

Diffusion processes

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Contents

1	Free Diffusion	2
1.1	Diffusion equation	2
1.2	Solution of the diffusion equation	3
2	Diffusion in presence of forces	4
2.1	Smoluchowski equation	4
2.2	An example – diffusion in a harmonic potential	5
3	Probabilistic description of diffusion processes	7
3.1	Conditional probabilities for particle displacements	7
3.2	Stochastic equations of motion	8
3.3	Time-dependent mean squared displacements	10
3.3.1	Free diffusion	11
3.3.2	Confined diffusion	11
4	Colloids and macromolecular systems	14
4.1	Many-body Smoluchowski equation and stochastic equations of motion	14
4.2	Elementary hydrodynamics	14
5	Diffusion in velocity space	16
5.1	Smoluchowski equation in velocity space	16
5.2	Mean square displacement in velocity space	17
5.3	Ornstein-Uhlenbeck process in velocity space and Langevin equation	17
5.4	Velocity autocorrelation function and mean square displacement	19
5.5	Mean square displacement of a Rayleigh particle	20
6	Anomalous free diffusion	22
6.1	Introduction	22
6.2	Mean square displacement	23
6.3	Kubo relation for the (fractional) diffusion constant	23

7 Fractional Ornstein-Uhlenbeck process	25
7.1 Introduction	25
7.2 Fourier spectrum of the autocorrelation function	27
7.3 Relaxation rate spectrum of the autocorrelation function	27
7.4 Diffusion in a “rough” harmonic potential	28
8 Applications in neutron scattering	29
8.1 Basic neutron scattering theory	29
8.2 Single-atom motion as an Ornstein-Uhlenbeck process	30
8.3 Fractional Ornstein-Uhlenbeck process for collective variables	33

1 Free Diffusion

1.1 Diffusion equation

Diffusion is an elementary transport problem describing the spreading of molecules, or microscopic particles (solutes) in general, in a solution. The first theoretical description has been given by Adolf Fick [1] and was inspired by Fourier’s description of heat conduction. Later a derivation was given by Einstein [2], which can be considered as a first step towards a description of diffusion processes in terms of stochastic displacements of individual particles. Considering a diluted solution, where interactions between the solute particles can be neglected, and neglecting external forces on them, their time- and space-dependent concentration is described by the following partial differential equation,

$$\partial_t c(\mathbf{x}, t) = D\Delta c(\mathbf{x}, t) \tag{1.1}$$

Here D is the diffusion constant and $\Delta = \partial_x^2 + \partial_y^2 + \partial_z^2$ is the Laplace operator. The diffusion constant is a so-called transport coefficient and has the physical dimension m^2/s in SI units. The derivation of the diffusion equation needs two basic ingredients:

1. A model for the the solute current density, $\mathbf{j}(\mathbf{x}, t)$, which describes the tendency to diminish concentration gradients and to establish a uniform solute concentration at long times. To describe this well-known phenomenon, Fick proposed to express the current density $\mathbf{j}(\mathbf{x}, t)$ in the form (“Fick’s law”)

$$\mathbf{j}(\mathbf{x}, t) = -D\nabla c(\mathbf{x}, t) \tag{1.2}$$

The solute current density is thus supposed to be proportional and opposed to the gradient of the solute concentration, with the diffusion constant D being the constant of proportionality. It can be interpreted as transport reaction on a given solute gradient and for this reason, the diffusion constant is a transport coefficient.

2. The conservation of the total number of solute molecules, $N = \int d^3r c(\mathbf{x}, t) = 1$, which yields the condition

$$\partial_t c(\mathbf{x}, t) + \nabla \cdot \mathbf{j}(\mathbf{x}, t) = 0 \tag{1.3}$$

for the solute current density. One sees immediately that insertion of Expression (1.2) into Eq. (1.3) leads to the diffusion equation (1.1). Eq. (1.3) is known as equation of continuity,

and appears in other fields of physics in the context of conservation laws. Its integral form is derived with Gauss' theorem and reads

$$\partial_t \underbrace{\int_V d^3r c(\mathbf{x}, t)}_{N_V(t)} = - \underbrace{\oint_{\partial V} d\mathbf{a} \cdot \mathbf{j}(\mathbf{x}, t)}_{I_{\partial V}(t)} = 0, \quad (1.4)$$

where $N_V(t)$ is the number of solute particles in the volume V and $I_{\partial V}(t)$ the net current of solute particles across the surface of V . Under physically reasonable assumptions $\lim_{V \rightarrow \infty} I_{\partial V}(t) = 0$, such that $\lim_{V \rightarrow \infty} N_V(t) = \text{const.}$, where the constant is the total number N of solute particles.

1.2 Solution of the diffusion equation

The diffusion equation is easily solved by spatial Fourier transformation. Introducing the Fourier transform pair

$$\tilde{f}(\mathbf{k}) = \int d^3r e^{-i\mathbf{k} \cdot \mathbf{x}} f(\mathbf{x}), \quad (1.5)$$

$$f(\mathbf{x}) = \frac{1}{(2\pi)^3} \int d^3k e^{i\mathbf{k} \cdot \mathbf{x}} \tilde{f}(\mathbf{k}), \quad (1.6)$$

Fourier transform of the diffusion equation (1.1) leads to

$$\partial_t \tilde{c}(\mathbf{k}, t) = -D|\mathbf{k}|^2 \tilde{c}(\mathbf{k}, t), \quad (1.7)$$

and thus transforms a partial differential equation into an ordinary differential equation, which can be solved to give

$$\tilde{c}(\mathbf{k}, t) = \tilde{c}(\mathbf{k}, 0) e^{-D|\mathbf{k}|^2 t}, \quad (1.8)$$

where $\tilde{c}(\mathbf{k}, 0)$ is the Fourier transform of the initial solute concentration. If we make the idealized assumption that all solute particles are initially concentrated at the origin, $\mathbf{x} = \mathbf{0}$, of the coordinate system, we have

$$c(\mathbf{x}, 0) = N\delta(\mathbf{x}) \longleftrightarrow \tilde{c}(\mathbf{k}, 0) = N. \quad (1.9)$$

In the case of freely diffusing particles in a homogenous system, there no reason to chose a particular initial point, and therefore $\mathbf{x}_0 = \mathbf{0}$ can be chosen. For the Fourier transform of the solution (1.8) back into real space we can use that in one dimension

$$g(x) = \frac{e^{-\frac{1}{2}(x/\sigma)^2}}{\sqrt{2\pi}\sigma} \longleftrightarrow \tilde{g}(k) = e^{-\frac{1}{2}(\sigma k)^2}.$$

Setting $\sigma = \sqrt{2Dt}$ and factorizing $\tilde{c}(\mathbf{k}, t) = N\tilde{g}(k_x, t)\tilde{g}(k_y, t)\tilde{g}(k_z, t)$, leads then to the solution

$$\boxed{c(\mathbf{x}, t) = N \frac{e^{-\frac{|\mathbf{x}|^2}{4Dt}}}{(\sqrt{4\pi Dt})^3}} \quad (1.10)$$

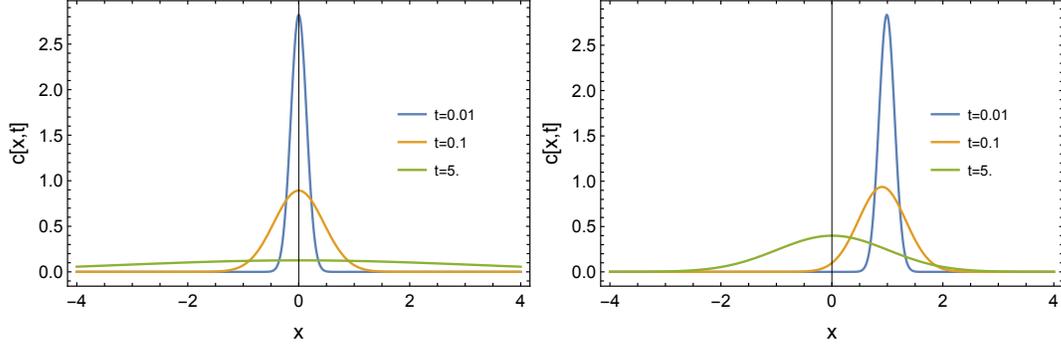


Figure 1: **Left panel:** Time evolution of the concentration for free diffusion. **Right panel:** Time evolution of the concentration for diffusion in a harmonic potential. More details are given in the text.

One recognizes that $\lim_{t \rightarrow 0} c(\mathbf{x}, t) = N\delta(\mathbf{x})$. The left panel of fig. 1 shows the spreading of the concentration profile for free diffusion in one dimension. The solution (1.10) may be used to extract the velocity field of the diffusing solute particles, writing

$$\mathbf{j}(\mathbf{x}, t) = c(\mathbf{x}, t)\mathbf{v}(\mathbf{x}, t) \quad (1.11)$$

and using here the definition (1.2) of the solute current density, $\mathbf{j}(\mathbf{x}, t)$. The result is

$$\mathbf{v}(\mathbf{x}, t) = \frac{\mathbf{x}}{2t}, \quad (1.12)$$

showing that the velocity has radial symmetry and tends from initially infinite values to zero as the equilibrium state is attained.

2 Diffusion in presence of forces

2.1 Smoluchowski equation

The diffusion equation has been extended by Marian Smoluchowski in order to account for explicit driving forces acting on the solute particles [3]. His idea was to supplement Fick's law (1.2) by a term containing the driving force, $\mathbf{F}(\mathbf{x})$, writing

$$\mathbf{j}(\mathbf{x}, t) = -D\nabla c(\mathbf{x}, t) + D\frac{\mathbf{F}(\mathbf{x})}{k_B T}c(\mathbf{x}, t) \quad (2.1)$$

Here $k_B T$ is the Boltzmann constant multiplied by the temperature T in Kelvin. As in the case of free diffusion the equation of continuity (1.3) must be fulfilled to guarantee the conservation of the total number of particles. Assuming that the driving force derives from a potential

$$\mathbf{F}(\mathbf{x}) = -\nabla V(\mathbf{x}), \quad (2.2)$$

leads to the modified diffusion equation

$$\partial_t c(\mathbf{x}, t) = D\nabla \cdot \left\{ \nabla c(\mathbf{x}, t) + \frac{\nabla V(\mathbf{x})}{k_B T} c(\mathbf{x}, t) \right\} \quad (2.3)$$

which is referred to as the Smoluchowski equation.

The presence of an external driving force leads to non-trivial stationary solutions, $c_s(\mathbf{x})$. Setting $\partial_t c_s(\mathbf{x}, t) = 0$, it follows from the Smoluchowski equation (2.3) that

$$\nabla c_s(\mathbf{x}) + \frac{\nabla V(\mathbf{x})}{k_B T} c_s(\mathbf{x}) = 0, \quad (2.4)$$

which may be written in the form

$$\nabla \log(c_s(\mathbf{x})) = -\frac{\nabla V(\mathbf{x})}{k_B T}, \quad (2.5)$$

showing that $\log(c_s(\mathbf{x})) \propto -\frac{V(\mathbf{x})}{k_B T}$. The normalized solution for $c_s(\mathbf{x})$ is thus

$$c_s(\mathbf{x}) = N \frac{\exp\left(-\frac{V(\mathbf{x})}{k_B T}\right)}{Z_c} \equiv c_{eq}(\mathbf{x}) \quad (2.6)$$

where it is supposed that

$$Z_c = \int d^3r \exp\left(-\frac{V(\mathbf{x})}{k_B T}\right) \quad (2.7)$$

exists. Being proportional to the configurational Boltzmann factor, $c_s(\mathbf{x})$ has the form of an equilibrium distribution function in statistical mechanics, and Z_c is the corresponding partition function. It is also important to note that the equilibrium concentration, $c_{eq}(\mathbf{x})$, does not depend on the diffusion constant. The latter determines how fast an arbitrary initial concentration $c(\mathbf{x}, 0)$ approaches $c_{eq}(\mathbf{x})$.

2.2 An example – diffusion in a harmonic potential

We consider now the concrete situation, where the systematic force driving the solute particles in a suspension derives from an isotropic harmonic potential,

$$V(\mathbf{x}) = \frac{1}{2} K |\mathbf{x}|^2, \quad K > 0. \quad (2.8)$$

Defining the relaxation constant¹

$$\eta = \frac{DK}{k_B T}, \quad (2.9)$$

the Smoluchowski equation (2.3) takes the form

$$\partial_t c(\mathbf{x}, t) = D \Delta c(\mathbf{x}, t) + \eta \nabla \cdot \{\mathbf{x} c(\mathbf{x}, t)\} \quad (2.10)$$

¹The physical dimension is s^{-1} .

