Lecture

I

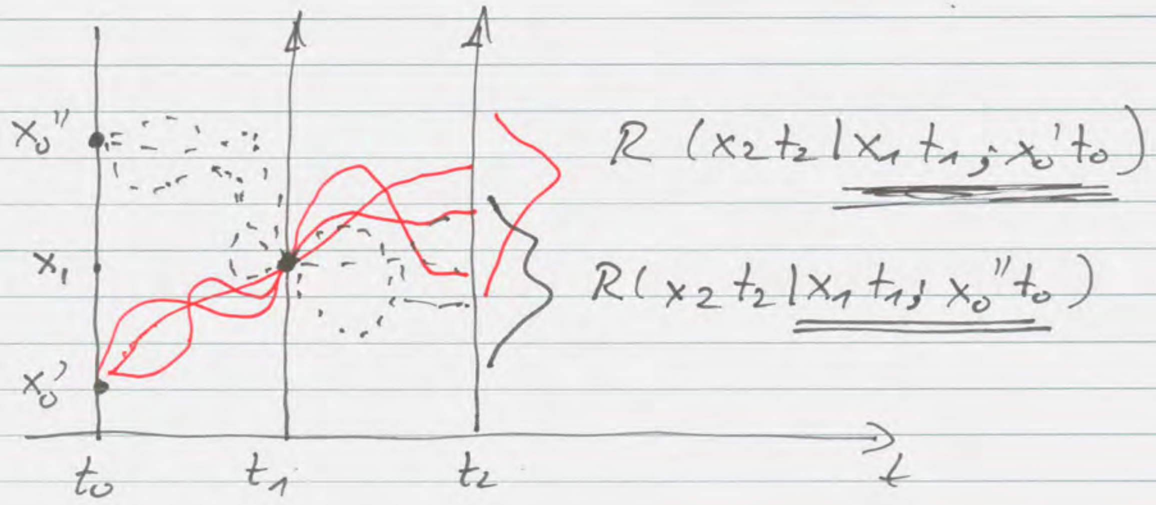
1 + 2

Fluctuation Theorems

(1) Response Theory & Fluctuations

(2) A Primer on the 2-nd Law

(3) Work-Theorems (mostly classical) & Relation to the Second Law



<u>Note</u> $R(x_2 t_2 | x_1 t_1)$ depends generally on $p_0(x_0)$

e.g. $p_0(x_0) = \delta(x - x_0')$

$$R(x_2 t_2 | x_1 t_1) = \frac{p_2(x_2 t_2, x_1 t_1)}{p(x_1 t_1)}$$

$$p(x_1 t_1) = \int R(x_1 t_1 | x_0 t_0)\, p_0(x_0)\, dx_0$$

$$p_2(x_2 t_2, x_1 t_1) = \int \frac{p_3(x_2 t_2, x_1 t_1, x_0 t_0)}{p_2(x_1 t_1, x_0 t_0)} \cdot \frac{p_2(x_1 t_1, x_0 t_0)}{p_0(x_0)} \cdot p(x_0)\, dx_0$$

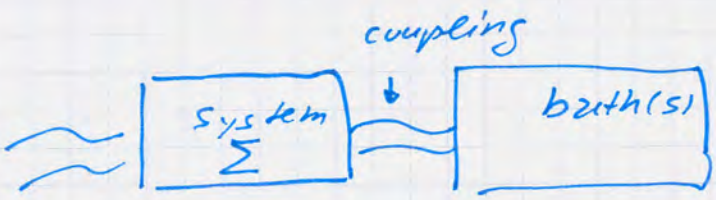
$$= \int R(x_2 t_2 | x_1 t_1, x_0 t_0) \cdot R(x_1 t_1 | x_0 t_0)\, \underbrace{p(x_0)}_{\delta(x_0 - x_0')}\, dx_0$$

$$= R(x_2 t_2 | x_1 t_1, x_0' t_0)\; p(x_1 t_1)$$

$$\Rightarrow \underline{R(x_2 t_2 | x_1 t_1)} = \frac{p_2(x_2 t_2, x_1 t_1)}{p(x_1 t_1)} = \underline{R(x_2 t_2 | x_1 t_1, x_0' t_0)}$$

