Internship report M1 – 2022

Brownian Motion near a Soft Surface

Yilin YE

SUPERVISORS: Yacine AMAROUCHENE, David DEAN, Thomas SALEZ - *Univ. Bordeaux, CNRS, Laboratoire Ondes et Matière d'Aquitaine, UMR 5798, F-33400, Talence, France*

Abstract
We consider the Brownian motion of a particle in 2D near a soft surface. We invoke previous deterministic soft-lubrication predictions for the forces and torques at leading order in compliance, and incorporate further thermal fluctuations in the description. Specifically here, a simple but model Winkler's response – equivalent to a simple layer of independent springs – is assumed for the soft substrate.

From the Fokker-Planck equation and the equilibrium constraint, we obtain the effective friction matrix as a function of the z-position variable and the geometric, viscous and elastic parameters. We also derive the proper noise correlators and spurious drifts to be used in the inertial Langevin equation. Solving numerically the latter requires a multi-dimensional discretisation. Our results demonstrate the influence of softness on various statistical observables.

Keywords
Brownian motion — soft surface — Langevin equation — noise correlator — Fokker-Planck equation

Introduction

In 1827, Robert Brown, the British botanist, reported on the random motion of pollen particles under a microscope. [1] The same thing happens with coal dust, leading to nothing about alive matters, which matched earlier observations of Jan Ingenhousz. Brown speculated that the apparent random motion of colloids is a result of the thermal movement of surrounding solvent molecules, implying indirect evidences of atoms.

In 1905, Albert Einstein proposed a stochastic model for Brownian motion [2], indicating clean connection with the impacts with atoms. With flux conservation, he recovered the microscopic diffusion equation $\frac{\partial \rho}{\partial t} = D\frac{\partial^2 \rho}{\partial x^2}$, where ρ is the probability density of particles as a function of time t and displacement x, while D refers to the diffusion coefficient, which describes the mobility of the particle inside a given liquid. At the same time, he also obtained $D = \frac{RT}{N_A \cdot 6\pi\eta r}$, where η refers to viscocity, r radius of particle, and N_A Avogadro number. Specifically, free Brownian motion in the bulk could be characterized by a typical spatial extent evolving as the square root of time, as well as Gaussian displacements. Hence, one can measure the average displacement λ after a delay τ as $\lambda = \sqrt{2D\tau}$.

After Einstein's theoretical explanation, French physicist Jean Perrin did experiments and measured N_A with different techniques, which confirmed Einstein's prediction, and the existence of atoms. For this achievement, he was honored with the Nobel Prize for Physics in 1926. [3]

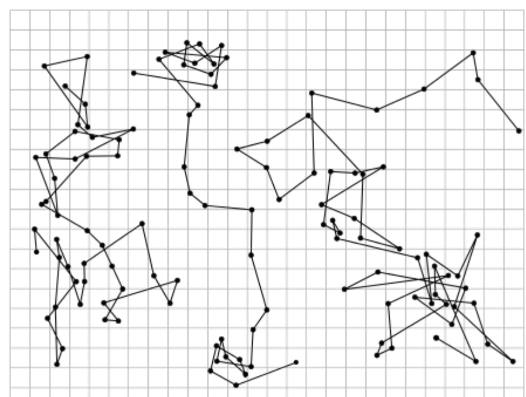

Figure 1. Three tracings of the motion of colloidal particles by Jean Perrin. [4]

The force required to move one particle in the fluid is proportional to its velocity, with friction coefficient $\zeta = 6\pi\eta r$ shown by Stokes in the 1850s. However, this result will lead to a zero velocity at long time, conflicting with the nature that particles will never stop. Based on that, Paul Langevin in 1908 furnished the formation in term of equations of motions. He introduced the concept of a random force or noise, toward the famous Langevin equation: [5]

$$m\dot{v} = -\zeta v + \delta F \tag{1}$$

where the first term refers to Stokes force, while the second term δF refers to random impacts due to thermal fluctuations of solvent molecules. Generally, there is no preferred direction for this fictive noise, so $\langle \delta F(t) \rangle = 0$. Also, Gaussian white noise is assumed and thus $\langle \delta F(\tau_1)\delta F(\tau_2)\rangle = 2k_B T\zeta\delta(\tau_1-\tau_2)$, which could reflect well the fluctuation-dissipation theorem [6], Stokes-Einstein relation [7], and Green-Kubo relations [8].

Brownian motion has been a central paradigm in modern science, which presents numerous applications in physics, biology, and even finance for instance on share prices. In addition, motility of confined microscopic biological matters towards certain targets is a paramount question of biophysics, as evidenced by: DNA replication, antibody recognition, and various examples self-assembly. Ideally, this problem could be simplified to mechanics through a basic combination of necessary ingredients: confined environment, elastic boundaries, electric charges, thermal fluctuations, and viscous flow.

In soft matter, an emergent ElastoHydroDynamic (EHD) lift force was theoretically predicted [9] for elastic bodies moving past each other in a viscous fluid, despite the low Reynolds number. This intriguing effect has thus been explored with various deterministic models and experiments, showing its potential relevance for biological and nanoscale systems. The EMetBrown project aims at combining the two elements of context above, confined Brownian motion and elastohydrodynamics, in order to address the influence of soft and complex boundaries on Brownian motion. Besides experimental setups, it involves three core theoretical models: soft lubrication, stochastic theory and Langevin simulations. Indeed, several preliminary results have been published previously, containing EHD force measurement in 2020 [10], confined Brownian motion in 2021 [11, 12], rigid sphere near elastic wall in 2022 [13]

The study of Brownian motion in soft-lubricated environments appears here as a canonical problem of biophysics and nanophysics. However, it is intriguing to note that studies are scarce on this topic. Therefore, a key mission arises, namely how to combine continuum ingredients, especially hydrodynamics and elasticity, together with molecular fluctuations at small scales.

In this internship report, we aim to develop a theoretical framework to incorporate soft lubrication forces into a Langevin problem including multiplicative noise and external potential, and then derive the effective friction and modified noise correlators. Besides, numerical simulations with multi-dimensional discretisation have also been completed to verify the predictions. The core strategy is to employ perturbation theory leading order in compliance, on a simple 2D spring-like system in order to demonstrate the effect of softness on various statistical variables. Apart from this report, see the *Supporting Information* for more details. yiliny/EHD_LOMA.

