\lambda_i(t)}_{perturbation} + \xi_i(t)$$

- Consider a response of an average of a local observable $\langle \mathcal{A}[\boldsymbol{x}(t)] \rangle$ at t due to a perturbation $\lambda_i(t')$ at t'.
- Linear response

$$R^i_{\mathcal{A}}(t,t') = \left. \frac{\delta \langle \mathcal{A}[\boldsymbol{x}(t)] \rangle}{\delta \lambda_i(t')} \right|_{\lambda=0}$$

- Nonlinear responses

$$R^i_{\mathcal{A}}(t;t',t'') = \left. \frac{\delta^2 \langle \mathcal{A}[\boldsymbol{x}(t)] \rangle}{\delta \lambda_i(t') \delta \lambda_i(t'')} \right|_{\lambda=0}, \quad \text{etc.}$$

- Causality: $R^i_{\mathcal{A}}(t,t') = 0$ if $t < t'$. $R^i_{\mathcal{A}}(t;t',t'') = 0$ if $t < t'$ or $t < t''$.

$$\langle \mathcal{A}[\boldsymbol{x}(t)] \rangle = \int dt'\ R^i_{\mathcal{A}}(t,t')\lambda_i(t') + \frac{1}{2}\int dt' \int dt''\ R^i_{\mathcal{A}}(t;t',t'')\lambda_i(t')\lambda_i(t'') + \cdots$$

Use of Response Field $\hat{\boldsymbol{x}}$

- In the action S_0, we have an additional term

$$-i \int dt \hat{x}_i(t) \lambda_i(t).$$

- Taking a derivative w.r.t. $\lambda_i(t')$ brings down a factor of $i\hat{x}_i(t')$ in front of the exponential.
- $\hat{x}(t)$: Response Field
- No need to introduce λ; All averages are w.r.t. the unperturbed action.

Response Field Formalism

$$R^i_{\mathcal{A}}(t,t') = \langle \mathcal{A}[\boldsymbol{x}(t)] i\hat{x}_i(t') \rangle.$$
$$R^i_{\mathcal{A}}(t;t',t'') = \langle \mathcal{A}[\boldsymbol{x}(t)] i\hat{x}_i(t') i\hat{x}_i(t'') \rangle, \quad \text{etc.}$$

Time-reversal Transformations

$\mathcal{R}$-transformation

$$\mathcal{R} : \begin{cases} \boldsymbol{x}(t) & \to \quad \boldsymbol{x}^{\mathrm{R}}(t) \equiv \boldsymbol{x}(\tau - t) \\ \hat{\boldsymbol{x}}(t) & \to \quad \hat{\boldsymbol{x}}^{\mathrm{R}}(t) \equiv \hat{\boldsymbol{x}}(\tau - t) - i\mathtt{D}^{-1} \cdot \frac{d}{dt}\boldsymbol{x}(\tau - t) \end{cases}$$

- Integration measure:

$$\mathcal{D}\boldsymbol{x}\mathcal{D}\hat{\boldsymbol{x}} = \mathcal{D}\boldsymbol{x}^{\mathrm{R}}\mathcal{D}\hat{\boldsymbol{x}}^{\mathrm{R}}$$

- Jacobian

$$
\begin{aligned}
S_J[\boldsymbol{x}] \to S_J[\boldsymbol{x}^{\mathrm{R}}] &= \theta(0)\int_0^\tau dt\, \sum_i \frac{\partial}{\partial x_i^{\mathrm{R}}} f_i(\boldsymbol{x}^{\mathrm{R}}) \\
&= \theta(0)\int_0^\tau dt\, \sum_i \frac{\partial}{\partial x_i(\tau-t)} f(\boldsymbol{x}(\tau-t)) \\
&= S_J[\boldsymbol{x}]
\end{aligned}
$$

after changing the integration variable from $t \to t' = \tau - t$.