One dimensional case. To construct the solution the Smoluchowski equation (2.10), we consider first the one-dimensional case,

$$\partial_t c(x, t) = D \frac{\partial^2}{\partial x^2} c(x, t) + \eta \frac{\partial}{\partial x} \{x c(x, t)\}. \quad (2.11)$$

As in the case of free diffusion we apply a Fourier transform to obtain

$$\partial_t \tilde{c}(k, t) = -Dk^2 \tilde{c}(k, t) - \eta k \frac{\partial}{\partial k} \tilde{c}(k, t). \quad (2.12)$$

We use here the correspondences $\partial_x f(x) \leftrightarrow ik \tilde{f}(k)$ and $xf(x) \leftrightarrow i \partial_k \tilde{f}(k)$. We suppose that the solution has still Gaussian form – as in the case of free diffusion – and make the *ansatz* [4]

$$c(x, t) = N \frac{e^{-\frac{(x-\mu(t))^2}{2\sigma(t)^2}}}{\sqrt{2\pi\sigma(t)}} \longleftrightarrow \tilde{c}(k, t) = N e^{-\frac{1}{2}\sigma(t)^2 k^2 - i\mu(t)k}, \quad (2.13)$$

where $\mu(t)$ and $\sigma(t)$ are the time-dependent mean and variance, respectively, of this Gaussian. Ordinary differential equations for $\mu(t)$ and $\sigma(t)$ are obtained by inserting the Fourier transform $\tilde{c}(k, t)$ of the Gaussian Ansatz (2.13) into the Fourier transformed Smoluchowski equation (2.12). Observing that the resulting equation must be separately fulfilled for its real and imaginary part, one obtains the differential equations

$$\begin{aligned} \sigma(t) (\eta\sigma(t) + \sigma'(t)) &= D, \\ \eta\mu(t) + \mu'(t) &= 0, \end{aligned}$$

respectively. Assuming that the solute particles are initially concentrated at $x(0) = x_0$,

$$\lim_{t \rightarrow 0} c(x, t) = N \delta(x - x_0), \quad (2.14)$$

the initial conditions are $\sigma(0) = 0$ and $\mu(0) = x_0$, which leads to

$$\sigma(t) = \frac{\sqrt{D(1 - e^{-2\eta t})}}{\sqrt{\eta}}, \quad (2.15)$$

$$\mu(t) = x_0 e^{-\eta t}. \quad (2.16)$$

Inserting this into the general Gaussian form of the solute concentration, which is given by the lefthand side of the Fourier transform pair (2.13), one obtains

$$c(x, t) = N \left(\frac{\eta}{2\pi D(1 - e^{-2\eta t})} \right)^{1/2} \exp \left(-\frac{\eta (x - x_0 e^{-\eta t})^2}{2D(1 - e^{-2\eta t})} \right). \quad (2.17)$$

Inserting $\lim_{t \rightarrow 0} \mu(t) = x_0$ and $\lim_{t \rightarrow 0} \sigma(t) = 0$ into the *ansatz* (2.13) for the solution the initial condition (2.14) of the solution is well retrieved. Concerning the long time limit, we have

$$\lim_{t \rightarrow \infty} \mu(t) = 0, \quad (2.18)$$

$$\lim_{t \rightarrow \infty} \sigma(t) = \sqrt{D/\eta} = \sqrt{k_B T/K}, \quad (2.19)$$

which shows that $\lim_{t \rightarrow \infty} c(x, t)$ is a centered Gaussian function, irrespective of the localization, x_0 , of the initial concentration. The concrete form is

$$\lim_{t \rightarrow \infty} c(x, t) = \left(\frac{K}{2\pi k_B T} \right)^{1/2} \exp \left(-\frac{Kx^2}{2k_B T} \right) = c_{eq}(x), \quad (2.20)$$

where is the equilibrium concentration, noting that $c_{eq}(x) \propto \exp \left(-\frac{V(x)}{k_B T} \right)$, with $V(x) = Kx^2/2$. The right panel of Figure 1 shows the solution for a concrete example, where $D = 1$, $\eta = 1$, $x_0 = 1$ in dimensionless units. One sees clearly that the solution evolves towards the equilibrium concentration (black solid line), which is a centered Gaussian.

Three dimensional case. The results of the previous paragraph are immediately generalized to three dimensions, noting that the potential $V(\mathbf{x})$ is isotropic, and therefore $c(\mathbf{x}, t) = \prod_{i=1}^3 c(r_i, t)$:

$$c(\mathbf{x}, t) = N \left(\frac{\eta}{2\pi D(1 - e^{-2\eta t})} \right)^{3/2} \exp \left(-\frac{\eta |\mathbf{x} - \mathbf{x}_0 e^{-\eta t}|^2}{2D(1 - e^{-2\eta t})} \right), \quad (2.21)$$

$$\lim_{t \rightarrow \infty} c(\mathbf{x}, t) = N \left(\frac{K}{2\pi k_B T} \right)^{3/2} \exp \left(-\frac{K|\mathbf{x}|^2}{2k_B T} \right) = c_{eq}(\mathbf{x}). \quad (2.22)$$

3 Probabilistic description of diffusion processes

3.1 Conditional probabilities for particle displacements

The probabilistic description of diffusion processes is based on the concept of conditional probabilities for the displacements of individual particles, instead of using a macroscopic approach in terms concentrations of ensembles of particles according to Fick, Einstein, and Smoluchowski. The link between the two approaches is that concentrations of a very large number of diffusers ($N \approx 10^{23}$) can be considered as valid "histogram approximations" for conditional probability densities if the initial concentrations correspond to the situation that all particles start at the same point, $c(\mathbf{x}, 0) = N\delta(\mathbf{x} - \mathbf{x}_0)$. One may therefore write

$$d^3r p(\mathbf{x}, t | \mathbf{x}_0, 0) \approx d^3r \frac{c(\mathbf{x}, t)}{N}. \quad (3.1)$$

where $p(\mathbf{x}, t | \mathbf{x}_0, 0)$ is the conditional probability to find a tagged particle at time t at some position, \mathbf{x} , given that this particle started at time 0 at some given initial position, \mathbf{x}_0 . Its time evolution is given by the Smoluchowski equation

$$\partial_t p(\mathbf{x}, t | \mathbf{x}_0, 0) = D \nabla \cdot \left\{ \nabla p(\mathbf{x}, t | \mathbf{x}_0, 0) + \frac{\nabla V(\mathbf{x})}{k_B T} p(\mathbf{x}, t | \mathbf{x}_0, 0) \right\} \quad (3.2)$$

which has to be solved with the initial condition

$$p(\mathbf{x}, t | \mathbf{x}_0, 0) = \delta(\mathbf{x} - \mathbf{x}_0). \quad (3.3)$$

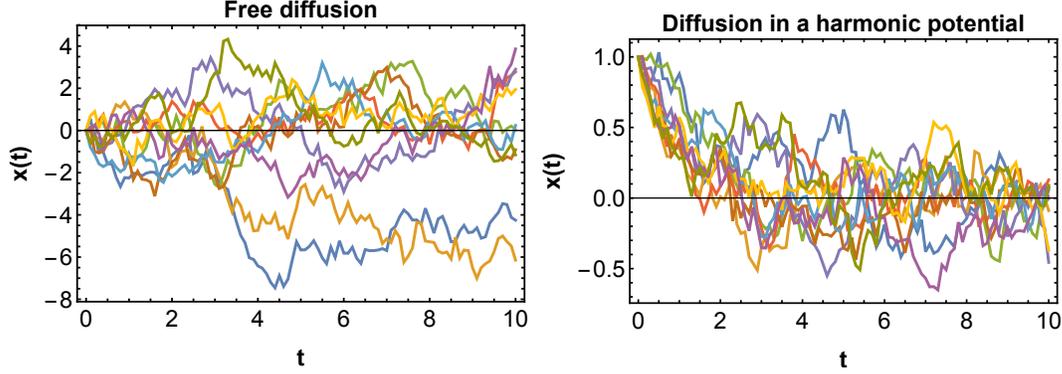


Figure 2: **Left panel:** A sample of 10 stochastic trajectories for free diffusion, setting $D = 1$ and $\Delta t = 0.1$. **Right panel:** A sample of 10 stochastic trajectories for diffusion in a quadratic potential (Ornstein-Uhlenbeck process), setting $D = 0.05$, $\eta = 1$, $x_0 = 1$, and $\Delta t = 0.1$.

In the case of free diffusion the localization \mathbf{x}_0 was arbitrarily set to $\mathbf{x}_0 = \mathbf{0}$, since the diffusion equation is invariant under a translation of the coordinate system. The example of the Smoluchowski equation for a harmonic potential shows that such a translational invariance does not exist in general, and the form of the solution will thus in general depend on \mathbf{x}_0 . Taking again diffusion in a harmonic potential as a concrete example, we have

$$\partial_t p(\mathbf{x}, t | \mathbf{x}_0, 0) = D \Delta p(\mathbf{x}, t | \mathbf{x}_0, 0) + \eta \nabla \cdot \{ \mathbf{x} p(\mathbf{x}, t | \mathbf{x}_0, 0) \}, \quad (3.4)$$

with the solution

$$p(\mathbf{x}, t | \mathbf{x}_0, 0) = \left(\frac{\eta}{2\pi D(1 - e^{-2\eta t})} \right)^{3/2} \exp \left(-\frac{\eta |\mathbf{x} - \mathbf{x}_0 e^{-\eta t}|^2}{2D(1 - e^{-2\eta t})} \right), \quad (3.5)$$

$$\lim_{t \rightarrow \infty} p(\mathbf{x}, t | \mathbf{x}_0, 0) = \left(\frac{K}{2\pi k_B T} \right)^{3/2} \exp \left(-\frac{K |\mathbf{x}|^2}{2k_B T} \right) = p_{eq}(\mathbf{x}) \quad (3.6)$$

for the initial condition (3.3).

3.2 Stochastic equations of motion

The probabilistic interpretation of diffusion processes is based on the idea to follow individual tagged particles and to consider conditional probability densities for their displacements rather than concentrations of many particles. It is therefore meaningful to ask the question if the Smoluchowski can be used to derive probabilistic (or stochastic) equations of motions describing the time evolution of their random trajectories. For this purpose we introduce the moment generating function for the particle displacements,

$$G(\mathbf{k}, t) = \int d^3 u e^{-i\mathbf{k} \cdot (\mathbf{x} - \mathbf{x}_0)} p(\mathbf{x}, t | \mathbf{x}_0, 0), \quad (3.7)$$

which yields the tensorial displacement moments via

$$\underbrace{\langle \mathbf{x} \otimes \dots \otimes \mathbf{x} \rangle}_{k \text{ times}}(t) = i^k \underbrace{\nabla \otimes \dots \otimes \nabla}_{k \text{ times}} G(\mathbf{k}, t)|_{\mathbf{k} \rightarrow \mathbf{0}}. \quad (3.8)$$

Considering now a small time increment, Δt , we can approximate

$$G(\mathbf{k}, \Delta t) \approx \int d^3 r e^{-i\mathbf{k} \cdot (\mathbf{x} - \mathbf{x}_0)} \underbrace{\left(\delta(\mathbf{x} - \mathbf{x}_0) + \Delta t \partial_t p(\mathbf{x}, t | \mathbf{x}_0, 0) \right)}_{p(\mathbf{x}, \Delta t | \mathbf{x}_0, 0)},$$

where $\partial_t p(\mathbf{x}, t | \mathbf{x}_0, 0)$ is given by the r.h.s. of the Smoluchowski equation (3.2),

$$G(\mathbf{k}, \Delta t) \approx \int d^3 r e^{-i\mathbf{k} \cdot (\mathbf{x} - \mathbf{x}_0)} \left(\delta(\mathbf{x} - \mathbf{x}_0) + \Delta t \left\{ D \nabla \cdot \left\{ \nabla \delta(\mathbf{x} - \mathbf{x}_0) + \frac{\nabla V(\mathbf{x})}{k_B T} \delta(\mathbf{x} - \mathbf{x}_0) \right\} \right\} \right).$$

Applying particle integrations, the derivatives of the delta distribution can be transformed in derivatives of the plane wave $\exp(-i\mathbf{k} \cdot (\mathbf{x} - \mathbf{x}_0))$, leading to

$$\begin{aligned} G(\mathbf{k}, \Delta t) &\approx \int d^3 r e^{-i\mathbf{k} \cdot (\mathbf{x} - \mathbf{x}_0)} \left(\delta(\mathbf{x} - \mathbf{x}_0) + \Delta t \left\{ D \nabla \cdot \left\{ \nabla \delta(\mathbf{x} - \mathbf{x}_0) + \frac{\nabla V(\mathbf{x})}{k_B T} \delta(\mathbf{x} - \mathbf{x}_0) \right\} \right\} \right) \\ &= 1 - \int d^3 r D |\mathbf{k}|^2 e^{-i\mathbf{k} \cdot (\mathbf{x} - \mathbf{x}_0)} \delta(\mathbf{x} - \mathbf{x}_0) + \int d^3 r i D \mathbf{k} \cdot \frac{\nabla V(\mathbf{x})}{k_B T} e^{-i\mathbf{k} \cdot (\mathbf{x} - \mathbf{x}_0)} \delta(\mathbf{x} - \mathbf{x}_0), \end{aligned}$$

and integration over \mathbf{x} leads to

$$G(\mathbf{k}, \Delta t) \approx 1 - D |\mathbf{k}|^2 \Delta t + i D \mathbf{k} \cdot \frac{\nabla V(\mathbf{x}_0)}{k_B T} \Delta t. \quad (3.9)$$

Applying now the rule (3.8) for the computation of the tensorial moments, we obtain

$$\langle (\mathbf{x} - \mathbf{x}_0) \rangle = -D \frac{\nabla V(\mathbf{x}_0)}{k_B T} \Delta t, \quad (3.10)$$

$$\langle (\mathbf{x} - \mathbf{x}_0) \otimes (\mathbf{x} - \mathbf{x}_0) \rangle = 2D \Delta t \mathbf{1}. \quad (3.11)$$

Noting that $\langle \mathbf{x}_0 \rangle = \mathbf{x}_0 = \mathbf{x}(t_0)$, the above equations can be translated into the stochastic equation of motion

$$\boxed{\mathbf{x}(t_0 + \Delta t) = \mathbf{x}(t_0) - D \frac{\nabla V(\mathbf{x}(t_0))}{k_B T} \Delta t + \delta \boldsymbol{\xi}} \quad (3.12)$$

where $\delta \boldsymbol{\xi}$ is a stochastic displacement verifying

$$\langle \delta \boldsymbol{\xi} \rangle = \mathbf{0}, \quad (3.13)$$

$$\langle \delta \boldsymbol{\xi} \otimes \delta \boldsymbol{\xi} \rangle = 2D \Delta t \mathbf{1}. \quad (3.14)$$

Eq (3.12) is a discrete equation of motion, and describes, in fact, the first step $t_0 \rightarrow t_1 = t_0 + \Delta t$. Successive applications $t_1 \rightarrow t_2 = t_1 + \Delta t$, $t_2 \rightarrow t_3 = t_2 + \Delta t$, etc. lead to the discrete trajectory

$$T = \{\mathbf{x}(t_0), \mathbf{x}(t_1), \mathbf{x}(t_2), \mathbf{x}(t_3), \dots\}.$$

As examples we consider the case of free diffusion and diffusion in a harmonic potential.

