

Linear response theory

$h(t) \leftarrow$ small perturbation



$h=0$ equilibrium

$$\begin{aligned} \langle m(t) \rangle_h - \langle m \rangle_0 &= \int_{-\infty}^t ds \chi(t-s) h(s) \end{aligned}$$

$$\chi(t) = -\beta \frac{d}{dt} \langle m(t) m(0) \rangle$$

* h could be some other field, or pressure. In that case

$$\chi(t) = -\beta \frac{d}{dt} \langle m(t) v(0) \rangle$$

↑ is the ~~conjugate~~ thermodynamic conjugate variable of h .

[Ref. Book of Sethna]

What happens outside equilibrium?

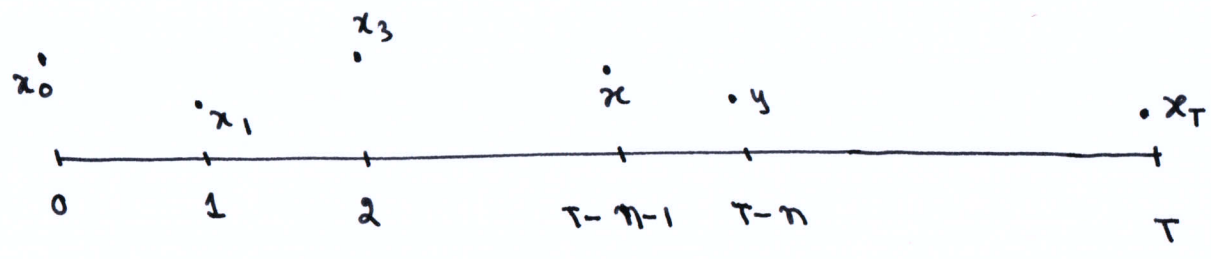
$$\begin{aligned} \chi(t) = & -\frac{\beta}{2} \frac{d}{dt} \left\{ \langle m(t) v(0) \rangle + \langle m(0) v(t) \rangle \right\} \\ & + \left\{ \langle m(t) a(0) \rangle + \langle m(0) a(t) \rangle \right\} \\ & \quad \uparrow \\ & \quad \text{[activity]} \end{aligned}$$

Ref: TS & Derrida. 2016, *J stat mech*, 113202

See last appendix.

Time-reversed process

[Book by Stroock
An Intro to Markov Processes]



Forward evolution:

$$C(t) \equiv \{ c_0 = x_0, c_1 = x_1, \dots, c_T = x_T \}$$

Prob evolves by $M(c', c)$

Time-reversed evolution:

$$c^*(t) = c(T-t)$$

$$c^*(t) = \{ c_0^* = x_T, c_1^* = x_{T-1}, \dots, c_T^* = x_0 \}$$

Q: ~~How does~~ what dynamics describe $c^*(t)$?
Is it Markovian?

Answer:

$$P^*(c_{n+1}^* = x, c_n^* = y, \dots, c_0^* = x_T) = P(c_{T-n-1} = x, c_{T-n} = y, \dots, c_T = x_T)$$

$$\Rightarrow \text{JMP}^*(c_{n+1}^* = x | c_n^* = y, \dots, c_0^* = x_T) P^*(c_n^* = y, \dots, c_0^* = x_T) = \dots$$

Also

$$P^*(c_n^* = y, \dots, c_0^* = x_T) = P(c_{T-n} = y, \dots, c_T = x_T)$$

• Taking ratio

$$\begin{aligned}
M^*(c_{n+1}^* = x \mid c_n^* = y, \dots, c_0^* = x_T) &= \frac{P(c_{T-n-1} = x, c_{T-n} = y, \dots, c_T = x_T)}{P(c_{T-n} = y, \dots, c_T = x_T)} \\
&= \frac{P(c_{T-n-1} = x) M(x \rightarrow y) M(y \rightarrow x_{T-n+1}) \dots M(x_{T-1} \rightarrow x_T)}{P(c_{T-n} = y) M(y \rightarrow x_{T-n+1}) \dots M(x_{T-1} \rightarrow x_T)} \\
&= \frac{P(c_{T-n-1} = x)}{P(c_{T-n} = y)} M(y, x) \quad [M(x \rightarrow y) \equiv M(y, x)]
\end{aligned}$$

This means that the time reversed dynamics is also Markovian (because it only depends on y, and not on $c_{n-1}^*, c_{n-2}^* ; \dots, c_0^*$).