Change in S_0:

$$
\begin{aligned}
S_0[\boldsymbol{x}^{\mathrm{R}}, \hat{\boldsymbol{x}}^{\mathrm{R}}] &= \int_0^\tau dt\Big[\{\hat{\boldsymbol{x}}(\tau-t) - i\mathtt{D}^{-1}\cdot \frac{d}{dt}\boldsymbol{x}(\tau-t)\}\cdot \mathtt{D} \\
&\qquad \cdot \{\hat{\boldsymbol{x}}(\tau-t) - i\mathtt{D}^{-1}\cdot \frac{d}{dt}\boldsymbol{x}(\tau-t)\} \\
&\quad + i\{\hat{\boldsymbol{x}}(\tau-t) - i\mathtt{D}^{-1}\cdot \frac{d}{dt}\boldsymbol{x}(\tau-t)\}\cdot\{\frac{d}{dt}\boldsymbol{x}(\tau-t) - \boldsymbol{f}(\boldsymbol{x}(\tau-t))\}\Big] \\
&= \int_0^\tau dt[\{\hat{\boldsymbol{x}}(t) + i\mathtt{D}^{-1}\cdot \frac{d}{dt}\boldsymbol{x}(t)\}\cdot \mathtt{D}\cdot\{\hat{\boldsymbol{x}}(t) + i\mathtt{D}^{-1}\cdot \frac{d}{dt}\boldsymbol{x}(t)\} \\
&\quad + i\{\hat{\boldsymbol{x}}(t) + i\mathtt{D}^{-1}\cdot \frac{d}{dt}\boldsymbol{x}(t)\}\cdot\{-\frac{d}{dt}\boldsymbol{x}(t) - \boldsymbol{f}(\boldsymbol{x}(t))\}] \\
&= S_0[\boldsymbol{x}, \hat{\boldsymbol{x}}] + \underbrace{\int_0^\tau dt\, \dot{\boldsymbol{x}}(t)\cdot \mathtt{D}^{-1}\cdot \boldsymbol{f}(\boldsymbol{x}(t))}_{\equiv \Delta S[\boldsymbol{x}]}
\end{aligned}
$$

- Suppose that (cf. DB condition)

$$
\boldsymbol{f}(\boldsymbol{x}) = -\mathtt{D}\cdot\boldsymbol{\nabla}\phi(\boldsymbol{x}), \quad \text{and} \quad P_i(\boldsymbol{x}(0)) = P^s(\boldsymbol{x}(0)) = \exp(-\phi(\boldsymbol{x}(0)))
$$

- Then

$$
\Delta S[\boldsymbol{x}] = -\int_0^\tau dt\, \dot{\boldsymbol{x}}(t)\cdot\boldsymbol{\nabla}\phi(\boldsymbol{x}) = -\int_0^\tau dt\, \frac{d}{dt}\phi(\boldsymbol{x}(t)) = -[\phi(\boldsymbol{x}(\tau)) - \phi(\boldsymbol{x}(0))].
$$

- We then have the symmetry

$$
\begin{aligned}
\langle \mathcal{O}[\boldsymbol{x}, \hat{\boldsymbol{x}}]\rangle &= \int \mathcal{D}\boldsymbol{x}\int \mathcal{D}\hat{\boldsymbol{x}}\; \mathcal{O}[\boldsymbol{x}, \hat{\boldsymbol{x}}]e^{-S_0[\boldsymbol{x},\hat{\boldsymbol{x}}]-S_J[\boldsymbol{x}]}P_i(\boldsymbol{x}(0)) \\
&= \int \mathcal{D}\boldsymbol{x}^{\mathrm{R}}\int \mathcal{D}\hat{\boldsymbol{x}}^{\mathrm{R}}\; \mathcal{O}[\boldsymbol{x}^{\mathrm{R}}, \hat{\boldsymbol{x}}^{\mathrm{R}}]e^{-S_0[\boldsymbol{x}^{\mathrm{R}},\hat{\boldsymbol{x}}^{\mathrm{R}}]-S_J[\boldsymbol{x}^{\mathrm{R}}]}P_i(\boldsymbol{x}^{\mathrm{R}}(0)) \\
&= \int \mathcal{D}\boldsymbol{x}\int \mathcal{D}\hat{\boldsymbol{x}}\; \mathcal{O}[\boldsymbol{x}^{\mathrm{R}}, \hat{\boldsymbol{x}}^{\mathrm{R}}]e^{-S_0[\boldsymbol{x},\hat{\boldsymbol{x}}]-\Delta S[\boldsymbol{x}]-S_J[\boldsymbol{x}]}P_i(\boldsymbol{x}(\tau)) \\
&= \int \mathcal{D}\boldsymbol{x}\int \mathcal{D}\hat{\boldsymbol{x}}\; \mathcal{O}[\boldsymbol{x}^{\mathrm{R}}, \hat{\boldsymbol{x}}^{\mathrm{R}}]e^{-S_0[\boldsymbol{x},\hat{\boldsymbol{x}}]-S_J[\boldsymbol{x}]+\{\phi(\boldsymbol{x}(\tau))-\phi(\boldsymbol{x}(0))\}}P_i(\boldsymbol{x}(\tau)) \\
&= \int \mathcal{D}\boldsymbol{x}\int \mathcal{D}\hat{\boldsymbol{x}}\; \mathcal{O}[\boldsymbol{x}^{\mathrm{R}}, \hat{\boldsymbol{x}}^{\mathrm{R}}]e^{-S_0[\boldsymbol{x},\hat{\boldsymbol{x}}]-S_J[\boldsymbol{x}]}P_i(\boldsymbol{x}(0)) \\
&= \langle \mathcal{O}[\boldsymbol{x}^{\mathrm{R}}, \hat{\boldsymbol{x}}^{\mathrm{R}}]\rangle
\end{aligned}
$$