Free diffusion. In absence of a external forces it follows from Eq. (3.12) that the updates of the particle positions are given by

$$\mathbf{x}(t_0 + \Delta t) = \mathbf{x}(t_0) + \delta\xi, \quad (3.15)$$

where the random displacements satisfy the conditions (3.13) and (3.14). Fig. 2 shows two examples for stochastic trajectories corresponding to one-dimensional diffusion processes. The left panel of Fig. 2 shows 10 sample trajectories for free one-dimensional diffusion, where the equation of motion (3.15) becomes $x(t_0 + \Delta t) = x(t_0) + \delta\xi$. The parameters are here $D = 1$ and $\Delta t = 0.1$ and all trajectories start at $x_0 = 0$.

Ornstein-Uhlenbeck process. If we consider diffusion in a harmonic potential,

$$V(\mathbf{x}) = \frac{1}{2}K|\mathbf{x}|^2, \quad K > 0,$$

it follows from Eq. (3.12) that the updates of the positions are given by

$$\mathbf{x}(t_0 + \Delta t) = \mathbf{x}(t_0) - \eta\mathbf{x}(t_0)\Delta t + \delta\xi, \quad (3.16)$$

where $\eta = DK/k_B T$ (see Eq. (2.9)) and the random displacements satisfy again the conditions (3.13) and (3.14). Eq. (3.16) defines a stochastic process which is referred to as Ornstein-Uhlenbeck (OU) process [5–7]. The right panel of Fig. 2 displays 10 sample trajectories corresponding to the one-dimensional OU process. Note that all trajectories start at $x_0 = 1$, i.e. displaced with respect to the minimum of the potential. The remaining parameters are $D = 0.05$, $\eta = 1$, and $\Delta t = 0.1$. It is well visible that all trajectories fluctuate for long times around the minimum of the potential, which is at $x = 0$. This observation is coherent with the time evolution of the concentration of diffusing particles in a harmonic potential, which is displayed in Fig. 1.

3.3 Time-dependent mean squared displacements

The time-dependent mean squared displacement (MSD) is the fundamental quantity characterizing the diffusion of individual particles. In a system at thermal equilibrium it is defined through

$$W(t) \equiv \langle |\mathbf{x}(t) - \mathbf{x}(0)|^2 \rangle = \int \int d^3r d^3r_0 |\mathbf{x} - \mathbf{x}_0|^2 p(\mathbf{x}, t | \mathbf{x}_0, 0) p_{eq}(\mathbf{x}_0) \quad (3.17)$$

where $p_{eq}(\mathbf{x}_0)$ is the equilibrium probability density for finding the particle at time 0 at position \mathbf{x}_0 . We have seen that the stochastic trajectory of a diffusing particle is entirely determined by the conditional probability density $p(\mathbf{x}, t | \mathbf{x}_0, 0)$ to go from a well-defined starting position, \mathbf{x}_0 , to some position, \mathbf{x} , within a time span, t . The calculation of an MSD must in addition account for the weighting of the initial position, which is given by $p_{eq}(\mathbf{x}_0)$. Otherwise we would compute an MSD for a particular initial position. Using Bayes' law,² we see that

$$p(\mathbf{x}, t | \mathbf{x}_0, 0) p_{eq}(\mathbf{x}_0) = p(\mathbf{x}, t; \mathbf{x}_0, 0) \quad (3.18)$$

is the *joint* probability density to find the particle at time 0 at the position \mathbf{x}_0 and at time t at the position \mathbf{x} .

²The usual form uses probabilities and not probability densities and says that the joint probability $p(A, B)$ for finding A and B can be written in the two equivalent forms $p(A, B) = p(A|B)p(B) = p(B|A)p(A)$, where $p(A|B)$ is the conditional probability to find A given B and $p(B|A)$ is the conditional probability to find B given A .

3.3.1 Free diffusion

In case of free diffusion there are no external forces, $V(\mathbf{x}) \equiv 0$, such that

$$\partial_t p(\mathbf{x}, t | \mathbf{x}_0, 0) = D \Delta p(\mathbf{x}, t | \mathbf{x}_0, 0). \quad (3.19)$$

Free diffusion implies a translationally (and rotationally) homogeneous system, such that

$$p_{eq}(\mathbf{x}_0) = \frac{1}{V}, \quad (3.20)$$

where $V \rightarrow \infty$ is the volume of the macroscopic system in which the diffusion process takes place. Correspondingly, the diffusion equation (3.19) is translationally invariant, and the variable transform $\mathbf{x} \rightarrow \mathbf{u} = \mathbf{x} - \mathbf{x}_0$ will not change its form,

$$\partial_t p(\mathbf{u}, t | \mathbf{0}, 0) = D \Delta p(\mathbf{u}, t | \mathbf{0}, 0). \quad (3.21)$$

For the MSD we have

$$W(t) = \int d^3 u |\mathbf{u}|^2 p(\mathbf{u}, t | \mathbf{0}, 0),$$

noting that $\int_V d^3 r_0 (1/V) = 1$. To compute $W(t)$ we establish first a simple differential equation

$$\partial_t W(t) = \int d^3 u |\mathbf{u}|^2 \partial_t p(\mathbf{u}, t | \mathbf{0}, 0),$$

where $\partial_t p(\mathbf{u}, t | \mathbf{0}, 0)$ is to be replaced by the r.h.s. of Eq. (6.3). We may then use double partial integration to obtain

$$\partial_t W(t) = D \int d^3 u |\mathbf{u}|^2 \Delta p(\mathbf{u}, t | \mathbf{0}, 0) = D \int d^3 u \underbrace{\{\Delta |\mathbf{u}|^2\}}_{=6} p(\mathbf{u}, t | \mathbf{0}, 0) = 6D,$$

from which it follows immediately that

$$W_{\text{free}}(t) = 6Dt \quad (3.22)$$

Working more generally in n dimensions this becomes

$$\boxed{W_{\text{free}}(t) = 2nDt} \quad (3.23)$$

3.3.2 Confined diffusion

We consider now the situation that a potential $V(\mathbf{x})$ prevents the diffusing particle to escape to infinity, such that

$$\langle |\mathbf{x}|^2 \rangle \equiv \int d^3 r p_{eq}(\mathbf{x}) |\mathbf{x}|^2 < \infty. \quad (3.24)$$

Expanding $|\mathbf{x} - \mathbf{x}_0|^2 = |\mathbf{x}|^2 + |\mathbf{x}_0|^2 - 2\mathbf{x} \cdot \mathbf{x}_0$ in Expression (3.17) for the MSD and using that, according to Bayes' law,

$$p(\mathbf{x}, t | \mathbf{x}_0, 0) p_{eq}(\mathbf{x}_0) = p(\mathbf{x}_0, t | \mathbf{x}, 0) p_{eq}(\mathbf{x}), \quad (3.25)$$

we obtain

$$W(t) = \int \int d^3r d^3r_0 |\mathbf{x}_0|^2 p(\mathbf{x}, t | \mathbf{x}_0, 0) p_{\text{eq}}(\mathbf{x}_0) + \int \int d^3r d^3r_0 |\mathbf{x}|^2 p(\mathbf{x}_0, t | \mathbf{x}, 0) p_{\text{eq}}(\mathbf{x}) \\ - 2 \int \int d^3r d^3r_0 \mathbf{x} \cdot \mathbf{x}_0 p(\mathbf{x}, t | \mathbf{x}_0, 0) p_{\text{eq}}(\mathbf{x}_0).$$

Since $\int d^3r p(\mathbf{x}, t | \mathbf{x}_0, 0) = 1$ and $\int d^3r_0 p(\mathbf{x}_0, t | \mathbf{x}, 0) = 1$ we are left with

$$W(t) = \int d^3r_0 |\mathbf{x}_0|^2 p_{\text{eq}}(\mathbf{x}_0) + \int d^3r |\mathbf{x}|^2 p_{\text{eq}}(\mathbf{x}) - 2 \int \int d^3r d^3r_0 \mathbf{x} \cdot \mathbf{x}_0 p(\mathbf{x}, t | \mathbf{x}_0, 0) p_{\text{eq}}(\mathbf{x}_0).$$

The first two integrals are trivially identical and using an abbreviated notation we have thus

$$\boxed{W(t) = \langle |\mathbf{x}(t) - \mathbf{x}(0)|^2 \rangle = 2 (\langle |\mathbf{x}|^2 \rangle - \langle \mathbf{x}(t) \cdot \mathbf{x}(0) \rangle)} \quad (3.26)$$

Defining the normalized position autocorrelation function

$$\boxed{\phi(t) = \frac{\langle \mathbf{x}(t) \cdot \mathbf{x}(0) \rangle}{\langle |\mathbf{x}|^2 \rangle}} \quad (3.27)$$

the MSD takes the form

$$\boxed{W(t) = 2 \langle |\mathbf{x}|^2 \rangle (1 - \phi(t))} \quad (3.28)$$

Since $\phi(t)$ relaxes for long times to zero, the MSD grows to the plateau value

$$W(\infty) = 2 \langle |\mathbf{x}|^2 \rangle. \quad (3.29)$$

In case of confined diffusion the trick to establish a simple differential equation for the MSD, which was used in the case of free diffusion, does not work and the computation has to be performed via the correlation function (3.27). Here again one can try to establish a simple differential equation and as an example consider the Ornstein-Uhlenbeck process, i.e. a particle diffusing in a quadratic potential. For simplicity we consider first the one-dimensional case and define the unnormalized correlation function

$$c_{xx}(t) \equiv \langle x(t)x(0) \rangle = \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} dx_t dx_0 x_t x_0 p(x_t, t | x_0, 0) p_{\text{eq}}(x_0). \quad (3.30)$$

The time derivative of this function is then given by

$$\begin{aligned} \partial_t c_{xx}(t) &= \partial_t \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} dx_t dx_0 x_t x_0 p(x_t, t | x_0, 0) p_{\text{eq}}(x_0) \\ &= \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} dx_t dx_0 x_t x_0 \{ \partial_t p(x_t, t | x_0, 0) \} p_{\text{eq}}(x_0) \\ &= \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} dx_t dx_0 x_t x_0 \left\{ D \frac{\partial^2}{\partial x_t^2} + \eta \frac{\partial}{\partial x_t} x_t \right\} p(x_t, t | x_0, 0) p_{\text{eq}}(x_0) \\ &= \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} dx_t dx_0 p(x_t, t | x_0, 0) p_{\text{eq}}(x_0) \left\{ D \frac{\partial^2}{\partial x_t^2} - x_t \eta \frac{\partial}{\partial x_t} \right\} x_t x_0 \\ &= -\eta \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} dx_t dx_0 x_t x_0 p(x_t, t | x_0, 0) p_{\text{eq}}(x_0) = -\eta c_{xx}(t). \end{aligned}$$

Here Eq. (3.4) and partial integration have been used, assuming that $\lim_{x_t \rightarrow \pm\infty} p(x_t, t|x_0, 0) = 0$ and $\lim_{x_t \rightarrow \pm\infty} x_t p(x_t, t|x_0, 0) = 0$. Noting that

$$c_{xx}(0) = \langle x^2 \rangle = \int_{-\infty}^{+\infty} dx_0 x_0^2 p_{\text{Eq}}(x_0) = \frac{k_B T}{K}, \quad (3.31)$$

we obtain

$$c_{xx}(t) = \frac{k_B T}{K} e^{-\eta t} \quad (3.32)$$

for the unnormalized correlation function.

The normalized correlation function is then a decaying exponential function,

$$\phi(t) = e^{-\eta t}, \quad (3.33)$$

independent of the dimension, n . Using that

$$\langle x^2 \rangle = n \frac{k_B T}{K} \quad (3.34)$$

the MSD in n dimensions becomes

$$W(t) = 2n \frac{k_B T}{K} (1 - e^{-\eta t}), \quad (3.35)$$

and with Relation (2.9) we may also write

$$W(t) = 2n \frac{D}{\eta} (1 - e^{-\eta t}). \quad (3.36)$$

Since $\eta \propto K$, the limit $\eta \rightarrow 0$ corresponds thus to the limit $K \rightarrow 0$, i.e. to considering vanishing force constant, one one retrieves the MSD for free diffusion,

$$\lim_{K \rightarrow 0} W(t) = \lim_{\eta \rightarrow 0} W(t) = 2nDt. \quad (3.37)$$

It is finally worthwhile noting that this law for the MSD arises also in the short time limit

$$W(t) \stackrel{\eta t \ll 1}{\approx} 2nDt, \quad (3.38)$$

which simply means that on time scales $t \ll 1/\eta$ the particle diffuses seemingly freely. Fig. 3 shows the MSD for a particle diffusing in one dimension in a harmonic potential (solid blue line), setting $n = 1$, $D = 1$ and $\eta = 1$ in dimensionless units. The dashed blue line indicates the corresponding plateau value. For comparison the MSD for free diffusion is shown (orange solid line). One sees that the MSD for confined and free diffusion are identical for $t \ll 1/\eta$.

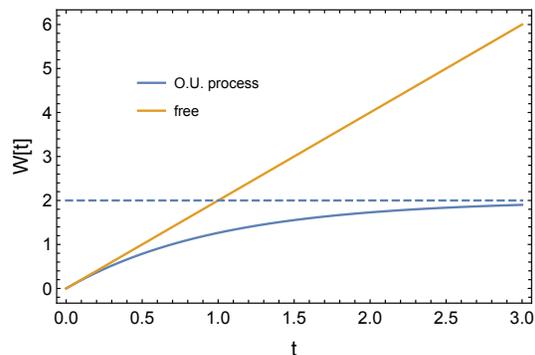


Figure 3: MSD for the one-dimensional Ornstein-Uhlenbeck process (blue solid line) and the corresponding plateau value (blue dashed line). The orange line indicates the MSD for a freely diffusing particle. More details are given in the text.

