Markov property:

$$\boxed{p_k(x_k \mid x_{k-1}, x_{k-2}, \ldots, x_1; t_1, \ldots, t_k) = p_2(x_k \mid x_{k-1}; t_{k-1}, t_k)}$$

Memory does not go beyond one step.

Gaussian Markov process:

Need only to know

$$\underbrace{\langle x(0)\, x(\tau) \rangle}$$

The autocorrelation function.

Diffusion process:

Langevin equation $\dot{x}(t) = \eta(t)$

This process is <u>not stationary.</u>

We add a <u>friction</u> term:

$$\boxed{\dot{x}(t) = \underbrace{-\beta x(t)}_{} + \eta(t)}$$

(Newton's second law: $m\ddot{x} = -\beta\dot{x} + \eta$)

$\langle \eta \rangle = 0$

$\underbrace{\langle \eta(t)\eta(t') \rangle = A\delta(t-t')}$.

Uncorrelated white noise.

We integrate the Langevin equation:

$$\boxed{x(t) = x(0)e^{-\beta t} + \int_0^t e^{-\beta(t-t')}\eta(t')\,dt'}$$

We now calculate the autocorrelation function $\langle x(t_1)\, x(t_2)\rangle$ using $\langle \eta(t)\rangle = 0$ and $\langle \eta(t)\,\eta(t')\rangle = A\,\delta(t-t')$:

$$\langle x(t_1)\, x(t_2)\rangle = \Big\langle \Big(x(0)\, e^{-\beta t_1} + \int_0^{t_1} e^{-\beta(t_1-t')}\, \eta(t')\, dt' \Big)$$

$$\Big(x(0)\, e^{-\beta t_2} + \int_0^{t_2} e^{-\beta(t_2-t'')}\, \eta(t'')\, dt'' \Big)\Big\rangle$$

$$= \langle x(0)^2 \rangle\, e^{-\beta(t_1+t_2)}$$

$$+ \Big\langle x(0)\, e^{-\beta t_1} \int_0^{t_2} e^{-\beta(t_2-t'')}\, \eta(t'')\, dt'' \Big\rangle$$

$$+ \Big\langle x(0)\, e^{-\beta t_2} \int_0^{t_1} e^{-\beta(t_1-t')}\, \eta(t')\, dt' \Big\rangle$$

$$+ \Big\langle \int_0^{t_1} e^{-\beta(t_1-t')}\, \eta(t')\, dt' \int_0^{t_2} e^{-\beta(t_2-t'')}\, \eta(t'')\, dt'' \Big\rangle$$

$$= x(0)^2\, e^{-\beta(t_1+t_2)}$$

$$+ x(0)\, e^{-\beta t_1} \int_0^{t_2} e^{-\beta(t_2-t'')} \langle \eta(t'')\rangle\, dt''$$

$$+ x(0)\, e^{-\beta t_2} \int_0^{t_1} e^{-\beta(t_1 - t')} \langle \eta(t') \rangle \, dt'$$

$$+ \int_0^{t_1} dt' \int_0^{t_2} dt'' \, e^{-\beta(t_1 - t') - \beta(t_2 - t'')}$$

$$\langle \eta(t'') \eta(t') \rangle$$

$$= x(0)^2 \, e^{-\beta(t_1 + t_2)}$$

$$+ A \int_0^{t_1} dt' \int_0^{t_2} dt'' \, e^{-\beta(t_1 + t_2) + \beta(t' + t'')}$$

$$\delta(t' - t'')$$

$$= x(0)^2 \, e^{-\beta(t_1 + t_2)}$$

$$+ A \int_0^{t_1} dt' \, e^{-\beta(t_1 + t_2) + 2\beta t'}$$

$$= \left(x(0)^2 + \frac{A}{2\beta} \left(e^{2\beta t_1} - 1 \right) \right) e^{-\beta(t_1 + t_2)}$$

$$= \left(x(0)^2 - \frac{A}{2\beta} \right) e^{-\beta(t_1 + t_2)} + \frac{A}{2\beta} e^{-\beta(t_1 - t_2)}$$

