Numerical Calculation of the Diffusion Coefficient in Langevin Equation with periodic potentials

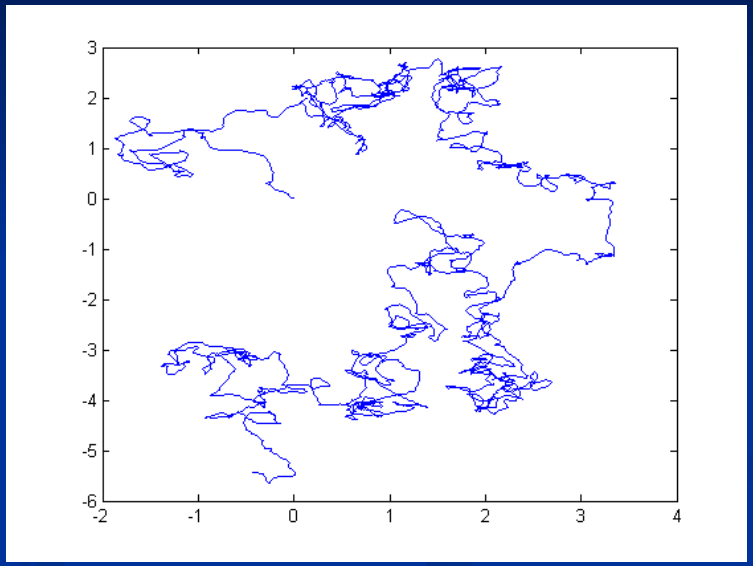
Anastasios Vogiannou
Aristotle University of Thessaloniki
Grigoris Pavliotis
Imperial College London

Contents

The Langevin Equation

- Brownian motion is the irregular, almost random motion observed in many physical problems like the motion of pollen grains suspended in a liquid.
- The problem of Brownian motion was solved many years after it's formulation by Einstein.
- Langevin proposed a different (and more simple) way to approach Brownian motion. He used the following equation

$$\ddot{q} = -V'(q) - \gamma\dot{q} + \xi$$



- The above equation is a second order stochastic differential equation (SDE).
- It is equivalent to the Newtonian equation of motion for a force derived from a potential plus a drift and a stochastic term.
- The stochastic term is a white noise Gaussian process. It is equal to

$$\xi = \sqrt{2\gamma\beta^{-1}}\dot{W}_t$$

$$W_0 = 0$$

W_t is continouous

$$W_t - W_s : N(0, t-s), \text{ for } 0 \quad s < t$$

The Langevin Equation – Example

Formulation

- Consider a particle inside a liquid whose mass is greater but comparable to the mass of the molecules of the liquid. The particle is under the influence of gravity field.
- The equations of motion for the particle is

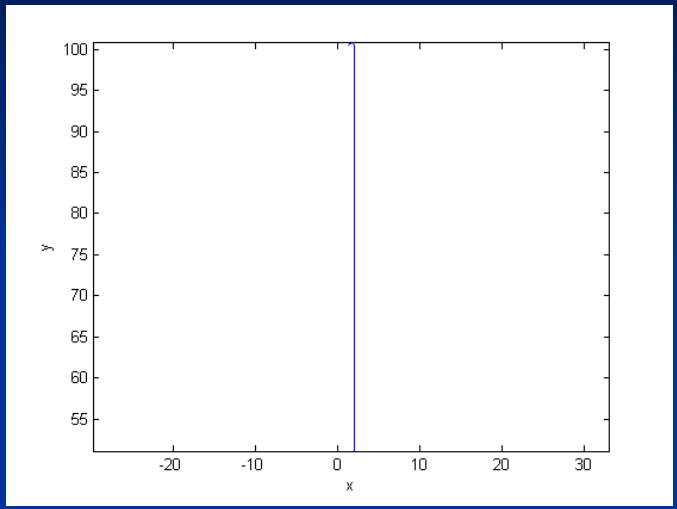
$$\ddot{x} = -\gamma\dot{x} + \xi_x$$
$$\ddot{y} = -g - \gamma\dot{y} + \xi_y$$

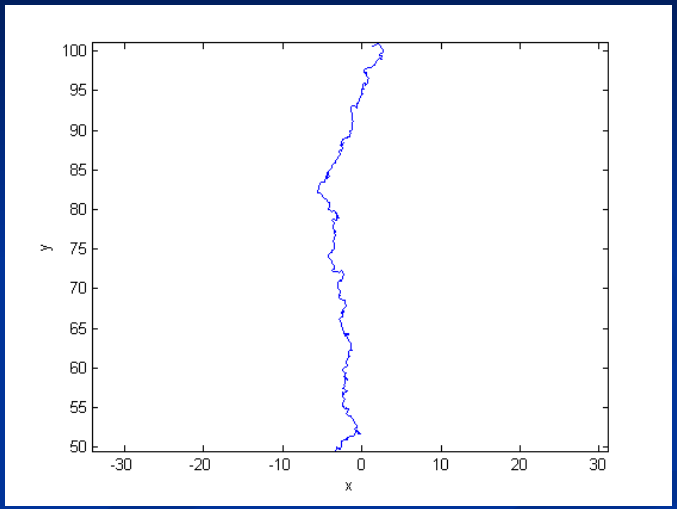
- In the Langevin equation the potential is the gravity field, the drift term represents the friction caused by the motion of the particle inside the liquid and the stochastic term is due to the unpredictable collisions of the particle with the molecules of the liquid.
- We study the motion of the particle in a vertical plane (2 dimensions).

