Accelerated approach to equilibrium

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May 3, 2017

1 Introduction

We would be studying an optimization problem for a classical non-equilibrium problem. Our model under consideration would be a Langevin particle coupled to a heat bath. We would be driving the system from one equilibrium state to another through a certain protocol.

On one hand, if the system is driven slow enough, then the system takes infinite time in reaching the new equilibrium configuration. On the other hand, if the system is driven really fast, then the sytem is in non-equilibrium and it takes some time to relax to the new equilibrium configuration.

Can we choose an optimized protocol that allows the system to equilibriate in arbitrary small time?

2 Preliminary thoughts

The task is to find a protocol for control variable such that equilibrium is reached in a time arbitrary smaller than the usual time. For example, if you expand the piston of gas very fast, then the gas molecules will take some time (characteristic time τ) to reach equilbrium. Of course, you can expand the piston quasi-statically, and then the gas molecules will never go out of equilibrium. But then it will take infinite amount of time to expand the piston upto certain height. That's bad! So, you are looking for a clever way (a protocol) to expand the piston so that you can expand the piston upto certain height and and still take arbitrarily small time compared to τ.

It's like eating the apple and having it too. How is it possible? Physically speaking, you should pay an enormous amount of energy.

Also note that it sounds similar to shortcut to adiabaticity but it is NOT. What's the difference?

3 Definition of thermal equilibrium

For a system to be in thermal equilibrium configuration, we should have:

- For each degree of freedom, the average kinetic K and potential V energy will follow equipartition theorem, i.e $\langle K\rangle = \langle V\rangle = k_BT/2$. In our model of overdamped Browinan particle in Harmonic potential, there is no kinetic energy. Hence, we will get $\langle E\rangle = \langle V\rangle = \kappa\langle x^2/2\rangle = k_BT/2$.
- Properties of the system should be time-independent.

4 Langevin dynamics

Let's write the general equation of a particle under a harmonic potential of stiffness κ and dissipation γ:

$$m\ddot{x} = -\kappa x - \gamma\dot{x} + \xi(t) \tag{1}$$

$$\langle\xi(t)\rangle = 0, \quad \langle\xi(t)\xi(t')\rangle = 2D\delta(t-t') \tag{2}$$

where $\xi(t)$ is white noise. Its' first and second moments are given in equation 2.What does condition on the second moment mean? Noise for different times is uncorrelated. For the same time, we see that second moment diverges. It's chosen for analytical convenience. While doing numerical simulations, we will have to see how to implement it.

This model has two degrees of freedom position x and velocity $\dot{x} = v$. We would focus here on position degree of freedom[1]. To understand the affect of noise and dissipation, we would first study two subcases: random walker (one with only noise term) and tired walker in position (the one with only dissipation term).

Random walker: affect of noise

Langevin equation for a random walker is given by:

$$\dot{x} = \xi(t) \tag{3}$$

Now, from equation 3, we can compute the mean and variance of position. We find that mean position $\langle \Delta x \rangle = 0$ (figure 1) and variance $\langle \Delta x^2 \rangle = 2Dt$ (figure 2), where $\Delta x = x(t) - x(0)$. Hence, we find that random walker never relaxes to equilibrium since $\langle \Delta x^2 \rangle$ always grows in time.

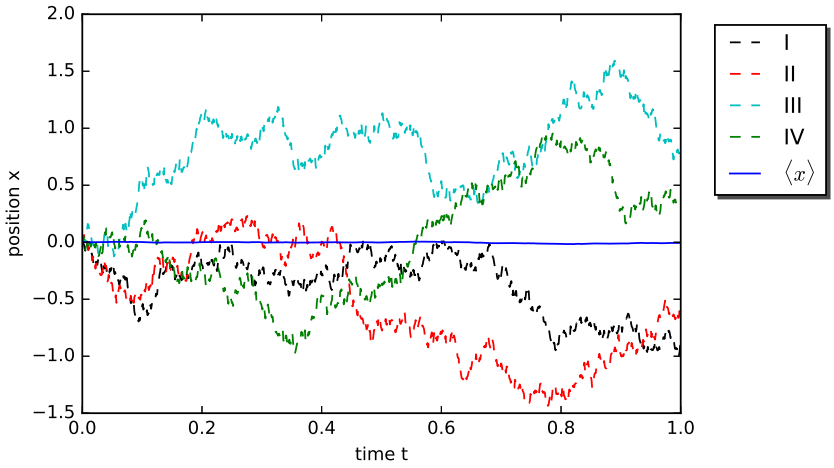

Figure 1: I, II, III and IV represent position of the random walker obtained as a function of time in first, second, third and fourth realization of noise. $< x >$ is the mean position of the random walker averaged over 1000 realizations.