Theoretical Analysis

Situation of the problem

Herein, we consider a 2D Brownian motion near a model soft surface (see Figure 2), based on a previous deterministic approach [14]. Below are the dimensionless deterministic equations of motion, with three coupled variables: X_G, Δ for parallel, vertical displacements, and Θ the rotation angle.

$$\ddot{X}_G + \frac{2\varepsilon\xi}{3}\frac{\dot{X}_G}{\sqrt{\Delta}} + \frac{\kappa\varepsilon\xi}{6}\left[\frac{19}{4}\frac{\dot{\Delta}\dot{X}_G}{\Delta^{7/2}} - \frac{\dot{\Delta}\dot{\Theta}}{\Delta^{7/2}} + \frac{1}{2}\frac{\ddot{\Theta}-\ddot{X}_G}{\Delta^{5/2}}\right] = 0$$

$$\ddot{\Delta} + \xi\frac{\dot{\Delta}}{\Delta^{3/2}} + \frac{\kappa\xi}{4}\left[21\frac{\dot{\Delta}^2}{\Delta^{9/2}} - \frac{(\dot{\Theta}-\dot{X}_G)^2}{\Delta^{7/2}} - \frac{15}{2}\frac{\ddot{\Delta}}{\Delta^{7/2}}\right] + 1 = 0$$

$$\ddot{\Theta} + \frac{4\varepsilon\xi}{3}\frac{\dot{\Theta}}{\sqrt{\Delta}} + \frac{\kappa\varepsilon\xi}{3}\left[\frac{19}{4}\frac{\dot{\Delta}\dot{\Theta}}{\Delta^{7/2}} - \frac{\dot{\Delta}\dot{X}_G}{\Delta^{7/2}} + \frac{1}{2}\frac{\ddot{X}_G-\ddot{\Theta}}{\Delta^{5/2}}\right] = 0$$

where ε is the ratio of initial height and particle radius; ξ the ratio of free fall time and typical lubrication damping time; $\kappa \ll 1$, dimensionless compliance.

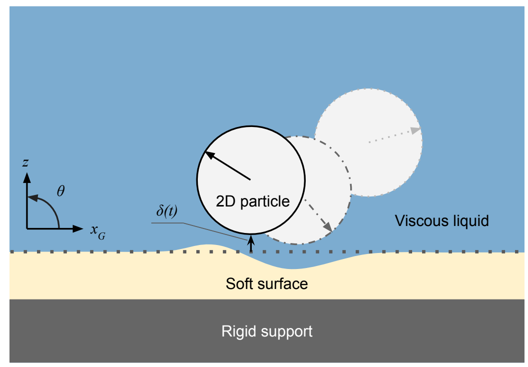

Figure 2. Schematic of the system. A negatively buoyant cylindrical colloid (grey) falls down under the influence of gravity, inside a viscous fluid (blue), and follows a Brownian-like motion in the vicinity of a thin soft wall (yellow). The ensemble lies atop an infinitely rigid support (black).

In these equations, the perpendicular height Δ plays a significant, nonlinear and singular role. Also, velocities $\dot{X}_G, \dot{\Delta}, \dot{\Theta}$ interact with each other, at leading order in κ. Moreover, extra acceleration terms emerge with non-zero κ.

The topic of my work is to further consider Brownian motion for such forces and torques. Thus, we should describe the corresponding friction coefficient, and random force correlator. We define v_x, v_z, v_θ for $\dot{X}_G, \dot{\Delta}, \dot{\Theta}$.

Langevin equation
$\downarrow$
$\boxed{v(t)} \rightarrow \boxed{\langle v^2(t)\rangle} \rightarrow$ noise amplitudes
$\downarrow$
$\boxed{\langle v(0)v(t)\rangle} \rightarrow$ MSD, diffusion coefficients

Figure 3. Calculation procedure

Herein, we will first start from Langevin equation for obtaining the formal expressions of velocities $v(t)$. See Figure 3, by computing the time average of the squared velocity $\langle v^2(t) \rangle$, we figure out the noise correlator amplitudes $\langle \delta F(\tau_1)\delta F(\tau_2)\rangle$. Also, from $\langle v(0)v(t)\rangle$ we derive the mean square displacement (MSD) $\langle \Delta r^2 \rangle$ and the diffusion coefficients as well.

Effective friction matrix

In the Langevin equation, the parameter ζ in Eq. (1) reflects the friction property of a given environment. We introduce a new parameter $\gamma = \frac{\zeta}{m}$, which controls several important quantities. Therefore, in this subsection, we will derive effective friction matrix according to the equations of motion, considering prefactors in front of velocities as friction and those in front of accelerations as effective mass. See Figure 4.

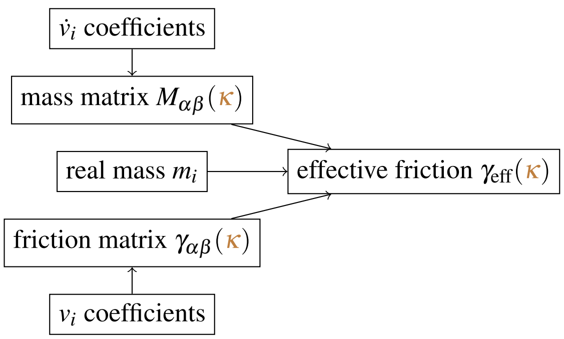

Figure 4. How to calculate the effective friction matrix

Mass matrix

Consider the deterministic equation with Einstein summation convention on β:

$$m_\alpha \cdot \dot{v}_\alpha = \left[F_{1\alpha}(\mathbf{x}) + F_{2\alpha\beta}(\mathbf{x})\dot{v}_\beta\right] - m_\alpha \cdot \gamma_{\alpha\beta} v_\beta$$

where $\mathbf{x}$ is the position vector, $F_{1\alpha}(\mathbf{x})$ refers to forces only depending on positions like external potentials, $F_{2\alpha\beta}(\mathbf{x})$ are coefficients for accelerations, and $\gamma_{\alpha\beta}$ those in front of velocities. For Δ, X components, the mass $m_\alpha = m = \pi r^2 \rho$, namely the mass of the cylindrical particle (per unit length); while $m_\theta = mr^2/2$ refers to the moment of inertia.