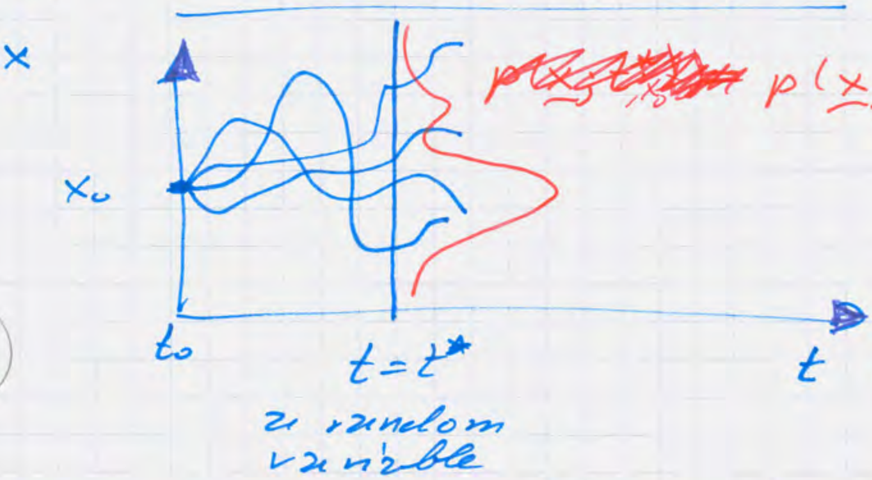
$R(x_2 t_2 | x_1 t_1)$ depends on $\underline{p_0}$!

$$p(t + dt) = \underbrace{R(t + dt | t)}_{\text{funct of } p_0}\, p(t)$$



$\underline{x}$: state variables
those are subject to
(1) Fluctuations from baths
(2) external forces acting on the system.

$\underline{x}(t)$: a stochastic process



include Detour!

$p(\underline{x}, t^* | \underline{x}_0, t = t_0)$

can be chosen randomly $\rho(\underline{x}_0)$

$p(x, t = t^*)$
$= \int d\underline{x}_0\, \rho(\underline{x}_0)\, p(\underline{x} t^* | \underline{x}_0 t_0)$

$p(\underline{x}\ t_0) \rightarrow p(\underline{x}, t^*) \rightarrow p(\underline{x}; t)$
Undergoes a time evolution!

$\dot{p}(\underline{x}, t) = \Pi\, p(\underline{x}, t)$: master operator
(Markov-processes!)

Markov:

Propagator

$$p^{(n)}(\underline{x}_n t_n, \ldots, \underline{x}_0 t_0) = R(\underline{x} t_n | \underline{x}_{n-1} t_{n-1})\, R(x_{n-1} t_{n-1} | x_{n-2} t_{n-2}) \times \ldots R(\underline{x}_1 t_1 | \underline{x}_0 t_0)\, p(\underline{x}_0, t_0)$$

non-Markov:

$$p(t) = R(t|t_0)\, p(t_0)$$
$$\dot{p}(t) = \underbrace{\dot{R}(t|t_0)\, R^{-1}(t|t_0)}\, p(t)$$
$$= \Pi_{t_0}(t)\, p(t)$$