Tired walker: affect of dissipation

For **overdamped** situation $\gamma \gg m$, we find that we get dissipation in position (rather than velocity $\dot{x}$):

$$\dot{x} = -\frac{\kappa}{\gamma} x \tag{4}$$

We get $x(t) = x(0)e^{-\kappa t/\gamma}$ as solution. It means as $t \to \infty$, position (and velocity)of particle goes to zero no matter what is the initial position (and velocity). Here, dissipation takes away total energy of the system.

"Note:" velocity should be zero because of our overdamped assumption. What do we learn? On one hand, with only noise term, the variance keeps growing in time. It will perpetually stay in non-equilibrium. On the other hand, when we have only dissipation term, the particle always relaxes to zero position. The final state is in equilibrium, but it's not useful for modelling anything

[1]see appendix for model involving velocity degree of freedom

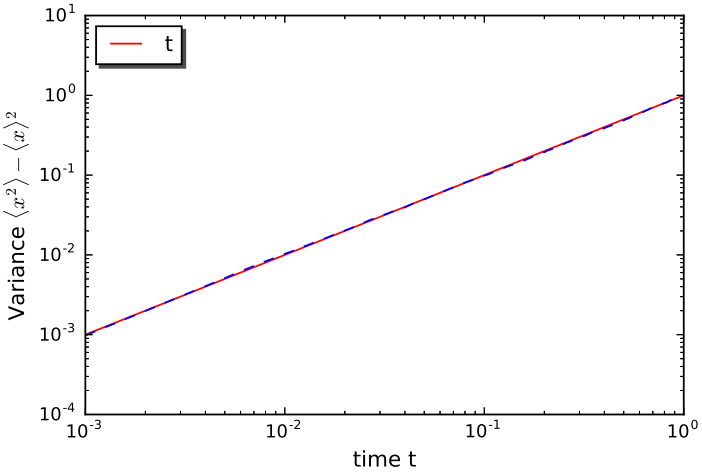

Figure 2: Variance $\langle \Delta x^2 \rangle$ of the random walker as a function of time with $D = 1/2$(dashed blue line). Red line is the fitted line linear in time t.

because average energy is zero. Hence, we will study equilibrium with both of the terms present. We will find that due to dissipation-fluctuation relationship, our system reaches equilibrium.

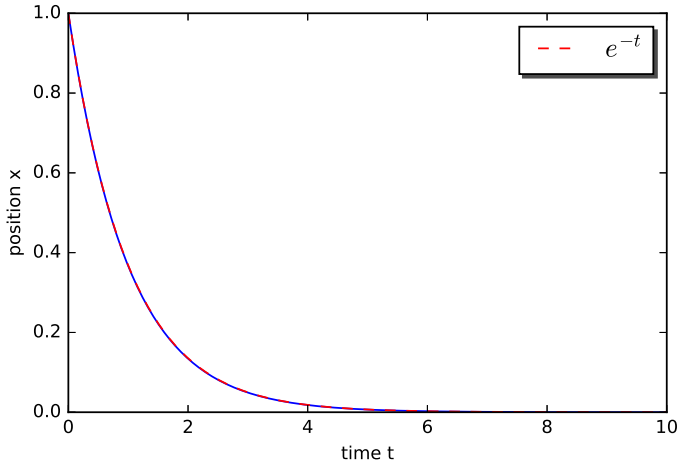

Figure 3: Position of the tired walker as a function of time with $\kappa/\gamma = 1$ and $x(0) = 1$. Euler method was used with $\Delta t = 0.01$.

Overdamped Brownian particle

Now let's consider overdamped Brownian particle with dissipation constant γ in a harmonic potential with spring stiffness κ. We assume $\gamma \gg \sqrt{\kappa/m}$ and thus, momentum $m\dot{q}$ is assumed to be constant. It follows:

$$\dot{x} = -\frac{\kappa(t)}{\gamma}x + \xi(t) \tag{5}$$

Characteristic time scale of our model is $\tau = \dfrac{\gamma}{\kappa}$. We should make the equation dimensionless while simulating it on computer. This will help us to describe dynamics in the units of the τ.