4 Colloids and macromolecular systems

4.1 Many-body Smoluchowski equation and stochastic equations of motion

Many applications of the theory of diffusion processes concern many particle systems, such as colloids, polymers, and biological macromolecules. Neglecting rotational degrees of freedom, the configurations of such systems are defined by the the positions of all N constituents, $\{\mathbf{x}_1, \dots, \mathbf{x}_N\}$. The Smoluchowski equation (3.2) describing the the diffusion of all N particles keeps its general form,

$$\partial_t p(\mathbf{x}, t | \mathbf{x}_0, 0) = \nabla \cdot \mathbf{D}(\mathbf{x}) \cdot \left\{ \nabla p(\mathbf{x}, t | \mathbf{x}_0, 0) + \frac{\nabla V(\mathbf{x})}{k_B T} p(\mathbf{x}, t | \mathbf{x}_0, 0) \right\} \quad (4.1)$$

where the position for a single particle is replaced by an $3N$ -dimensional vector,

$$\mathbf{x} = \begin{pmatrix} \mathbf{x}_1 \\ \vdots \\ \mathbf{x}_N \end{pmatrix}, \quad (4.2)$$

the potential function

$$V(\mathbf{x}) \equiv V(\mathbf{x}_1, \dots, \mathbf{x}_N) \quad (4.3)$$

accounts for both external and inter-particle forces, and the diffusion constant, D , becomes a positive definite $3N \times 3N$ matrix depending on the positions of all particles, and accounts for hydrodynamic interactions,

$$\mathbf{D}(\mathbf{x}) = \begin{pmatrix} \mathbf{D}_{11}(\mathbf{x}) & \dots & \mathbf{D}_{1N}(\mathbf{x}) \\ \vdots & \ddots & \vdots \\ \mathbf{D}_{N1}(\mathbf{x}) & \dots & \mathbf{D}_{NN}(\mathbf{x}) \end{pmatrix}. \quad (4.4)$$

The corresponding stochastic equations of motion are

$$\mathbf{x}(t_0 + \Delta t) = \mathbf{x}(t_0) - \mathbf{D}(\mathbf{x}) \cdot \frac{\nabla V(\mathbf{x}_0)}{k_B T} \Delta t + \delta \boldsymbol{\xi} \quad (4.5)$$

where $\delta \boldsymbol{\xi}$ is a stochastic displacement verifying

$$\langle \delta \boldsymbol{\xi} \rangle = \mathbf{0}, \quad (4.6)$$

$$\langle \delta \boldsymbol{\xi} \otimes \delta \boldsymbol{\xi} \rangle = 2\mathbf{D}(\mathbf{x}) \Delta t \mathbf{1}. \quad (4.7)$$

Hydrodynamic interactions are mediated by the solvent and arise only if the solute particles are in motion. They are usually computed on the basis of the laws of continuum mechanics solving the Navier-Stokes equation with appropriate boundary conditions for the solvent at the boundary of the solute particles [8,9]. This aspect is briefly discussed in the next section.

4.2 Elementary hydrodynamics

To understand the construction of the diffusion matrix $\mathbf{D}(\mathbf{x})$ on the basis of continuum hydrodynamics we start with the concept of friction. If we consider a spherical solute article of radius

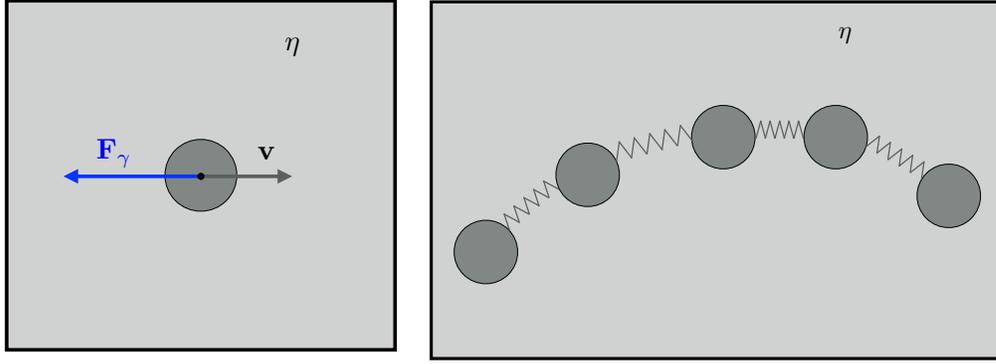


Figure 4: **Left panel:** Friction force F_γ exerted on a sphere moving with velocity v . **Right panel:** A simple Rouse chain of identical spherical monomers.

a and move it with constant velocity v across a solvent of viscosity η , the necessary driving force must exactly balance the frictional force (see Fig. 4),

$$\mathbf{F}_\gamma = -\gamma \mathbf{v}. \quad (4.8)$$

where the friction constant γ is given by [8]

$$\gamma = 6\pi\eta a. \quad (4.9)$$

The so-called Stokes-Einstein relation puts in relation the friction constant γ given above and the diffusion constant of the diffusing solute particle. It puts, in fact, in relation dissipation (friction) and fluctuation (diffusion), noting that in general $D = k_B T \mu$, where $\mu = 1/\gamma$ is the mobility coefficient of a diffusing particle. With Formula (4.9) one obtains thus.

$$D = \frac{k_B T}{6\pi\eta a}. \quad (4.10)$$

The computation of the diffusion tensor for finite distances is a difficult task. The general solution, including rotational degrees and lubrication forces, i.e. hydrodynamic interactions at very short distances, has been presented in Ref. [9]. A good approximation for polymers, where lubrication needs not to be considered, is the Rotne-Prager tensor [10]. It has been developed to describe polymer dynamics, where a polymer is described by a chain of spherical monomer “beads” which have all the same radius, a . An illustration is given in Fig. 4 (right panel), where the springs represent interactions between the monomers keeping them at a prescribed mean distance. Rotational degrees of freedom of individual monomers need not be considered, since rotational motions of the monomers are essentially blocked. The block matrices $\mathbf{D}_{ij}(\mathbf{x})$ in the general form (4.4) of the Diffusion matrix are here given by

$$\mathbf{D}_{ii}(\mathbf{x}) = \frac{k_B T}{6\pi\eta a}, \quad (4.11)$$

$$\mathbf{D}_{ij}(\mathbf{x}) = \frac{k_B T}{8\pi\eta |\mathbf{x}_{ij}|^3} \left\{ (|\mathbf{x}_{ij}|^2 \mathbf{1} + \mathbf{x}_{ij} \otimes \mathbf{x}_{ij}) + \frac{2a_i^2}{|\mathbf{x}_{ij}|^2} \left(\frac{1}{3} |\mathbf{x}_{ij}|^2 \mathbf{1} - \mathbf{x}_{ij} \otimes \mathbf{x}_{ij} \right) \right\}, \quad i \neq j, \quad (4.12)$$

where $\mathbf{x}_{ij} = \mathbf{x}_i - \mathbf{x}_j$. If the solute particles are spaced such that $|\mathbf{x}_i - \mathbf{x}_j| \rightarrow \infty$ for any pair (i, j) with $i \neq j$, the diffusion matrix takes the diagonal form,

$$\mathbf{D}(\mathbf{x}) \approx \begin{pmatrix} D_1 \mathbf{1} & \mathbf{0} & \dots & \mathbf{0} \\ \mathbf{0} & D_2 \mathbf{1} & \dots & \mathbf{0} \\ \vdots & \ddots & \dots & \vdots \\ \mathbf{0} & \mathbf{0} & \dots & D_N \mathbf{1} \end{pmatrix}, \quad (4.13)$$

as it should be. It should be noted that the approach to the diagonal form is very slow, $\propto 1/|\mathbf{x}_{ij}|$. From this point of view hydrodynamic interactions resemble electrostatic interactions.

5 Diffusion in velocity space

Diffusion processes are not limited to position space. Instead of considering the position \mathbf{x} of a particle as stochastic variable, one can for instance consider its velocity. In the following we discuss free diffusion of a Brownian particle in velocity space, i.e. on a finer time scale which allows to resolve relaxation processes of the velocity and which is finer compared to the one which is characteristic for diffusion in position space. A Brownian particle moving in velocity space is referred to as ‘‘Rayleigh particle’’ [7].

5.1 Smoluchowski equation in velocity space

The equilibrium distribution for the velocity of a diffusing particle in a liquid or in a dense gas is known to be the Maxwell distribution, which has Gaussian form,

$$P_{eq}(\mathbf{v}) = \left(\frac{M}{2\pi k_B T} \right)^{3/2} \exp \left(-\frac{M|\mathbf{v}|^2}{2k_B T} \right). \quad (5.1)$$

This distribution function may be compared with the one for a particle diffusing in a harmonic potential of the form $V(\mathbf{x}) = K|\mathbf{x}|^2/2$ (OU process),

$$p_{eq}(\mathbf{x}) = \left(\frac{K}{2\pi k_B T} \right)^{3/2} \exp \left(-\frac{K|\mathbf{x}|^2}{2k_B T} \right), \quad (5.2)$$

the one-dimensional case of which has been discussed earlier. Comparing the distributions (5.1) and (5.2), shows that the kinetic energy, $T = M|\mathbf{v}|^2/2$, in the Boltzmann factor of distribution (5.1) is replaced by the potential energy, $V = K|\mathbf{x}|^2/2$, in the Boltzmann factor of distribution (5.2). Since both T and V are quadratic functions, the corresponding Smoluchowski equations for the respective variables \mathbf{v} and \mathbf{x} must have the the same form, and one can infer from the Smoluchowski equation (3.2) that the time evolution of the the conditional probability density $p(\mathbf{v}, t|\mathbf{v}_0, 0)$ reads

$$\partial_t P(\mathbf{v}, t|\mathbf{v}_0, 0) = D_v \nabla_v \cdot \left\{ \nabla_v P(\mathbf{v}, t|\mathbf{v}_0, 0) + \frac{\nabla_v T(\mathbf{v})}{k_B T} P(\mathbf{v}, t|\mathbf{v}_0, 0) \right\}. \quad (5.3)$$

Noting that the diffusion constant for the OU process in position space is given by $D = \langle x^2 \rangle \eta$, where η is a relaxation constant with the physical dimension 1/s, its follows that

$$\boxed{D_v = \langle v_x^2 \rangle \eta = \eta \frac{k_B T}{M}} \quad (5.4)$$

With this definition and $T = M|\mathbf{v}|^2/2$ one obtains from Eq. (5.3) that

$$\boxed{\partial_t P(\mathbf{v}, t|\mathbf{v}_0, 0) = \eta \nabla_v \cdot \left\{ \mathbf{v} P(\mathbf{v}, t|\mathbf{v}_0, 0) \right\} + \eta \frac{k_B T}{M} \Delta_v P(\mathbf{v}, t|\mathbf{v}_0, 0)} \quad (5.5)$$

where $\nabla_v = \partial/\partial\mathbf{v}$ and $\Delta_v = (\partial/\partial\mathbf{v}) \cdot (\partial/\partial\mathbf{v})$. Using the solution for spatial diffusion in a harmonic potential (voir Eqs. (3.5) et (3.6)) we find

$$P(\mathbf{v}, t|\mathbf{v}_0, 0) = \left(\frac{M}{2\pi k_B T (1 - e^{-2\eta t})} \right)^{3/2} \exp \left(-\frac{M |\mathbf{v} - \mathbf{v}_0 e^{-\eta t}|^2}{2k_B T (1 - e^{-2\eta t})} \right), \quad (5.6)$$

$$\lim_{t \rightarrow \infty} P(\mathbf{v}, t|\mathbf{v}_0, 0) = \left(\frac{M}{2\pi k_B T} \right)^{3/2} \exp \left(-\frac{M |\mathbf{v}|^2}{2k_B T} \right) = P_{eq}(\mathbf{v}), \quad (5.7)$$

where $P_{eq}(\mathbf{v})$ is the Maxwell distribution.