But $M^*(x, y)$ depends on time (n) \implies a time inhomogeneous process.

Remark ◦ If the forward process has reached a stationary state, i.e. $P(c_n = x) = P_{st}(x)$, then

$$\boxed{M^*(x, y) = \frac{P_{st}(x)}{P_{st}(y)} M(y, x)} \quad \text{time-homogeneous.} \quad (\text{check: } \sum_x M^*(x, y) = 1)$$

Remark ◦ note, generally $M^*(x, y) \neq M(x, y)$. This equality happens only for equilibrium by detailed balance condition.

Remark ◦ continuous time case can be obtained by

$$M^*(x, y) = \delta_{x, y} + \Delta t w^*(x, y) + \dots = \frac{P(x) + \Delta t h(x)}{P(y) + \Delta t h(y)} \cdot (\delta_{y, x} + \Delta t w(y, x))$$

5 Entropy and convergence to stationary state [van-Kampen Book ch V, Sec 5]

A physics way of showing that system evolves towards its stationary state.

Similar to Boltzmann's H-theorem, (but simpler)

Let $f(x)$ is a strictly convex function, and ~~is~~ non-negative

$f(x) \geq 0$ and $f'(x) > 0$ for $x \in [0, \infty)$

Let's define

$H(t) = \sum_c P_{eq}(c) f\left(\frac{P_t(c)}{P_{eq}(c)}\right)$ Assume that $P_{eq}(c)$ exist.

Then,

$\frac{dH(t)}{dt} = \sum_c \cancel{P_{eq}(c)} \cdot f'(x_t(c)) \cdot \frac{1}{\cancel{P_{eq}(c)}} \cdot \frac{dP_t(c)}{dt}$

$= \sum_c f'(x_t(c)) \sum_{c'} \{ \omega(c, c') P_t(c') - \omega(c', c) P_t(c) \}$

$= \sum_{c'} \sum_c f'(x_t(c)) \cdot x_t(c') \cdot \omega(c, c') P_{eq}(c') - \underbrace{\sum_c \sum_{c'} f'(x_t(c)) \cdot x_t(c) \cdot \omega(c', c) P_{eq}(c)}_{\text{exchange } c \leftrightarrow c'}$

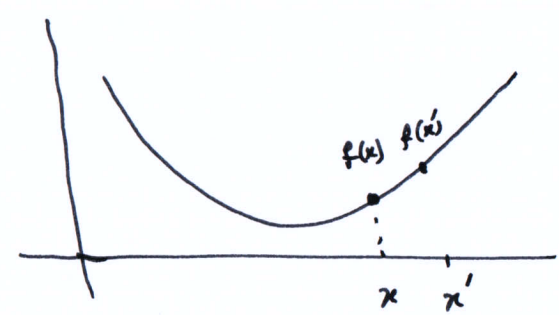
$= \sum_c \sum_{c'} \omega(c, c') \cdot P_{eq}(c') \cdot x_t(c') [f'(x_t(c)) - f'(x_t(c'))]$

use detailed balance

$= \frac{1}{2} \sum_c \sum_{c'} \omega(c, c') \cdot P_{eq}(c') \cdot (x_t(c') - x_t(c)) (f'(x_t(c)) - f'(x_t(c')))$

$$\Rightarrow \frac{dH(t)}{dt} = -\frac{1}{2} \sum_c \sum_{c'} \omega(c, c') \cdot P_{eq}(c') \cdot (x_t(c) - x_t(c')) \left(f'(x_t(c)) - f'(x_t(c')) \right)$$

≤ 0 for convex $f(x)$



This means, $H(t)$ monotonically decreases with time.