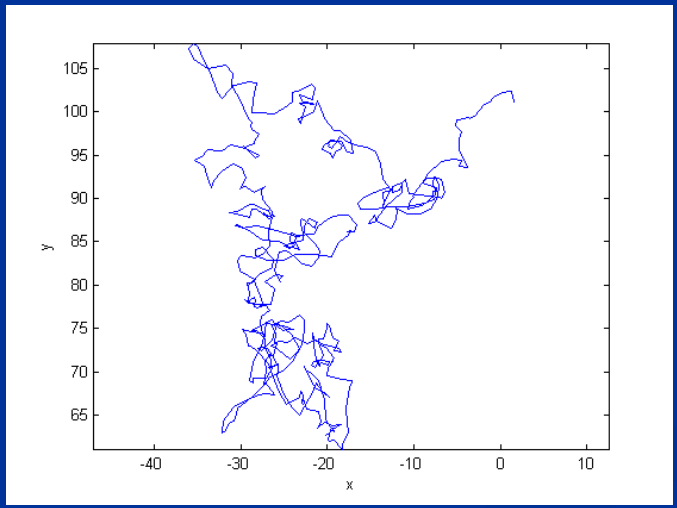
Solution

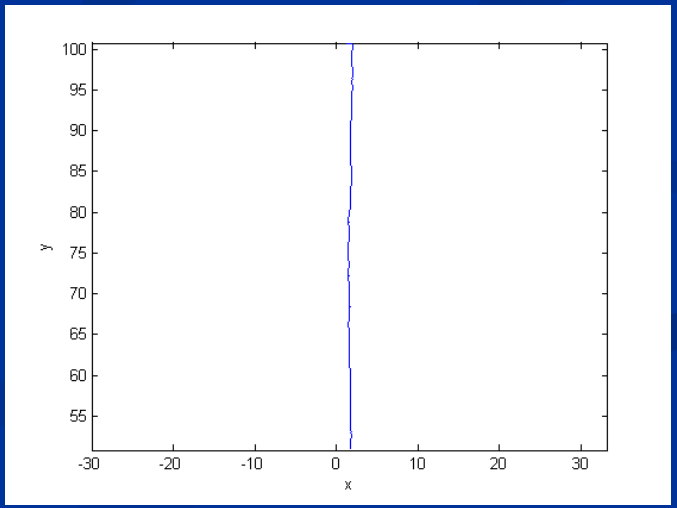
- In the absence of the stochastic term there is a unique solution for specific initial conditions.
- For low intensity noise the orbit of the particle is slightly perturbed. For higher intensity noise the orbit is completely different.
- The averaged orbit $x(t) = \langle x_i(t) \rangle,\ y(t) = \langle y_i(t) \rangle$ is same with the one of the noise-free system

The Langevin Equation – Example









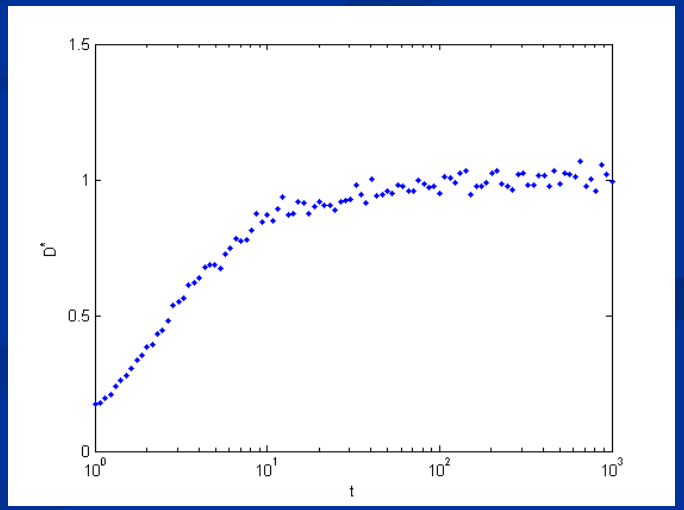
The Diffusion Coefficient

- An essential phenomenon that characterizes many stochastic systems, like those described by the Langevin equation, is that if the particles of the system are in a small area, after some time they will spread in space.
- This process is quantified with the diffusion coefficient defined as

$$D = \lim_{t} \frac{1}{2t} \left\langle \left(q(t) - q(0) \right)^2 \right\rangle$$

- Higher value of the diffusion coefficient means that the particles spread in space faster.
- If the second moment of space grows linearly with time, for some time interval, we say that the system is in normal diffusion. If it grows faster we have superdiffusion and if slower we have subdiffusion.
- The experimental calculation of diffusion is practical impossible. A quantity that describes the diffusive behavior of a system and we are able to calculate is

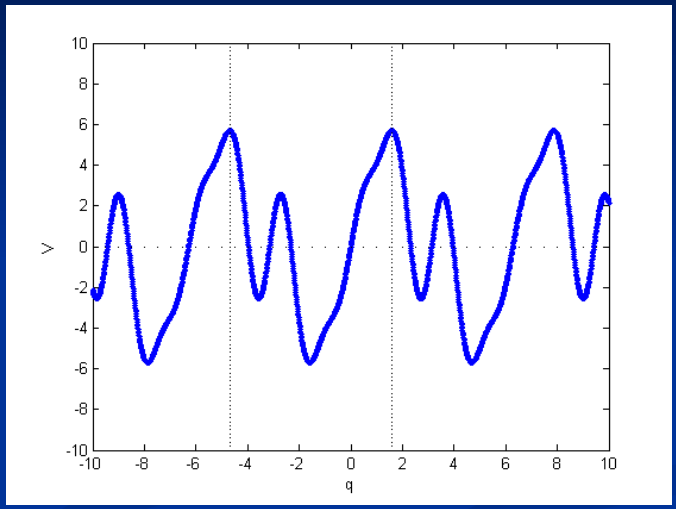
$$D^*(t) = \frac{1}{2t} \left\langle \left(q(t) - q(0) \right)^2 \right\rangle$$



- A feature of many stochastic systems, like the ones we are going to study, is that they reach normal diffusion state after some time.