5.2 Mean square displacement in velocity space

As for a Brownian particle diffusing in a harmonic potential in position space, one can define a mean square velocity displacement,

$$W_v(t) = \langle |\mathbf{v}(t) - \mathbf{v}(0)|^2 \rangle = 2 \left(\langle |\mathbf{v}|^2 \rangle - \langle \mathbf{v}(t) \cdot \mathbf{v}(0) \rangle \right), \quad (5.8)$$

which may be written in the form

$$\boxed{W_v(t) = 2 \langle |\mathbf{v}|^2 \rangle (1 - \phi_{vv}(t))} \quad (5.9)$$

where

$$\phi_{vv}(t) = \frac{\langle \mathbf{v}(t) \cdot \mathbf{v}(0) \rangle}{\langle |\mathbf{v}|^2 \rangle} = e^{-\eta t} \quad (5.10)$$

is the normalized *velocity* autocorrelation function (VACF). Since $\phi_{vv}(t)$ relaxes for long times to zero, the MSD grows to the plateau value

$$W(\infty) = 2 \langle |\mathbf{v}|^2 \rangle = \frac{n k_B T}{m}. \quad (5.11)$$

5.3 Ornstein-Uhlenbeck process in velocity space and Langevin equation

As for the Smoluchowski equation in position space, one may derive a stochastic equation of motion for the velocity from Eq. (5.3), and in analogy to Eq. (3.12) one obtains

$$\mathbf{v}(t_0 + \Delta t) = \mathbf{v}(t_0) - D_v \frac{\nabla T(\mathbf{v}(t_0))}{k_B T} \Delta t + \delta \boldsymbol{\xi}_v, \quad (5.12)$$

or, equivalently,

$$\boxed{\mathbf{v}(t_0 + \Delta t) = \mathbf{v}(t_0) - \eta \mathbf{v}(t_0) \Delta t + \delta \boldsymbol{\xi}_v} \quad (5.13)$$

where the stochastic displacement in velocity space verifies

$$\langle \delta \boldsymbol{\xi}_v \rangle = \mathbf{0}, \quad (5.14)$$

$$\langle \delta \boldsymbol{\xi}_v \otimes \delta \boldsymbol{\xi}_v \rangle = 2nD_v \Delta t \mathbf{1} = 2n\eta \frac{k_B T}{M} \Delta t \mathbf{1}, \quad (5.15)$$

where n is the dimensions of v . Approximating

$$\frac{\mathbf{v}(t_0 + \Delta t) - \mathbf{v}(t_0)}{\Delta t} \approx \dot{\mathbf{v}}(t_0),$$

the stochastic equation of motion (5.13) can be considered as analogue to the Langevin equation [11] (the notation is here adapted),

$$\boxed{\dot{\mathbf{v}}(t) + \eta \mathbf{v}(t) = \mathbf{f}_s(t)} \quad (5.16)$$

which is named after Paul Langevin who introduced this equation in 1908 to describe Brownian motion. Here $\mathbf{f}_s(t)$ is a stochastic acceleration verifying

$$\langle \mathbf{f}_s(t) \rangle_\tau = \mathbf{0}, \quad (5.17)$$

$$\langle \mathbf{f}_s(t) \otimes \mathbf{f}_s(t') \rangle_\tau = 2D_v \mathbf{1} \delta(t - t'). \quad (5.18)$$

The averages $\langle \dots \rangle_\tau$ are here *time averages*,

$$\langle \mathbf{f}_s(t) \rangle_\tau \equiv \lim_{T \rightarrow \infty} \frac{1}{T} \int_{-T/2}^{T/2} d\tau \mathbf{f}_s(\tau) \quad (5.19)$$

$$\langle \mathbf{f}_s(t) \otimes \mathbf{f}_s(t') \rangle_\tau \equiv \lim_{T \rightarrow \infty} \frac{1}{T} \int_{-T/2}^{T/2} d\tau \mathbf{f}_s(t + \tau) \otimes \mathbf{f}_s(t' + \tau). \quad (5.20)$$

in this picture, $\mathbf{f}_s(t)$ is Gaussian white noise and it follows from the Langevin equation (5.16) that

$$\frac{d}{dt} \langle \mathbf{v}(0) \cdot \mathbf{v}(t) \rangle_\tau + \eta \langle \mathbf{v}(0) \cdot \mathbf{v}(t) \rangle_\tau = \langle \mathbf{v}(0) \cdot \mathbf{f}_s(t) \rangle_\tau.$$

Since $\mathbf{f}_s(t)$ is Gaussian white noise, it follows that

$$\boxed{\langle \mathbf{v}(0) \cdot \mathbf{f}_s(t) \rangle_\tau = 0} \quad (5.21)$$

such that

$$\frac{d}{dt} \langle \mathbf{v}(0) \cdot \mathbf{v}(t) \rangle_\tau + \eta \langle \mathbf{v}(0) \cdot \mathbf{v}(t) \rangle_\tau = 0. \quad (5.22)$$

Therefore the velocity autocorrelation function is an exponential function

$$c_{vv}(t) = \langle \mathbf{v}(0) \cdot \mathbf{v}(t) \rangle_\tau = \langle |\mathbf{v}(0)|^2 \rangle_\tau e^{-\eta t}, \quad (5.23)$$

leading to

$$\boxed{\phi_{vv}^{(\tau)}(t) = \frac{\langle \mathbf{v}(0) \cdot \mathbf{v}(t) \rangle_\tau}{\langle |\mathbf{v}|^2 \rangle_\tau} = e^{-\eta t}} \quad (5.24)$$

Assuming that

$$\langle |\mathbf{v}|^2 \rangle_\tau = \langle |\mathbf{v}|^2 \rangle = n \frac{k_B T}{M}, \quad (5.25)$$

corresponds to the assumption of ergodicity, where generally time averages are assumed to be equal to the corresponding ensemble averages. In this context it is worthwhile noting that Eq. (5.21) can be interpreted as a time scale separation between the dynamics of the “slow” variable $\mathbf{v}(t)$ and the “fast” variable $\mathbf{f}_s(t)$. This is the picture of Brownian motion, where a massive and slow Brownian particle is kicked around by rapidly varying forces arising from the collisions with the surrounding molecules of the solvent in which the Brownian particle (“solute”) is immersed.

The Langevin equation is one of the pivots of modern statistical physics, which uses a stochastic equations of motion to describe Brownian motion on the basis of single particle motion instead of using the concept of distribution functions, as Fick, Einstein, and Smoluchowski. It must, however, be emphasized that a description in terms of probability distributions is more complete, since the underlying probability density cannot be inferred from the Langevin equation without further assumptions.

5.4 Velocity autocorrelation function and mean square displacement

The time-dependent mean square displacement of a particle in position space,

$$W(t) := \langle |\mathbf{x}(t) - \mathbf{x}(0)|^2 \rangle,$$

is closely related to its velocity autocorrelation function (VACF). Since

$$\mathbf{x}(t) - \mathbf{x}(0) = \int_0^t dt' \mathbf{v}(t'),$$

one can write

$$W(t) = \int_0^t dt' \int_0^t dt'' \langle \mathbf{v}(t') \cdot \mathbf{v}(t'') \rangle.$$

Supposing that $\mathbf{v}(t)$ is described by a stationary stochastic process, such that its autocorrelation function depends only on time differences,

$$\langle \mathbf{v}(t') \cdot \mathbf{v}(t'') \rangle = \langle \mathbf{v}(t' - t'') \cdot \mathbf{v}(0) \rangle,$$

the MSD may be written in the form

$$W(t) = \int_0^t dt' \int_0^t dt'' c_{vv}(t' - t''),$$

where $c_{vv}(t)$ denotes the (unnormalized) velocity autocorrelation function,

$$c_{vv}(t) = \langle \mathbf{v}(t) \cdot \mathbf{v}(0) \rangle.$$

A more useful expression can be obtained by introducing the new variables

$$\begin{aligned} u &= t' - t'', \\ v &= t'', \end{aligned}$$

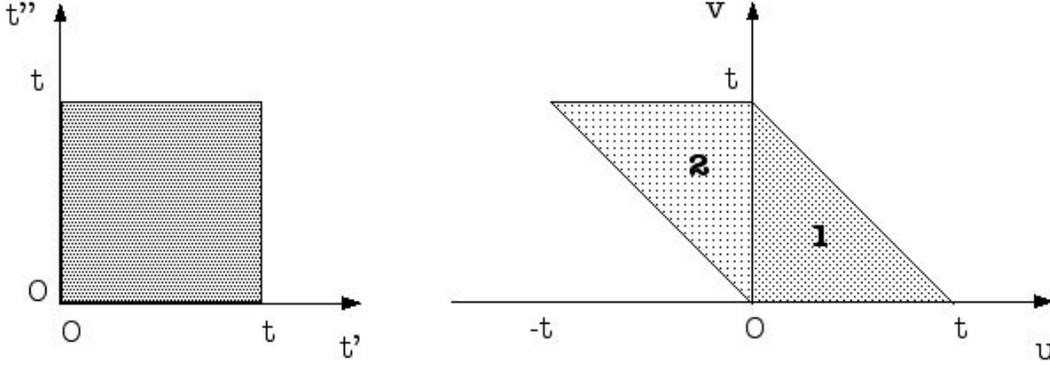


Figure 5: Integration domains for the variables (t', t'') and (u, v) .

for which the corresponding Jacobi matrix reads

$$\mathbf{J} = \begin{pmatrix} \frac{\partial u}{\partial t'} & \frac{\partial u}{\partial t''} \\ \frac{\partial v}{\partial t'} & \frac{\partial v}{\partial t''} \end{pmatrix} = \begin{pmatrix} 1 & -1 \\ 0 & 1 \end{pmatrix}.$$

Since the determinant of \mathbf{J} equals one, $|\mathbf{J}| = 1$, the volume element is transformed as $dudv = |\mathbf{J}|dt'dt'' = dt'dt''$. In the new variables u and v the MSD thus takes the form

$$W(t) = \int_0^t dv \int_{-v}^{t-v} du c_{vv}(u),$$

and Fig. 5 shows that one may also write

$$W(t) = \underbrace{\int_0^t du \int_0^{t-u} dv c_{vv}(u)}_{\text{triangle 1}} + \underbrace{\int_{-t}^0 du \int_{-u}^t dv c_{vv}(u)}_{\text{triangle 2}}.$$

With a new variable change $u \rightarrow -u$ for the integration over triangle 2 and using that $c(u) = c(-u)$ for a classical (stationary) time correlation function one finds

$$W(t) = 2 \int_0^t du (t-u) c_{vv}(u) \quad (5.26)$$

Using the normalised form of the VACF, this may be written as

$$W(t) = n \frac{2k_B T}{M} \int_0^t du (t-u) \phi_{vv}(u) \quad (5.27)$$

5.5 Mean square displacement of a Rayleigh particle

In the preceding section we have derived a relation between the MSD and the VACF and Relation (5.27) will now be used to derive the MSD for the concrete case of a freely diffusing Brownian

particle, whose motion is described by an OU process in velocity space – the Rayleigh particle. For this purpose it is very convenient to work with the Laplace transform. For an arbitrary function $f(t) = \Theta(t)f(t)$ the Laplace transform and its inverse and its inverse are defined by

$$\hat{f}(s) = \int_0^{\infty} dt \exp(-st)f(t) \quad (5.28)$$

$$f(t) = \frac{1}{2\pi i} \oint_C ds \hat{f}(s) \exp(-st). \quad (5.29)$$

The Laplace transform of $f(t)$ exists if one can find a constant $a > 0$ such that $|f(t)| < \exp(at)$. The variable s must be chosen such that $\Re\{s\} > a$. The contour C in relation (5.29) includes all singularities of $\hat{f}(s)$. In many cases one uses the residue method to obtain $f(t)$ from relation (5.29). In some cases the notations

$$\hat{f}(s) \equiv \mathcal{L}\{f(t), t, s\}, \quad (5.30)$$

$$f(t) = \mathcal{L}^{-1}\{\hat{f}(s), s, t\}. \quad (5.31)$$

will also be used.

Expression (5.27) shows that the MSD is formally proportional to a convolution of the functions $f(t) = t$ and $g(t) = \phi_{vv}(t)$. The general form for the convolution integral is

$$(f * g)(t) := \int_0^t d\tau f(t - \tau)g(\tau), \quad (5.32)$$

where $f(t) = \Theta(t)f(t)$ and $g(t) = \Theta(t)g(t)$. It is easy to prove that

$$\mathcal{L}\{(f * g)(t), t, s\} = \hat{f}(s)\hat{g}(s). \quad (5.33)$$

Applying the above convolution theorem to relation (5.27) yields thus

$$\hat{W}(s) = n \frac{2k_B T}{M} \frac{\hat{\phi}_{vv}(s)}{s^2}, \quad (5.34)$$

since $\mathcal{L}\{t, t, s\} = 1/s^2$. For a freely diffusing Brownian particle we have $\phi_{vv}(t) = \exp(-\gamma t)$, and the corresponding Laplace transform is given by

$$\hat{\phi}_{vv}(s) = \frac{1}{s + \eta}. \quad (5.35)$$

Inserting the above expression into (5.34) yields thus

$$\hat{W}(s) = n \frac{2k_B T}{M} \frac{1}{s^2(s + \eta)} \quad (5.36)$$

and an inverse Laplace transform leads to the MSD in the time domain,

$$W(t) = n \frac{2k_B T}{M} \left\{ \frac{\exp(-\eta t) - 1 + \eta t}{\eta^2} \right\} \quad (5.37)$$

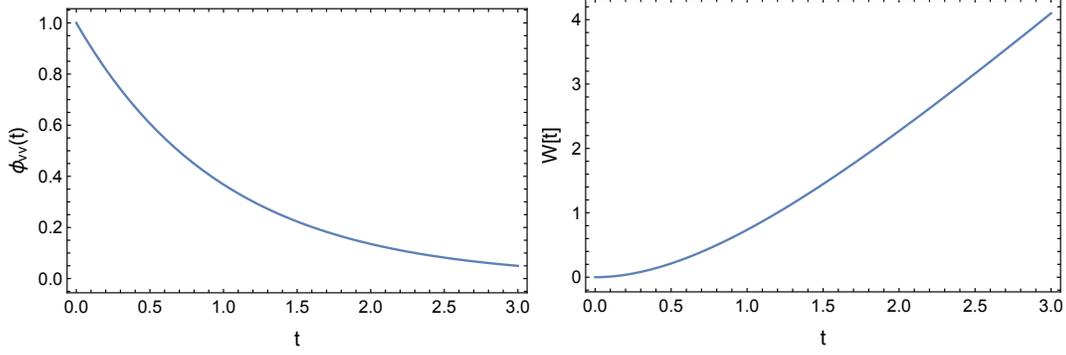


Figure 6: The normalised VACE, $\phi_{vv}(t)$, of a Brownian particle and the corresponding MSD. All quantities are given in dimensionless units, i.e. $t \leftarrow \eta t$ and $W(t) \leftarrow W(t)\eta^2/\langle|\mathbf{v}|^2\rangle$.

For times much longer than the inverse relaxation rate, $t \gg \eta^{-1}$, the MSD grows linearly with time

$$\boxed{W(t) \approx 2nDt} \quad (5.38)$$

Here D is the *diffusion constant*

$$\boxed{D = \frac{k_B T}{M\eta}} \quad (5.39)$$

and the above relation is often referred to as *Einstein relation*. Fig 6 illustrates the form of the MSD for a freely diffusing Brownian particle. The linear growth with time is attained for $t \gg \eta^{-1}$. If, in contrast, $t \ll \eta^{-1}$ one can approximate $\exp(-\eta t) \approx 1 - \eta t + (\eta t)^2/2$. In this case one finds

$$\boxed{W(t) \approx \langle|\mathbf{v}|^2\rangle t^2 = \frac{nk_B T}{M} t^2} \quad (5.40)$$

Fig 6. shows indeed a parabolic form of the MSD in the initial phase.