Detour

normal vs. anomalous diffusion

normal:

$$\dot{p}(x,t) = D \frac{\partial^2}{\partial x^2} p(x,t)$$

more general $\dot{p}(x,t) = \frac{\partial}{\partial x} D(x) \frac{\partial}{\partial x} p(x,t)$

$$\left(j(x,t) = -D(x) \frac{\partial p}{\partial x} \Rightarrow \dot{p} + \mathrm{div}\, j = 0 \Rightarrow \dot{p} = \frac{\partial}{\partial x} D(x) \frac{\partial}{\partial x} p \right)$$

position-position-correlation

$$\langle x(t)\, x(s) \rangle = \phi(t,s)$$

$$\langle [x(t) - x(s)]^2 \rangle = \langle x^2(t) \rangle + \langle x^2(s) \rangle - 2\phi(t,s)$$

stationary increments

$$\langle [x(t) - x(s)]^2 \rangle = \langle x^2(t-s) \rangle$$

Thus: $\phi(t,s) = \frac{1}{2} \left[\langle x^2(t) \rangle + \langle x^2(s) \rangle - \langle x^2(t-s) \rangle \right]$

anomalous diffusion

$$\langle [x(t) - x(s)]^2 \rangle = \langle x^2(t-s) \rangle = \underline{\underline{K(t-s)^\alpha}}, \quad t > s$$

example fract. Brownian motion
with $\langle x^2(t) \rangle = K t^\alpha \Rightarrow \phi(t,s) = \frac{K}{2} \left(t^\alpha + s^\alpha - |t-s|^\alpha \right)$

independent increments

$$t > s; \quad \phi(t,s) = \langle x(t) x(s) \rangle = \langle [x(s) + \underbrace{\{x(t) - x(s)\}] x(s)}_{= 0} \rangle$$

$$\Rightarrow \phi(t,s) = \langle x(t) x(s) \rangle = \langle x^2(s) \rangle$$

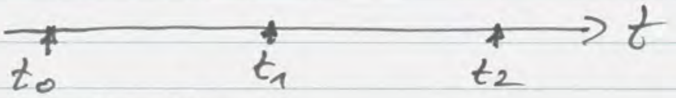
$\Rightarrow \langle [x(t)-x(s)]^2 \rangle = \langle x^2(t)\rangle + \langle x^2(s)\rangle - 2\langle x^2(s)\rangle$

$= \langle x^2(t)\rangle - \langle x^2(s)\rangle$

with $\langle x^2(t)\rangle = Kt^\alpha$

$\Rightarrow \langle [x(t)-x(s)]^2\rangle = K(t^\alpha - s^\alpha)$

same only for $\alpha = 1$ (normal diffusion)



preparation time!

stationary increments:

$\langle [x(t_2-t_0) - x(t_1-t_0)]^2\rangle = \langle x^2(t_2 - t_0 - \{t_1 - t_0\})\rangle = K(t_2-t_1)^\alpha$

NO AGE

uncorrelated increments (independent)

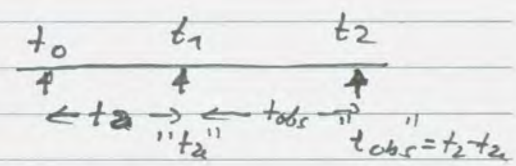
$\langle [x(t_2 - t_0) - x(t_1-t_0)]^2\rangle = K[(t_2-t_0)^\alpha - (t_1-t_0)^\alpha]$

→ can determine AGE of system dynamics (CTRW, ..., Fractional F-P-eqs.)

age of the system at the beginning of observation

$t_{a,\,\text{Anfang}} = t_1 - t_0$

$t_{observation} = t_2 - t_a$



~~Ex~~ $\cancel{t_1 = t_a + t_0};\ \cancel{t_{obs} + t_a = t_2 - t_0} + t_a$

$\langle x^2(t_{obs}, t_a)\rangle = K[(t_{obs}+t_a)^\alpha - t_a^\alpha] = K t_a^\alpha \left[\left(\frac{t_{obs}}{t_a}+1\right)^\alpha - 1\right]$

