III. Fokker-Planck equations

Gerald Kneller
Centre de Biophysique Moléculaire, CNRS Orléans
Université d'Orléans
Synchrotron Soleil, St Aubin

Stochastic processes

$$\boxed{Y = f(X, t)}$$

X is a stochastic variable

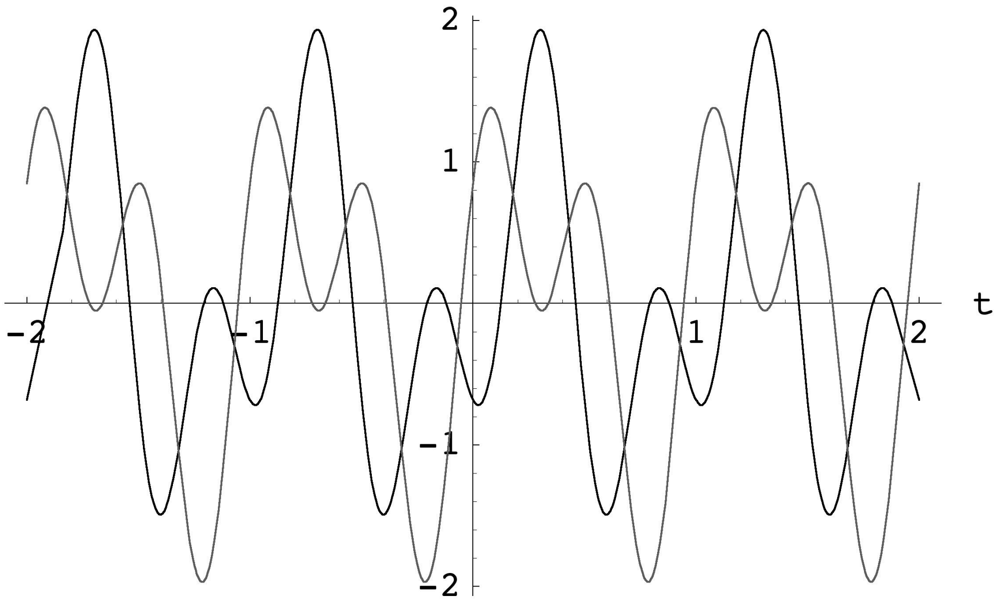
$$\boxed{p_Y(y,t) = \int_{-\infty}^{+\infty} dx\, \delta\Big(y - f(x,t)\Big) p_X(x)}$$

Construct the probability density

Example

$$Y = \sin(2\pi t) + \sin(4\pi t + X)$$

$$p_X(x) = \begin{cases} \frac{1}{2\pi} & x \in [0, 2\pi], \\ 0 & \text{sinon.} \end{cases}$$



- Probability density order *n*

$$p_n^{(Y)}(y_n, t_n; \ldots; y_1, t_1) = \int_{-\infty}^{+\infty} dx\, \delta\Big(y_1 - f(x, t_1)\Big) \ldots \delta\Big(y_n - f(x, t_n)\Big) p_X(x)$$

- Several "hidden" variables

$$Y = f(X_1, \ldots, X_m, t)$$

$$p_n^{(Y)}(y_n, t_n; \ldots; y_1, t_1) = \int_{-\infty}^{+\infty} dx_1 \ldots \int_{-\infty}^{+\infty} dx_m\, \delta\Big(y_1 - f(x_1, \ldots, x_m, t_1)\Big) \ldots \times \delta\Big(y_n - f(x_1, \ldots, x_m, t_n)\Big) p_m^{(X)}(x_1, \ldots, x_m).$$

- Moments

$$\langle Y^{m_1}(t_1) \ldots Y^{m_k}(t_k) \rangle = \int_{-\infty}^{+\infty} \ldots \int_{-\infty}^{+\infty} y_1^{m_1} \ldots y_k^{m_k} p_n^{(Y)}(y_n, t_n; \ldots; y_1, t_1)$$

- Correlation functions

$$\boxed{c_{yy}(t_2, t_1) := \langle (Y(t_2) - \langle Y(t_2) \rangle)(Y(t_1) - \langle Y(t_1) \rangle) \rangle}$$

- At equilibrium - stationarity

$$\boxed{p_n^{(Y)}(y_n, t_n; \ldots; y_1, t_1) = p_n^{(Y)}(y_n, t_n + \tau; \ldots; y_1, t_1 + \tau)}$$

$$\Rightarrow \quad \langle Y(t_1) \rangle \equiv \langle Y \rangle$$

$$\Rightarrow \quad \boxed{c_{yy}(t_2, t_1) = c_{yy}(|t_2 - t_1|, 0) \equiv c_{yy}(t_2 - t_1)}$$

Markov processes

Conditional probability densities

$$p_{r|n-r}(y_n, t_n; \ldots; y_{n-r+1}, t_{n-r+1}|y_{n-r}, t_{n-r}; \ldots; y_1, t_1)$$

$$:= \frac{p_n(y_n, t_n; \ldots; y_1, t_1)}{p_{n-r}(y_{n-r}, t_{n-r}; \ldots; y_1, t_1)}$$

Markov property

$$\boxed{p_{1|n-1}(y_n, t_n|y_{n-1}, t_{n-1}; \ldots; y_1, t_1) = p_{1|1}(y_n, t_n|y_{n-1}, t_{n-1})}$$

"Markov chain"

$$\boxed{p_n(y_n, t_n; \ldots; y_1, t_1) = p_{1|1}(y_n, t_n|y_{n-1}, t_{n-1}) \ldots p_{1|1}(y_2, t_2|y_1, t_1) p_1(y_1, t_1)}$$