In particular

$$
\langle \mathcal{A}[\boldsymbol{x}(t)]\hat{x}_i(t')]\rangle = \left\langle \mathcal{A}[\boldsymbol{x}(\tau-t)]\left\{\hat{x}_i(\tau-t') - i\sum_j [D^{-1}]_{ij}\frac{d}{dt'}x_j(\tau-t')\right\}\right\rangle
$$

or

$$R^i_{\mathcal{A}}(t,t') = R^i_{\mathcal{A}}(\tau-t,\tau-t') + \sum_j [D^{-1}]_{ij} \frac{d}{dt'} \left\langle \mathcal{A}[\boldsymbol{x}(\tau-t)] x_j(\tau-t') \right\rangle$$

By changing $\tau - t \to t$ and $\tau - t' \to t'$,

FDR 1 (DB)

$$R^i_{\mathcal{A}}(t,t') - R^i_{\mathcal{A}}(\tau-t,\tau-t') = \sum_j [D^{-1}]_{ij} \left\langle \mathcal{A}[\boldsymbol{x}(t)] \dot{x}_j(t') \right\rangle$$

$\mathcal{U}$-transformation

$$\mathcal{U}: \begin{cases} \boldsymbol{x}(t) & \to & \boldsymbol{x}^{\mathrm{U}}(t) \equiv \boldsymbol{x}(\tau-t) \\ \hat{\boldsymbol{x}}(t) & \to & \hat{\boldsymbol{x}}^{\mathrm{U}}(t) \equiv -\hat{\boldsymbol{x}}(\tau-t) + i\mathtt{D}^{-1}\cdot \boldsymbol{f}(\boldsymbol{x}(\tau-t)) \end{cases}$$

- One can show again with the same ΔS that (see Problems)

$$S_0[\boldsymbol{x}^{\mathrm{U}}, \hat{\boldsymbol{x}}^{\mathrm{U}}] = S_0[\boldsymbol{x}, \hat{\boldsymbol{x}}] + \Delta S[\boldsymbol{x}] \tag{6}$$

- The Jacobians and the measure are invariant as well.
- If the DB holds and the initial state is given by the stationary state, then

$$\langle \mathcal{O}[\boldsymbol{x}, \hat{\boldsymbol{x}}]\rangle = \langle \mathcal{O}[\boldsymbol{x}^{\mathrm{U}}, \hat{\boldsymbol{x}}^{\mathrm{U}}]\rangle \tag{7}$$

$$\left\langle \mathcal{A}[\boldsymbol{x}(t)] \hat{x}_i(t')] \right\rangle = \left\langle \mathcal{A}[\boldsymbol{x}(\tau-t)] \left\{ -\hat{x}_i(\tau-t') + i \sum_j [D^{-1}]_{ij} f_j(\boldsymbol{x}(\tau-t')) \right\} \right\rangle \tag{8}$$

FDR 2 (DB)

$$R^i_{\mathcal{A}}(t,t') + R^i_{\mathcal{A}}(\tau-t,\tau-t') = -\sum_j [D^{-1}]_{ij} \left\langle \mathcal{A}[\boldsymbol{x}(t)] f_j(\boldsymbol{x}(t')) \right\rangle \tag{9}$$