$t_{obs} \ll t_a$

fully aging

$\sim (\cancel{1} + \alpha \frac{t_{obs}}{t_a} - \cancel{1})$

$\langle x^2(t_{obs}, t_a)\rangle \simeq K_\alpha t_a^{\alpha-1} t_{obs}$

age-dependent diffusion

examples

I. Focker-Planck-eq.:

$$\dot{p}(\underline{x},t) = -\frac{\partial}{\partial \underline{x}} \underline{j}(x,t) \Leftrightarrow \dot{p} + \mathrm{div}\, \underline{j} = 0$$

conservation of probability

$$= -\frac{\partial}{\partial \underline{x}} \left\{ \underline{f}(\underline{x})\, p(\underline{x},t) - \underline{\underline{D}}(\underline{x}) \frac{\partial}{\partial \underline{x}} p(\underline{x},t) \right\}$$

$\Updownarrow$ relation to a stochastic diff. eq.

$$\underline{\underline{D}}(\ldots) = \underline{\underline{g}}(\ldots)\, \underline{\underline{g}}^t(\ldots) \qquad \dot{\underline{x}} = \underline{f}(\underline{x}) + \underline{\underline{g}}(\underline{x}) \,:\, \frac{d\underline{w}(t)}{dt}$$

$\uparrow$ stoch. calculus

$t \quad t+dt$

Ito S post-point

Ito $\rightarrow \underline{\underline{D}}(\underline{x}) \frac{\partial^2}{\partial \underline{x}^2} p(\underline{x},t)$

Stratonovich $\rightarrow \frac{\partial}{\partial \underline{x}} \underline{\underline{g}}(x) \frac{\partial}{\partial \underline{x}} \underline{\underline{g}}(x)\, p(\underline{x},t)$

Hänggi (postpoint) $\frac{\partial}{\partial \underline{x}} \underline{\underline{D}}(\underline{x}) \frac{\partial}{\partial \underline{x}} p(\underline{x},t)$ (transport form)

II. Liouville eq.

$\underline{X} \rightarrow$ phase space $(q_1, p_1, q_2, p_2, \ldots q_N, p_N)$

Poisson bracket: $\{f,g\} = \sum_i \left\{ \frac{\partial f}{\partial p_i} \frac{\partial g}{\partial q_i} - \frac{\partial f}{\partial q_i} \frac{\partial g}{\partial p_i} \right\}$

$$\dot{p}(\underline{X},t) = \{ H(\underline{X}), p(\underline{X},t) \}$$

Now: perturbation acting on system only

$$H_0 \rightarrow H_0 - \lambda(t)\, Q(\underline{X}) \;;\quad H_0 = \frac{p^2}{2m} + U(x)$$

$$m\ddot{x} = -\frac{\partial U}{\partial x} + \lambda(t) + \sqrt{2 D(x)} :: \frac{dw}{dt}$$

$$\Leftrightarrow \Gamma(t) = \Gamma_0 - \lambda(t) \frac{\partial}{\partial x} \;;\quad \dot{p}(\underline{x},t) = \Gamma_0\, p(\underline{x},t) - \lambda(t) \frac{\partial}{\partial x} p(\underline{x},t)$$

Linear Response Theory

$$\Gamma_{total} = \underset{\text{no perturbation}}{\Gamma_0} + \underset{\text{imposed perturbation}}{\Gamma_{ext}(t)}$$

we set: $\Gamma_{ext}(t) \equiv \lambda(t)\,\Omega$

$$\dot p(x,t) = \int \Gamma_{total}(x,y;t)\, p(y,t)\, dy$$

$$= \int \{\Gamma_0(x,y) + \lambda(t)\Omega(x,y)\}\, p(y,t)\,dy$$

conservation of probability

$$\Rightarrow \int \Gamma(x,y;t)\,dx = 0 \Leftrightarrow \int \Gamma_0(x,y)\,dx = 0 \;\&\; \int \Omega(x,y)\,dx = 0$$

Dyson-Eq.