Periodic Potentials – Dynamics

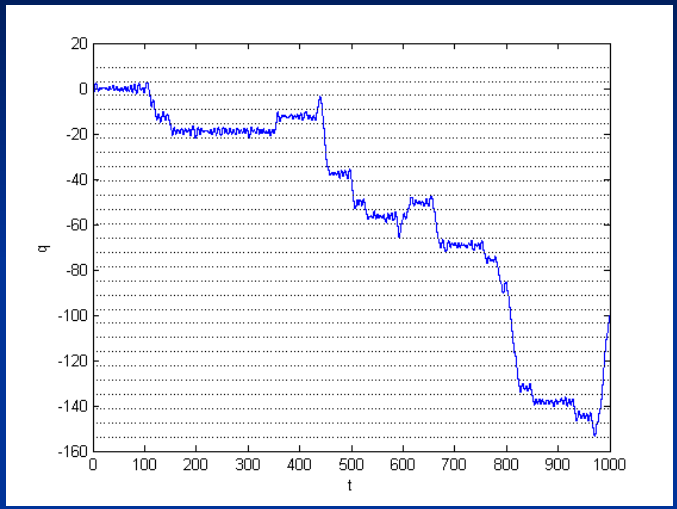
- If the potential in the Langevin equation is a smooth periodic function of space then there exist global minima and global maxima. The interval of length equal to the period that has end points global maxima of the potential is called a well.
- The potential can be seen as a sequence of wells
- The motion of the Brownian particle is characterized by jumps between the wells and trapping inside them.

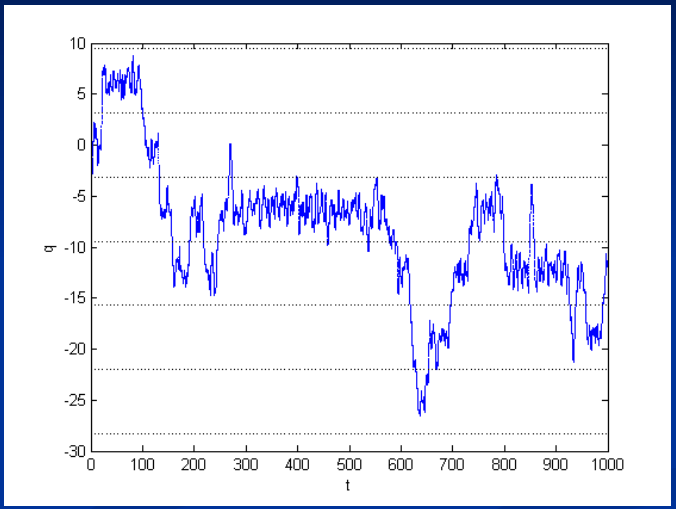


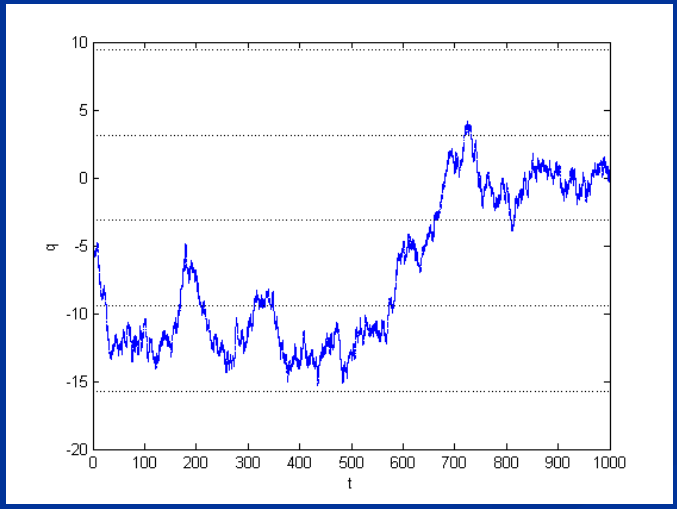
- The possibility a jump will occur in a certain period of time is called jump rate.
- The particle may pass many wells before it gets trapped again. Thus we have jumps with various lengths.
- The jump rate and jump lengths depend on friction, temperature and the potential.
- The diffusion coefficient can be calculated from the formula

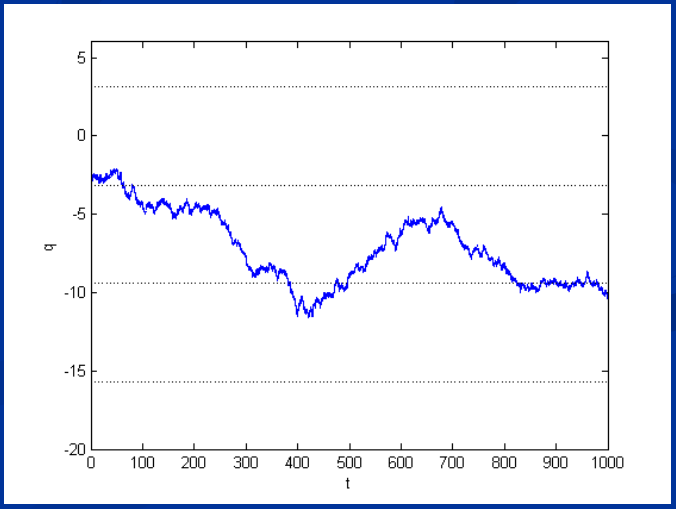
$$D = \frac{1}{2}\kappa\left\langle l^2 \right\rangle$$

Periodic Potentials – Time Series









Underdamped & Overdamped Limit

Underdamped limit

- For the case that γ is far less than 1 a formula for the diffusion is available. This formula is valid for low temperatures and for cosine potential is equal to

$$D = \frac{1}{\gamma}\frac{\pi}{2\beta}e^{-2\beta}$$

- As we can see, the diffusion coefficient increases when we raise the temperature β^{-1} and decreases when we raise the friction γ.