Chapman-Kolmogoroff relation

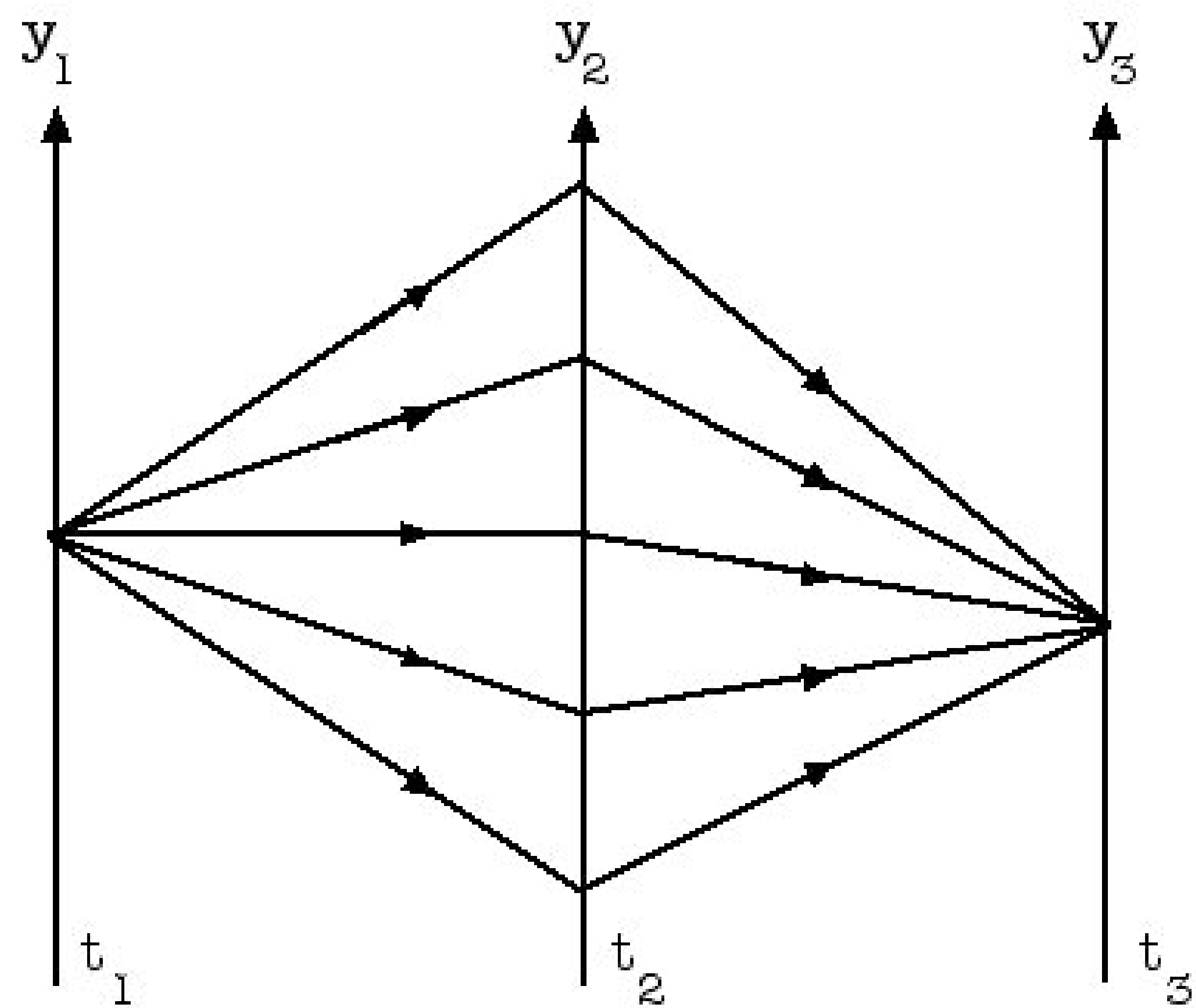
For $t_1 < t_2 < t_3$

$$p_3(y_3, t_3; y_2, t_2; y_1, t_1) = p_{1|1}(y_3, t_3 | y_2, t_2) p_{1|1}(y_2, t_2 | y_1, t_1) p_1(y_1, t_1)$$

Integration over y_2

$$p_2(y_3, t_3; y_1, t_1) = p_{1|1}(y_3, t_3 | y_1, t_1) p_1(y_1, t_1)$$
$$= \left\{ \int_{-\infty}^{+\infty} dy_2 \, p_{1|1}(y_3, t_3 | y_2, t_2) p_{1|1}(y_2, t_2 | y_1, t_1) \right\} p_1(y_1, t_1)$$

$$\boxed{p_{1|1}(y_3, t_3 | y_1, t_1) = \int_{-\infty}^{+\infty} dy_2 \, p_{1|1}(y_3, t_3 | y_2, t_2) p_{1|1}(y_2, t_2 | y_1, t_1)}$$



$$p_{1|1}(y_3, t_3|y_1, t_1) = \int_{-\infty}^{+\infty} dy_2\, p_{1|1}(y_3, t_3|y_2, t_2) p_{1|1}(y_2, t_2|y_1, t_1)$$

Master equation

$$T(y_2, \tau | y_1) \equiv p_{1|1}(y_2, \tau | y_1, 0)$$ Transition probability

$$\begin{aligned} \int_{-\infty}^{+\infty} dy_2 \, T(y_2, \tau | y_1) &= 1, \\ \lim_{\tau \to 0} T(y_2, \tau | y_1) &= \delta(y_2 - y_1). \end{aligned}$$

