Simulation of small systems

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Introduction

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- Whereas fluctuations have a time evolution which appears stochastic, their statistical properties exhibit strong constraints and are the signature of intrinsic properties of the system.
- In linear response theory, the role of fluctuations is well understood when the system is close to equilibrium. Several major steps have been done on fluctuations by the findings of different relations, so called fluctuation theorems.

Brownian dynamics

A basic stochastic differential equation

$$\frac{dx(t)}{dt} = a(x,t) + b(x,t)\xi(t)$$

where $\xi(t)$ is a Gaussian white noise, $< \xi(t) >= 0$ and $< \xi(t)\xi(t') >= 2\delta(t - t')$

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A formal solution of the stochastic differential equation in the time interval Δt reads

$$x(t+\Delta t) = x(t) + \int_t^{t+\Delta t} dt'(a(x,t') + b(x,t'))\xi(t') \quad (1)$$

$$= x(t) + \int_t^{t+\Delta t} dt' a(x,t') + \int_t^{t+\Delta t} dW(t) b(x,t') \quad (2)$$

where $w(t)$ is a Wiener process, such that $dW(t) = \xi(t)dt$.

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- $\langle W(t)W(t') \rangle = \mathrm{Min}(t, t')$.
- (An elementary proof consists in writing $\langle W(t)W(t') \rangle = \langle W(t)(W(t') - W(t) + W(t)) \rangle$ and if $t' > t$, the first is equal to zero and the second term to t (diffusion term)).

Stochastic calculus

One has to calculate integrals as

$$\int_{t_0}^{t} f(t) dW(t) \tag{3}$$

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$$S_n = \sum_{i=1}^{n} f(\tau_i)(W(t_i) - W(t_{i-1})) \tag{4}$$

where τ_i is a intermediate time between t_{i-1} and t_i.

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By choosing $f(t) = W(t)$, the mean value of the integral is given

$$< S_n >= \sum_{i=1}^{n} (\mathrm{Min}(\tau_i, t_i) - \mathrm{Min}(\tau_i, t_{i-1})) \tag{5}$$

$$= \sum_{i=1}^{n} (\tau_i - t_{i-1}) \tag{6}$$

Stochastic calculus

If one chooses τ_i as the barycenter of the time interval

$$\tau_i = \alpha t_i + (1-\alpha) t_{i-1} \tag{7}$$

with α between 0 and 1, one obtains for the mean value of S_n

$$< S_n >= \alpha(t - t_0) \tag{8}$$

which leads to a result depending on the intermediate point, even after the average over all realizations!

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$$\int_{t_0}^{t} f(t) dW(t) = \lim_{n\to\infty} \sum_{i=1}^{n} f(t_{i-1})(W(t_i) - W(t_{i-1})) \tag{9}$$

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The Ito's choice corresponds to the fact that the integral is calculated by taking a value of the function f indépendent of the behavior of the Wiener process in the future. A principle similar to the causality principle! However, it yields $< f(t).dW(t) >=< f(t) >< dW(t) >= 0$ and raises question for the computation of the work along a stochastic trajectory.

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The Stratonovitch's choice implies that
$< f(t).dW(t) >\neq< f(t) >< dW(t) >\neq 0$, which leads to adopt this choice in the stochastic thermodynamics.

Stratanovitch's and Ito's calculus

Let us introduce the Stratonovitch calculus and the usual notation, one has

$$\begin{aligned} f(x,t) \circ dW &= f(x + dx/2, t + dt/2)dW \\ &\simeq (f(x) + f'_x(x)dx/2)dW \end{aligned}$$

Comparaison

In order to obtain the same trajectory either calculated by the Ito calculus or by the Stratonovitch calculus, one has to compare with the stochastic differential equation $dx = a(x)dt + b(x)dW$.
For the Stratonovitch calculus, one has

$$\begin{aligned} b(x,t) \circ dW(t) &= (b(x,t) + \frac{\partial b(x,t)}{2\partial x} dx) dW \\ &= b(x,t)dW + b(x,t)\frac{\partial b(x,t)}{2\partial x} dt \end{aligned} \tag{10}$$

to the lowest order in dt.

$$b(x,t) \circ dW(t) = b(x,t)dW(t) + \frac{b(x,t)}{2}\frac{\partial b(x,t)}{\partial x} dt$$

by using $dW^2 = dt$.

Comparison

Finally, the Langevin equation of the Ito calculus $dx(t) = a(x,t)dt + b(x,t)dW$ can be expressed as

$$dx(t) = \left(a(x) - \frac{b(x,t)}{2} \frac{\partial b(x,t)}{\partial x} \right) dt + b(x) \circ dW(t)$$

with the Stratanovich calculus.