~~Let's choose~~
Let's choose $f(x) = x \log x$

$$\text{Then } H(t) = \sum_c P_{eq}(c) \cdot \frac{P_t(c)}{P_{eq}(c)} \cdot \log \frac{P_t(c)}{P_{eq}(c)}$$

$$= \sum_c P_t(c) \log \frac{P_t(c)}{P_{eq}(c)} \quad \text{has minimum zero, (bounded below)}$$

[Kullback-Leibler divergence]

\Rightarrow As time grows, $H(t)$ could only monotonically decrease, ~~but it~~
~~can't reach~~ then at $t \rightarrow \infty$ it can only reach $H=0$.

$$\Rightarrow P_\infty(c) = P_{eq}(c).$$

Remark: You can use ~~the same~~ ^a very similar analysis to show that P_{eq} is unique.

This method is powerful, and typically used to prove unique asymptotic solution of ODE. One non-trivial example is solution of Hamilton-Jacobi equation $\frac{\partial S}{\partial t} = -H(q, \frac{\partial S}{\partial q})$
[Derrida & TS: J. Stat. Phys. 177, 151 (2015)]

Remark: What happens if no detailed balance? What is non-equilibrium generalization of entropy? $S(t) = -k_B H(t) + S_{eq}$

More reading: Book of Sethna. Ch 5.

⑥ If there is detailed balance, then we can ~~make~~ ^{transform} ~~W~~-matrix symmetric, by a similarity transformation.

Then, we can use all nice properties of ~~Hermitian~~ Hermitian matrices, just like in Q.M. (A-very useful trick)

How? use detailed balance

$$W(c', c) P_{eq}(c) = W(c, c') P_{eq}(c')$$

$$\left. \begin{array}{l} \text{divide by} \\ \sqrt{P_{eq}(c') P_{eq}(c)} \end{array} \right\} \Rightarrow \frac{1}{\sqrt{P_{eq}(c')}} \cdot W(c', c) \cdot \sqrt{P_{eq}(c)} = \frac{1}{\sqrt{P_{eq}(c)}} \cdot W(c, c') \sqrt{P_{eq}(c')}$$

$$\Rightarrow \boxed{H(c', c) = H(c, c')}$$

This means,

$S^{-1} \cdot W \cdot S = H$ is a symmetric matrix.

$$S = \begin{pmatrix} \sqrt{P(c_1)} & & & 0 \\ & \ddots & & \\ & & \sqrt{P(c_2)} & \\ 0 & & & \ddots \end{pmatrix}$$

~~Example~~

Symmetric matrix is diagonalizable and left eigenvector = right eigenvector

$$H|\psi_\lambda\rangle = \lambda |\psi_\lambda\rangle$$

$$\Rightarrow S^{-1} W S |\psi_\lambda\rangle = \lambda |\psi_\lambda\rangle$$

$$\Rightarrow W(S|\psi_\lambda\rangle) = \lambda (S|\psi_\lambda\rangle)$$

$$\Rightarrow \boxed{|\alpha_\lambda\rangle = S|\psi_\lambda\rangle}$$

$$\langle \psi_\lambda | H = \lambda \langle \psi_\lambda |$$

$$\Rightarrow \boxed{\langle \alpha_\lambda | = \langle \psi_\lambda | S^{-1}}$$

* Same eigen spectrum.

* Steady state ($\lambda=0$) then corresponds to ground state of $-H$.

* Then any solution $|P_t\rangle$ can be expressed in terms of complete eigen states

$$|P_t\rangle = |P_{st}\rangle + e^{\lambda_1 t} s |P_1\rangle e_1 + e^{\lambda_2 t} s |P_2\rangle e_2 + \dots$$

with $0 > \lambda_1 > \lambda_2 > \dots$

This way, the time scale to reach stationary state is given by

$$\tau = \frac{1}{|\lambda_1|}$$

and this question of ~~how long~~ reaching a unique st state reduces to finding ~~any~~ non-zero spectral gap OR bound states for a QM hamiltonian.

A famous example:

Exclusion process \longleftrightarrow ~~xxxx~~ - spin chain

Deepak Dhar 1986.

Cwaj & spohn, 1992.