For short times

$$T(y_2, \tau | y_1) \approx \Big(1 - \tau a_0(y_1)\Big)\delta(y_2 - y_1) + \tau W(y_2 | y_1)$$

- $W(y_2|y_1)$ is a transition *rate* for the transition $y_1 \to y_2 \in [y_2, y_2 + dy_2]$
- $a_0(y_1) = \int_{-\infty}^{+\infty} dy_2 \, W(y_2|y_1)$

with Chapman-Kolmogorov

$$p_{1|1}(y_3, \tau + \tau' | y_1, 0) = \int_{-\infty}^{+\infty} dy_2 \, p_{1|1}(y_3, \tau + \tau' | y_2, \tau) p_{1|1}(y_2, \tau | y_1, 0)$$

τ' small

$$T(y_3, \tau + \tau' | y_1) = \int_{-\infty}^{+\infty} dy_2 \, T(y_3, \tau' | y_2) T(y_2, \tau | y_1)$$

$$= \int_{-\infty}^{+\infty} dy_2 \, \left\{ \Big(1 - \tau' a_0(y_2)\Big) \delta(y_3 - y_2) + \tau' W(y_3 | y_2) \right\} T(y_2, \tau | y_1)$$

$$T(y_3, \tau + \tau' | y_1) = \Big(1 - \tau' a_0(y_3)\Big) T(y_3, \tau | y_1) + \tau' \int_{-\infty}^{+\infty} dy_2 \, W(y_3 | y_2) T(y_2, \tau | y_1)$$

$$\frac{T(y_3, \tau + \tau' | y_1) - T(y_3, \tau | y_1)}{\tau'} = - \underbrace{\left\{ \int_{-\infty}^{+\infty} dy_2 \, W(y_2 | y_3) \right\}}_{a_0(y_3)} T(y_3, \tau | y_1) + \int_{-\infty}^{+\infty} dy_2 \, W(y_3 | y_2) T(y_2, \tau | y_1).$$

Master equation

$$\frac{\partial T(y_3,\tau|y_1)}{\partial \tau} = \int_{-\infty}^{+\infty} dy_2 \left\{ W(y_3|y_2)T(y_2,\tau|y_1) - W(y_2|y_3)T(y_3,\tau|y_1) \right\}$$

"gain" "perte"

Compact notation

$$P(y,t) \equiv T(y,t|y_0), \quad P(y,0) = \delta(y-y_0)$$

$$\frac{\partial P(y,t)}{\partial t} = \int_{-\infty}^{+\infty} dy' \left\{ W(y|y')P(y',t) - W(y'|y)P(y,t) \right\}$$

Fokker-Planck equations

$$\Omega(y-y',y') = W(y|y')$$

$$\zeta(y') \equiv y - y'$$

$$\frac{\partial P(y,t)}{\partial t} = \int_{-\infty}^{+\infty} d\zeta \left\{ \Omega(\zeta, y-\zeta) P(y-\zeta, t) - \Omega(-\zeta, y) P(y,t) \right\}$$

- $$\Omega(\zeta, y-\zeta)P(y-\zeta,t) \approx \Omega(\zeta,y)P(y,t) - \zeta \frac{\partial}{\partial y}\left\{\Omega(\zeta,y)P(y,t)\right\} + \frac{\zeta^2}{2}\frac{\partial^2}{\partial y^2}\left\{\Omega(\zeta,y)P(y,t)\right\}$$
- $$\int_{-\infty}^{+\infty} d\zeta\, \Omega(-\zeta,y) = \int_{-\infty}^{+\infty} d\zeta\, \Omega(\zeta,y)$$

$$\Rightarrow \quad \boxed{\frac{\partial P(y,t)}{\partial t} = -\frac{\partial}{\partial y}\left\{a_1(y)P(y,t)\right\} + \frac{1}{2}\frac{\partial^2}{\partial y^2}\left\{a_2(y)P(y,t)\right\}}$$

$$\boxed{a_k(y) = \int_{-\infty}^{+\infty} d\zeta\, \zeta^k \Omega(\zeta,y)}$$

Equation of motion

Moment generating function

$$G(k,t) = \int_{-\infty}^{+\infty} dy\ \exp(-iky) P(y,t)$$

$$\Rightarrow \quad G(k,\Delta t) \approx \int_{-\infty}^{+\infty} dy\ \exp(-iky) \left\{ P(y,0) + \Delta t\ \frac{\partial P(y,t)}{\partial t}\bigg|_{t=0} \right\}$$

$$G(k,\Delta t) \approx \int_{-\infty}^{+\infty} dy\ \exp(-iky) \left\{ \delta(y-y_0) + \Delta t \left(-\frac{\partial}{\partial y}\left[a_1(y)P(y,t)\right] + \frac{1}{2}\frac{\partial^2}{\partial y^2}\left[a_2(y)P(y,t)\right] \right)\bigg|_{t=0} \right\}$$

$$\Rightarrow \quad \boxed{G(k,\Delta t) \approx \left(1 - ika_1(y_0)\Delta t - \frac{k^2}{2} a_2(y_0)\Delta t\right) \exp(-iky_0)}$$

$$G(k,\Delta t) \approx \left(1 - ika_1(y_0)\Delta t - \frac{k^2}{2}a_2(y_0)\Delta t\right)\exp(-iky_0)$$

$$\langle y \rangle = i\frac{\partial}{\partial k}G(k,\Delta t)\bigg|_{k=0} = y_0 + \Delta t a_1(y_0),$$

$$\langle y^2 \rangle = i^2\frac{\partial^2}{\partial k^2}G(k,\Delta t)\bigg|_{k=0} = y_0^2 + \Delta t a_2(y_0) + 2\Delta t a_1(y_0)y_0.$$

$$\begin{aligned} \langle y - y_0 \rangle &= \Delta t a_1(y_0) \\ \langle (y - y_0)^2 \rangle &= \Delta t a_2(y_0) \end{aligned}$$