We introduce the mass matrix as $M_{\alpha\beta} = \delta_{\alpha\beta} \cdot m_\alpha - F_{2h\alpha\beta}(\mathbf{x})$. We extract easily all non-zero $F_{2h\alpha\beta}(\mathbf{x})$ according to extra acceleration terms:

$$F_{2hzz} = -\frac{m_z a_5}{\Delta^{7/2}} \qquad F_{2hxx} = -\frac{m_x b_5}{\Delta^{5/2}} \qquad F_{2hx\theta} = -\frac{m_x b_4}{\Delta^{5/2}}$$
$$F_{2h\theta x} = -\frac{m_\theta c_4}{\Delta^{5/2}} \qquad F_{2h\theta\theta} = -\frac{m_\theta c_5}{\Delta^{5/2}}$$

where $a_5 = -\frac{15\kappa\xi}{8}$, $b_4 = -b_5 = \frac{\kappa\xi\varepsilon}{12}$, $c_4 = -c_5 = \frac{\kappa\xi\varepsilon}{6}$. As a result, we have the mass matrix M, and its inverse matrix M^{-1} at first-order in κ:

$$M^{-1} \simeq \begin{pmatrix} \frac{1}{m_z} + \frac{15\kappa\xi}{8\Delta^{5/2} m_z} & 0 & 0 \\ 0 & \frac{1}{m_x} + \frac{\kappa\xi\varepsilon}{12\Delta^{5/2} m_x} & -\frac{\kappa\xi\varepsilon}{12\Delta^{5/2} m_\theta} \\ 0 & -\frac{\kappa\xi\varepsilon}{6\Delta^{5/2} m_x} & \frac{1}{m_\theta} + \frac{\kappa\xi\varepsilon}{6\Delta^{5/2} m_\theta} \end{pmatrix}$$

Fokker-Planck equation for friction matrix

Consider the following deterministic equation $\mathrm{d}\mathbf{x} = \mathbf{v}\mathrm{d}t$ and $\mathrm{d}\mathbf{v} = -\mathbf{U}\mathrm{d}t - \nabla\phi(\mathbf{x})\mathrm{d}t$. We assume that $\mathbf{U}$ is generated by hydrodynamic interactions, which do not however affect the equilibrium Gibbs-Boltzmann distribution which is

$$P_{\text{eq}}(\mathbf{x}, \mathbf{v}) = \frac{1}{\bar{Z}} \exp\left(-\frac{\beta \mathbf{v}^2}{2} - \beta\phi(\mathbf{x})\right)$$

where $\beta^{-1} = k_{\mathrm{B}}T$. To follow the evolution of the distribution probability $P(\mathbf{x}, \mathbf{v}, t)$, we exploit the Fokker-Planck equation, solving

$$\frac{\partial P}{\partial t} = \frac{\partial}{\partial v_\alpha}\left[T\gamma_{\alpha\beta} \cdot \frac{\partial P}{\partial v_\beta} + U_\alpha P + \frac{\partial \phi}{\partial x_\alpha} \cdot P\right] - \frac{\partial}{\partial x_\alpha}(v_\alpha P)$$

The last two terms vanish, so we have

$$\frac{\partial P}{\partial t} = \frac{\partial}{\partial v_\alpha}\left(T\gamma_{\alpha\beta} \cdot \frac{\partial P}{\partial v_\beta} + U_\alpha P\right) = \frac{\partial}{\partial v_\alpha}\left(-\gamma_{\alpha\beta} \cdot v_\beta P + U_\alpha P\right)$$

Therefore, at equilibrium $\frac{\partial P}{\partial t} = 0$, and we obtain the Gibbs-Boltzmann distribution for the steady state if

$$U_\alpha = \gamma_{\alpha\beta} \cdot v_\beta \tag{2}$$

Following the format of Langevin equation, the $\gamma_{\alpha\beta}$ matrix above only contains terms with first derivatives

$$\gamma_{Z\beta} v_\beta = a_1 \frac{\dot{\Delta}}{\Delta^{3/2}} + a_2 \frac{\dot{\Delta}^2}{\Delta^{9/2}} + a_3 \frac{\dot{\Theta}^2 + \dot{X}^2}{\Delta^{7/2}} + a_4 \frac{\dot{\Theta}\dot{X}}{\Delta^{7/2}}$$
$$\gamma_{X\beta} v_\beta = b_1 \frac{\dot{X}}{\sqrt{\Delta}} + b_2 \frac{\dot{\Delta}\dot{X}}{\Delta^{7/2}} + b_3 \frac{\dot{\Delta}\dot{\Theta}}{\Delta^{7/2}}$$
$$\gamma_{\Theta\beta} v_\beta = c_1 \frac{\dot{\Theta}}{\sqrt{\Delta}} + c_2 \frac{\dot{\Delta}\dot{\Theta}}{\Delta^{7/2}} + c_3 \frac{\dot{\Delta}\dot{X}}{\Delta^{7/2}}$$

with reduced parameters like $a_1 = \xi$, $b_1 = \frac{2\varepsilon\xi}{3}$, and so on for convenience. To be general, we write γ for small velocities as

$$\gamma_{\alpha\beta} \cdot v_\beta = \lambda_{\alpha\beta}(\mathbf{x}) \cdot v_\beta + \Lambda_{\alpha\beta\gamma}(\mathbf{x}) \cdot v_\beta v_\gamma$$

where the term $\lambda_{\alpha\beta}(\mathbf{x})$ is just the friction tensor without any elastic effects. Additional efforts should be taken on the second term by symmetry. We suppose that

$$\gamma_{\alpha\beta} = \lambda_{\alpha\beta} + \gamma_{2\alpha\beta} \qquad \gamma_{2\alpha\beta} = \Gamma_{\alpha\beta\gamma} \cdot v_\gamma$$

Consequently, we have $\Gamma_{\alpha\beta\gamma}(\mathbf{x}) \cdot v_\beta v_\gamma = \Lambda_{\alpha\beta\gamma}(\mathbf{x}) \cdot v_\beta v_\gamma$. Then without loss of generality, we take $\Lambda_{\alpha\beta\gamma} = \Lambda_{\alpha\gamma\beta}$, which gives $\Gamma_{\alpha\beta\gamma} + \Gamma_{\alpha\gamma\beta} = 2\Lambda_{\alpha\beta\gamma}$. In fact, velocity terms on different directions contribute equally for products, so $\Lambda_{\alpha\beta\gamma} = \Lambda_{\alpha\gamma\beta}$. Also, mutual interactions means that terms with v_α contribute equally toward $\gamma_{\alpha\beta} v_\beta$, hence we obtain another constraint $\Gamma_{\alpha\beta\gamma} = \Gamma_{\beta\alpha\gamma}$, and then all $\Gamma_{\alpha\beta\gamma}$.