6 Anomalous free diffusion

6.1 Introduction

We consider here a generalization of the diffusion equation, which has the form

$$\boxed{\partial_t p(\mathbf{x}, t|\mathbf{x}_0, 0) = {}_0\partial_t^{1-\alpha} p(\mathbf{x}, t|\mathbf{x}_0, 0), D_\alpha \Delta p(\mathbf{x}, t|\mathbf{x}_0, 0)} \quad (6.1)$$

where ${}_0\partial_t^{1-\alpha}$ denotes a fractional derivative of order $1 - \alpha$. For an arbitrary function $f(\cdot)$ the latter is defined through

$$\boxed{{}_0\partial_t^{1-\alpha} f(t) = \frac{d}{dt} \int_0^t du \frac{(t-u)^{\alpha-1}}{\Gamma(\alpha)} f(u)} \quad (6.2)$$

where $\Gamma(\cdot)$ is the Gamma function or generalized factorial, which is defined for complex arguments [12]. The fractional derivative introduces memory effects and the underlying stochastic processes are non-markovian. It leads in particular to an MSD which grows $\propto t^\alpha$, with $0 \leq \alpha < 2$. The regime $0 < \alpha < 1$ is referred to as “subdiffusion” and the regime $1 < \alpha < 2$ as “superdiffusion”. There is a large amount of literature on fractional diffusion models and Refs. [13–15] can be taken as starting point to explore the subject.

6.2 Mean square displacement

For the calculation of the MSD we follow the same steps as for normal free diffusion and use in addition the Laplace transform as a powerful tool. The first step is to change $\mathbf{x} \rightarrow \mathbf{u} \equiv \mathbf{x} - \mathbf{x}_0$ and to write the fractional diffusion equation in the form

$$\partial_t p(\mathbf{u}, t | \mathbf{0}, 0) = {}_0\partial_t^{1-\alpha} D_\alpha \Delta p(\mathbf{u}, t | \mathbf{0}, 0). \quad (6.3)$$

For the time derivative of the MSD we have then

$$\begin{aligned} \partial_t W(t) &= \int d^3 u |\mathbf{u}|^2 \partial_t p(\mathbf{u}, t | \mathbf{0}, 0) \\ &= \int d^3 u |\mathbf{u}|^2 {}_0\partial_t^{1-\alpha} D_\alpha \Delta p(\mathbf{u}, t | \mathbf{0}, 0) = D_\alpha \left\{ {}_0\partial_t^{1-\alpha} \int d^3 u |\mathbf{u}|^2 \Delta p(\mathbf{u}, t | \mathbf{0}, 0) \right\} \\ &= D_\alpha \left\{ {}_0\partial_t^{1-\alpha} \int d^3 u p(\mathbf{u}, t | \mathbf{0}, 0) \underbrace{\{\Delta |\mathbf{u}|^2\}}_{2n} \right\} = {}_0\partial_t^{1-\alpha} \{2n D_\alpha\}. \end{aligned}$$

Applying here the Laplace transform leads to

$$s \hat{W}(s) - \underbrace{W(0)}_{=0} = s^{1-\alpha} \left(\frac{2n D_\alpha}{s} \right) = 2n D_\alpha s^{-(1+\alpha)},$$

which yields in the domain

$$\boxed{W(t) = 2n D_\alpha \frac{t^\alpha}{\Gamma(1 + \alpha)}} \quad (6.4)$$

Noting that $\Gamma(2) = 1$, the well-known expression for normal free diffusion is retrieved for $\alpha \rightarrow 1$.

6.3 Kubo relation for the (fractional) diffusion constant

The example of a Rayleigh particle has shown that the linear evolution of the mean square displacement with time, which follows from the diffusion equation according to Eq. (3.22), is obtained as an *asymptotic regime*, where $t \gg \eta^{-1}$, with η being the relaxation constant of the velocity autocorrelation function. Since the latter decays exponentially, the diffusion constant given by Formula (5.39) can be written as $D = k_B T / M \int_0^\infty dt \phi_{vv}(t)$. Using that $c_{vv}(0) = nk_B T / M$, where n is the dimension of the diffusion problem, we can write

$$\boxed{D = \frac{1}{n} \int_0^\infty dt c_{vv}(t)} \quad (6.5)$$

which is an example in which a transport coefficient – here the diffusion constant – is expressed as an integral over a time correlation function. The derivation, which is based on linear response theory, is due to Ryogo Kubo.³ It will now be shown that this formula can be obtained without any further assumption from Expression (5.26), by using a theorem from asymptotic analysis, which is due to Jovan Karamata.⁴ The concept has been described in Ref. [16] and more details can be found there. Karamata’s theorem relates the asymptotic form of a certain class of functions $f(t)$ for large t with the asymptotic form of its Laplace transform, $F(s)$, for small s . It states that

$$f(t) \stackrel{t \rightarrow \infty}{\sim} L(t)t^\alpha \Leftrightarrow F(s) \stackrel{s \rightarrow 0}{\sim} L(1/s) \frac{\Gamma(1+\alpha)}{s^{1+\alpha}}, \quad (6.6)$$

with the condition $\alpha > -1$. The function $L(t)$ is here a “slowly varying function”, which is defined through the property $\lim_{t \rightarrow \infty} L(\lambda t)/L(t) = 1$, where $\lambda > 0$ is an arbitrary scaling parameter. It can easily be checked that the logarithm, $L(t) = \log(t)$, is such a function, and here we will make the assumption that $L(t)$ obeys the stronger condition

$$\lim_{t \rightarrow \infty} L(t) = 1. \quad (6.7)$$

Obviously any function with this property is slowly growing in the sense of Karamata’s theorem. The latter can then be applied to the mean square displacement,

$$W(t) \stackrel{t \rightarrow \infty}{\sim} L(t)2nDt \Leftrightarrow W(s) \stackrel{s \rightarrow 0}{\sim} L(1/s) \frac{2nD}{s^2}, \quad (6.8)$$

noting that $\Gamma(2) = 1$. From a physical point of view, $L(t)$ refines the asymptotic regime of the MSD, but here a concrete form is not needed. We use simply that it follows from Expression (5.26) that

$$\hat{W}(s) = \frac{2\hat{c}_{vv}(s)}{s^2}, \quad (6.9)$$

and therefore

$$D = \lim_{s \rightarrow 0} \frac{1}{n} \hat{c}_{vv}(s) = \frac{1}{n} \int_0^\infty dt c_{vv}(t) \quad (6.10)$$

which is exactly Expression (6.5).

These results can be straightforwardly generalized to the case of anomalous diffusion, considering instead of Eq. (6.8)

$$W(t) \stackrel{t \rightarrow \infty}{\sim} L(t)2nD_\alpha t^\alpha \Leftrightarrow W(s) \stackrel{s \rightarrow 0}{\sim} L(1/s)2nD_\alpha \frac{\Gamma(1+\alpha)}{s^{1+\alpha}}. \quad (6.11)$$

Using that $\lim_{t \rightarrow \infty} L(t) = 1$ we obtain here instead of the Kubo formula (6.10) the fractional generalization [17]

$$D_\alpha = \lim_{s \rightarrow 0} \frac{1}{n} \frac{s^{\alpha-1}}{\Gamma(1+\alpha)} \hat{c}_{vv}(s) = \frac{1}{n} \int_0^\infty dt {}_0\partial_t^{\alpha-1} c_{vv}(t) \quad (6.12)$$

where ${}_0\partial_t^{\alpha-1}$ is a fractional derivative of order $\alpha - 1$,

$${}_0\partial_t^{\alpha-1} f(t) = \frac{d}{dt} \int_0^t du \frac{(t-u)^{1-\alpha}}{\Gamma(2-\alpha)} f(u). \quad (6.13)$$

³Ryogo Kubo, Japanese physicist, 1920 – 1995, famous for his work in the field of non-equilibrium statistical physics.

⁴Jovan Karamata, Serbian mathematician, 1902-1967.

It is interesting that the case $\alpha = 0$ can be explicitly included

$$D_0 = \frac{1}{n} \langle |\mathbf{u}|^2 \rangle = \frac{k_B T}{K} \quad (6.14)$$

where $\mathbf{u} = \mathbf{x} - \mathbf{x}_0$. The proof is given in Ref. [17]. Confined diffusion can thus be formally considered as extreme cas of anomalous diffusion, where $\alpha = 0$, and the fractional diffusion constant is here the mean square position fluctuation.

7 Fractional Ornstein-Uhlenbeck process

7.1 Introduction

We consider here the fractional Smoluchowski equation

$$\partial_t p(\mathbf{x}, t | \mathbf{x}_0, 0) = {}_0\partial_t^{1-\alpha} \{ D_\alpha \Delta p(\mathbf{x}, t | \mathbf{x}_0, 0) + \eta_\alpha \nabla \cdot \{ \mathbf{x} p(\mathbf{x}, t | \mathbf{x}_0, 0) \} \}, \quad (7.1)$$

where D_α can be considered as fractional short time diffusion coefficient (see discussion below), with physical dimensions $\text{m}^2/\text{s}^\alpha$, and η_α as fractional relaxation constant, with physical units $\text{s}^{-\alpha}$. Instead of Relation (2.9) we have here

$$\eta_\alpha = \frac{D_\alpha K}{k_B T}, \quad (7.2)$$

and, again, the MSD can be derived via Eq. (3.26), inserting the correlation function $c_{xx}(t) \equiv \langle \mathbf{x}(t) \cdot \mathbf{x}(0) \rangle$. As for the case of the normal OU process we perform the computation first for the one-dimensional case, starting from the definition (3.30) for $c_{xx}(t)$. It follows then that

$$\begin{aligned} \partial_t c_{xx}(t) &= {}_0\partial_t^{1-\alpha} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} dx_t dx_0 x_t x_0 \{ \partial_t p(x_t, t | x_0, 0) \} p_{\text{eq}}(x_0) \\ &= {}_0\partial_t^{1-\alpha} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} dx_t dx_0 x_t x_0 \left\{ D \frac{\partial^2}{\partial x_t^2} + \eta \frac{\partial}{\partial x_t} x_t \right\} p(x_t, t | x_0, 0) p_{\text{eq}}(x_0) \\ &= {}_0\partial_t^{1-\alpha} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} dx_t dx_0 p(x_t, t | x_0, 0) p_{\text{eq}}(x_0) \left\{ D \frac{\partial^2}{\partial x_t^2} - x_t \eta \frac{\partial}{\partial x_t} \right\} x_t x_0 \\ &= -\eta {}_0\partial_t^{1-\alpha} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} dx_t dx_0 x_t x_0 p(x_t, t | x_0, 0) p_{\text{eq}}(x_0) = -\eta {}_0\partial_t^{1-\alpha} c_{xx}(t). \end{aligned}$$

The only difference with respect to the normal OU process is the appearance of the the fractional derivative ${}_0\partial_t^{1-\alpha}$ on the r.h.s of the above equations, which leads to the fractional differential equation

$$\partial_t c_{xx}(t) = -\eta {}_0\partial_t^{1-\alpha} c_{xx}(t). \quad (7.3)$$

Applying the Laplace transform one obtains

$$s \hat{c}_{xx}(s) - c_{xx}(0) = -\eta s^{1-\alpha} \hat{c}_{xx}(s),$$

which may be solved to yield

$$\hat{c}_{xx}(s) = c_{xx}(0) \frac{1}{s(1 + \eta_\alpha s^{-\alpha})}.$$

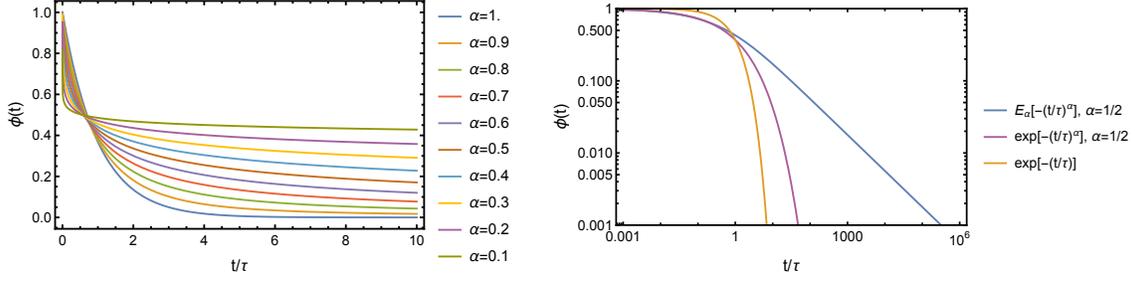


Figure 7: **Left panel:** Stretched Mittag-Leffler function for different values of α . **Right panel:** Comparison to stretched and a normal exponential on a log-log scale.