Constant spring stiffness

We can solve this equation analytically when spring stiffness $\kappa(t) = \kappa$ is a constant. Then, we get:

$$x(t) = x(0)e^{-\kappa t/\gamma} + \int_0^t ds\xi(s)e^{-\kappa(t-s)/\gamma} \tag{6}$$

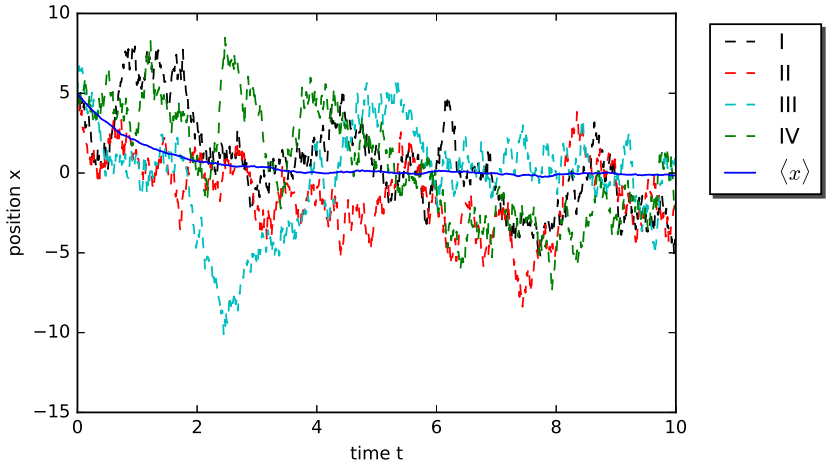

Figure 4: With $\kappa/\gamma = 1$ and $x(0) = 5$, I, II, III and IV represent position of the Brownian particle as a function of time in first, second, third and fourth realization of noise. $< x >$ is the mean position of the random walker averaged over 1000 realizations . Euler-Maruyama method was used with $\Delta t = 0.01$.

The above equation gives us information about how position [2] of particle evolves in time. We would be interested in the position at really long time ($t \to \infty$). Since $\langle x(t)\rangle = 0$, let's compute second raw moment [3].

$$\langle x^2(t)\rangle = \langle x^2(0)\rangle e^{-2\kappa t/\gamma} + \frac{D\gamma}{\kappa}(1 - e^{-2\kappa t/\gamma}) \tag{7}$$

For long time, we see that Brownian particle reaches equilibrium since $\langle x^2(t \to \infty)\rangle$ becomes time -independent. Thus, we expect it to satisfy equipartition theorem, i.e $\langle x^2\rangle = k_B T/\kappa$. This would mean that $D = k_B T/\gamma$. We obtain a fluctuation-dissipation relation in this way.

Linear ramp of spring's stiffness

The central idea is that we would be studying transition between two equilibrium configuration defined by spring constants $\kappa(0) = 1$ and $\kappa(T_f) = 2$ at initial and final time, respectively. Linear ramp of spring constant (figure 6) is given by:

$$\kappa(t) = \begin{cases} 1 & , 0 < t < 10 \\ 1 + t/t_f & , 10 < t \leq t_f \\ 2 & , t_f \leq t_f + 10 \end{cases} \tag{8}$$

where t_f is the time it takes for spring constant to ramp from $\kappa = 1$ to $\kappa = 2$. Thus, smaller the t_f, higher is the slope $\dot{\kappa} = 1/t_f$. We have chosen 10 time units as the time interval that we give our particle to relax to equilibrium because in figure 5, we find that it relaxes to equilibrium before 10 time units. Hence, initially, with $\kappa(0) = 1$, we give 10 time units for our Brownian particle to relax to equilibrium, and then after $t = t_f$ with $\kappa(t > t_f) = 2$, we again wait for 10 time units.

[2] To find velocity, we can take a time derivative of equation 6. However, we see that it violates our assumpation that momentum is constant in time. What's happening here?

[3] In equation 7, if we take $\kappa/\gamma \to 0$ so as that to get back variance of random walker, we get wrong answer. The blame should go to the step in which averaging was done of the solution from equation 6. Before averaging, equation 6 does give us correct answer in this limit.