Corresponding to the case without taking the mass into account, the Langevin equation reads:

$$\frac{\mathrm{d}v_\alpha}{\mathrm{d}t} = -U_\alpha - \frac{\partial \phi}{\partial x_\alpha} + k_{\mathrm{B}}T \frac{\partial \gamma_{\alpha\beta}}{\partial v_\beta} + \delta F_\alpha$$

which could be written as

$$\frac{\mathrm{d}v_\alpha}{\mathrm{d}t} = -\gamma_{\alpha\beta} \cdot v_\beta - \frac{\partial \phi}{\partial x_\alpha} + k_\mathrm{B} T \Gamma_{\alpha\beta\beta} + \delta F_\alpha$$

where the first term refers to the friction, $-\frac{\partial \phi}{\partial x_\alpha} + k_\mathrm{B} T \Gamma_{\alpha\beta\beta}$ the external and spurious forces, and δF_α the random force. Note, we only have non-zero $\Gamma_{\alpha\beta\beta}$ along the vertical direction. To be exact, we have

$$\Gamma_{zzz} = \frac{21\kappa\xi}{4\Delta^{9/2}} \qquad \Gamma_{zxx} = -\frac{\kappa\xi}{4\Delta^{7/2}} \qquad \Gamma_{z\theta\theta} = -\frac{\kappa\xi}{4\Delta^{7/2}}$$

Since $\gamma_{\alpha\beta} = \lambda_{\alpha\beta} + \Gamma_{\alpha\beta\gamma} \cdot v_\gamma$, we could calculate all $\gamma_{\alpha\beta}$. Below is its approximation at leading-order in κ:

$$\begin{aligned}
\gamma_{zz} &\simeq \frac{\xi}{\Delta^{3/2}} + \frac{21\kappa\xi v_z}{4\Delta^{9/2}} \\
\gamma_{xx} &\simeq \frac{2\varepsilon\xi}{3\sqrt{\Delta}} + \frac{(6+19\varepsilon)\kappa\xi v_z}{24\Delta^{7/2}} \\
\gamma_{\theta\theta} &\simeq \frac{4\varepsilon\xi}{3\sqrt{\Delta}} + \frac{(3+19\varepsilon)\kappa\xi v_z}{12\Delta^{7/2}}
\end{aligned}$$

$$\begin{aligned}
\gamma_{zx} = \gamma_{xz} &\simeq \frac{\kappa\xi\left((3+\varepsilon)v_\theta - 3v_x\right)}{12\Delta^{7/2}} \\
\gamma_{z\theta} = \gamma_{\theta z} &\simeq \frac{\kappa\xi\left((3-\varepsilon)v_x - 3v_\theta\right)}{12\Delta^{7/2}} \\
\gamma_{x\theta} = \gamma_{\theta x} &\simeq -\frac{\kappa\xi(\varepsilon+1)v_z}{4\Delta^{7/2}}
\end{aligned}$$

Effective friction matrix

We return to the deterministic equation with the mass matrix,

$$m_\alpha \cdot \dot{v}_\alpha - F_{2\alpha\beta}(\mathbf{x})\dot{v}_\beta = M_{\alpha\beta}\dot{v}_\beta = F_{1\alpha}(\mathbf{x}) - m_\alpha \cdot \gamma_{\alpha\beta} v_\beta$$

where $F_{1\alpha}(\mathbf{x}) = -\frac{\partial \phi}{\partial x_\alpha} + k_\mathrm{B} T \Gamma_{\alpha\beta\beta}$. We write the Langevin equation with the mass matrix as

$$\dot{v}_\beta = M^{-1}_{\alpha\beta}\left[F_{1\alpha}(\mathbf{x}) - m_\alpha \cdot \gamma_{\alpha\beta} v_\beta + \delta F_\alpha\right]$$

Thus we find the effective friction matrix as

$$\gamma_{\mathrm{eff},\alpha\beta} = M^{-1}_{\alpha\beta} \cdot m_\alpha \cdot \gamma_{\alpha\beta} \tag{3}$$

with elements below

$$\begin{aligned}
\gamma_{\mathrm{eff},zz} &\simeq \frac{\xi}{\Delta^{3/2}} + \kappa\left(\frac{15\xi^2}{8\Delta^4} + \frac{21\xi v_z}{4\Delta^{9/2}}\right) \\
\gamma_{\mathrm{eff},xx} &\simeq \frac{2\xi\varepsilon}{3\sqrt{\Delta}} + \frac{\kappa\xi\left(4\sqrt{\Delta}\xi\varepsilon^2 + 18v_z + 57\varepsilon v_z\right)}{72\Delta^{7/2}} \\
\gamma_{\mathrm{eff},\theta\theta} &\simeq \frac{4\xi\varepsilon}{3\sqrt{\Delta}} + \frac{\kappa\xi\left(8\sqrt{\Delta}\xi\varepsilon^2 + 57\varepsilon v_z + 9v_z\right)}{36\Delta^{7/2}} \\
\gamma_{\mathrm{eff},xz} = \gamma_{\mathrm{eff},zx} &\simeq \frac{\kappa\xi\left((\varepsilon+3)v_\theta - 3v_x\right)}{12\Delta^{7/2}} \\
\gamma_{\mathrm{eff},\theta z} = \gamma_{\mathrm{eff},z\theta} &\simeq \frac{\kappa\xi\left((3-\varepsilon)v_x - 3v_\theta\right)}{12\Delta^{7/2}} \\
\gamma_{\mathrm{eff},\theta x} = \gamma_{\mathrm{eff},x\theta} &\simeq -\frac{\kappa\xi\left(16\Delta^3\xi\varepsilon^2 + 36\Delta^{5/2}(\varepsilon+1)v_z\right)}{144\Delta^6}
\end{aligned}$$

Modified noise correlator amplitude

In the bulk, it can be proved [6] that the amplitude of random force is just the square root of the parameter $\zeta = m\gamma$ in Eq. (1). Similarly, we consider the square root of γ_eff for the random forces and their correlator amplitudes. Suppose $\gamma_\mathrm{eff} \simeq \Psi + \kappa\Phi$, as well as $\gamma_\mathrm{eff}^{1/2} \simeq \psi + \kappa\chi$. Then we have:

$$\psi_{ij} = \sqrt{\Psi_{ij}} \qquad \chi_{ij} = \frac{\Phi_{ij}}{\sqrt{\Psi_{ii}} + \sqrt{\Psi_{jj}}}$$

Even though the mass matrix should be taken into account later, we could always continue the same procedure.