As t_1 and $t_2 \to \infty$, the initial transient dies out, and we are left with

$$\underline{\underline{\langle x(t_1)\, x(t_2)\rangle = \frac{A}{2\beta}\, e^{-\beta(t_2-t_1)}}}$$

Hence, apart from the initial transient, the <u>process is stationary to second order.</u>

We also calculate

$$\langle x(t)^2\rangle = \langle \left(x(0)\, e^{-\beta t} + \int_0^t e^{-\beta(t-t')}\, \eta(t')\, dt'\right)$$

$$\left(x(0)\, e^{-\beta t} + \int_0^t e^{-\beta(t-t'')}\, \eta(t'')\, dt''\right)\rangle$$

$$= x(0)^2 e^{-2\beta t} + \int_0^t dt' \int_0^t dt''\, e^{-\beta(t-t')-\beta(t-t'')}$$

$$\underbrace{\langle \eta(t')\, \eta(t'')\rangle}_{=A\,\delta(t'-t'')}$$

$$= x(0)^2 e^{-2\beta t} + \frac{A}{2\beta}\left(1 - e^{-2\beta t}\right)$$

$$\rightarrow \frac{A}{2\beta} \quad \text{as } t \to \infty .$$

We now use these results to construct an

Algorithm for generating a stationary Gaussian Markov chain.

$$\dot{x}(t) = -\beta x(t) + \eta(t)$$

We integrate this from t_n to t_{n+1}:

$$x(t_{n+1}) = x(t_n)\, e^{-\beta \Delta t} + \int_0^{\Delta t} e^{-\beta(\Delta t - t')} \eta(t_n + t')\, dt'$$

where $\Delta t = t_{n+1} - t_n$.

A, β and Δt are given parameters.

We set $x_{n+1} = x(t_{n+1})$ and

$$x_n = x(t_n).$$

We now define

$$z_n = \int_0^{\Delta t} e^{-\beta(\Delta t - t')} \eta(t_n + t')\,dt'$$

$$\langle z_n^2 \rangle = \frac{A}{2\beta}\left(1 - e^{-2\beta\Delta t}\right)$$

Set $x_0 = 0$

$$\langle x \rangle = 0$$

$$\langle x^2 \rangle = \frac{A}{2\beta}$$

Algorithm:

(1) Draw z_n from a gaussian distribution with $\langle z \rangle = 0$ and $\langle z^2 \rangle = \frac{A}{2\beta}\left(1 - e^{-2\beta\Delta t}\right)$.

(2)

Construct

$$\underline{x_{n+1} = x_n e^{-\beta \Delta t} + z_n.}$$

Example:

Velocity component of a massive molecule diffusing in a solution.

Maxwell velocity distribution:

$$p_1(v) = e^{-mv^2/2k_B T} \Big/ \sqrt{2\pi k_B T/m}$$

Langevin equation:

$$\dot{v}(t) = -\beta v(t) + \eta(t)$$

Time scale not present in p_1.

One can show that molecules follow this equation.

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

$$\langle \eta(0)\, \eta(\tau) \rangle = \frac{2\beta k_B T}{m}\, \delta(\tau).$$

Chose $A = \dfrac{2\beta k_B T}{m} \rightarrow$

$$\langle z^2 \rangle = \frac{k_B T}{m} \left(1 - e^{-2\beta \Delta t}\right)$$

This gives $\underline{\langle v(0)\, v(\tau) \rangle = \frac{k_B T}{m}\, e^{-\beta t}}$

"Brownian dynamics".

From Markov to Memory.

Autoregressive processes.

Gaussian Markov process:

$$x_{n+1} = a x_n + z_n$$

Uncorrelated gaussian noise