Overdamped limit

- For the case that γ is far bigger than 1 the left hand term in the Langevin equation is negligible and the equation reduces to the 1 dimensional SDE (after elimination of γ)

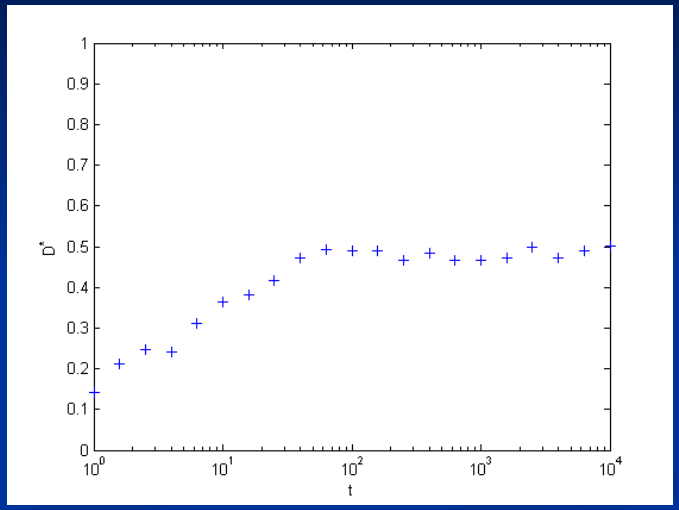
$$\dot{q} = -V'(q) + \sqrt{2\beta^{-1}}\dot{W}$$

- It is easier and more efficient to study the above equation instead of the original one.
- For the overdamped case an analytic formula is also available. This formula, for cosine potential is

$$D = \frac{\beta^{-1}}{\gamma J_0^2(\beta)}$$

The Monte Carlo Integration Method

- The concept of this method is to integrate the Langevin equation using a numerical scheme, for large enough time and a large enough number of particles and then calculate the diffusion through the definition formula.
- If we don't know the time needed for the system to reach normal diffusion state we should estimate it experimentally with a graph of D^* versus t.
- In order to apply a numerical scheme we have to rewrite the Langevin equation as a system



$$dp = \left(-\quad V(q) - \gamma p\right) dt + \sqrt{2\gamma\beta^{-1}}\, dW$$

$$dq = p\,dt$$

- In numerical analysis, the term *dW* is translated as a gaussian random number of mean value zero and variance 1, denoted as *N(0,1)*.
- The second equation can be integrated as an ordinary differential equation.
- For SDE there are two types of convergence, the strong (convergence of a single orbit) and the weak (convergence of averaged quantities).

The Monte Carlo Integration Method

Euler-Maruyama scheme

- The Euler-Maruyama scheme is a generalization of the Euler scheme for ODE.
- For a differential equation of the form

$$dx = a(x,t) + b(x,t)dW$$

- The Euler-Maruyama scheme is

$$x_{n+1} = x_n + a_n \Delta t + b_n \Delta W$$

- The orders of convergence are 0.5 for strong and 1 for weak.

Milstein scheme

- The Milstein scheme is

$$x_{n+1} = x_n + a_n \Delta t + b_n \Delta W + \frac{1}{2} b_n b_n \left(\Delta W \right)^2 - \Delta t$$

- The orders of convergence are 1 for strong and 2 for weak.
- The difference with the Euler-Maruyama scheme is a term that is proportional to the derivative of *b(x,t)*. Since in the Langevin equation this term is constant the two methods coincide.

The Monte Carlo Integration Method

Convergence

- There are several parameters that affect the convergence in the Monte Carlo method. Particularly
  - The time step dt: The Milstein scheme has weak rate of convergence 2. That means that the error is proportional to $(\Delta t)^2$. The usual values of the time step are between 10^{-2} and 10^{-3}.
  - The integration time T: The integration time has to be equal or greater from the time needed so that the system will reach state of normal diffusion. A main factor that affects this time is the friction coefficient γ. For low values of dissipation the necessary time is at least one order of magnitude greater than $1/\gamma$. For mid to large values of dissipation we usually use $T = 1000$.
  - The number of particles m: The usual number for the particles are between 10^3 and 10^4.
  - The friction γ, the temperature β^{-1} and the potential $V(q)$: They determine the value of the diffusion coefficient. This value itself affect the time needed for the system to reach normal diffusion.
  - The quality of the Gaussian Random Number Generator.

The Jumps Method

- The jumps method is based in the formula for the diffusion coefficient in periodic potentials

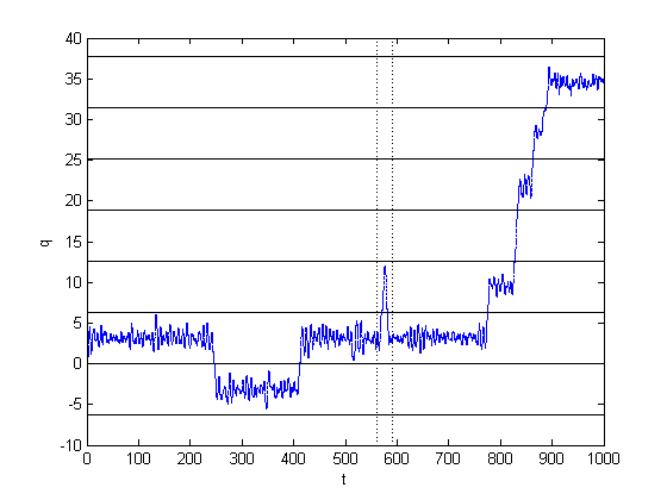
$$D = \frac{1}{2}\kappa\left\langle l^2 \right\rangle$$