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with the Stratanovich calculus.
For a white noise, b is a constant, the trajectories are the same!

Stochastic differential equations and Python

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- Brownian motion in two dimensions

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  3. Different algoritms:

Langevin dynamics

Underdamped motion

Let us consider a particle in one dimension with an applied force deriving from a potential energy $U(x, \lambda)$ and in thermal environment, where λ is a parameter which depends on time in general.

$$\begin{cases} \frac{dp}{dt} &= -\frac{\partial U(x,\lambda)}{\partial x} - \gamma \frac{p}{m} + \xi(t) \\ \frac{dx}{dt} &= \frac{p}{m} \end{cases}$$

where $\xi(t)$ is a Gaussian white noise characterized by the two first moments

$$\langle \xi(t) \rangle = 0, \quad \langle \xi(t)\xi(t') \rangle = 2\gamma k_b T \delta(t - t') \tag{11}$$

and $-\gamma \frac{p}{m}$ is a viscous damping force coming from the thermal environment.

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and $-\gamma \frac{p}{m}$ is a viscous damping force coming from the thermal environment.
In the absence of the external force, one easily checks that the system obeys the Einstein relation, and leads the system to equilibrium. It is easy to show that $\langle \frac{p^2}{m} \rangle = k_B T$.

Langevin dynamics

Overdamped motion

If one assumes that the variation of λ is slow, and the time step Δt for solving the equation of motion is larger than m/γ, the velocity distribution of the particle is always at equilibrium and the derivative of the momentum in the Langevin is much smaller than $\gamma p/m$. The motion is then overdamped and the Langevin equation becomes

$$0 = -\frac{\partial U(x,\lambda)}{\partial x} - \gamma \frac{p}{m} + \xi(t)$$

which can be reexpressed as

$$\frac{dx}{dt} = \frac{1}{\gamma}\left(-\frac{\partial U(x,\lambda)}{\partial x} + \xi(t)\right) \tag{12}$$

Fokker-Planck and Kramers equations

Whereas the Langevin equation is well adapted for obtaining information for a single trajectory, the Fokker-Planck and Kramers equation describe the evolution of the probability $P(x, p, t)$ which corresponds to an average over a large number of trajectories.

underdamped motion

$$\frac{\partial P(x,p,t)}{\partial t} = \left[-\frac{\partial}{\partial x}\frac{p}{m} + \frac{\partial}{\partial p}\left(\frac{\partial U(x,\lambda)}{\partial x} + \gamma \frac{p}{m} \right) + \frac{\partial^2}{\partial p^2} \gamma k_B T \right] P(x,p,t)$$

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The Kramers equation is an equation of continuity in the phase space.

$$\frac{\partial P(x,p,t)}{\partial t} = -\frac{\partial J_x}{\partial x} - \frac{\partial J_p}{\partial p} = -\vec{\nabla}.\vec{J} \tag{13}$$

where J is the flux of probability at point (x, p).

$$\vec{J} = \begin{cases} J_x &= \frac{p}{m} P(x,p,t) \\ J_p &= \left(-\frac{\partial U(x,\lambda)}{\partial x} - \gamma \frac{p}{m} \right) P(x,p,t) - \frac{\partial}{\partial p}(\gamma k_B T P(x,p,t)) \end{cases} \tag{14}$$

Fokker-Planck and Kramers equations

Underdamped motion

Note that when λ and T are constant, the Kramers equation evolves to equilibrium, which means that the stationary probability is given as $P(x, v) = f(x)g(p)$ Inserting the ansatz in the Fokker-Planck equation, one obtains

$$0 = -\frac{p}{m}g(p)\frac{df(x)}{dx} + f(x)\frac{\partial U(x)}{\partial x}\frac{dg(p)}{dp} + \frac{\gamma}{m}f(x)\frac{dpg(p))}{dp} + f(x)\gamma k_B T\frac{d^2g(v)}{dv^2} \tag{15}$$

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By dividing the above equation by $f(x)g(p)$, one obtains

$$\frac{p}{m} \frac{d\ln(f(x))}{dx} - \frac{\partial U(x)}{\partial x} \frac{d\ln(g(p))}{dp} = \frac{\gamma}{mg(p)} \frac{dpg(p))}{dp} + \frac{\gamma k_B T}{g(p)} \frac{d^2 g(v)}{dv^2} \tag{16}$$

Underdamped motion

Both sides of the equation must be equal to 0 in the stationary state (because at equilibrium, no flux is present in the system). One first obtains that

$$\frac{p}{m} g(p) + k_B T \frac{dg(p)}{dp} = 0 \tag{17}$$

which gives

$$g(p) \propto e^{-\frac{p^2}{2mkBT}} \tag{18}$$

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Inserting this solution in the left-hand side of stationary equation, one obtains the differential equation for $f(x)$

$$\frac{p}{m} \left(\frac{d \ln(f(x))}{dx} + \frac{1}{k_B T} \frac{\partial U(x)}{\partial x} \right) = 0 \tag{19}$$

with the solution $f(x) \propto e^{-\beta U(x)}$.