Exact symmetry of MSR action

- Consider the following transformation

  $\mathcal{E}$-transformation

$$\mathcal{E}: \begin{cases} \boldsymbol{x}(t) & \to & \boldsymbol{x}^{\mathrm{E}}(t) \equiv \boldsymbol{x}(t) \\ \hat{\boldsymbol{x}}(t) & \to & \hat{\boldsymbol{x}}^{\mathrm{E}}(t) \equiv -\hat{\boldsymbol{x}}(t) - i\mathtt{D}^{-1}\cdot (\dot{\boldsymbol{x}}(t) - \boldsymbol{f}(\boldsymbol{x}(t))) \end{cases}$$

- Unlike $\mathcal{R}$ and $\mathcal{U}$, they don't involve *time reversal.*
- One can show that it is an exact symmetry: (see Problems)

$$S_0[\boldsymbol{x}^{\mathrm{E}}, \hat{\boldsymbol{x}}^{\mathrm{E}}] = S_0[\boldsymbol{x}, \hat{\boldsymbol{x}}] \tag{10}$$

- Without assuming DB or stationary initial distribution, we have

$$\langle \mathcal{O}[\boldsymbol{x}, \hat{\boldsymbol{x}}]\rangle = \langle \mathcal{O}[\boldsymbol{x}^{\mathrm{E}}, \hat{\boldsymbol{x}}^{\mathrm{E}}]\rangle \tag{11}$$

- It follows that

$$\langle \mathcal{A}[\boldsymbol{x}(t)]\hat{x}_i(t')]\rangle = -\langle \mathcal{A}[\boldsymbol{x}(t)]\hat{x}_i(t')\rangle \\ - i\sum_j [D^{-1}]_{ij}\langle \mathcal{A}[\boldsymbol{x}(t)]\dot{x}_j(t')\rangle + i\sum_j [D^{-1}]_{ij}\langle \mathcal{A}[\boldsymbol{x}(t)]f_j(\boldsymbol{x}(t'))\rangle \tag{12}$$

- We therefore have an important identity

  Identity

$$2\sum_j D_{ij}R^j_{\mathcal{A}}(t,t') = \left\langle \mathcal{A}[\boldsymbol{x}(t)]\ \dot{x}_i(t')\right\rangle - \left\langle \mathcal{A}[\boldsymbol{x}(t)]\ f_i(\boldsymbol{x}(t'))\right\rangle$$

- This nonperturbative relation can also be obtained from the identity

$$\begin{aligned} 0 &= \int \mathcal{D}\boldsymbol{x}(t)\int \mathcal{D}\hat{\boldsymbol{x}}(t)\ \frac{\delta}{\delta\hat{x}_i(t')}\left[\mathcal{A}[\boldsymbol{x}]e^{-S_0[\boldsymbol{x},\hat{\boldsymbol{x}}]-S_J[\boldsymbol{x}]}P_i(\boldsymbol{x}(0))\right] \\ &= -2\sum_j D_{ij}\left\langle \mathcal{A}[\boldsymbol{x}(t)]\hat{x}_j(t')\right\rangle - i\left\langle \mathcal{A}[\boldsymbol{x}(t)]\dot{x}_i(t')\right\rangle + i\left\langle \mathcal{A}[\boldsymbol{x}(t)]f_i(\boldsymbol{x}(t'))\right\rangle \end{aligned}$$

- This relation can be used to study the violation of the FDR in nonequilibrium

4.3 Time-Reversal Transformations in Nonequilibrium

Contents

Use of Time-reversal Transformations in Nonequilibrium

- Consider an overdamped system driven by the time-dependent protocol λ_t

$$\gamma\dot{x} = f(x,\lambda_t) + \xi(t), \quad \text{or} \quad \dot{x} = \gamma^{-1}f(x,\lambda_t) + \eta(t),$$

  where $\langle\eta(t)\eta(t')\rangle = 2D\delta(t-t')$ and $\langle\xi(t)\xi(t')\rangle = 2D\gamma^2\delta(t-t')$ with the Einstein relation $\gamma D = T$.