$$\dot p = (\Gamma + \Gamma_{ext})\, p$$

$$p(t) = R(t|s)\,p(s) \;;\; R(t|s)\text{: Propagator}$$

$$\Rightarrow \dot p(t) = \dot R(t|s)\,p(s)$$

$$= \Gamma(t)\underbrace{R(t|s)\,p(s)}_{p(t)} = \Gamma(t)\,p(t)$$

$$\boxed{\dot R(t|s) = (\Gamma_0 + \Gamma_{ext}(t))\,R(t|s)} \;;\; R(t|t) = R(t_0|t_0) = \mathbb{1}$$

$$\langle x|R(t_0|t_0)|y\rangle = \delta(x-y)$$

solution: $t \geq t_0;\; s \geq t_0;\; t \geq s$

EXACT: $$R(t|t_0) = R_0(t|t_0) + \int_{t_0}^{t} R_0(t|s)\,\Gamma_{ext}(s)\,R(s|t_0)\,ds$$

$$\dot R(t|t_0) = \Gamma_0\, R_0(t|t_0) + \Gamma_0 \int_{t_0}^{t} R_0(t|s)\,\Gamma_{ext}(s)\,R(s|t_0)\,ds$$

$$\Gamma_0\, R(t|t_0)$$

$$+ \underbrace{R_0(t|t)}_{\mathbb{1}}\,\Gamma_{ext}(t)\,R(t|t_0)$$

$$= (\Gamma_0 + \Gamma_{ext}(t))\,R(t|t_0) \quad \text{q.e.d.}$$

Linear Response

replace $R(t|s)$ with unperturbed solution

$$R(t|s) \Rightarrow R_0(t|s) = \exp \Gamma_0 (t-s)$$

$$p(t) = p_0(t) + \int_{t_0}^{t} R_0(t|s)\, \cancel{\lambda(s)}\, \Omega\, p_0(s)$$

from now on $p_0 = \bar{p}$: stationary solution $\Gamma_0 \bar{p} = 0$

consider an observable $x(t)$

Linear response $\langle \delta x(t) \rangle = \langle x(t) \rangle_{p(t)} - \langle x(t) \rangle_{\bar{p}}$

$$:= \int_{t_0}^{t} \chi(t-s)\, \lambda(s)\, ds$$

where $$\chi(t-s) = \underset{\substack{\Uparrow \\ \text{causality}}}{\Theta(t-s)} \iint dx\, dy\;\, x \{\Omega \bar{p}\}(y)\, R_0(x; t-s | y)$$

Fluctuation-Theorem (Linear Response)

P. H.; Helv. Phys. Acta **51**, 202 (1978); Phys. Rep. 88: 207 (1982)

Define: $\varphi(x)\bar{p}(x) = (\Omega \bar{p})(x)$; $\int \varphi(x)\bar{p}(x) = \int [\Omega \bar{p}](x)\, dx$

$$\Rightarrow \langle \varphi(x) \rangle_{\bar{p}} = \underbrace{\int dx \Big(\underbrace{\int \Omega(x, y)\bar{p}(y)\, dy}_{[\Omega \bar{p}](x)} \Big)}_{0} \overset{!}{=} 0$$

a stationary correlation!

$$\Rightarrow \chi(t-s) = \chi(\tau) = \Theta(t-s) \langle x(\tau)\, \delta\varphi(0) \rangle_{\bar{p}}$$

$$= \cancel{\Theta(t-s) \langle \delta x(\tau)\, \delta(\ldots) \rangle_{\bar{p}}}$$

$$:= \Theta(t-s) \langle \delta x_\tau\, \varphi(x(0)) \rangle_{\bar{p}}$$

"Linear Response measures the stationary correlation between $\delta x = x(t) - \langle x \rangle_{\bar{p}}$ & $\varphi(x(0))$

alternative Result for $\chi(\tau)$

$$\Gamma(t) = \left[\Gamma_0 + \lambda(t)\,\Omega\right]_{\substack{\text{accompanying}\\ \text{frozen}}} = 0$$

linear response δp_a:

$$\Gamma_0\, \delta p_a + (\Omega \bar{p})\,\lambda(t) = 0$$

define: $\delta p_a(x;\lambda(t)) := \psi(x)\,\bar{p}(x)\,\lambda(t)$

$$\Rightarrow \quad [\Omega \bar{p}](x) = -\int \Gamma_0(x,z)\,\psi(z)\,\bar{p}(z)\,dz$$

again one can show $\langle \psi(x)\rangle_{\bar{p}} = 0$

$$\Rightarrow \chi(\tau) = -\Theta(\tau) \int\!\!\int\!\!\int x\, R_0(x;\tau|y)\,\Gamma_0(y,z)\,\psi(z)\,\bar{p}(z)\,dx\,dy\,dz$$

$$R_0 = \exp(\Gamma_0 \tau) \quad \text{with} \quad \frac{dR_0}{d\tau} = \Gamma_0 R_0(\tau) = R_0(\tau)\,\Gamma_0$$

$$= -\Theta(\tau)\,\frac{d}{d\tau} \int\!\!\int dx\,dz \;\; \delta x\; R_0(x;\tau|z)\,\psi(z)\,\bar{p}(z)$$

$$\boxed{\chi(\tau) \overset{!}{=} -\Theta(\tau)\,\frac{d}{d\tau}\,\langle \delta x(\tau)\,\psi(x(0))\rangle_{\bar{p}}}$$

2-nd Fluctuation-Theorem

Examples

Isolated system $\dot{\rho}(X,t) = \{(H_0 + H_{ext}), \rho\}$

Liouville eq.

$$H_{ext}(t) = -\lambda(t) x$$

$$\Rightarrow \Omega = -\{x, ..\} \quad \& \quad \bar{\rho}(X) = Z^{-1} \exp(-\beta H_0(X))$$

canonical Gibbs!

$$\varphi(X)\bar{\rho}(X) \equiv [\Omega\bar{\rho}]_X \Rightarrow \varphi(X) = \{x, H_0(X)\}\beta = \beta\dot{x}$$

likewise: $\psi(x) = \beta x$

Therefore: $\chi(\tau) = \Theta(\tau)\beta\langle\delta x(\tau)\dot{x}(0)\rangle_{\bar{\rho}=\rho_{eq.}}$

$$= -\Theta(\tau)\beta \cdot \frac{d}{d\tau}\langle\delta x(\tau)\delta x(0)\rangle_{\bar{\rho}=\rho_{eq}}$$

$$= -\Theta(\tau)\frac{1}{k_B T}\frac{d}{d\tau}\langle\delta x(\tau)\delta x(0)\rangle$$

Kubo - classical Fluctuation-Dissipation Theorem (1960)

Quantum Generalization Callen-Welton (1951)

$$\chi_{xx}(\tau) = \frac{i\,\Theta(\tau)}{\hbar}\langle [x(\tau), x(0)]\rangle_\beta$$
$$= -\Theta(\tau)\int_0^\beta \langle x(-i\hbar\lambda)\,\dot{x}(\tau)\rangle_\beta\, d\lambda$$
$$\left(-\Theta(\tau)\,\beta\,\langle \delta\dot{x}(\tau)\,\delta x(0)\rangle\right)$$

$$\chi''(\omega) = \frac{1}{\hbar}\tanh(\hbar\omega\beta/2)\, S_{xx}(\omega)$$

$\frac{1}{2}\langle(\delta x(\tau)\delta x(0) + \delta x(0)\delta x(\tau))\rangle_\beta$

symmetrized

Therefore: ~~$S_{xx}(\omega) = \hbar\coth(\hbar\beta\omega/2)$~~

$$S_{xx}(\omega) = \hbar\coth(\hbar\omega\beta/2)\,\chi''(\omega)$$

one measures the response to the single-time observable:

$$\delta x(t) = \langle x(t)\rangle - \langle x(t)\rangle_{\rho_{eq}}$$

One does not do a two-time measurement of a quantum correlation!