Realization for a stochastic process

$$\boxed{y(t_0 + \Delta t) = y(t_0) + \Delta t a_1(y(t_0)) + \xi}$$

$$\boxed{\overline{\xi} = 0 \quad \text{and} \quad \overline{\xi^2} = \Delta t a_2(y(t_0))}$$

Equilibrium, stationary solutions

$$\frac{\partial P(y,t)}{\partial t} + \frac{\partial J(y,t)}{\partial y} = 0$$

Equation of continuity

$$J(y,t) = a_1(y)P(y,t) - \frac{a_2(y)}{2}\frac{\partial P(y,t)}{\partial y}$$

systematic entropic

Probability current

Equilibrium

$$J_{eq}(y) \equiv \lim_{t\to\infty} J(y,t) = 0$$

$$P_{eq}(y) = C \exp\left(\int_{-\infty}^{y} dy' \, \frac{2a_1(y')}{a_2(y')}\right)$$

Stationary regime

$$J_s(y) \equiv \lim_{t\to\infty} J(y,t), \qquad \frac{\partial J_s(y)}{\partial y} = 0$$

Wiener process - free diffusion

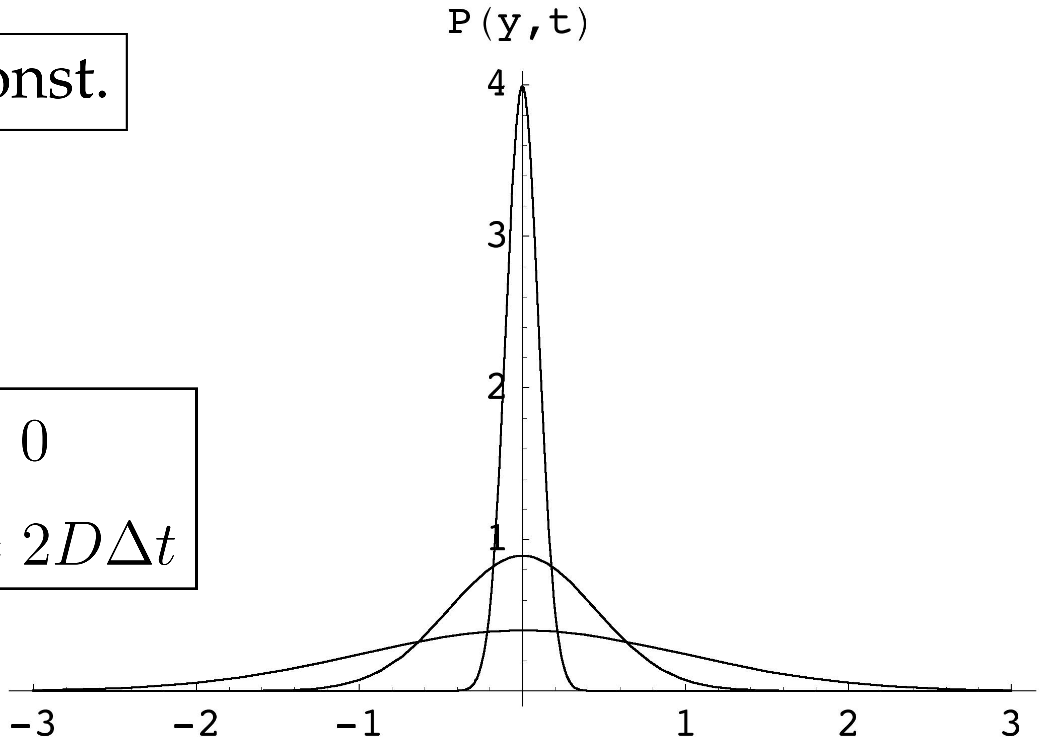
- $$a_1(y) = 0, \qquad a_2(y) = 2D = \text{const.}$$

$$\frac{\partial P(y,t)}{\partial t} = D\frac{\partial^2 P(y,t)}{\partial y^2}$$

$$y(t_0 + \Delta t) = y(0) + \xi$$

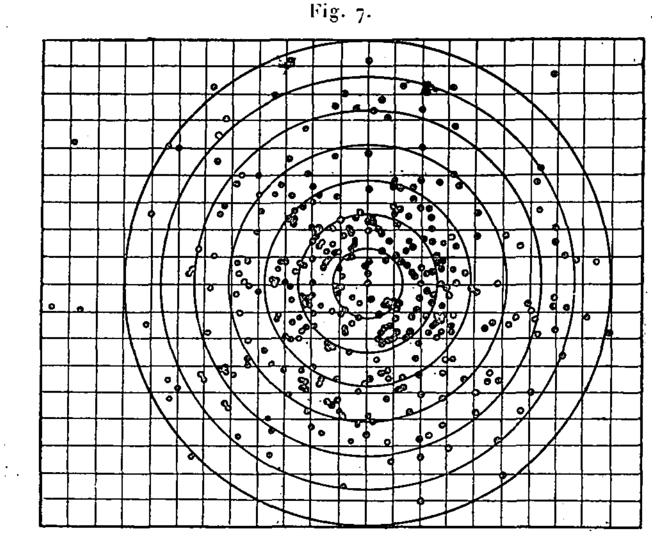
$$\overline{\xi} = 0$$
$$\overline{\xi^2} = 2D\Delta t$$