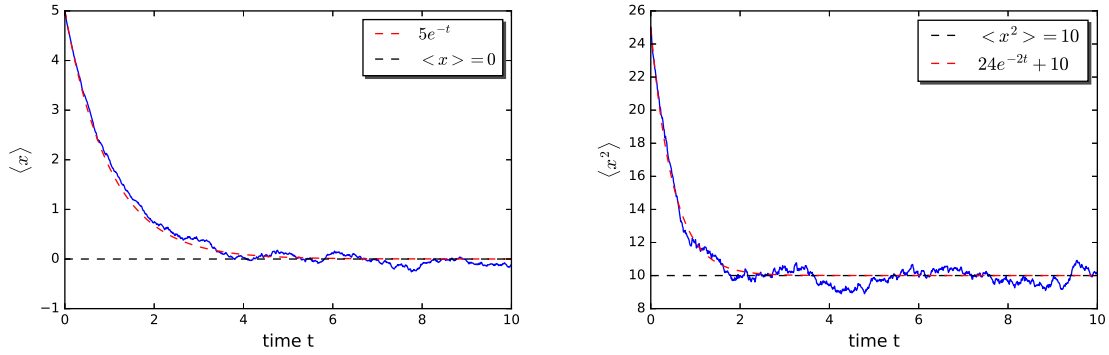

Figure 5: First $< x >$ and second $< x^2 >$ raw moments of the position of the Brownian particle as a function of time with $D = 10$, $\kappa/\gamma = 1$ and $x(0) = 5$. Euler-Maruyama method was used with $\Delta t = 0.01$. We can note that physical quantities after some time starts fluctuating around their equilibrium value

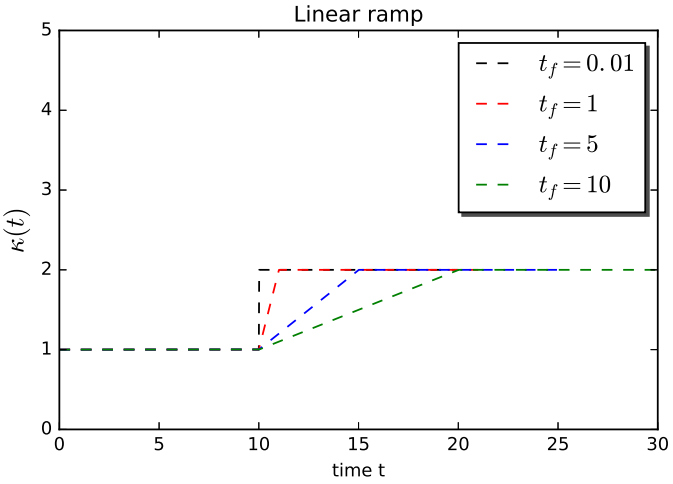

Figure 6: Ramp protocol

Note that relaxation time for mean of position $< x >$ is $\tau = \frac{\gamma}{\kappa} = 1$ unit. And relaxation time for second raw moment of position $< x^2 >$ is $\tau = \frac{\gamma}{2\kappa} = 0.5$ units. When $\kappa = 2$, then $\tau = 0.25$. We see that even with $t_f < \tau$, then we still see that particle relaxes to equilibrium! It's very surprising, and doesn't match with Nature Physics '16 paper.

Here are a few expectations from the numerical simulation before we can start trusting these results:

- The time it takes to relax to equilibrium should NOT depend on N_{exp} and Δt. Generally speaking, N_{exp} should be large enough and Δt small enough so that our numerical results don't depend on these two parameters.
- All of linear ramp protocol should give the same value for $0 < t < 10$. This expectation is met.

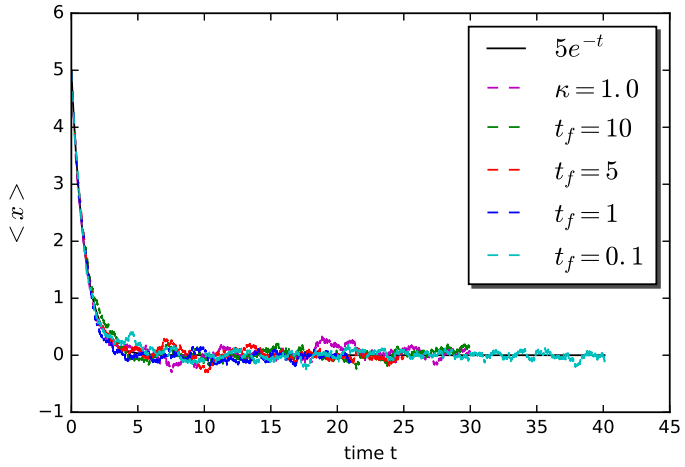

Figure 7: $\Delta t = 0.001, D = 10, \gamma = 1$ and number of noise realizations $N_{exp} = 1000$ over which it is averaged. For all linear protocol ramps, mean $< x >$ matches with that of mean of equation 6