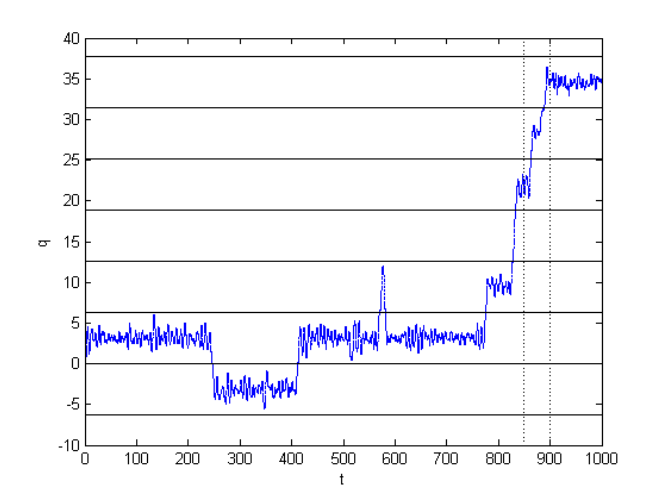
- To calculate the diffusivity we apply the following steps
  - We integrate the Langevin equation once with a numerical scheme that was described before and we store the orbit in a vector. The integration time is far bigger than the one used in Monte Carlo integration method.
  - From the vector of positions we get a vector of the wells in which the particle was.
  - We write the sequence of the wells the particle followed
  - We remove from the sequence the wells in which the particle stayed there for less than some time τ. We merge the consecutive terms that refer to the same well.
  - From the number of the elements of the sequence we get the number of the jumps, and therefore the jump rate
  - From the differences in the sequence we get the lengths of the jumps. We calculate the mean squared jump length.
  - We apply the above to the formula for the diffusion

The Jumps Method

The definition of jump

- We say that a particle is trapped in a potential well if it stays there for more than the relaxation time.
- A jump occurs when a particle is trapped in a well and then, after some time gets trapped in a different well. The difference of the wells is the jump length.
- In case that a particle moves from one well to a next one and then returns to the first one this may not be a jump, depending on how long the particle stayed there.
- In case that a particle moves from one well to the next one and then to the very next one this may be 2 jumps of length 1 or 1 jump of length 2, depending on the time the particle stayed in the intermediate well.





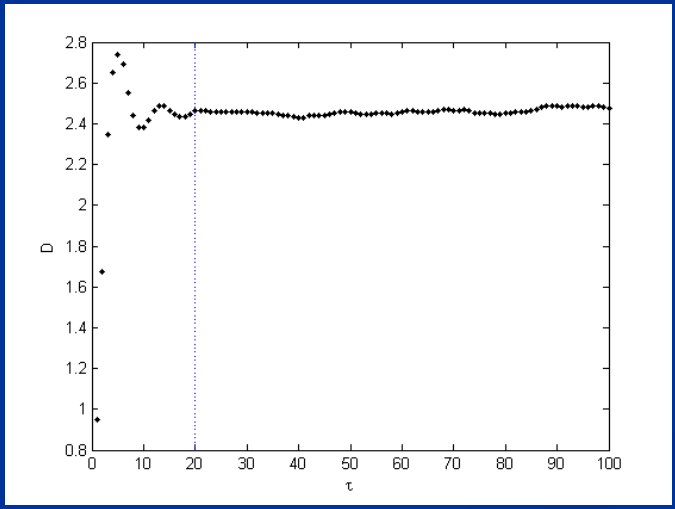
The Jumps Method

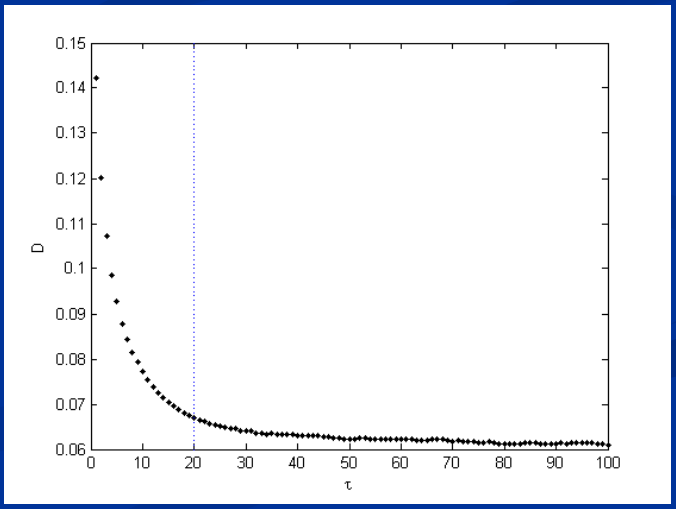
The trapping time

- The relaxation time for cosine potential in the underdamped and overdamped limits is

$$\tau_{rel} = \frac{2}{\gamma}, \quad \gamma = 1 \quad \text{and} \quad \tau_{rel} = 2\gamma, \quad \gamma ? \; 1$$

- If instead of the relaxation time we use some other time τ as a minimum trapping time then the results we are going to get will be quite different if $\tau < \tau_{rel}$ and (almost) the same if $\tau > \tau_{rel}$, but not far bigger. This is illustrated in the following pictures