Wiener process



- $$P(y,t) = \frac{1}{\sqrt{4\pi Dt}}\exp\left(-\frac{(y-y_0)^2}{4Dt}\right)$$

- $$W(t) = \int_{-\infty}^{+\infty} dy\, y^2 P(y,t) = 2Dt$$



J. Perrin, Ann. Chim. Phys. 1909

Ornstein-Uhlenbeck process

- $$a_1(y) = -\eta y, \qquad a_2(y) = 2D$$

$$\frac{\partial P(y,t)}{\partial t} = \eta \frac{\partial}{\partial y}\left\{ yP(y,t) \right\} + D\frac{\partial^2 P(y,t)}{\partial y^2}$$

$$y(t_0 + \Delta t) = y(t_0) - \Delta t \eta y(t_0) + \xi$$

$$\overline{\xi} = 0$$
$$\overline{\xi^2} = 2D\Delta t$$

Processus de Ornstein-Uhlenbeck

- $$P(y,t) = \frac{1}{\sqrt{2\pi\sigma(t)}} \exp\left(-\frac{\{y - M(y_0,t)\}^2}{2\sigma(t)} \right)$$

$$\begin{aligned} M(y_0,t) &= y_0 \exp(-\eta t), \\ \sigma(t) &= \frac{D}{\eta}\left\{ 1 - \exp(-2\eta t) \right\}. \end{aligned}$$

Short and long time limits

- $\sigma(t) \approx 2Dt \quad \textbf{si} \quad t \ll \eta^{-1}$

  "free" diffusion

$$\boxed{P(y,t) \approx \frac{1}{\sqrt{4\pi D t}} \exp\left(-\frac{(y-y_0)^2}{4Dt}\right)}$$

- $\sigma(t) \approx \dfrac{D}{\eta} \qquad \textbf{si} \quad t \gg \eta^{-1}$

$$\boxed{P_{eq}(y) = \sqrt{\frac{\eta}{2\pi D}} \exp\left(-\frac{\eta y^2}{2D}\right)}$$

$$\langle y^2 \rangle_{eq} = \int_{-\infty}^{+\infty} dy\, y^2 P_{eq}(y) = \frac{D}{\eta}$$

Position autocorrélation function

$$c_{yy}(t) \equiv \langle y(t)y(0)\rangle = \int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} dy_t dy_0\, y_t y_0 p(y_t, t; y_0, 0)$$

$$\tilde{p}(k_t, t; k_0, 0) = \int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} dy_t dy_0\, \exp(-i[k_t y_t + k_0 y_0])p(y_t, t; y_0, 0)$$

$$c_{yy}(t) = -\left.\frac{\partial^2}{\partial k_t \partial k_0}\tilde{p}(k_t, t; k_0, 0)\right|_{k_t=0, k_0=0}$$

$$\tilde{p}(k_t, t; k_0, 0) = \int_{-\infty}^{+\infty} dy_0\, \exp(-ik_0 y_0)p_{eq}(y_0) \underbrace{\int_{-\infty}^{+\infty} dy_t\, \exp(-ik_t y_t)p(y_t, t|y_0, 0)}_{\exp(-iM(t,y_0)-\frac{1}{2}k_t^2\sigma(t))}$$

$$= \exp\left(-\frac{1}{2}k_t^2\sigma(t)\right) \underbrace{\int_{-\infty}^{+\infty} dy_0\, \exp(-i[k_0 + k_t \exp(-\eta t)]y_0)p_{eq}(y_0)}_{\exp(-\frac{1}{2}\langle y^2\rangle_{eq}[k_0+k_t\exp(-\eta t)]^2)}.$$

$$\tilde{p}(k_t, t; k_0, 0) = \exp\left(-\frac{1}{2}\langle y^2\rangle_{eq}\left\{(k_t^2 + k_0^2) + 2k_0 k_t \exp(-\eta t)\right\}\right)$$

$$\Rightarrow \boxed{c_{yy}(t) = \langle y^2\rangle_{eq}\exp(-\eta t)}$$

Mean square displacement

Note that

$$\langle \{y(t) - y(0)\}^2 \rangle = \langle y^2(t) + y^2(0) - 2y(t)y(0) \rangle = 2\langle y^2 \rangle_{eq} - 2c_{yy}(t)$$

$$\boxed{W(t) = 2\langle y^2 \rangle_{eq} \{1 - \exp(-\eta t)\}}$$

- $t \ll \eta^{-1}$ $\quad W(t) \approx 2\langle y^2 \rangle_{eq} \eta t$

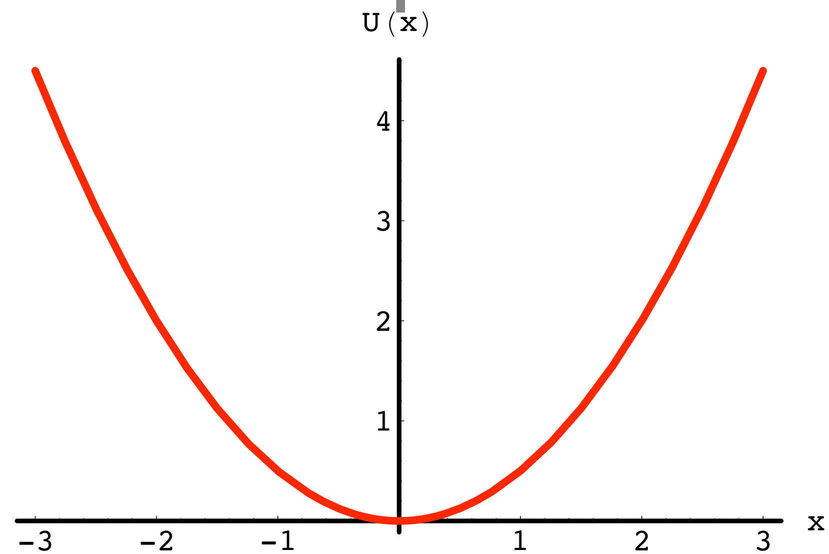
  $D \approx 2\langle y^2 \rangle_{eq} \eta$ Short time diffusion coefficient