The fraction on the r.h.s. of the equation is the Laplace transform of the “stretched” Mittag-Leffler (ML) function [18]

$$E_\alpha(-\eta_\alpha t^\alpha) \longleftrightarrow \frac{1}{s(1 + \eta_\alpha s^{-\alpha})}, \quad (7.4)$$

where the ML function itself is defined by the series

$$E_\alpha(z) = \sum_{k=0}^{\infty} \frac{z^k}{\Gamma(1 + \alpha k)}$$

with $z, \alpha \in \mathbb{C}$. One recognizes that the exponential function is retrieved for the case $\alpha = 1$, noting that $\Gamma(1 + k) = k!$. Defining

$$\tau := \eta_\alpha^{-1/\alpha} \quad (7.5)$$

we obtain for the correlation function

$$c_{xx}(t) = \frac{k_B T}{M} E_\alpha(-(t/\tau)^\alpha) \quad (7.6)$$

instead of the exponentially decaying function given in Expression (3.32). An important feature of the stretched ML function is its asymptotic power-law decay,

$$E_\alpha(-(t/\tau)^\alpha) \stackrel{t \rightarrow \infty}{\sim} \frac{(t/\tau)^{-\alpha}}{\Gamma(1 - \alpha)} \quad (7.7)$$

The long-time tail vanishes as $\alpha \rightarrow 1$, noting that $\lim_{z \rightarrow 0} \Gamma(z) = \infty$. In n dimensions we have thus

$$c_{\mathbf{x}\mathbf{x}}(t) = n \frac{k_B T}{M} E_\alpha(-(t/\tau)^{-\alpha}), \quad (7.8)$$

and the MSD becomes

$$W(t) = 2n \frac{k_B T}{K} (1 - E_\alpha(-(t/\tau)^{-\alpha})) \quad (7.9)$$

For short times we have

$$W(t) \stackrel{t \rightarrow 0}{\sim} 2n \frac{k_B T}{K} (t/\tau)^{-\alpha} = 2n D_\alpha t^\alpha, \quad (7.10)$$

which confirms that D_α can be considered as short time diffusion coefficient.

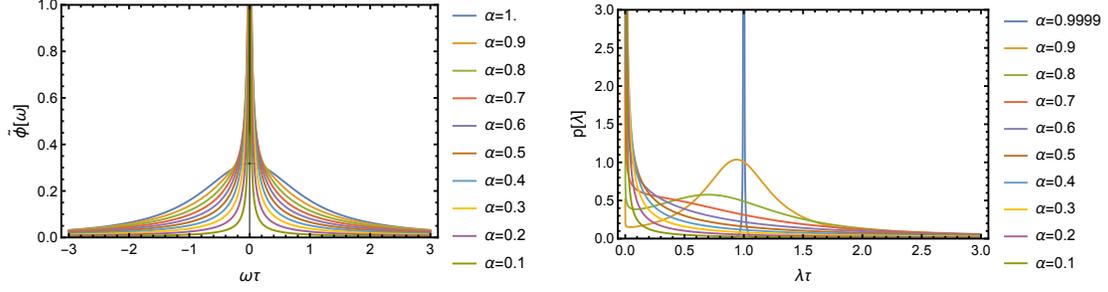


Figure 8: **Left panel:** Fourier spectrum of the stretched Mittag-Leffler function for different values of α . **Right panel:** Corresponding relaxation rate spectra.

7.2 Fourier spectrum of the autocorrelation function

The autocorrelation function of the fractional OU process can be straightforwardly obtained from its Laplace transform. Considering the normalized form,

$$\phi(t) \equiv \frac{\langle x(0)x(t) \rangle}{\langle x^2 \rangle}, \quad (7.11)$$

the Fourier transform

$$\tilde{\phi}(\omega) = \int_{-\infty}^{+\infty} dt e^{-i\omega t} \phi(t) \quad (7.12)$$

can be obtained via

$$\tilde{\phi}(\omega) = \lim_{\epsilon \rightarrow 0} \frac{1}{\pi} \Re \{ \hat{\phi}(i\omega + \epsilon) \}, \quad \omega \geq 0, \quad (7.13)$$

where the Laplace transform is given by (see Eq. (7.4))

$$\hat{\phi}(s) = \frac{1}{s(1 + \eta_\alpha s^{-\alpha})}.$$

The result is a ‘‘generalized Lorentzian’’,

$$\tilde{\phi}(\omega) = \frac{\sin\left(\frac{\pi\alpha}{2}\right)}{\pi\omega \left((\omega\tau)^{-\alpha} + (\omega\tau)^\alpha + 2\cos\left(\frac{\pi\alpha}{2}\right) \right)}, \quad \omega \geq 0 \quad (7.14)$$

where τ is defined through Eq. (7.5) and $0 < \alpha \leq 1$. The normal Lorentzian is retrieved for $\alpha \rightarrow 1$.

7.3 Relaxation rate spectrum of the autocorrelation function

The autocorrelation function of the fractional OU process can be written as a superposition of a continuous spectrum of exponentially decaying functions,

$$\phi(t) = \int_0^\infty d\lambda p(\lambda) e^{-\lambda t} \quad (7.15)$$

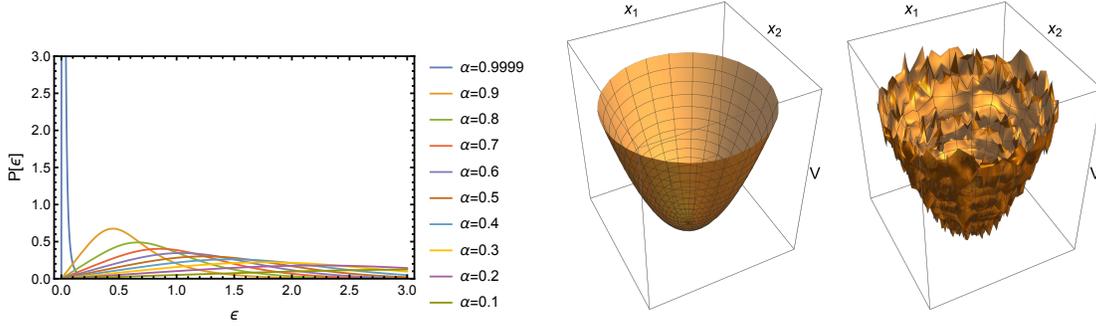


Figure 9: **Left panel:** Energy barrier distribution for various values of α . **Right panel:** Smooth and rough harmonic potential energy surface in two dimensions.

where the relaxation rate spectrum, $p(\lambda)$, can be derived as well from the Laplace transform via

$$p(\lambda) = \lim_{\epsilon \rightarrow 0} \frac{1}{\pi} \Im \{ \hat{\phi}(-i\lambda - \epsilon) \}. \quad (7.16)$$

With the relaxation time τ defined through Eq. (7.5) this leads to the analytical formula

$$p(\lambda) = \frac{\sin(\pi\alpha)}{\pi\lambda((\lambda\tau)^{-\alpha} + (\lambda\tau)^\alpha + 2\cos(\pi\alpha))} \quad (7.17)$$

For $\alpha \rightarrow 1$ the relaxation rate spectrum tends to $p(\lambda) = \delta(\lambda - \eta)$.

7.4 Diffusion in a “rough” harmonic potential

The time correlation function derived in the preceding section can also be derived from an energy landscape perspective, considering a particle that diffuses in a “rough” harmonic potential. In the context of protein dynamics and protein folding, multi-minima energy landscapes have been considered by Frauenfelder, Wolynes, and co-workers [19–22], considering high-dimensional (free) energy profiles as functions of the $3N$ coordinates of proteins containing N atoms. The many minima in these energy landscapes, which are referred to as “conformational substates”, are separated by energy barriers of different heights hindering more or less the diffusion on the global (free) energy envelope. To formalize the deceleration of the diffusion process, Zwanzig [23] has considered the diffusion of a particle in some smooth potential, $U(x)$, which is modulated by at each drawing a modulation δU from a Gaussian distribution with a fixed standard deviation δG , which is independent of x , such that $\langle \delta U^2 \rangle(x) = \delta G^2$. He found that the short time diffusion coefficient, D , of the Smoluchowski equation describing the diffusion in the smooth potential becomes

$$D^* = D e^{-\epsilon^2}, \quad \text{where} \quad \epsilon = \frac{\delta G}{k_B T}. \quad (7.18)$$

For a harmonic potential the short time diffusion coefficient is related through $D = \langle x^2 \rangle \eta$ with the relaxation constant describing the exponential decay of the position autocorrelation function,

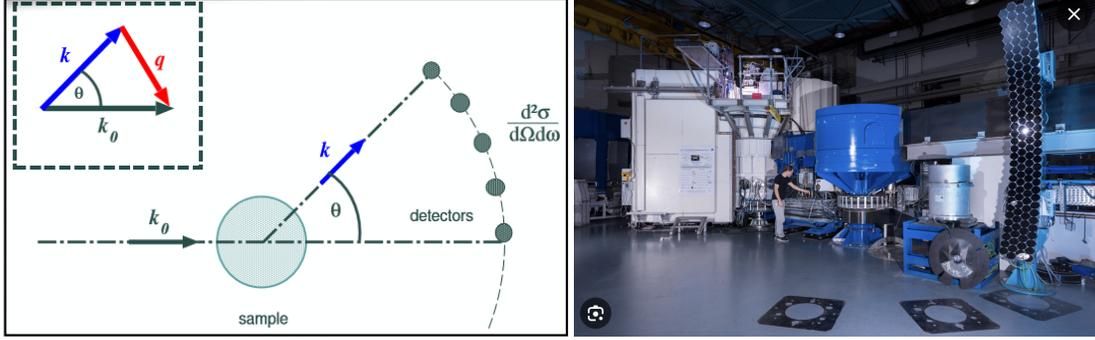


Figure 10: **Left panel:** Scheme of a neutron scattering experiment. **Right panel:** The IN16B spectrometer at the Institut Laue-angevin in Grenoble.

$c_{xx}(t) \equiv \langle x(t)x(0) \rangle$, and setting $\lambda \equiv \eta$, the relaxation rate is thus modulated as

$$\lambda^* = \lambda e^{-\epsilon^2}. \quad (7.19)$$

This relation enable the conversion of a spectrum of relaxation rates into a spectrum energy barriers, noting that the latter is a standard deviation of a Gaussian distribution describing the modulation δU of the smooth harmonic potential. The conversion is described by

$$P(\epsilon) = p(\lambda(\epsilon)) \left| \frac{d\lambda}{d\epsilon} \right| \quad (7.20)$$

and leads to

$$P(\epsilon) = \frac{2\epsilon \sin(\pi\alpha)}{\pi (e^{-\alpha\epsilon^2} + e^{\alpha\epsilon^2} + 2 \cos(\pi\alpha))} \quad (7.21)$$

8 Applications in neutron scattering

We will new discuss some applications of the theory of diffusion described in the previous sections to model quasielastic neutron scattering spectra (QENS) from liquids and biomolecular systems. Within the classical interpretation of neutron scattering QENS probes essentially stochastic motions of the atoms in the sample.

8.1 Basic neutron scattering theory

In neutron scattering experiments the sample of interest is exposed to a beam of incident neutrons with momentum $\hbar k_0$ and one one records energy histograms of the scattered neutrons as a function of the scattering angle. These histograms are proportional to the differential scattering cross section,

$$\frac{d^2 \sigma}{d\Omega d\omega} = \frac{k}{k_0} S(\mathbf{q}, \omega) \quad (8.1)$$

where $S(\mathbf{q}, \omega)$ is the dynamic structure factor containing the information about the structural dynamics of the scattering system, k_0 and k are the wave numbers of the incident and scattered neutrons, and $\mathbf{q} = \mathbf{k}_0 - \mathbf{k}$ and $\omega = (E_0 - E)/\hbar$ are the momentum and energy transfer in units of \hbar . Usually \mathbf{q} is referred to a scattering vector. The dynamic structure factor is given by

$$S(\mathbf{q}, \omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} dt e^{-i\omega t} F(\mathbf{q}, t), \quad (8.2)$$

$$F(\mathbf{q}, t) \approx \frac{1}{N} \sum_{j,k} \Gamma_{jk} \left\langle e^{-i\mathbf{q} \cdot \hat{\mathbf{x}}_j(0)} e^{i\mathbf{q} \cdot \hat{\mathbf{x}}_k(t)} \right\rangle, \quad (8.3)$$

where $F(\mathbf{q}, t)$ is the intermediate scattering function. Here N is the number of hydrogen atoms, $\hat{\mathbf{x}}_j(t)$ is the time-dependent position operator of hydrogen atom j , \mathbf{q} the scattering vector, and the symbol $\langle \dots \rangle$ denotes a quantum ensemble average and the weighting factors Γ_{jk} have the form

$$\Gamma_{jk} = \overline{b_j^* b_k} + \delta_{jk} |b_j - \overline{b_j}|^2, \quad (8.4)$$

where b_j and b_k are the (complex) scattering lengths [24,25] of the atoms j and k , respectively. For a selected atom the average runs over all isotopes and combinations of the nuclear and neutron spins and $b_{j,\text{coh}} \equiv \overline{b_j}$ and $b_{j,\text{inc}} \equiv (|b_j - \overline{b_j}|^2)^{1/2}$ are, respectively, the coherent and incoherent scattering lengths of atom j .