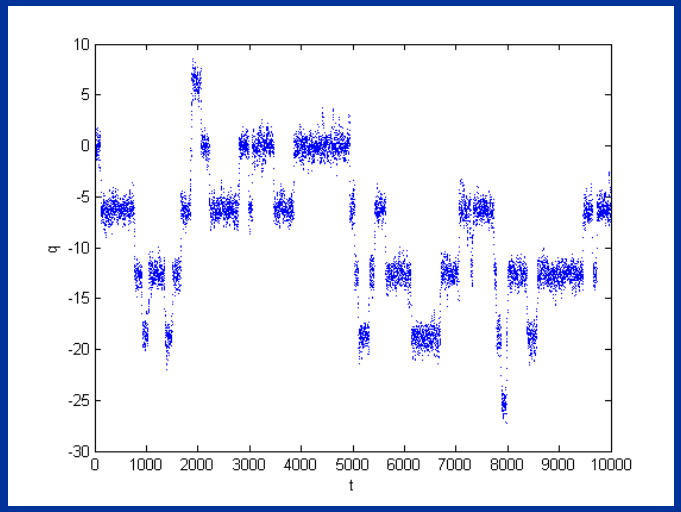


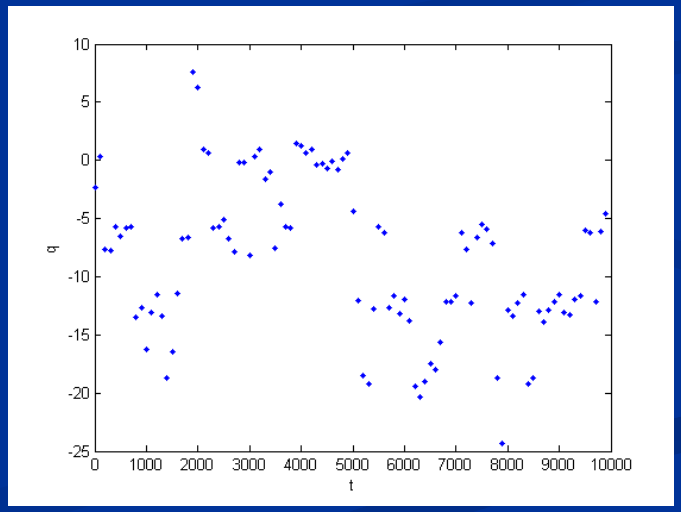


The Jumps Method

Storing data

- Storing all the positions of the orbit is much memory consuming. For this reason we store only a percentage of them, for example 1 point for every 100.
- The less we store the less memory and processing time is needed. But subtracting too many points may lead to poor results, because the orbit may not look like the original one at all.
- To apply the above we use an inner loop while integrating.

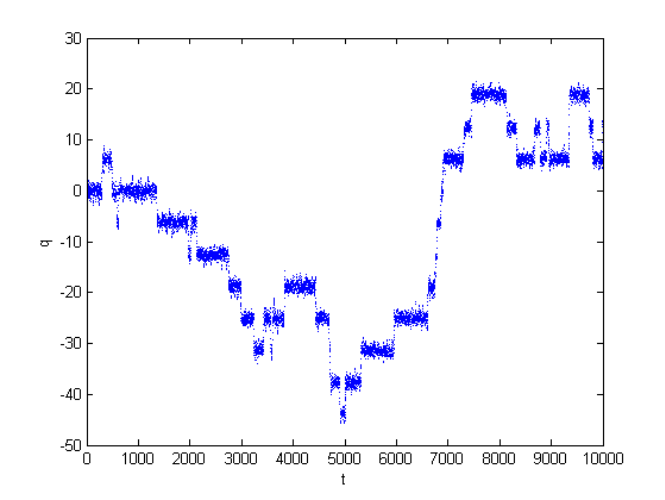


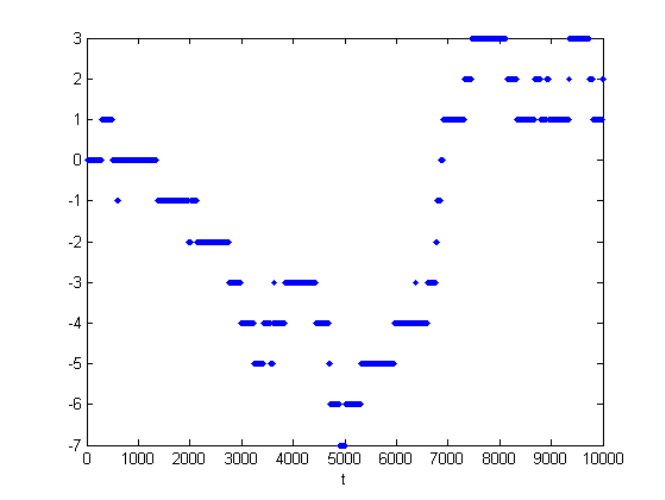


The Jumps Method

The transformation & the sequence of wells

- From the vector of positions (the orbit) we get the vector of wells if we divide each element with the period and round to the nearest integer. This transformation can be seen in the following pictures
- From the vector of wells we separate the orbit of the particle in time intervals in which the particle is inside the same well.
- From these intervals we remove the ones that the particle was not trapped and then we merge the consecutive terms that refer to the same well to get the sequence of the wells where the particle was trapped.





The Jumps Method

Convergence

- There are several parameters that affect the convergence in the Jumps method. Particularly
  - The time step *dt*: The same with the Monte Carlo method. Almost every time we use time step equal to 10^{-2}.
  - The integration time *T*: We usually get good results for integration time 10^6. For more accuracy we use 10^7 and for fast results we use 10^5.
  - The friction γ, the temperature β^{-1} and the potential $V(q)$: They determine the value of the diffusion coefficient. For low values of diffusivity a very long integration time is needed in order to get affordable number of jumps. From the diffusion coefficient formula we get $D : \kappa \langle l^2 \rangle \quad \kappa : \frac{D}{\langle l^2 \rangle} \quad m : \frac{DT}{\langle l^2 \rangle}$

    If the diffusion is of order of 10^{-5} then for T = 10^6 we have about 1 jump, leading to poor results.
  - The quality of the Gaussian Random Number Generator.

The Poisson Equation Method

- The Poisson equation method is derived from Multiscale analysis.
- The diffusion coefficient is calculated from the formula

$$D = \int_{\mathrm{T}} p\phi\rho_\beta(q,p)\,dqdp$$

where the function ϕ is the solution of the Poisson equation

$$-L\phi = p$$

and ρ_β is the Maxwell-Boltzmann distribution

$$\rho_\beta(q,p) = Z^{-1}e^{-\beta H(q,p)},\quad Z = \int_{\mathrm{T}} e^{-\beta H(q,p)}\,dqdp$$

- The differential operator L that appears in the Poisson equation is

$$L + = + V(+q) + - = \quad p \quad {}_q \quad \gamma\left(\quad p \quad {}_p \quad \beta^{-1} \quad {}^2_p \right) \quad L_1 \quad \gamma L_0$$

- The integral of diffusion can be calculated numerically. Our work for calculating the diffusion reduces to finding the function ϕ.