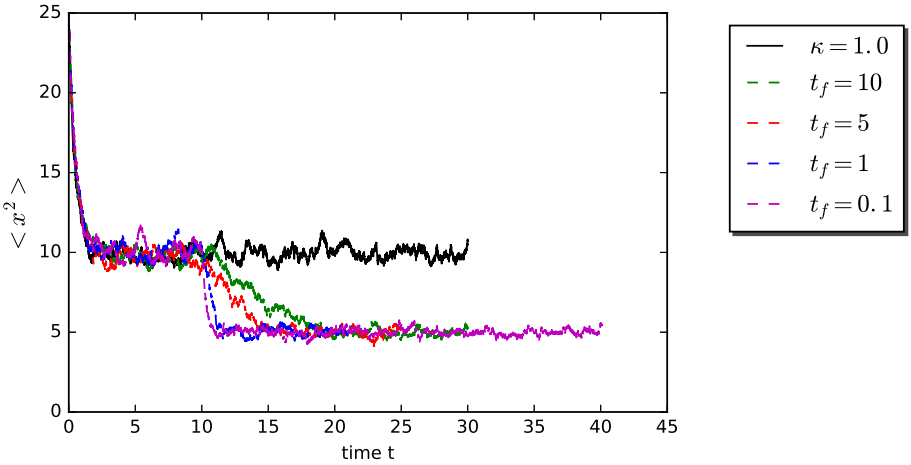

Figure 8: $\Delta t = 0.001, D = 10, \gamma = 1$ and number of noise realizations $N_{exp} = 1000$ over which it is averaged.

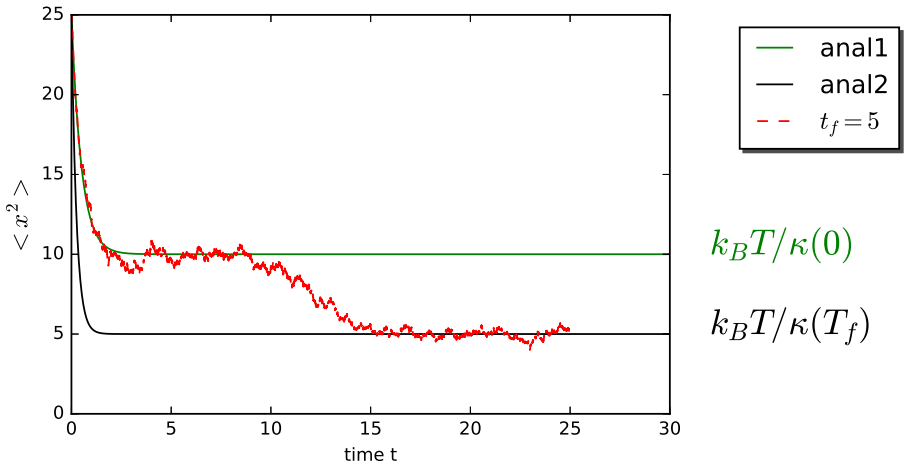

Figure 9: $\Delta t = 0.001, D = 10, \gamma = 1$ and number of noise realizations $N_{exp} = 1000$ over which it is averaged.

5 Fokker-Planck dynamics

When we average over position over all noise realization, we get Fokker-Planck equation. It describes the time evolution of probability distribution of position. To understand it, let's first study random walker.

Random walker

We expect that the probability of a random walker should be a guassian with zero mean and a variance growing linearly in time. Let's derive it from Fokker Planck equation.

$$\frac{\partial \rho}{\partial t} = D \frac{\partial^2 \rho}{\partial x^2} \tag{9}$$

We assume that the random walker initially was located at origin, i.e. $\rho(x, 0) = \delta(x)$. Then, we get $\rho(x, t) = \frac{1}{\sqrt{4\pi D t}} e^{-x^2/(4Dt)}$

By comparing it with the standard form of guassian distribution $P(x) = \frac{1}{\sqrt{2\pi\sigma^2}} e^{-\frac{(x-\mu)^2}{2\sigma^2}}$, we can find mean μ and variance σ^2. It matches with what we got in Langevin dynamics, i.e. $\langle \Delta x \rangle = 0$ and $\langle \Delta x^2 \rangle = 2Dt$, where $\Delta x = x(t) - x(0)$ [4] .