⊛ Continuous time + continuous space.

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$$\frac{d}{dt} P_t(x) = \int dy \left\{ w(x,y) P_t(y) - w(y,x) P_t(x) \right\}$$

$$\boxed{\frac{d}{dt} |P_t\rangle = W |P_t\rangle}$$

Generalization of Perron-Frobenius theorem

→ Perron-Frobenius - Jentzsch theorem

⊛ ~~⊛~~ In most real examples, on "real" space, there are local jumps. \Rightarrow at very small time dt , ~~$w(x,y)$~~ $w(x,y)$ decays very fast with $x-y$.

For such processes, the integral operator W can be reduced to a differential operator

$$\frac{d}{dt} P_t(x) = [\mathcal{L} \cdot P_t](x)$$

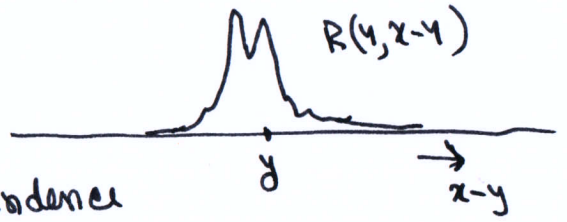
This equation is known as the Fokker-Planck equation.

This transformation is done by Kramers-Moyal expansion.

$$\frac{dP_F(x)}{dt} = \int dy \{ W(x,y) P_F(y) - W(y,x) P_F(x) \}$$

let $W(x,y) = R(y, x-y)$

slow dependence fast dependence



$$\begin{aligned} \Rightarrow \frac{dP_F(x)}{dt} &= \int dy \{ R(y, x-y) P_F(y) - R(x, y-x) P_F(x) \} \\ &= \int dy \{ R(x-x-y, x-y) P_F(x-x-y) - R(x, y-x) P_F(x) \} \\ &= - \int dx \{ R(x-x, x) P_F(x-x) - R(x, -x) P_F(x) \} \\ &= - \underbrace{\int dx \{ R(x, x) P_F(x) - R(x, -x) P_F(x) \}}_0 + \frac{d}{dx} [a_1(x) P_F(x)] \\ &\quad + \frac{d^2}{dx^2} [a_2(x) P_F(x)] - \dots \end{aligned}$$

with $a_n(x) = - \int dx \frac{(-x)^n}{n!} R(x, x)$

$$\Rightarrow \boxed{\frac{dP_F(x)}{dt} = \frac{d}{dx} (a_1(x) P_F(x)) + \frac{d^2}{dx^2} (a_2(x) P_F(x)) + \dots} = - \int dy \frac{(y-x)^n}{n!} \dots w(y, x)$$

If we truncate at second order, it is called the FP equation.

Remark: this is usually justified if there is a scaling parameter l such that $x-y \sim l$ small.

Example: Wiener process

$$R(x, x) = \frac{1}{\sqrt{2\pi} l} e^{-\frac{(x-lm)^2}{2l^2}} \quad [\text{think CLT}]$$

$\Rightarrow a_1(x) = + \ell \cdot m(x), \quad a_2(x) = -\ell + \ell^2, \quad a_3 = \ell^2 + \dots$

Then, for small ℓ ,

$\frac{d}{dt} P_t(x) = \ell \frac{d}{dx} (mP) - \ell \cdot \frac{d^2}{dx^2} P + O(\ell^2)$

One can absorb ℓ by redefining time $t \times \ell$

This, we will see is justified for Langevin equations, and particularly for stochastic differential equations.

~~Remark: ... jumps~~

~~Another example: Ornstein-Uhlenbeck process~~

~~...~~

Remark: of course, there are cases where long jumps are allowed, one can not truncate the series.

For example Lévy processes do not have a FP description.

Instead there is a description using ~~FP-type~~ FP-type equation with fractional derivatives.

Ref! EPL, 46, 431 (1999).

→ search in youtube channel "veubingx"

Remark: F-P equation, when written as

$\frac{\partial}{\partial t} P_t = - \partial_x j \quad ; \quad j = - a_1(x)P - \frac{d}{dx} (a_2(x)P)$


$j :=$ probability current.