As for γ_eff, several velocities have been included. In the bulk case, we make a Laplace transform,

$$\mathscr{L}_t\left[f(t)\right](s) = \int_0^t f(t)e^{-st}\mathrm{d}t = \widetilde{f}$$

and then its inverse transform for solutions. So here we have to consider that as a matrix equation

$$\widetilde{\dot{\mathbf{v}}} = -\widetilde{\gamma_\mathrm{eff} \cdot \mathbf{v}} + \widetilde{M^{-1} \cdot \delta\mathbf{F}}$$

Note, γ_eff is not a constant matrix, and thus is included inside the Laplace transform.

Dissecting γ_eff as $\gamma_\mathrm{eff} = \gamma_0 + \gamma_1(\kappa) + \gamma_{1v}(\kappa, v_i)$, where γ_0 is a constant matrix, independent on κ; γ_1 depends on κ; and γ_{1v} depends on κ and velocities, as:

$$\gamma_0 = \begin{pmatrix} \frac{\xi}{\Delta^{3/2}} & 0 & 0 \\ 0 & \frac{2\xi\varepsilon}{3\sqrt{\Delta}} & 0 \\ 0 & 0 & \frac{4\xi\varepsilon}{3\sqrt{\Delta}} \end{pmatrix}$$

$$\gamma_1 = \begin{pmatrix} \frac{15\kappa\xi^2}{8\Delta^4} & 0 & 0 \\ 0 & \frac{\kappa\xi^2\varepsilon^2}{18\Delta^3} & -\frac{\kappa\xi^2\varepsilon^2}{9\Delta^3} \\ 0 & -\frac{\kappa\xi^2\varepsilon^2}{9\Delta^3} & \frac{2\kappa\xi^2\varepsilon^2}{9\Delta^3} \end{pmatrix}$$

$$\gamma_{1v} = \begin{pmatrix} \frac{21\kappa\xi v_z}{4\Delta^{9/2}} & \frac{\kappa\xi((\varepsilon+3)v_\theta - 3v_x)}{12\Delta^{7/2}} & \frac{\kappa\xi((3-\varepsilon)v_x - 3v_\theta)}{12\Delta^{7/2}} \\ \frac{\kappa\xi((\varepsilon+3)v_\theta - 3v_x)}{12\Delta^{7/2}} & \frac{\kappa\xi(6+19\varepsilon)v_z}{24\Delta^{7/2}} & -\frac{\kappa\xi(\varepsilon+1)v_z}{4\sqrt{\Delta}} \\ \frac{\kappa\xi((3-\varepsilon)v_x - 3v_\theta)}{12\Delta^{7/2}} & -\frac{\kappa\xi(\varepsilon+1)v_z}{4\sqrt{\Delta}} & \frac{\kappa\xi(19\varepsilon+3)v_z}{12\Delta^{7/2}} \end{pmatrix}$$

we could separate the transform as

$$\widetilde{\gamma_\mathrm{eff} \cdot \mathbf{v}} = \gamma_0 \cdot \widetilde{\mathbf{v}} + \gamma_1 \cdot \widetilde{\mathbf{v}} + \widetilde{\gamma_{1v} \cdot \mathbf{v}}$$

Since γ_0 is a diagonal matrix, we write $\gamma_{0,ii}$ as γ_{i0} for the convenience. Also, we suppose that $\gamma_{1v,ij} = g_{ij\alpha} v_\alpha$, where $g_{ij\alpha}$ refers to the coefficient of v_α in $\gamma_{1v,ij}$, such as $g_{12x} = -\frac{\kappa\xi}{4\Delta^{7/2}}$. Symmetric γ_eff results in symmetric γ_0, γ_1, and $g_{ij\alpha}$.

Due to the perturbation on κ, we write $\mathbf{v} = \mathbf{v}_0 + \mathbf{v}_1$, where the former is of 0 order while the latter is of 1 order. Similarly, the mass matrix and random forces are treated in the same way, leading to:

$$\begin{aligned}
\dot{\mathbf{v}} &= \dot{\mathbf{v}}_0 + \dot{\mathbf{v}}_1 = -\gamma_\mathrm{eff} \cdot \mathbf{v} + M^{-1} \cdot \delta\mathbf{F} \\
&= -(\gamma_0 + \gamma_1 + \gamma_{1v}) \cdot (\mathbf{v}_0 + \mathbf{v}_1) + (M_0^{-1} + M_1^{-1}) \cdot (\delta\mathbf{F}_0 + \delta\mathbf{F}_1)
\end{aligned}$$

We only keep terms of 0 and 1 orders in κ:

$$\dot{\mathbf{v}}_0 = -\gamma_0 \cdot \mathbf{v}_0 + M_0^{-1} \cdot \delta \mathbf{F}_0$$

$$\dot{\mathbf{v}}_1 = -\gamma_0 \cdot \mathbf{v}_1 - \gamma_1 \cdot \mathbf{v}_0 - \gamma_{1v} \cdot \mathbf{v}_0 + M_0^{-1} \cdot \delta \mathbf{F}_1 + M_1^{-1} \cdot \delta \mathbf{F}_0$$

After Laplace transform $\mathscr{L}_t\left[f(t)\right](s) = \widetilde{f}$, we have

$$s\widetilde{\mathbf{v}}_0 - \mathbf{v}(0) = -\gamma_0 \cdot \widetilde{\mathbf{v}}_0 + M_0^{-1} \cdot \widetilde{\delta \mathbf{F}_0}$$

$$s\widetilde{\mathbf{v}}_1 = -\gamma_0 \cdot \widetilde{\mathbf{v}}_1 - \gamma_1 \cdot \widetilde{\mathbf{v}}_0 - \widetilde{\gamma_{1v} \cdot \mathbf{v}_0} + M_0^{-1} \cdot \widetilde{\delta \mathbf{F}_1} + M_1^{-1} \cdot \widetilde{\delta \mathbf{F}_0}$$