- Let us apply the $\mathcal{R}$-transformation in this case

$$\begin{aligned} S_0[x^{\mathrm{R}},\hat{x}^{\mathrm{R}};\lambda] &= \int_0^\tau dt\ [D\{\hat{x}(\tau-t) - \frac{i}{D}\frac{d}{dt}x(\tau-t)\}^2 \\ &+ i\{\hat{x}(\tau-t) - \frac{i}{D}\frac{d}{dt}x(\tau-t)\}\{\frac{d}{dt}x(\tau-t) - \gamma^{-1}f(x(\tau-t),\lambda_t)\}] \\ &= \int_0^\tau dt\ [D\{\hat{x}(t) + \frac{i}{D}\frac{d}{dt}x(t)\}^2 \\ &+ i\{\hat{x}(t) + \frac{i}{D}\frac{d}{dt}x(t)\}\{-\frac{d}{dt}x(t) - \gamma^{-1}f(x(t),\lambda_{\tau-t})\}] \\ &= S_0[x,\hat{x};\lambda^{\mathrm{R}}] + \frac{1}{T}\int_0^\tau dt\ \dot{x}(t)f(x(t),\lambda^{\mathrm{R}}_t), \end{aligned}$$

  where $\lambda^{\mathrm{R}}_t \equiv \lambda_{\tau-t}$ corresponds to the reverse protocol.

- We can write this as

$$S_0[x^{\mathrm{R}},\hat{x}^{\mathrm{R}};\lambda] = S_0[x,\hat{x};\lambda^{\mathrm{R}}] + \Delta S[x;\lambda^{\mathrm{R}}],$$

  where

$$\Delta S[x;\lambda^{\mathrm{R}}] = \frac{1}{T}\int_0^\tau dt\ \dot{x}(t)f(x(t),\lambda^{\mathrm{R}}_t) = -\Delta S[x^{\mathrm{R}};\lambda]$$

- Jacobian:

$$\begin{aligned} S_J[x;\lambda] \to S_J[x^{\mathrm{R}};\lambda] &= \theta(0)\int_0^\tau dt\, \sum_i \frac{\partial}{\partial x_i^{\mathrm{R}}}[\gamma^{-1} f_i(x^{\mathrm{R}};\lambda_t)] \\ &= \theta(0)\int_0^\tau dt\, \sum_i \frac{\partial}{\partial x_i(\tau - t)}[\gamma^{-1} f(x(\tau-t);\lambda_t)] \\ &= S_J[x;\lambda^{\mathrm{R}}] \end{aligned}$$

- We again have

$$\mathcal{D}x\mathcal{D}\hat{x} = \mathcal{D}x^{\mathrm{R}}\mathcal{D}\hat{x}^{\mathrm{R}}$$

Now consider

$$\begin{aligned} & \left\langle \mathcal{O}[x,\hat{x}] e^{-\Delta S[x;\lambda] - \ln \rho_i(x(0)) + \ln \rho_f(x(\tau))} \right\rangle \\ = & \int \mathcal{D}x \int \mathcal{D}\hat{x}\; \mathcal{O}[x,\hat{x}] e^{-S_0[x,\hat{x};\lambda] - S_J[x;\lambda] - \Delta S[x;\lambda]} \frac{\rho_f(x(\tau))}{\rho_i(x(0))}\rho_i(x(0)) \\ = & \int \mathcal{D}x^{\mathrm{R}} \int \mathcal{D}\hat{x}^{\mathrm{R}}\; \mathcal{O}[x^{\mathrm{R}},\hat{x}^{\mathrm{R}}] e^{-S_0[x^{\mathrm{R}},\hat{x}^{\mathrm{R}};\lambda] - S_J[x^{\mathrm{R}};\lambda] - \Delta S[x^{\mathrm{R}};\lambda]} \rho_f(x^{\mathrm{R}}(\tau)) \\ = & \int \mathcal{D}x \int \mathcal{D}\hat{x}\; \mathcal{O}[x^{\mathrm{R}},\hat{x}^{\mathrm{R}}] e^{-S_0[x,\hat{x};\lambda^{\mathrm{R}}] - \Delta S[x;\lambda^{\mathrm{R}}] - S_J[x;\lambda^{\mathrm{R}}] + \Delta S[x;\lambda^{\mathrm{R}}]} \rho_f(x(0)) \\ = & \int \mathcal{D}x \int \mathcal{D}\hat{x}\; \mathcal{O}[x^{\mathrm{R}},\hat{x}^{\mathrm{R}}] e^{-S_0[x,\hat{x};\lambda^{\mathrm{R}}] - S_J[x;\lambda^{\mathrm{R}}]} \rho_f(x(0)) \\ \equiv & \left\langle \mathcal{O}[x^{\mathrm{R}},\hat{x}^{\mathrm{R}}] \right\rangle_{\mathrm{R}}, \qquad \cdots\cdots \quad (\dagger) \end{aligned}$$

where $\langle \cdots \rangle_{\mathrm{R}}$ is the average evaluated with the reverse protocol λ^{R} and the initial distribution ρ_f