~~In equilibrium $j(x,t) = 0$. Example: particle in a potential.~~

* Most common example

$$\frac{d}{dt} P_F(x) = \frac{d}{dx} [U'(x) P_F(x)] + k_B T \frac{d^2}{dx^2} P_F(x)$$

describes a Brownian particle in a potential $U(x)$ at temperature $k_B T$.

If $U(x)$ is a confining potential , system reaches an equilibrium stationary state, with zero current

$$U'(x) P_{eq}(x) + k_B T \frac{d}{dx} P_{eq}(x) = 0$$

$$\Rightarrow P_{eq}(x) \propto e^{-\frac{1}{k_B T} U(x)}$$

In operator formulation:

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FP equation

$$\frac{\partial P_t(x)}{\partial t} = \mathcal{A}_t \cdot P_t(x)$$

time independent case.

$$\text{Here } \mathcal{A}_t \cdot P_t(x) = \frac{d}{dx} a_1(x) P_t(x) + \frac{d^2}{dx^2} a_2(x) P_t(x)$$

is a differential operator.

Formal solution

$$P_t(x) = e^{t\mathcal{A}} \cdot P_0(x)$$

~~Remark~~
Remark: In general \mathcal{A} is not hermitian (not self-adjoint).

There is a subtle difference.

[If we define an inner product

$$\langle \ell | \eta \rangle = \int dx \ell^*(x) \eta(x)$$

Then, ~~the~~ \mathcal{A}^\dagger is defined by

$$\langle \mathcal{A}^\dagger \ell | \eta \rangle = \langle \ell | \mathcal{A} \eta \rangle$$

(a) \mathcal{A} is Hermitian if $\mathcal{A}^\dagger \equiv \mathcal{A}$, meaning

$$\langle \mathcal{A} \ell | \eta \rangle = \langle \ell | \mathcal{A} \eta \rangle$$

(b) But, note that domain of \mathcal{A} may not be same as domain of \mathcal{A}^\dagger .
functional space on which \mathcal{A} acts.

If both domains are same, then \mathcal{A} is self-adjoint.

This ~~subtle~~ subtle difference has important consequences in QM.

An example: considers $\mathcal{A} := \frac{d^2}{dx^2}$

acting on all functions on $0 \leq x < \infty$ that vanish at $x \rightarrow \infty$ and $\int_0^\infty dx \ell(x) \eta(x) = \text{Finite}$.

Then $\langle \ell | \mathcal{A} \eta \rangle = \int_0^\infty dx \ell(x) \eta''(x)$ [$\ell \eta'' = \ell'' \eta - (\ell' \eta - \ell \eta')$]

using integration by parts $= \int_0^\infty dx \ell''(x) \eta(x) + \ell(0) \eta'(0) - \ell'(0) \eta(0)$

vanish if

Case 1: $\eta(0) = 0 = \eta'(0)$

Case 2: $\eta(0) = 0 = \ell(0)$

Both cases give

$\langle \mathcal{A}^\dagger \ell | \eta \rangle = \langle \ell | \mathcal{A} \eta \rangle = \int dx \ell''(x) \eta(x)$

$\Rightarrow \mathcal{A}^\dagger := \frac{d^2}{dx^2}$ ~~is the same as~~ \mathcal{A} thus Hermitian.

But in case 1: ^{space} ~~domain~~ of functions $\eta \subseteq$ ^{space} ~~domain~~ of ℓ

\Rightarrow domain of $\mathcal{A} \subseteq$ domain of \mathcal{A}^\dagger

so \mathcal{A} is not self-adjoint

Case 2: both domains same $\Rightarrow \mathcal{A}$ is self-adjoint

Remark: This has interesting consequences in QM.

Ref 1: Araujo, Coutinho & Perez, Am. J. Phys. 73, 203 (2004)

Ref 2: Bonneau, Faraut, Valent, Am. J. Phys. 69, 322 (2001)

Generally, the Fokker-Planck operator is not self-adjoint.