The intermediate scattering function fulfills the symmetry relations

$$F^*(\mathbf{q}, t) = F(\mathbf{q}, -t), \quad (8.5)$$

$$F(\mathbf{q}, t) = F(-\mathbf{q}, -t + i\beta\hbar). \quad (8.6)$$

and the model calculations concern the symmetrized version

$$F^{(+)}(\mathbf{q}, t) = \frac{F(\mathbf{q}, t + i\beta\hbar/2)}{F(\mathbf{q}, i\beta\hbar/2)}, \quad (8.7)$$

which can be associated with the classical intermediate scattering function

$$F_{\text{cl}}(\mathbf{q}, t) = F^{(+)}(\mathbf{q}, t) \quad (8.8)$$

using Schofield's semiclassical approximation [26]. For simplicity we will consider the self correlation function for a single atom j ,

$$f_s(\mathbf{q}, t) = \left\langle e^{-i\mathbf{q} \cdot \hat{\mathbf{x}}_j(0)} e^{i\mathbf{q} \cdot \hat{\mathbf{x}}_j(t)} \right\rangle, \quad (8.9)$$

and the version describing collective dynamics,

$$f_c(\mathbf{q}, t) = \frac{1}{N} \sum_{j,k} \left\langle e^{-i\mathbf{q} \cdot \hat{\mathbf{x}}_j(0)} e^{i\mathbf{q} \cdot \hat{\mathbf{x}}_k(t)} \right\rangle. \quad (8.10)$$

8.2 Single-atom motion as an Ornstein-Uhlenbeck process

We consider now neutron scattering from a single atom which diffuses in a harmonic potential, which keeps the atom close to its equilibrium position. This is the simplest possible model for an

atom in a protein, whose motion is hindered by interactions with the “cage” of the surrounding atoms. For simplicity we consider a fixed direction “ x ” which is defined by the direction of the scattering vector. In this case the intermediate scattering function has the form

$$f_s(q, t) = \langle e^{-iq\hat{x}(0)} e^{iq\hat{x}(t)} \rangle \quad (8.11)$$

and we consider the semiclassical approximation

$$f_s^{(\text{cl})}(q, t) \approx f_s^{(+)}(q, t), \quad (8.12)$$

using the OU process as a stochastic model for the dynamics of the atomic position, x . Defining $f_s^{(\text{OU})}(q, t) \equiv f_s^{(\text{cl})}(q, t)$, we write

$$f_s^{(\text{OU})}(q, t) = \int \int dx_t dx_0 e^{iq(x_t - x_0)} p(x_t, t | x_0, 0) p_{\text{eq}}(x_0). \quad (8.13)$$

where $p(x_t, t | x_0, 0)$ fulfills the differential equation (2.11),

$$\partial_t p(x_t, t | x_0, 0) = D \frac{\partial^2}{\partial x^2} p(x_t, t | x_0, 0) + \eta \frac{\partial}{\partial x} \{x p(x_t, t | x_0, 0)\},$$

and the equilibrium distribution function $p_{\text{eq}}(x_0)$ is given by

$$p_{\text{eq}}(x_0) = \lim_{t \rightarrow \infty} p(x_t, t | x_0, 0).$$

According to Baye’s rule, $p(x_t, t | x_0, 0) p_{\text{eq}}(x_0)$ is the joint probability to find the atom at time 0 at position x_0 and at time t at position x_t . The solution and the spatial Fourier transform of the latter can be read off from Eq. (2.13),

$$p(x_t, t | x_0, 0) = \frac{e^{-\frac{(x - \mu(t))^2}{2\sigma(t)^2}}}{\sqrt{2\pi\sigma(t)}} \longleftrightarrow \tilde{p}(k, t | x_0, 0) = e^{-\frac{1}{2}\sigma(t)^2 k^2 - i\mu(t)k},$$

where $\sigma(t)$ and $\mu(t)$ are given by Eqs. (2.15) and (2.16), respectively,

$$\sigma(t) = \frac{\sqrt{D(1 - e^{-2\eta t})}}{\sqrt{\eta}},$$

$$\mu(t) = x_0 e^{-\eta t}.$$

In order to evaluate $f_s^{(\text{OU})}(q, t)$ we write

$$f_s^{(\text{OU})}(q, t) = \int dx_0 p_{\text{eq}}(x_0) e^{-iqx_0} \int dx_t e^{iqx_t} p(x_t, t | x_0, 0),$$

noting that the second integral is the Fourier transform of the conditional probability density, $p(x_t, t | x_0, 0)$ evaluated at the Fourier variable $k = q$,

$$\tilde{p}(q, t | x_0, 0) = \int dx_t e^{iqx_t} p(x_t, t | x_0, 0).$$

This leads to

$$f_s^{(\text{OU})}(q, t) = e^{-\frac{q^2}{2}\sigma(t)^2} \int dx_0 p_{\text{eq}}(x_0) e^{-iq(1+e^{-\eta t})x_0}$$

which is the spatial Fourier transform of the equilibrium distribution evaluated at the Fourier variable $k = q(1 + \exp(-\eta t))$. Noting that

$$\tilde{p}_{\text{eq}}(k) = \lim_{t \rightarrow \infty} \tilde{p}(k, t | x_0, 0) = e^{-\frac{1}{2}\sigma(\infty)k^2},$$

it follows that

$$f_s^{(\text{OU})}(q, t) = e^{-Dq^2 \frac{(1-\exp(-\eta t))}{\eta}} \quad (8.14)$$

Writing the diffusion constant in the form

$$D = \langle x^2 \rangle \eta$$

one obtains the equivalent expression

$$f_s^{(\text{OU})}(q, t) = e^{-q^2 \langle x^2 \rangle (1-e^{-\eta t})} \quad (8.15)$$

noting that $\langle x^2 \rangle = k_B T / K$, with K being the force constant of the potential. For an isotropic harmonic potential it follows that

$$f_s^{(\text{OU})}(\mathbf{q}, t) = e^{-|\mathbf{q}|^2 \frac{D(1-e^{-\eta t})}{\eta}} \quad (8.16)$$

or, equivalently,

$$f_s^{(\text{OU})}(\mathbf{q}, t) = e^{-\frac{|\mathbf{q}|^2 \langle \mathbf{x}^2 \rangle}{3} (1-e^{-\eta t})} \quad (8.17)$$

noting that

$$D = \langle x^2 \rangle \eta = \frac{\langle \mathbf{x}^2 \rangle}{3} \eta. \quad (8.18)$$

Writing $\eta = D / \langle x^2 \rangle$ shows that η vanishes if $K \rightarrow 0$, i.e. if the scattering atom feels no elastic force. The intermediate scattering function for a free particle is thus given by

$$f_s^{(\text{free})}(\mathbf{q}, t) = \lim_{\eta \rightarrow 0} f_s^{(\text{OU})}(\mathbf{q}, t) = e^{-D|\mathbf{q}|^2 t} \quad (8.19)$$

A physical meaningful interpretation is here that small q -values are considered, such that the motion of a whole protein can be described by the motion of a “representative” atom. It finally worthwhile mentioning that the intermediate scattering function for the OU process fulfills the so-called Gaussian approximation in the classical approximation [27] exactly, and for an isotropic potential one has

$$f_s^{(\text{OU})}(\mathbf{q}, t) = e^{-\frac{|\mathbf{q}|^2}{6} W(t)} \quad (8.20)$$

where $W(t)$ is the MSD

$$W(t) = \langle |\mathbf{x}(t) - \mathbf{x}(0)|^2 \rangle = 2\langle \mathbf{x}^2 \rangle (1 - e^{-\eta t}) \quad (8.21)$$

8.3 Fractional Ornstein-Uhlenbeck process for collective variables

In the preceding section we have described the intermediate scattering function of a tagged atom by a stochastic model for the time evolution of its position. Formally, this approach can be generalized to the N atoms of a macromolecule considering their collective diffusion in a $3N$ -dimensional harmonic potential [28,29], but this approach necessitates a realistic force field for molecular dynamics simulations and is not suited to develop simple models which can be fitted directly to experimental neutron scattering data. An alternative is to consider anomalous diffusion of the collective variable

$$a_{\mathbf{q}}(\mathbf{x}_1, \dots, \mathbf{x}_N) = \frac{1}{\sqrt{N}} \sum_{j=1}^N e^{i\mathbf{q} \cdot \mathbf{x}_j} \quad (8.22)$$

which leads to a non-exponentially decaying correlation function, which typical for complex systems. Here $N = 1$ is admitted to model incoherent (“self”) scattering. For the following considerations we split $a_{\mathbf{q}}$ into a static and a dynamic part,

$$a_{\mathbf{q}}(t) = \langle a_{\mathbf{q}} \rangle + \xi_{\mathbf{q}}(t), \quad (8.23)$$

and write the intermediate scattering function in the form

$$f(\mathbf{q}, t) = |\langle a_{\mathbf{q}} \rangle|^2 + \langle \xi_{\mathbf{q}}^*(0) \xi_{\mathbf{q}}(t) \rangle \quad (8.24)$$

where $|\langle a_{\mathbf{q}} \rangle|^2$ is the elastic emplitude of the measured dynamic structure factor,

$$s(\mathbf{q}, \omega) = |\langle a_{\mathbf{q}} \rangle|^2 \delta(\omega) + \frac{1}{2\pi} \int_{-\infty}^{+\infty} dt e^{-i\omega t} \langle \xi_{\mathbf{q}}^*(0) \xi_{\mathbf{q}}(t) \rangle. \quad (8.25)$$

Using that $\langle |\xi_{\mathbf{q}}|^2 \rangle = \langle |a_{\mathbf{q}}|^2 \rangle - |\langle a_{\mathbf{q}} \rangle|^2$ the intermediate scattering function can be cast into the form

$$f(\mathbf{q}, t) = |\langle a_{\mathbf{q}} \rangle|^2 + (\langle |a_{\mathbf{q}}|^2 \rangle - |\langle a_{\mathbf{q}} \rangle|^2) \phi_{\xi\xi}(\mathbf{q}, t) \quad (8.26)$$

where $\phi_{\mathbf{q}}(t)$ is the normalized autocorrelation function

$$\phi_{\xi\xi}(\mathbf{q}, t) \equiv \frac{\langle \xi_{\mathbf{q}}^*(0) \xi_{\mathbf{q}}(t) \rangle}{\langle |\xi_{\mathbf{q}}|^2 \rangle} \quad (8.27)$$

and

$$\langle |a_{\mathbf{q}}|^2 \rangle = F(\mathbf{q}, 0) = S(\mathbf{q}) \quad (8.28)$$

is the static structure factor, which becomes $S(\mathbf{q}) = 1$ for a single atom.

To enable the use of stochastic models we introduce the vector variable

$$\boldsymbol{\xi}_{\mathbf{q}} \equiv \begin{pmatrix} \Re\{a_{\mathbf{q}} - \langle a_{\mathbf{q}} \rangle\} \\ \Im\{a_{\mathbf{q}} - \langle a_{\mathbf{q}} \rangle\} \end{pmatrix} \quad (8.29)$$

supposing that the $\langle a_{\mathbf{q}} \rangle$ is not strictly zero. This assumption is correct for any system where the scattering atom feels a force from its neighbors and assures that the two components of $\boldsymbol{\xi}_{\mathbf{q}}$ are

independent in the case $N = 1$, where a single atom is considered. In terms of the vector variable ξ_q the intermediate scattering function can be expressed as

$$\boxed{f(\mathbf{q}, t) = |\langle a_q \rangle|^2 + \langle \xi_q^T(0) \cdot \xi_q(t) \rangle} \quad (8.30)$$

noting that in the classical limit

$$\langle \xi_q^T(0) \cdot \xi_q(t) \rangle = \Re\{\langle \xi^*(\mathbf{q}, 0)\xi(\mathbf{q}, t) \rangle\}, \quad (8.31)$$

if $\langle \xi^*(\mathbf{q}, 0)\xi(\mathbf{q}, t) \rangle$ is invariant with respect to a reflection $\mathbf{q} \rightarrow -\mathbf{q}$, which can be assumed for proteins or other macromolecules in solution or powder samples. The explicit form of the auto-correlation function of ξ_q is

$$\langle \xi_q^T(0) \cdot \xi_q(t) \rangle = \int \int d^2\xi_0 d^2\xi_t \xi_0^T \cdot \xi_t p(\xi, t|\xi_0, 0) p_{\text{eq}}(\xi_0), \quad (8.32)$$

omitting the q -dependence of ξ on the r.h.s. of the above equation.

In the following we will consider the case that the time evolution of the dynamical vector variable $\xi_q(t)$ is described by an Ornstein-Uhlenbeck process [5–7] or its fractional variant [13–15], which describe here, respectively, normal and anomalous diffusion of ξ in an harmonic potential

$$V(\xi) = \frac{K}{2} |\xi|^2, \quad (8.33)$$

where $K > 0$ has the dimension of an energy. From a physical point of view this potential assures that $a(\mathbf{q})$ stays more or less close to its mean value $\langle a(\mathbf{q}) \rangle$ and the equilibrium probability density, $p_{\text{eq}}(\xi_0)$, has Gaussian form

$$p_{\text{eq}}(\xi) \propto e^{-\beta \frac{K}{2} |\xi|^2}, \quad (8.34)$$

with $\beta = 1/k_B T$. We will here discuss the case of the fractional O.U. process which contains the normal O.U. process as a special case. Applications concern so far only incoherent scattering from water and proteins in solution [30–35], which is described by scattering from a single atom in the framework of the model. The Smoluchowski (Fokker-Planck) equation for the transition probability of a fractional O.U. process has the form

$$\partial_t p(\xi, t|\xi_0, 0) = {}_0\partial_t^{1-\alpha} \left\{ D_\xi^{(\alpha)} \Delta p(\xi, t|\xi_0, 0) + \eta_\xi^{(\alpha)} \nabla \cdot (\xi p(\xi, t|\xi_0, 0)) \right\}, \quad (8.35)$$

where the fractional diffusion coefficient has here the dimension $1/s^\alpha$ and is related to the fractional relaxation constant though

$$D_\xi^{(\alpha)}(\mathbf{q}) = \eta_\xi^{(\alpha)}(\mathbf{q}) \langle |\xi_q|^2 \rangle. \quad (8.36)$$

To obtain the time autocorrelation function of $\xi_q(t)$ it is not necessary to solve the Smoluchowski equation explicitly, and following the same steps as for the position autocorrelation function described in Section (7) one finds

$$\boxed{c_{\xi\xi}(t) = \langle |\xi(\mathbf{q})|^2 \rangle E_\alpha \left(-\eta_\xi^{(\alpha)} t^\alpha \right)} \quad (8.37)$$

where the initial value is given by

$$\langle |\xi_{\mathbf{q}}|^2 \rangle = \langle |a_{\mathbf{q}}|^2 \rangle - |\langle a_{\mathbf{q}} \rangle|^2 \quad (8.38)$$

and the relaxation function is thus

$$\boxed{\phi_{\xi\xi}(\mathbf{q}, t) = E_{\alpha} \left(-\eta_{\xi}^{(\alpha)} t^{\alpha} \right)} \quad (8.39)$$

The parameters of the stretched Mittag-Leffler function are here \mathbf{q} -dependent, i.e. $\alpha \equiv \alpha(\mathbf{q})$ and $\eta_{\xi}^{(\alpha)} \equiv \eta_{\xi}^{(\alpha)}(\mathbf{q})$.

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