- Note that

$$\Delta S[x;\lambda] = \frac{1}{T}\int_0^\tau dt\, \dot{x}(t) f(x(t),\lambda_t) = -\frac{1}{T}\int_0^\tau dt\, \dot{x}[-\gamma\dot{x}(t) + \xi(t)]$$

  The quantity in $[\cdots]$ is the force from the reservoir and the integral can usually be interpreted as the heat flow ΔQ into the system. We therefore have

$$\Delta S[x;\lambda] = -\frac{\Delta Q}{T} = \Delta S_{\mathrm{env}}$$

  which is the entropy change in the environment (reservoir).

- Let us write the system entropy change as the change in Shannon entropy as

$$\Delta S_{\mathrm{sys}} = -\ln \rho_f(x(\tau)) + \ln \rho_i(x(0))$$

- The total entropy change is $\Delta S_{\mathrm{tot}} = \Delta S_{\mathrm{sys}} + \Delta S_{\mathrm{env}}$
- The above relation can the be written as

$$\boxed{\left\langle \mathcal{O}[x,\hat{x}] e^{-\Delta S_{\mathrm{tot}}} \right\rangle = \left\langle \mathcal{O}[x^{\mathrm{R}},\hat{x}^{\mathrm{R}}] \right\rangle_{\mathrm{R}}}$$

Integral Fluctuation Theorem

- For $\mathcal{O} = 1$, we have the integral fluctuation theorem

$$\boxed{\left\langle e^{-\Delta S_{\rm tot}} \right\rangle = 1}.$$

From Jensen's inequality $\langle e^x \rangle \geq e^{\langle x \rangle}$, the thermodynamic 2nd law follows

$$\langle \Delta S_{\rm tot} \rangle \geq 0$$

- For $\mathcal{O} = \mathcal{A}[x(t)]\hat{x}(t')$, we have a generalized FDR

$$\left\langle \mathcal{A}[x(t)]\hat{x}(t')e^{-S_{\rm tot}[x;\lambda]} \right\rangle = \left\langle \mathcal{A}[x(\tau - t)] \left\{ \hat{x}(\tau - t') - \frac{i}{D}\frac{d}{dt'}x(\tau - t') \right\} \right\rangle_{\rm R}$$

Jarzynski equality

- Consider the special case where $f(x(t);\lambda_t) = -\partial_x U(x;\lambda_t)$
- We have

$$\begin{aligned} \Delta S_{\rm env} &= \frac{1}{T}\int_0^\tau dt\, \dot{x}(t) f(x(t),\lambda_t) = -\frac{1}{T}\int_0^\tau dt\, \dot{x}(t)\partial_x U(x(t),\lambda_t) \\ &= -\frac{1}{T}\int_0^\tau dt\, \left[\frac{dU}{dt} - \dot{\lambda}_t \frac{\partial U}{\partial \lambda_t}\right] = -\frac{\Delta U}{T} + \frac{\Delta W}{T}, \end{aligned}$$

where $\Delta U = U(x(\tau);\lambda_\tau) - U(x(0);\lambda_0)$ and the Jarzynski work

$$\Delta W = \int_0^\tau dt\, \dot{\lambda}_t \frac{\partial U}{\partial \lambda_t}$$

- Consider also the case where the initial and final distributions are given by Boltzmann distribution as

$$\rho_i(x(0)) = \frac{1}{Z(0)} e^{-U(x(0);\lambda_0)/T}, \qquad \rho_f(x(\tau)) = \frac{1}{Z(\tau)} e^{-U(x(\tau);\lambda_\tau)/T}$$

- The system entropy change is

$$\Delta S_{\rm sys} = -\ln \rho_f(x(\tau),\lambda_\tau) + \ln \rho_f(x(0),\lambda_0) = \frac{1}{T}(\Delta U - \Delta F),$$

where $\Delta F = -T\ln Z(\tau) + T\ln Z(0)$ is the free energy difference.