- $t \gg \eta^{-1}$ $\quad \lim_{t \to \infty} D(t) = \lim_{t \to \infty} \frac{1}{2} \frac{d}{dt} W(t) = 0$

Diffusion in a harmonic potential

Here y≡x is the position of a Brownian particle

$$V(x) = \frac{1}{2}Kx^2, \qquad K > 0$$



Boltzmann weight:

$$p_{eq}(x) = \sqrt{\frac{K}{2\pi k_B T}} \exp\left(-\frac{Kx^2}{2k_B T}\right)$$

On the other hand $$p_{eq}(x) = \sqrt{\frac{\eta}{2\pi D}} \exp\left(-\frac{\eta x^2}{2D}\right)$$

$$\langle x^2 \rangle_{eq} = \frac{D}{\eta} = \frac{k_B T}{K}$$

O.U. process for the velocity of a particle

$$\eta \to \gamma \qquad D \to \gamma k_B T / M$$

- $$a_1(v) = -\gamma v, \qquad a_2(v) = 2\gamma \frac{k_B T}{M}$$

  $$\frac{\partial P(v,t)}{\partial t} = \gamma \frac{\partial}{\partial v}\left\{ v P(v,t) \right\} + \gamma \frac{k_B T}{M} \frac{\partial^2 P(v,t)}{\partial v^2}$$

  $$P(v,t) = \sqrt{\frac{M}{2\pi k_B T\{1-\exp(-2\gamma t)\}}} \exp\left(-\frac{M\{v - v_0 \exp(-\gamma t)\}^2}{2k_B T\{1-\exp(-2\gamma t)\}} \right)$$

- $$v(t_0 + \Delta t) = v(t_0) - \Delta t \gamma v(t_0) + \xi$$

  $$\overline{\xi} = 0$$

  $$\overline{\xi^2} = 2\gamma \frac{k_B T}{M} \Delta t$$

  $$\Updownarrow$$

  $$\dot{v} + \gamma v = f_s(t)$$ Langevin equation

- Equilibrium

$$\boxed{\lim_{t\to\infty} P(v,t) \equiv P_{eq}(v) = \sqrt{\frac{M}{2\pi k_B T}} \exp\left(-\frac{Mv^2}{2k_B T}\right)}$$

Maxwell distribution

- Autocorrelation function

$$\boxed{c_{vv}(t) = \langle v^2 \rangle_{eq} \exp(-\gamma t)}$$

$$\langle v^2 \rangle_{eq} = \frac{k_B T}{M}$$

O.U. process in phase space

- Fokker-Planck equation $\mathbf{y} = (x, v)^T$

$$\mathbf{a}^{(1)}(\mathbf{y}) = -\mathbf{A} \cdot \mathbf{y} \qquad \mathbf{a}^{(2)}(\mathbf{y}) = 2\mathbf{B}$$

$$\mathbf{A} = \begin{pmatrix} 0 & -1 \\ \omega_0^2 & \gamma \end{pmatrix} \qquad \mathbf{B} = \begin{pmatrix} 0 & 0 \\ 0 & \frac{k_B T}{M}\gamma \end{pmatrix}$$

$$\boxed{\frac{\partial P(\mathbf{y},t)}{\partial t} = \frac{\partial}{\partial \mathbf{y}} \cdot \left\{ \mathbf{A} \cdot \mathbf{y} P(\mathbf{y},t) \right\} + \frac{\partial}{\partial \mathbf{y}} \cdot \left\{ \mathbf{B} \cdot \frac{\partial}{\partial \mathbf{y}} P(\mathbf{y},t) \right\}}$$

- Equation of motion

$$\begin{pmatrix} x(t_0 + \Delta t) \\ v(t_0 + \Delta t) \end{pmatrix} = \begin{pmatrix} x(t_0) \\ v(t_0) \end{pmatrix} + \Delta t \begin{pmatrix} 0 & 1 \\ -\omega_0^2 & -\gamma \end{pmatrix} \cdot \begin{pmatrix} x(t_0) \\ v(t_0) \end{pmatrix} + \begin{pmatrix} 0 \\ \xi \end{pmatrix}$$

$$\Longleftrightarrow \quad \ddot{x} + \gamma \dot{x} + \omega_0^2 x = f_s(t)$$

Solution

- $$P(\mathbf{y},t) = \frac{1}{2\pi\sqrt{\det(\boldsymbol{\sigma}(t))}} \exp\left(-\frac{1}{2}\{\mathbf{y}-\mathbf{M}(t)\}^T \cdot \boldsymbol{\sigma}^{-1}(t)\cdot\{\mathbf{y}-\mathbf{M}(t)\}\right)$$

$$\begin{aligned}\mathbf{M}(t) &= \mathbf{G}(t)\cdot\mathbf{y}_0, \\ \boldsymbol{\sigma}(t) &= 2\int_0^t d\tau\, \mathbf{G}(\tau)\cdot\mathbf{B}\cdot\mathbf{G}^T(\tau).\end{aligned}$$

$$\mathbf{G}(t) = \exp(-\mathbf{A}t)$$

"propagator"