- There will be left and right eigenvectors

$$\mathcal{L} \cdot \pi_\lambda(x) = \lambda \pi_\lambda(x) \qquad \mathcal{L}^\dagger \cdot l_\lambda(x) = \lambda^* l_\lambda(x)$$

- Generalization of Perron-Frobenius theorem essentially applies when there is a spectral gap. ~~There are~~ In such case,

- (i) largest eigenvalue = 0
- (ii) $\pi_0(x) = P_{st}(x)$
- (iii) $l_0(x) = 1$.

- In good cases (most common) eigenbasis is

complete $\sum_\lambda l_\lambda^*(x) \pi_\lambda(x') = \delta(x-x')$

orthonormal $\int dx l_\lambda^*(x) \pi_{\lambda'}(x) = \delta_{\lambda,\lambda'}$

Then,

$$P_t(x) = \pi_0(x) + e^{t\lambda_1} \cdot \pi_1(x) \cdot a_1 + \dots$$

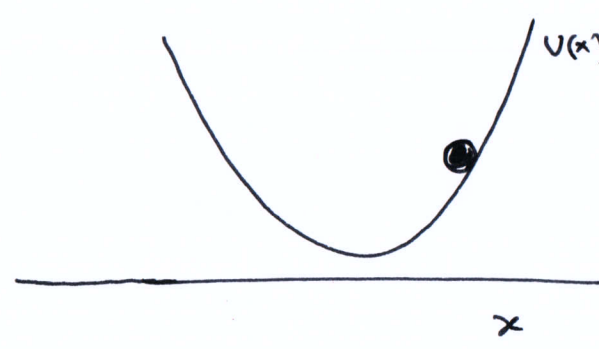
with $a_k = \int dx l_k^*(x) P_0(x)$

- Unlike in QM, here one needs to determine both the left and right eigenvectors.

* An explicit example: Brownian particle in a potential $U(x)$.

$$\frac{dP_t(x)}{dt} = \mathcal{L} \cdot P_t(x)$$

$$\mathcal{L} := \frac{d}{dx} U'(x) + k_B T \frac{d^2}{dx^2}$$



~~So physics intuition & our space of functions~~

If $U \rightarrow \infty$ for $|x| \rightarrow \infty$, then our physics intuition tells that ~~we should~~ ~~look at functions~~ ~~with, which~~ ~~mean~~ $P_t(x)$, and its derivative vanish at infinity.

So we look at functions $r(x)$ such that

$$\begin{aligned} \mathcal{L}^*(x) r(x) &\rightarrow 0 \text{ as } |x| \rightarrow \infty \\ \mathcal{L}^*(x) r'(x) &\rightarrow 0 \\ \mathcal{L}'(x) r(x) &\rightarrow 0 \end{aligned}$$

Then, for this space of functions (by integration by parts)

$$\mathcal{L}^{\dagger} := -U'(x) \frac{d}{dx} + k_B T \frac{d^2}{dx^2}$$

* So $\mathcal{L}^{\dagger} \neq \mathcal{L} \Rightarrow$ not Hermitian.

~~Expected value of $\langle x^2 \rangle = \frac{1}{2} k_B T$~~
~~Largest eigenvalue $\neq 0$ with ~~state~~ ~~probability~~~~
~~However, this problem can be fully solved~~

However, it can be made Hermitian by a similarity transformation.

↓
this links to Schrödinger equation.

F P equation \longrightarrow Schrödinger equation.

$$\frac{d}{dt} P_T(x) = \frac{d}{dx} U'(x) P_T(x) + k_B T \frac{d^2}{dx^2} P_T(x)$$

Define $P_T(x) = e^{-\frac{1}{2k_B T} U(x)} \Psi_T(x)$

Do the algebra and show that



$$-\frac{d}{dx} \Psi_T(x) = \left\{ -k_B T \frac{d^2}{dx^2} \Psi_T + V(x) \Psi_T \right\}$$

with effective potential

$$V(x) = \frac{1}{4k_B T} (U'(x))^2 - \frac{U''(x)}{2}$$

Remark: what does it mean for α -operator?

a choice \longrightarrow $H = - \left(P_{eq}(x) \right)^{\frac{1}{2}} \alpha \left(P_{eq}(x) \right)^{-\frac{1}{2}}$ $\left[P_{eq}(x) = e^{-\frac{U(x)}{k_B T}} \right]$
 $= -k_B T \frac{d^2}{dx^2} + V(x)$ is Hermitian.