Fokker-Planck and Kramers equations

Underdamped motion

By using the normalization of P, the equilibrium probability is given by

$$P_{eq}(x,p) = \frac{\exp\left(-\beta\left(\frac{p^2}{2m} + U(x)\right)\right)}{\sqrt{2\pi m/\beta}\int dx \exp\left(-\beta\left(\frac{p^2}{2m} + U(x)\right)\right)}$$

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Overdamped motion

the velocity distribution is always at equilibrium and the position distribution obeys the Fokker-Planck equation

$$\frac{\partial P(x,t)}{\partial t} = \frac{\partial}{\partial x}\left(\frac{1}{\gamma}\left[\frac{\partial U(x)}{\partial x} + \frac{\partial}{\partial x}k_B T\right]\right)P(x,t) = -\frac{\partial J}{\partial x}$$

where J is the probability flux

Fokker-Planck and Kramers equations

Overdamped motion

$$J = -\frac{1}{\gamma}\left(\frac{\partial U(x)}{\partial x} + \frac{\partial}{\partial x} k_B T\right) P(x, p, t) \tag{20}$$

It is worth noting that the position distribution also reaches equilibrium at long times by cancelling the flux J.

$$P_{eq}(x) = \frac{\exp\left(-\beta U(x)\right)}{\int dx \exp\left(-\beta U(x, \lambda)\right)}$$

Path integral approach

If $\xi(t)$ is a Gaussian white noise, with the two first moments $\langle \xi(t) \rangle = 0$ and $\langle \xi(t)\xi(t') \rangle = 2\gamma k_b T$. The probability of having a path $\xi(t)$ between 0 and t is given by

$$P[\xi] \propto \exp\left(-\frac{1}{4\gamma k_B T} \int_0^t du\, \xi^2(u) \right)$$

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The probability $P[\xi]$ is normalized by summing over paths:

$$\int d[\xi]\, P[\xi] = 1 \tag{21}$$

For an overdamped motion, the Langevin equation can be expressed as

$$\gamma \frac{dx}{dt} + \frac{\partial U(x,\lambda)}{\partial x} = \xi(t) \tag{22}$$

Path integral approach

When one solves the stochastic differential equation, the noise is converted in position fluctuations of the particle.
the probability of having a trajectory $x(t)$ is given by

$$P[x] \propto \exp\left(-\frac{1}{4\gamma k_B T}\int_0^t du\left\{\left[\gamma\frac{dx}{dt}+\frac{\partial U}{\partial x}\right]^2-2k_B T\frac{\partial^2 U}{\partial x^2}\right\}\right)$$

such that

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The second derivative of the potential comes from the Jacobian of the change of variable $\xi(t)$ to $x(t)$ in the path integral. Indeed, taking a finite time step, the Langevin equation is expressed as

$$\gamma((x_{n+1}-x_n)=-U'(x'_n)dt+\sqrt{2\gamma k_B T}(W_{n+1}-W_n)$$

where x'_n is a point choosing betwenn x_n and x_{n+1}.

Path integral approach

By choosing a Stratonovitch rule,

$$U'(x'_n = (U'(x_n) + \frac{1}{2}U''(x_n)(x_{n+1} - x_n)$$

which gives a Jacobian of the elementary transformation equal to

$$\frac{\partial(W_{n+1} - W_n)}{\partial(x_{n+1} - x_n)} = \frac{\gamma}{\sqrt{2\gamma k_B T}}(1 + \frac{\delta t}{2\gamma}U''(x_n)$$

Finally, one takes the limit $\Delta t \to 0$, and one obtains

$$\prod_{n=0}^{\frac{t}{\Delta t}}(1 + \frac{\delta t}{2\gamma}U''(x_n)) \to \exp\left(\frac{1}{2\gamma}\int_0^t U''(x)ds\right)$$

Contrary to Hamiltonian systems, the Langevin equation breaks the time-reversal symmetry (for a single trajectory). However, one can see that the time-reversal process $\xi(-t)$ occurs with the same probability.

Path integral approach

- At equilibrium, the probability of having the time-reversal trajectory $x(-t)$ is equal to the probability of having $x(t)$. This symmetry is called detailed balance.

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- At equilibrium, the probability of having the time-reversal trajectory $x(-t)$ is equal to the probability of having $x(t)$. This symmetry is called detailed balance.
- Consequently, no work can be extracted from the stochastic motion of the particle, corresponding to the prescription of the second law of thermodynamics.