Note, $\mathscr{L}_t\left[\int_0^t f(\tau)g(t-\tau)\,d\tau\right](s) = \left(\mathscr{L}_t[f(t)](s)\right)\left(\mathscr{L}_t[g(t)](s)\right)$. Hence, 0-order solutions are rather simple:

$$v_{i0}(t) = v_{i0}(0)e^{-\gamma_{i0}t} + \int_0^t \mathrm{d}\tau \frac{\delta F_{i0}(\tau)}{m_i} \exp\left[-\gamma_{i0}(t-\tau)\right] \quad (4)$$

which shows almost the same formula with the case in the bulk. In our case, the constant parameter γ just becomes the one γ_{i0} depending on the height Δ. Following the same process we have done previously, we get the amplitude of the noise correlator:

$$\left\langle \delta F_{i0}(\tau_1)\delta F_{j0}(\tau_2)\right\rangle = 2k_\mathrm{B}T m_i \gamma_{i0}\delta_{ij}\delta(\tau_1-\tau_2) \quad (5)$$

As for the 1-order correction v_{i1}, we have

$$(s+\gamma_{i0})\widetilde{v_{i1}} = -\sum_j \gamma_{1,ij}\widetilde{v_{j0}} - \sum_j\sum_k g_{ijk}(\widetilde{v_{j0}\cdot v_{k0}}) + M_{0i}^{-1}\widetilde{\delta F_{i1}} + \sum_j M_{1,ij}^{-1}\widetilde{\delta F_{j0}}$$

Laplace transform and its inverse transforms have been calculated. To be clear, we decompose $\mathbf{v}_1$ as:

$$\mathbf{v}_1 = \mathbf{v}_{gv} + \left(\mathbf{v}_{vv} + \mathbf{v}_{vf} + \mathbf{v}_{fv} + \mathbf{v}_{ff}\right) + \mathbf{v}_{fm} + \mathbf{v}_{mf}$$

In fact, while calculating the noise correlator amplitudes and diffusion coefficients, higher order correlation functions will be introduced due to $v_{vv}, v_{fv}, v_{vf}, v_{ff}$, such as $\left\langle v_i v_j v_k\right\rangle$, $\left\langle v_i v_j \delta F_{k0}\right\rangle$, $\left\langle v_i \delta F_{j0}\delta F_{k0}\right\rangle$, $\left\langle \delta F_{i0}\delta F_{j0}\delta F_{k0}\right\rangle$. Since we always pose that there is no correlation between velocities and random forces, namely $\left\langle v_i\cdot\delta F_j\right\rangle = 0$, also $\left\langle\delta F_{i0}\right\rangle = 0$, we are inclined to neglect these odd-power terms, only considering the terms below:

$$v_{i,gv} = \frac{\gamma_{1,ij}}{\gamma_{i0}-\gamma_{j0}}\left\{\left(e^{-\gamma_{i0}t} - e^{-\gamma_{j0}t}\right)v_j(0) + \int_0^t \mathrm{d}\tau \frac{\delta F_{j0}(\tau)}{m_j}\left[e^{-\gamma_{i0}(t-\tau)} - e^{-\gamma_{j0}(t-\tau)}\right]\right\}$$

$$v_{i,fm} = \int_0^t \mathrm{d}\tau \frac{\delta F_{i1}(\tau)}{m_i} e^{-\gamma_{i0}(t-\tau)}$$

$$v_{i,mf} = M_{1,ij}^{-1}\int_0^t \mathrm{d}\tau \delta F_{j0}(\tau) e^{-\gamma_{i0}(t-\tau)}$$

Note, as for $\mathbf{v}_{gv}$, $\lim_{\gamma_{i0}\to\gamma_{j0}} \frac{e^{-\gamma_{i0}t}-e^{-\gamma_{j0}t}}{\gamma_{i0}-\gamma_{j0}} = -te^{-\gamma_{i0}t}$. With all coefficients known, we could resolve $\mathbf{v}_1$. Then we take $v_{z1}(t)$ for instance for the following calculation:

$$v_{z1}(t) = -v_z(0)\gamma_{1,zz}te^{-\gamma_{z0}t} + \int_0^t \mathrm{d}\tau\, e^{-\gamma_{z0}(t-\tau)} \times \left\{\left[\frac{\delta F_{z1}(\tau)}{m_z} + M_{zz1}^{-1}\delta F_{z0}(\tau)\right] - \gamma_{1,zz}(t-\tau)\frac{\delta F_{z0}(\tau)}{m_z}\right\}$$

We consider the velocity square average up to κ:

$$\left\langle v_z^2(t)\right\rangle = \left\langle\left[v_{z0}(t)+v_{z1}(t)\right]^2\right\rangle \simeq \left\langle v_{z0}^2(t)\right\rangle + 2\left\langle v_{z0}(t)v_{z1}(t)\right\rangle$$

In the bulk case, we pose that there is correlation along the same direction shown in Eq. 5. It will be reasonable to insist that formula, only thinking the correlation between 0-order and 1-order random forces along the same direction. Also, we ignore the correlation between two 1-order random forces, which will be a 2-order correlation. Consider $\left\langle\delta F_{z0}(\tau_1)\delta F_{z1}(\tau_2)\right\rangle = K_z\cdot\delta(\tau_1-\tau_2)$. So at long time, $\left\langle v_z^2(t)\right\rangle$ will converge to

$$\left\langle v_z^2(t)\right\rangle = k_\mathrm{B}T\left[\frac{1}{m_z} + 2\left(M_{1,zz}^{-1} - \frac{\gamma_{1,zz}}{2m_z\gamma_{z0}}\right)\right] + \frac{K_z}{m_z^2\gamma_{z0}}$$

According to the equipartition theorem, we derive the amplitude by $\left\langle v_z^2(t)\right\rangle = k_\mathrm{B}T/m_z$:

$$K_z = k_\mathrm{B}Tm_z\left(\gamma_{1,zz} - 2\gamma_{z0}m_zM_{1,zz}^{-1}\right)$$