- Equilibrium

$$P_{eq}(\mathbf{y}) = \frac{1}{2\pi\sqrt{\det(\boldsymbol{\sigma}(\infty))}} \exp\left(-\frac{1}{2}\mathbf{y}^T\cdot\boldsymbol{\sigma}^{-1}(\infty)\cdot\mathbf{y}\right)$$

$$\boldsymbol{\sigma}(\infty) = \frac{k_BT}{M}\begin{pmatrix}\omega_0^{-2} & 0 \\ 0 & 1\end{pmatrix} = \langle \mathbf{y}\cdot\mathbf{y}^T\rangle$$

$$P_{eq}(x,v) = \frac{M\omega_0}{2\pi k_BT}\exp\left(-\frac{1}{k_BT}\left\{\frac{Mv^2}{2} + \frac{M\omega_0^2x^2}{2}\right\}\right)$$

Spectral representation of G(t)

- Left and right eigenvectors of A

$$\mathbf{A} = \begin{pmatrix} 0 & -1 \\ \omega_0^2 & \gamma \end{pmatrix}$$

$$\begin{aligned} \mathbf{A} \cdot \mathbf{u}_k &= \lambda_k \mathbf{u}_k, \\ \mathbf{A}^T \cdot \mathbf{v}_k &= \lambda_k \mathbf{v}_k. \end{aligned}$$

$$\mathbf{u}_i^T \cdot \mathbf{v}_j = \delta_{ij}$$

Bi-orthonormal systems of eigenvectors

$$\Rightarrow \quad \lambda_{1,2} = -\frac{\gamma}{2} \pm i\tilde{\omega}_0$$

$$\tilde{\omega}_0 = \sqrt{\omega_0^2 - \frac{\gamma^2}{4}}$$

$$\begin{aligned} \mathbf{u}_1 &= (-1, \lambda_1)^T, \\ \mathbf{u}_2 &= (-1, \lambda_2)^T, \\ \mathbf{v}_1 &= \frac{1}{\lambda_1 - \lambda_2}(\lambda_2, 1)^T, \\ \mathbf{v}_2 &= \frac{1}{\lambda_2 - \lambda_1}(\lambda_1, 1)^T. \end{aligned}$$

- $\mathbf{A} = \sum_k \lambda_k \mathbf{u}_k \cdot \mathbf{v}_k^T$ $\Rightarrow$ $\mathbf{G}(t) = \sum_k \exp(-\lambda_k t)\mathbf{u}_k \cdot \mathbf{v}_k^T$

$$\Rightarrow \quad \mathbf{G}(t) = \frac{\exp(-\lambda_1 t)}{\lambda_1 - \lambda_2} \begin{pmatrix} -\lambda_2 & -1 \\ \lambda_1\lambda_2 & \lambda_1 \end{pmatrix} + \frac{\exp(-\lambda_2 t)}{\lambda_2 - \lambda_1} \begin{pmatrix} -\lambda_1 & -1 \\ \lambda_1\lambda_2 & \lambda_2 \end{pmatrix}$$

Correlation functions

- Velocity

$$c_{vv}(t) = \frac{k_B T}{M} G_{22}(t)$$

$$\boxed{c_{vv}(t) = \frac{k_B T}{M} \exp\left(-\frac{\gamma t}{2}\right) \left\{\cos(\tilde{\omega}_0 t) - \frac{\gamma}{2\tilde{\omega}_0} \sin(\tilde{\omega}_0 t)\right\}}$$

- Position

$$c_{xx}(t) = \frac{k_B T}{M\omega_0^2} G_{11}(t)$$

$$\boxed{c_{xx}(t) = \frac{k_B T}{M\omega_0^2} \exp\left(-\frac{\gamma t}{2}\right) \left\{\cos(\tilde{\omega}_0 t) + \frac{\gamma}{2\tilde{\omega}_0} \sin(\tilde{\omega}_0 t)\right\}}$$

$$\boxed{W(t) = \frac{2k_B T}{M\omega_0^2} \left[1 - \exp\left(-\frac{\gamma t}{2}\right) \left\{\cos(\tilde{\omega}_0 t) + \frac{\gamma}{2\tilde{\omega}_0} \sin(\tilde{\omega}_0 t)\right\}\right]}$$

Smoluchowski equation

$$J(y,t) = a_1(y)P(y,t) - \frac{a_2(y)}{2}\frac{\partial P(y,t)}{\partial y}$$

General form of the probability current

$$J(x,t) = D\left(\frac{F(x)}{k_B T}P(x,t) - \frac{\partial P(x,t)}{\partial x}\right)$$

Diffusion in a harmonic potential

$$F(x) = -\frac{\partial V(x)}{\partial x} = -Kx$$

Harmonic force

$$\frac{\partial P(y,t)}{\partial t} + \frac{\partial J(y,t)}{\partial y} = 0$$

$$\frac{\partial P(x,t)}{\partial t} = D\frac{\partial}{\partial x}\left\{\frac{1}{k_B T}\frac{\partial V(x)}{\partial x}P(x,t) + \frac{\partial P(x,t)}{\partial x}\right\}$$

Smoluchowski equation for an arbitrary potential

Kramers equation

$$\frac{\partial P(\mathbf{y},t)}{\partial t} = \frac{\partial}{\partial \mathbf{y}} \cdot \left\{ \mathbf{A} \cdot \mathbf{y} P(\mathbf{y},t) \right\} + \frac{\partial}{\partial \mathbf{y}} \cdot \left\{ \mathbf{B} \cdot \frac{\partial}{\partial \mathbf{y}} P(\mathbf{y},t) \right\}$$