The Poisson Equation Method

Solution to the Poisson equation

- We will look for a solution of the form

$$\phi(q,p) = \sum_{n=0}^{+\infty} \sum_{k=-\infty}^{+\infty} \phi_{nk} e^{ikq} f_n(p)$$

where $f_n(p)$ are the eigenfunctions of the operator L_0 and are the normalized Hermite polynomials

$$f_n(p) = \frac{1}{\sqrt{n!}} H_n\left(\sqrt{\beta}\, p\right),$$

$$H_n(p) (-1)^n e^{\frac{p^2}{2}} \frac{d^n}{dp^n} e^{-\frac{p^2}{2}}$$

- The normalized Hermite polynomials are orthonormal with density

$$\rho_0(p) = \sqrt{\frac{\beta}{2\pi}} e^{-\frac{\beta p^2}{2}}$$

- The gradient of the potential that appears in L should also be expanded in Fourier series

The Poisson Equation Method

The diffusion integral

- The integral that gives the diffusion is

$$D = \int_{-\pi}^{\pi} \int_{-}^{+} p\phi(q,p)\,\rho_\beta(q,p)\,dqdp$$

- If we apply the expansion of ϕ in the above formula, after some calculations we get

$$D = \sqrt{2\pi}\,\beta^{-1} \int_{-\pi}^{\pi} \sum_{k=-}^{+} \phi_{1k} e^{ikq} e^{-\beta V(q)}\,dq$$

- Expanding the term $e^{-\beta V(q)}$ in a Fourier series we finally get

$$D = Z^{-1}(2\pi)^{3/2}\,\beta^{-1} \sum_{k=-}^{k=} \phi_{1k} U_{-k}$$

where U_k are the coefficients of the Fourier expansion of $e^{-\beta V(q)}$.

- Thus, in order to calculate the diffusion we only need the Fourier expansions of ϕ_1 and the one of $e^{-\beta V(q)}$.

The Poisson Equation Method

Derivation of the linear system

- Our goal is to find the coefficients ϕ_{nk} of the expansion of ϕ. In order to do that we substitute the expansion of ϕ in the Poisson equation and we follow the steps
  - We act with the operator L_0 on the functions $f_n(p)$.
  - We eliminate the operators p and d_p using the relations that hold for the normalized Hermite polynomials

$$= {}_p f_n(p) \quad \sqrt{n\beta}\, f_{n-1}(p)$$

$$p f_n(p) = \sqrt{n\beta^{-1}}\, f_{n-1}(p) + \sqrt{(n+1)\,\beta^{-1}}\, f_{n+1}(p), \quad n \quad 1$$

  - We make the suitable transformations for the indices and then we make the factorization with $f_n(p)$. Using the fact that $p_n = \sqrt{\beta^{-1}}\, f_n(p)$, we demand that the coefficients of the functions $f_n(p)$ are equal to zero.
  - We expand the gradient of the potential in Fourier series.
  - We make the suitable transformations for the indices and then we make the factorization with e^{-ikq}. We demand that the coefficients of e^{-ikq} areequal to zero.
- From the above process we get a linear system for the coefficients ϕ_{nk}.

The Poisson Equation Method

Formulation of the linear system

- The equation that we get from the previous process is

$$\sqrt{\beta}\sqrt{n+1}\sum_{k=-}^{+}\phi_{n+1\,(k+k)/2}V_{(k-k)/2}-i\sqrt{\beta^{-1}}\sqrt{n+1}k\phi_{n+1\,k}$$

$$-i\sqrt{\beta^{-1}}\sqrt{n}k\phi_{n-1\,k}+\gamma n\phi_{n\,k}=\sqrt{\beta^{-1}}\delta_{1n}\delta_{0k}$$

- The above equation represents a system of infinite equations and infinite variables. To solve it, we keep the first N+1 terms of the Hermite expansion and the first K+1 terms (both positive and negative) of the Fourier expansion. The term ϕ_{00} is absent and one equation is linearly dependent of the others. We remove the equation for n, k = 0. Thus, we get a finite system with (N+1)(2K+1)-1 equations and variables of the form $\mathbf{Ax}=\mathbf{b}$ with

$$x_i=\phi_{nk},\quad i=\begin{cases}k+K+1 & n=0,\ k<0\\ n(2K+1)+k+K & n=0,\ k>0 \ \text{ or } \ n \quad 0\end{cases}$$

- and α_{ij} is the coefficient of x_j in the i^{th} equation, which is for values of n and k

$$i=\begin{cases}k+K+1 & n=0,\ k<0\\ n(2K+1)+k+K & n=0,\ k>0 \ \text{ or } \ n \quad 0\end{cases}$$

The Poisson Equation Method

The numerical scheme

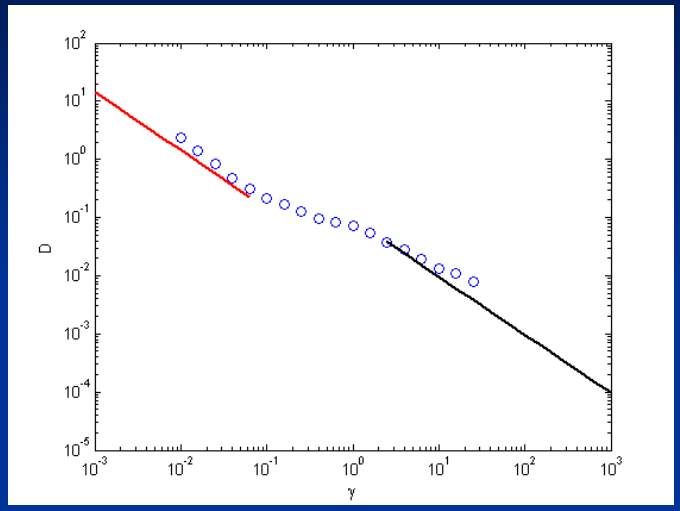
- An algorithm that uses this method to calculate the diffusion, briefly follows the steps
  - Create the square matrix **A** with zero elements of dimensions (N+1)(2K+1)-1. Using loops give values for the elements of **A**.
  - Create the vector **b** with zero elements of dimensions (N+1)(2K+1)-1. Give value for the non-zero element of **b**.
  - Inverse the Matrix **A**.
  - Multiply $\mathbf{A}^{-1}$ with **b** and store the result in a vector called **ϕ**.
  - Find the Fourier series (using an integrating routine) for $e^{-\beta V(q)}$ and store the first K+1 coefficients in a vector called **U**.
  - Find the factor Z (using an integrating routine).
  - Calculate the diffusion with the formula