Hence, up to 1-order correction, the modified noise amplitude for the force along z turns to:

$$\left\langle\delta F_z(\tau_1)\delta F_z(\tau_2)\right\rangle = 2k_\mathrm{B}Tm_z\delta(\tau_1-\tau_2)\cdot\left(\gamma_{z0}+\gamma_{1,zz}-2\gamma_{z0}m_zM_{1,zz}^{-1}\right)$$

Using $M_{1,zz}^{-1} = \frac{15\kappa\xi}{8\Delta^{5/2}m_z}$, $\gamma_{z0}+\gamma_{1,zz} = \frac{\xi}{\Delta^{3/2}} + \frac{15\kappa\xi^2}{8\Delta^4}$, we calculate

$$\gamma_{z0}+\gamma_{1,zz}-2\gamma_{z0}m_zM_{1,zz}^{-1} = \frac{\xi}{\Delta^{3/2}} - \frac{15\kappa\xi^2}{8\Delta^4}$$

leading to the central and amazingly concise result:

$$\left\langle\delta F_z(\tau_1)\delta F_z(\tau_2)\right\rangle = 2k_\mathrm{B}Tm_z\delta(\tau_1-\tau_2)\cdot(\gamma_{z0}-\gamma_{1,zz}) \quad (6)$$

which is valid at 1-order and generalized the fluctuation dissipation relation for the case of a soft boundary.

Furthermore, we could repeat the same procedure for v_{1x} and $v_{1\theta}$, deriving the modified noise correlator amplitudes K_x and K_θ. Again, we suppose that the noise amplitude for the force along x and θ reads: $\left\langle\delta F_{x0}(\tau_1)\delta F_{x1}(\tau_2)\right\rangle = K_x\cdot\delta(\tau_1-\tau_2)$, and $\left\langle\delta F_{\theta 0}(\tau_1)\delta F_{\theta 1}(\tau_2)\right\rangle = K_\theta\cdot\delta(\tau_1-\tau_2)$ for the calculations towards $\left\langle v_x^2\right\rangle$ and $\left\langle v_\theta^2\right\rangle$. At long time, they converge to:

$$\left\langle v_x^2(t)\right\rangle = k_\mathrm{B}T\left[\frac{1}{m_x} + 2\left(M_{1,xx}^{-1} - \frac{\gamma_{1,xx}}{2m_x\gamma_{x0}}\right)\right] + \frac{K}{m_x^2\gamma_{x0}}$$

$$\left\langle v_\theta^2(t)\right\rangle = k_\mathrm{B}T\left[\frac{1}{m_\theta} + 2\left(M_{1,\theta\theta}^{-1} - \frac{\gamma_{1,\theta\theta}}{2m_\theta\gamma_{x0}}\right)\right] + \frac{K}{m_\theta^2\gamma_{\theta 0}}$$

Since they should be equal to $\frac{k_\mathrm{B}T}{m_x}$, $\frac{k_\mathrm{B}T}{m_\theta}$, respectively, we get:

$$K_x = k_\mathrm{B}Tm_x\left(\gamma_{1,xx} - 2m_x M^{-1}_{1,xx}\gamma_{x0}\right)$$
$$K_\theta = k_\mathrm{B}Tm_\theta\left(\gamma_{1,\theta\theta} - 2m_\theta M^{-1}_{1,\theta\theta}\gamma_{\theta 0}\right)$$

Similar to the modified noise correlator on z, we obtain:

$$\begin{aligned}\langle\delta F_x(\tau_1)\delta F_x(\tau_2)\rangle &= 2k_\mathrm{B}Tm_x\delta(\tau_1-\tau_2)\cdot(\gamma_{x0}-\gamma_{1,xx})\\ \langle\delta F_\theta(\tau_1)\delta F_\theta(\tau_2)\rangle &= 2k_\mathrm{B}Tm_\theta\delta(\tau_1-\tau_2)\cdot(\gamma_{\theta 0}-\gamma_{1,\theta\theta})\end{aligned} \tag{7}$$

Mean square displacement

We have obtained noise correlator amplitudes from equipartition and $\langle v^2(t)\rangle$. In addition, we could also derive the mean square displacement (MSD) using $\langle v(0)v(t)\rangle$. We recall that there is no correlation between $v_i(t)$ and $\delta F_j(t)$, $\langle v_i(t_1)\delta F_j(t_2)\rangle = 0$. But we assume that $\langle v_x(0)v_\theta(0)\rangle = \langle v_\theta(0)v_x(0)\rangle = k_\mathrm{B}T/m_{x\theta}$; $\langle v_x^2(0)\rangle = k_\mathrm{B}T/m_x$, and $\langle v_\theta^2(0)\rangle = k_\mathrm{B}T/m_\theta$. Then we can calculate $\langle v_x(0)v_x(t)\rangle$ and $\langle v_\theta(0)v_\theta(t)\rangle$:

$$\begin{aligned}&\langle v_x(0)v_x(t)\rangle = \langle v_x(0)v_{x0}(t)\rangle + \langle v_x(0)v_{x1}(t)\rangle\\ &= \frac{k_\mathrm{B}T}{m_x}e^{-\gamma_{x0}t}\left(1-\gamma_{1,xx}t\right) + \frac{k_\mathrm{B}T}{m_{x\theta}}\frac{\gamma_{1,x\theta}}{\gamma_{x0}-\gamma_{\theta 0}}\left(e^{-\gamma_{x0}t}-e^{-\gamma_{\theta 0}t}\right)\end{aligned}$$

$$\begin{aligned}&\langle v_\theta(0)v_\theta(t)\rangle = \langle v_\theta(0)v_{\theta 0}(t)\rangle + \langle v_\theta(0)v_{\theta 1}(t)\rangle\\ &= \frac{k_\mathrm{B}T}{m_\theta}e^{-\gamma_{\theta 0}t}\left(1-\gamma_{1,\theta\theta}t\right) + \frac{k_\mathrm{B}T}{m_{x\theta}}\frac{\gamma_{1,\theta x}}{\gamma_{x0}-\gamma_{\theta 0}}\left(e^{-\gamma_{x0}t}-e^{-\gamma_{\theta 0}t}\right)\end{aligned}$$

We define the MSD as $\langle\Delta r_i^2(t)\rangle = \left\langle\int_0^t \mathrm{d}\tau_1\int_0^t \mathrm{d}\tau_2 v_i(\tau_1)v_i(\tau_2)\right\rangle$. We compute it by its derivative

$$\frac{\mathrm{d}}{\mathrm{d}t}\left\langle\Delta r_i^2(t)\right\rangle = 2\int_0^t \mathrm{d}\tau\,\langle v_i(0)v_i(\tau)\rangle$$