~~the operator is self-adjoint~~. This makes thing easy.

~~the eigenvalues of H are real.~~

① For H, both left and right eigenvectors are same. ~~use~~

② $\alpha \cdot \eta_\lambda = \lambda \eta_\lambda \implies H \Psi_\lambda = -\lambda \Psi_\lambda$ with $\eta_\lambda(x) = \sqrt{P_{eq}(x)} \cdot \Psi_\lambda(x)$

$\alpha^\dagger \cdot \xi_\lambda = \lambda \xi_\lambda \longrightarrow \xi_\lambda(x) = \frac{1}{\sqrt{P_{eq}(x)}} \Psi_\lambda(x)$

③ eigenvalues λ are real.

④ Eigenvalue of α is minus of eigenvalue of H .

\Rightarrow Steady state for $\alpha \iff$ ground state of H .

This has important meaning:

Generalization of Perron-Frobenius, which essentially means that there is spectral gap between largest and second largest eigenvalues (non-degeneracy) \iff question of spectral gap for H in QM \iff existence of Bound states.

[Bound states in QM: ① Brownstein, Am. J. Phys. 68 (2000), 160
② Landau & Lifshitz]

An explicit solution

Grostein-Uhlenbeck Process: Brownian particle in a harmonic potential. $V(x) = \frac{1}{2} x^2$

QM-potential $V(x) = \frac{x^2}{4k_B T} - \frac{1}{2}$ Harmonic oscillator problem.

Eigenvalues $\lambda_n = -n$ with $n = 0, 1, 2, \dots$

Eigen Functions $\Psi_n(x) = \left[\frac{1}{2\pi k_B T} \right]^{1/4} \cdot \frac{1}{\sqrt{2^n n!}} \cdot H_n \left(\frac{x}{\sqrt{2k_B T}} \right) e^{-\frac{x^2}{4k_B T}}$
Hermit polynomial.

$\Rightarrow \rho_n(x) = \Psi_n(x) \cdot e^{-\frac{x^2}{4k_B T}}$, $l_n(x) = \Psi_n(x) e^{+\frac{x^2}{k_B T}}$

Show: $\rho_0(x) = P_{st}(x) \propto e^{-\frac{x^2}{2k_B T}}$ and $l_0(x) = 1$ (after trivial re-scaling)

Other examples: (A) ~~Free~~ Free brownian particle ($\psi(x)=0$)

on infinite line.

• corresponding QM potential $V(x)=0$;

It has only propagating solutions $e^{\pm iKx}$

with eigenvalues of α -operator is continuous and given by

$$\lambda = -K^2 \cdot K_B T \quad \text{for } K \geq 0.$$

• There is no gap in eigen-spectrum, and this means the

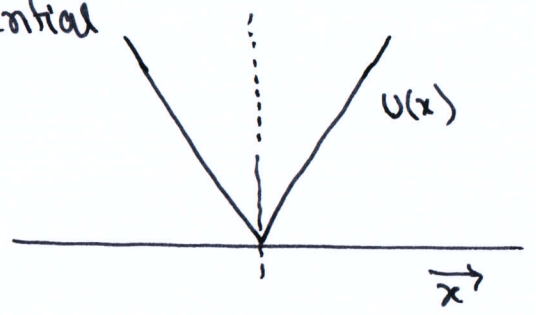
● Brownian particle takes infinite time to reach the uniform distribution.

Remark: do the same exercise on a ring, and show that the spectrum is discrete.



(B) Brownian particle in a linear potential

$$U(x) = |x|$$



⇒ QM potential

$$V(x) = \frac{1}{4 K_B T} - \delta(x)$$

There is only one bound-state, and that is the stationary state.

$$\text{Spectral gap} = \frac{1}{4 K_B T}$$