Overdamped Brownian particle

Fokker-Planck equation for the overdamped Brownian particle in Harmonic potential would have an additional term :

$$\partial_t \rho = \partial_x \left(\frac{\kappa(t)}{\gamma} x \rho \right) + D \partial_{xx} \rho \tag{10}$$

We would find that the equilibrium distribution would be again a guassian, whose variance would be linear in temperature [5] .

[4] For the wavefunction of free quantum particle, the Schrödinger equation looks exactly the same as the above classical diffusion equation. Now in that case, we find $\langle \Delta x_Q^2 \rangle \sim t^2$. Why it's different? It's because Schrödinger equation involves quantum probability amplitude $\psi(x)$, not probability $|\psi(x)|^2$. The variance of complex-valued $\psi(x)$ does spread linear in time, but that's different from quantum variance of position which grows quadratically in time as the later is computed from quantum probability. Hence, for quantum free particle $\langle \Delta x_Q^2 \rangle = \int x^2 P_Q(x,t) dx = \int x^2 |\psi(x,t)|^2 dx \sim t^2$ and for classical diffusive particle $\langle \Delta x_C^2 \rangle = \int x^2 P_C(x,t) dx \sim t$.

[5] This can be compared with variance of random walker which is linear in time.

In the experiment under consideration, particle is in equilibrium at the initial and final time. For time $t = 0$, we get:

$$\begin{aligned} D\partial_{xx}\rho + \partial_x\left(\frac{\kappa(0)}{\gamma}x\rho\right) &= 0 \\ \partial_{xx}\rho + \alpha(x\partial_x\rho + \rho) + &= 0 \end{aligned}$$

where $\alpha = \dfrac{\kappa(0)}{D\gamma} = \dfrac{\kappa(0)}{k_BT}$, using fluctuation-dissipation relation. We find that $\rho(x) = Ae^{-\alpha x^2/2}$, where A is a normalization constant, satisfies the above equation. Hence, we note that variance $1/\alpha \propto T$. Similarly, at time $t = t_f$, we find that particle's probability density ρ is a guassian with $\alpha = \dfrac{\kappa(t_f)}{D\gamma} = \dfrac{\kappa(t_f)}{k_BT}$.

We find that mean of distribution is zero and it's variance is constant in time, and linear in Temperature. This matches with what we had obtained from Langevin dynamics of overdamped particle in long time limit.

6 Thermodynamics calculation

Hamiltonian

Our model is an open classical system. It is in canonical ensemble where our Brownian particle is in contact with heat bath of temperature T. The affect of heat bath on the particle is two-fold: reducing the energy through dissipation and giving kick with a random force through noise term.

Hamitonian of the total system H_t is

$$H_t = H_b + H_s + H_{int} \tag{11}$$

where H_b, H_s, H_{int} are the Hamiltonian of bath, system and interaction between bath and system. If we follow standard statistical mechanics, heat bath would be weakly interacting so that we can ignore H_{int} term. Heat bath defines temperature T and we get partition function as $Z = \int d\Gamma e^{-\beta H}$, where β is inverse temperature and $d\Gamma$ is infinitesimal phase space volume $dpdq$.

Let's write the Hamitonian of the system generally. We would ignore the noise and dissipation term in equation 5 since it's because these terms are the effect of bath on the system.

$$H_s = \frac{p^2}{2m} + \frac{1}{2}\kappa(t)x^2 \tag{12}$$

For writing the Hamiltonian of system H_s of our overdamped Langevin particle, we should ignore kinetic energy term, and for underdamped we should ignore potential energy. Essentially, we are comparing which component of energy is bigger [6].

The Hamiltonian of system H_s of our overdamped Langevin particle [8]

$$H_s = \frac{1}{2}\kappa(t)x^2 \tag{13}$$

At time $t = 0$ and $t = t_f$, our particle is in equilibrium. Hence, we can find thermodynamic quantities like free energy, partition function, entropy and internal energy. Let's find partition function because other physical quantities can be derived from it.

[6] This nomenclature as defined in literature [7] is misleading if we compare it to textbook problem of damped harmonic oscillator. In the old problem, we would compare dissipation with product of mass and spring constant term.