O.U. process in phase space

$$\frac{\partial P}{\partial t} + v\frac{\partial P}{\partial x} - \omega_0^2 x \frac{\partial P}{\partial v} = \gamma \frac{\partial}{\partial v}\left\{ vP + \frac{k_B T}{M}\frac{\partial P}{\partial v} \right\}$$

$$\omega_0^2 x \rightarrow \frac{1}{M}\frac{\partial V}{\partial x}$$

$$\boxed{\frac{\partial P}{\partial t} + v\frac{\partial P}{\partial x} - \frac{1}{M}\frac{\partial V}{\partial x}\frac{\partial P}{\partial v} = \gamma \frac{\partial}{\partial v}\left\{ vP + \frac{k_B T}{M}\frac{\partial P}{\partial v} \right\}}$$

Kramers equation for an arbitrary potential

Solutions of FP equation in terms of eigenfunctions

$$\frac{\partial P(y,t)}{\partial t} = \mathcal{L}_{FP} P(y,t)$$

$$\mathcal{L}_{FP} = -\frac{\partial}{\partial y} a_1(y) + \frac{1}{2} \frac{\partial^2}{\partial y^2} a_2(y)$$

Fokker-Planck operator

Laplace transform

$$s\hat{P}(y,s) - P(y,0) = \mathcal{L}_{FP} \hat{P}(y,s)$$

$$\hat{P}(y,s) = \frac{1}{s - \mathcal{L}_{FP}} \delta(y - y_0)$$

$$\mathcal{L}_{FP} P_n(y) = -\lambda_n P_n(y)$$
$$\mathcal{L}_{FP}^{+} Q_n(y) = -\lambda_n Q_n(y)$$

$$\mathcal{L}_{FP}^{+} = a_1(y) \frac{\partial}{\partial y} + a_2(y) \frac{1}{2} \frac{\partial^2}{\partial y^2}$$

$$P_n(y) = Q_n(y) P_{eq}(y)$$

$$\delta(y - y_0) = \sum_n P_n(y) Q_n(y_0)$$

$$P(y,t) = \sum_n \exp(-\lambda_n t) P_n(y) Q_n(y_0)$$

Correlation function

$$
\begin{aligned}
c_{yy}(t) &= \int\int dy_0 dy\, y y_0 P(y,t|y_0,0) P_{eq}(y_0) \\
&= \sum_{n=1}^{\infty} \left(\int dy\, y P_n(y) \right)^2 \exp(-\lambda_n t)
\end{aligned}
$$

Multiexponential relaxation

$$\boxed{\tau_{max} = \frac{1}{\lambda_1}}$$

Slowest relaxation time scale

Example

$$\lambda_n = n\eta, \quad n = 0, 1, 2, \ldots .$$

$$\begin{aligned}\mathcal{L}_{FP} &= \eta \frac{\partial}{\partial x} x + D \frac{\partial^2}{\partial x^2}, \\ \mathcal{L}_{FP}^{+} &= -\eta x \frac{\partial}{\partial x} + D \frac{\partial^2}{\partial x^2}.\end{aligned}$$

$$P_n(y) = Q_n(y) P_{eq}(y)$$

$$Q_n(x) = \frac{1}{\sqrt{2^n n!}} H_n(x\sqrt{\eta/2D})$$

$$P_{eq}(x) = \sqrt{\frac{\eta}{2\pi D}} \exp\left(-\frac{\eta x^2}{2D}\right)$$

$$P(\xi, t) = \frac{\exp\left(-\frac{\xi^2}{2}\right)}{\sqrt{2\pi}} \sum_{n=0}^{\infty} \frac{1}{2^n n!} H_n\left(\frac{\xi}{\sqrt{2}}\right) H_n\left(\frac{\xi_0}{\sqrt{2}}\right) \exp(-n\eta t)$$

$$\xi = \frac{x}{\sqrt{\langle x^2 \rangle}}$$

$$\frac{D}{\eta} = \frac{k_B T}{K} = \langle x^2 \rangle$$

$$\sum_{n=0}^{\infty} \frac{\alpha^n}{n!} H_n(x) H_n(y) = \frac{1}{\sqrt{1-4\alpha^2}} \exp\left(\frac{4\alpha}{1-4\alpha^2}(xy - \alpha x^2 - \alpha y^2)\right)$$

$$P(\xi, t) = \sqrt{\frac{1}{2\{1-\exp(-2\eta t)\}}} \exp\left(-\frac{\{\xi - \xi_0 \exp(-\eta t)\}^2}{2\{1-\exp(-2\eta t)\}}\right)$$

Correlation function

$$
\begin{aligned}
c_{yy}(t) &= \int\int dy_0 dy\, y y_0 P(y,t|y_0,0) P_{eq}(y_0) \\
&= \sum_{n=1}^{\infty} \left(\int dy\, y P_n(y) \right)^2 \exp(-\lambda_n t)
\end{aligned}
$$

$$y \longrightarrow \xi$$

$$\int d\xi\, \xi P_n(\xi) = \delta_{n,1}$$

$$\boxed{c_{\xi\xi}(t) = \exp(-\eta t)}$$

$$x = \sqrt{\langle x^2 \rangle} \xi$$

$$\boxed{c_{xx}(t) = \langle x^2 \rangle \exp(-\eta t)}$$

References

[1] H. Risken. *The Fokker-Planck Equation*. Springer Series in Synergetics. Springer, Berlin, Heidelberg, New York, 2nd reprinted edition, 1996.

[2] C.W. Gardiner. *Handbook of Stochastic Methods*. Springer Series in Synergetics. Springer, Berlin, Heidelberg, New York, 2nd edition, 1985.

[3] N.G. van Kampen. *Stochastic Processes in Physics and Chemistry*. North Holland, Amsterdam, revised edition, 1992.