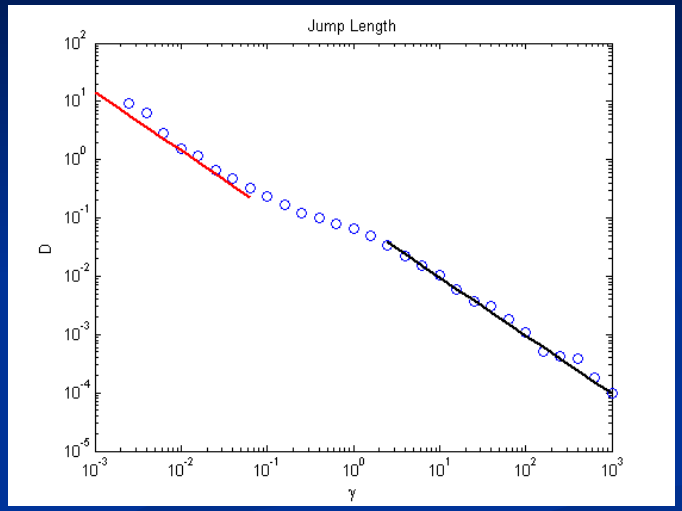
$$D = Z^{-1}\left(2\pi\right)^{3/2}\beta^{-1}\sum_{k=-}^{k=}\phi_{1k}U_{-k}$$

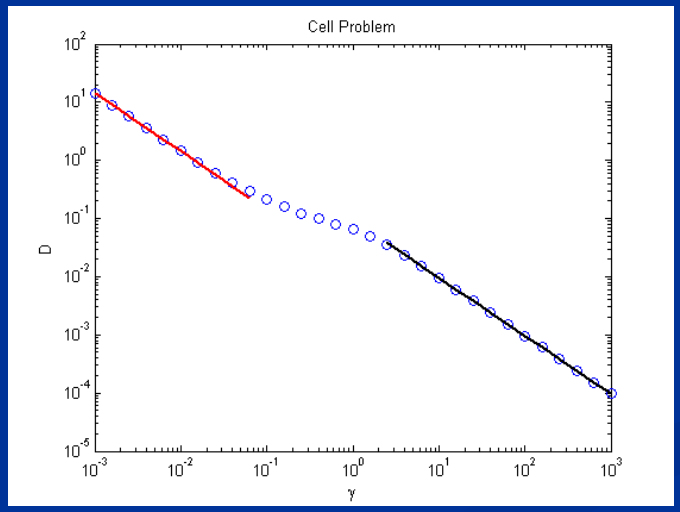
Comparison of Numerical Results

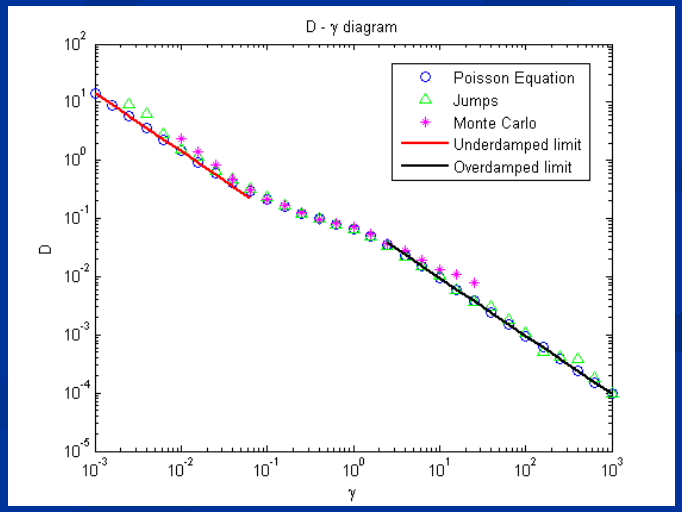
- Numerical results that obtained with the methods described before are presented in following pictures for comparison.
- The calculation time was the same for all the methods. The programs run in the same computer.
- The calculation time was far greater for low values of friction, since it is more difficult to get results in this case.
- With the Monte Carlo integration method we were not able to get affordable results for values of friction far from 1.
- With the Jumps method we can get results for a wider range of dissipation, but the values are not always perfectly accurate
- The Poisson equation method produces result that matches perfectly with the theoretical values for all the regimes of friction.
- From the above we can conclude that the Poisson equation method is superior to the others.
- The Poisson equation can give perfect results for large values of dissipation even with extremely small calculation time.

Comparison of Numerical Results









Conclusions

- We described the motion of a Brownian particle in a periodic potential. We presented three different methods to calculate the diffusivity.
- The Monte Carlo integration method is not limited to periodic potential and it is fast and easy to construct a program and get values for the diffusion. In contrast, it lacks of efficiency and for very low or very big values of dissipation gives very poor results. A generalization to more dimensions is straightforward.
- The Jumps method can be applied only to periodic potentials. It needs more time to construct a program, but is more efficient than the Monte Carlo integration method. Generalization to more dimensions is also straightforward.
- The Poisson equation method is the most efficient method and gives perfect result for a very wide range of dissipation. Needs more time to construct a program. The generalization to more dimensions is not obvious.

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THE END

To be continued…