[8] Trouble is that this doesn't give us correct equation of motion 5. But for now, we would go ahead because this hamiltonian does gives the free energy difference that matches exactly with that given in Nature phyiscs paper

Partition Function

Let's denote $\kappa(0) = \kappa$. Since, over-damped particle has a single degree of freedom x, we have partition function Z given by:

$$Z = \int dx e^{-\beta H} = \int dx e^{-\beta \kappa x^2/2\gamma} = \sqrt{\frac{2\pi}{\beta\kappa}} \tag{14}$$

Hence, we have free energy $F = -k_B T \ln Z = -\frac{k_B T}{2} \ln \frac{2\pi}{\beta\kappa}$. This means free energy difference between two equilibrium states will be $\Delta F = \frac{k_B T}{2} \ln \frac{\kappa(t_f)}{\kappa(0)}$.

Now let's talk about internal energy. $U = \langle E \rangle = \frac{k_B T}{2}$, which is the statement of equipartition theorem. Since the temperature is the same, $\Delta U = 0$.

$$\begin{aligned} F &= U - TS \\ \Delta F &= \Delta U - T\Delta S \\ \Delta F &= -T\Delta S \\ \Delta S &= -\Delta F/T = -\frac{k_B}{2} \ln \frac{\kappa(t_f)}{\kappa(0)} \end{aligned}$$

Work done

$\langle W \rangle = \int dH = \int \frac{\partial H}{\partial \kappa} d\kappa = \int \langle x(t)^2 \rangle \dot{\kappa} dt$

Hence, we note that work done for constant spring stiffness is zero. For linear ramp, we get $W \propto a$

A Model with velocity degree of freedom

Let's write the general equation of a particle with dissipation γ and noise term ξ:

$$m\ddot{x} = -\gamma \dot{x} + \xi(t) \tag{15}$$

This model has two degrees of freedom position x and velocity $\dot{x} = v$. We would focus here on velocity degree of freedom as we have already studied model involving position degree of freedom. Like before, to understand the affect of noise and dissipation, we would first study two subcases: random walker (one with only noise term) and tired walker in velocity(the one with only dissipation term).

Random walker in velocity space: affect of noise

Langevin equation for a random walker in velocity space (with $m = 1$) is given by:

$$\dot{v} = \xi(t) \tag{16}$$

We find that $\langle \Delta v \rangle = 0$ and $\langle \Delta v^2 \rangle = 2Dt$, where $\Delta v = v(t) - v(0)$.

Tired walker in velocity space: affect of dissipation

If there is no spring constant κ, then we find that we get dissipation in velocity:

$$\dot{v} = -\frac{\gamma}{m} v \tag{17}$$

We get $v(t) = v(0)e^{-\kappa t/\gamma}$ as solution. It means as $t \to \infty$, speed (and position) of particle goes to zero no matter what is the initial velocity (and position). Here, dissipation takes away kinetic energy of the system.

Brownian particle

Now let's consider Brownian particle with dissipation constant γ and noise ξ term together. It follows:

$$\dot{v} = -\frac{\gamma}{m}v + \xi(t) \tag{18}$$

We get equation of motion to be similar to what we obtained before with position x replaced by velocity v.

$$v(t) = v(0)e^{-\gamma t/m} + \int_0^t ds\xi(s)e^{-\gamma(t-s)/m} \tag{19}$$

$$\langle v^2(t)\rangle = \langle v^2(0)\rangle e^{-2\gamma t/m} + \frac{D\gamma}{m}(1 - e^{-2\gamma t/m}) \tag{20}$$

$$\langle \Delta x^2(t)\rangle = 2\frac{k_B T}{\gamma}\left[t - \frac{m}{\gamma} + \frac{m}{\gamma}e^{-\gamma t/m}\right] \tag{21}$$

Since $\langle \Delta x^2(t)\rangle = 2Dt$, we get $D = \dfrac{k_B T}{\gamma}$

B Numerical algorithm for Langevin equation

$$\dot{x} = -\frac{\kappa(t)}{\gamma}x + \xi(t) \tag{22}$$

$$dx_t = -\Omega x_t dt + \sqrt{2D}dW_t \tag{23}$$

$\Omega = \kappa/\gamma$, $D = T/\xi$

Weiner process is defined as

$$W_0 = 0, \langle W_t\rangle = 0, \langle (W_t - W_s)^2\rangle = |t - s| \tag{24}$$