- The total entropy change is

$$\Delta S_{\rm tot} = \Delta S_{\rm env} + \Delta S_{\rm sys} = \frac{\Delta W}{T} - \frac{\Delta F}{T}$$

- Applying this to Eq. (†), we have

$$e^{\Delta F/T} \left\langle \mathcal{O}[x,\hat{x}] e^{-\Delta W/T} \right\rangle = \left\langle \mathcal{O}[x^{\rm R},\hat{x}^{\rm R}] \right\rangle_{\rm R0},$$

where $\langle \cdots \rangle_{\rm R0}$ is the average using the reverse protocol and the Boltzmann distribution as an initial one.

- When $\mathcal{O} = 1$,

$$\boxed{\langle e^{-\Delta W} \rangle = e^{-\Delta F}}, \qquad \Rightarrow \langle \Delta W \rangle \geq \Delta F$$

5 Problems

Problem 1

Consider for a set of variables $\mathbf{a}(t) = \{a_i(t)\}$, $i = 1, 2, \ldots, N$

$$\frac{da_i}{dt} = \sum_j G_{ij} a_j + \xi_i(t), \quad \text{or} \quad \frac{d\mathbf{a}}{dt} = \mathtt{G} \cdot \mathbf{a} + \boldsymbol{\xi}(t),$$

where

$$\langle \xi_i(t) \rangle = 0, \qquad \langle \xi_i(t) \xi_j(t') \rangle = 2B_{ij}\delta(t - t')$$

The dissipation matrix $\mathtt{G} = \{G_{ij}\}$ is not necessarily a symmetric matrix whose eigenvalues have *negative* real parts. In the long time limit, we expect $\langle a_i(t) a_j(t) \rangle$ approaches the equilibrium value $\langle a_i a_j \rangle_{\text{eq}} = M_{ij}$. ($\mathtt{B}$ and $\mathtt{M}$ are by definition symmetric matrices.)

Find the relationship among the matrices $\mathtt{G}$, $\mathtt{B}$ and $\mathtt{M}$. (Hint: Try $\mathbf{a}(t) = e^{\mathtt{G}t} \cdot \mathbf{b}(t)$.)

Problem 2

In the Caldeira-Leggett model, $B(t)$ defined in Eq. (4) plays role of stochastic force from the bath.

(a) Show that

$$\langle B(t) \rangle = 0$$

$$\langle [B(t), B] \rangle = [B(t), B] = -\frac{2i\hbar}{\pi} \int_0^\infty d\omega\, J(\omega) \sin(\omega t)$$

$$\langle \{B(t), B\} \rangle = \frac{2\hbar}{\pi} \int_0^\infty d\omega\, J(\omega) \coth(\frac{1}{2}\beta\hbar\omega) \cos(\omega t),$$

where the average is evaluated with respect to the bath Hamiltonian, i.e. $\langle \cdots \rangle = \mathsf{Tr}[\rho_B(\cdots)]$ where $\rho_B = (1/Z)e^{-\beta H_B}$ with $Z = \mathsf{Tr}e^{-\beta H_B}$.

(b) Show that in the classical limit $\beta\hbar\omega \ll 1$,

$$\frac{1}{2}\langle \{B(t), B\} \rangle = k_B T \gamma(t)$$

Problem 3

In the Caldeira-Leggett Hamiltonian, Eq. (3), let us assume that the coupling between the system and the bath is nonlinear in system coordinates (but still linear in bath coordinates; we want an exact solution for the bath.). For example, suppose for an arbitrary $F(x)$,

$$H_I = -F(x) \sum_j \kappa_j q_j$$

and the corresponding counter term. Derive the final form for the quantum generalized Langevin equation corresponding to Eq. (5).

Problem 4

For a free quantum Brownian particle, the equation of motion is given by Eq. (5) with $U(x) = 0$. Let us assume the bath oscillators satisfy the Ohmic property, i.e. $J(\omega) = \gamma\omega$, then the equation looks very similar to the (Markov) Langevin equation Eq. (1) for the classical Brownian motion. Using the solution of the form Eq. (2), find the expressions for the average kinetic energy

$$\frac{1}{2m}\langle p^2(t) \rangle$$

and the mean square displacement

$$\langle [x(t) - x(t')]^2 \rangle$$

for the quantum Brownian motion. Try to separate out the terms that diverge when the frequency cutoff goes to infinity. This is related to the vacuum energy fluctuations of the bath oscillators. Find the asymptotic expressions in the long time limit. Check whether these expressions approach the known classical results .

Problem 5

Derive Eqs. (6)$\sim$(9) for $\mathcal{U}$-transformations and Eqs. (10)$\sim$(12) for $\mathcal{E}$-transformations