After two integrations, we have:

$$\begin{aligned}&\left\langle\Delta r_x^2(t)\right\rangle = \left\langle\Delta r_x^2(0)\right\rangle + k_\mathrm{B}T\times\\ &\left(\frac{\frac{e^{-t\gamma_{x0}}-1}{\gamma_{x0}}+t}{m_x\gamma_{x0}} + \frac{\gamma_{1,x\theta}\left(\frac{e^{-t\gamma_{x0}}-1}{\gamma_{x0}}+t\right)}{\gamma_{x0}m_{x\theta}\left(\gamma_{x0}-\gamma_{\theta 0}\right)}\right.\\ &\left.-\frac{\gamma_{1,x\theta}\left(\frac{e^{-t\gamma_{\theta 0}}-1}{\gamma_{\theta 0}}+t\right)}{\gamma_{\theta 0}m_{x\theta}\left(\gamma_{x0}-\gamma_{\theta 0}\right)} - \frac{\gamma_{1,xx}\left(t-\frac{2-e^{-t\gamma_{x0}}(t\gamma_{x0}+2)}{\gamma_{x0}}\right)}{m_x\gamma_{x0}^2}\right)\end{aligned}$$

$$\begin{aligned}&\left\langle\Delta r_\theta^2(t)\right\rangle = \left\langle\Delta r_\theta^2(0)\right\rangle + k_\mathrm{B}T\times\\ &\left(\frac{\frac{e^{-t\gamma_{\theta 0}}-1}{\gamma_{\theta 0}}+t}{m_\theta\gamma_{\theta 0}} + \frac{\gamma_{1,\theta x}\left(\frac{e^{-t\gamma_{x0}}-1}{\gamma_{x0}}+t\right)}{\gamma_{x0}m_{x\theta}\left(\gamma_{x0}-\gamma_{\theta 0}\right)}\right.\\ &\left.-\frac{\gamma_{1,\theta x}\left(\frac{e^{-t\gamma_{\theta 0}}-1}{\gamma_{\theta 0}}+t\right)}{\gamma_{\theta 0}m_{x\theta}\left(\gamma_{x0}-\gamma_{\theta 0}\right)} - \frac{\gamma_{1,\theta\theta}\left(t-\frac{2-e^{-t\gamma_{\theta 0}}(t\gamma_{\theta 0}+2)}{\gamma_{\theta 0}}\right)}{m_\theta\gamma_{\theta 0}^2}\right)\end{aligned}$$

Additionally, mean cross displacement could also been derived between x and θ.

$$\langle\Delta r_x(t)\cdot\Delta r_\theta(t)\rangle = \int_0^t\left[\frac{\mathrm{d}}{\mathrm{d}t}\langle\Delta r_x(\tau)\cdot\Delta r_\theta(\tau)\rangle\right]\mathrm{d}\tau + \langle\Delta r_x(0)\cdot\Delta r_\theta(0)\rangle$$

Since $\Delta r_x(t) = \int_0^t v_x(\tau)\mathrm{d}\tau$, $\Delta r_\theta(t) = \int_0^t v_\theta(\tau)\mathrm{d}\tau$, we have

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle\Delta r_x(t)\cdot\Delta r_\theta(t)\rangle = \int_0^t\langle v_x(t)v_\theta(\tau)\rangle\mathrm{d}\tau + \int_0^t\langle v_x(\tau)v_\theta(t)\rangle\mathrm{d}\tau$$

We consider the cross velocity product at 1-order in κ:

$$\begin{aligned}&\langle v_x(\tau_1)v_\theta(\tau_2)\rangle \simeq\\ &\quad\langle v_{x0}(\tau_1)v_{\theta 0}(\tau_2)\rangle + \langle v_{x0}(\tau_1)v_{\theta 1}(\tau_2)\rangle + \langle v_{x1}(\tau_1)v_{\theta 0}(\tau_2)\rangle\end{aligned}$$

Only taking $\langle v_x^2(0)\rangle$, $\langle v_\theta^2(0)\rangle$, $\langle v_x(0)v_\theta(0)\rangle = \frac{k_\mathrm{B}T}{m_{x\theta}}$ mentioned previously into account, and keeping $\langle\delta F_x(\tau_1)\delta F_\theta(\tau_2)\rangle = 0$, and $\langle v_i(\tau_1)\delta F_j(\tau_2)\rangle = 0$, we get

$$\begin{aligned}\langle v_{x0}(\tau_1)v_{\theta 0}(\tau_2)\rangle &= \langle v_x(0)v_\theta(0)\rangle e^{-\gamma_{0x}\tau_1}e^{-\gamma_{0\theta}\tau_2}\\ \langle v_{x0}(\tau_1)v_{\theta 1}(\tau_2)\rangle &= \left\langle v_x^2(0)\right\rangle\frac{e^{-\gamma_{0x}\tau_1}\gamma_{1,\theta x}}{\gamma_{0x}-\gamma_{0\theta}}\left(e^{-\gamma_{0x}\tau_2}-e^{-\gamma_{0\theta}\tau_2}\right)\\ &\quad-\langle v_x(0)v_\theta(0)\rangle\gamma_{1,\theta\theta}\tau_2 e^{-\gamma_{0x}\tau_1}e^{-\gamma_{0\theta}\tau_2}\\ \langle v_{x1}(\tau_1)v_{\theta 0}(\tau_2)\rangle &= \left\langle v_\theta^2(0)\right\rangle\frac{e^{-\gamma_{0\theta}\tau_2}\gamma_{1,x\theta}}{\gamma_{0x}-\gamma_{0\theta}}\left(e^{-\gamma_{0x}\tau_1}-e^{-\gamma_{0\theta}\tau_1}\right)\\ &\quad-\langle v_x(0)v_\theta(0)\rangle\gamma_{1,xx}\tau_1 e^{-\gamma_{0x}\tau_1}e^{-\gamma_{0\theta}\tau_2}\end{aligned}$$

We skip the explicit calculation process, giving the final result directly:

$$\begin{aligned}&\langle\Delta r_x(t)\cdot\Delta r_\theta(t)\rangle = \langle\Delta r_x(0)\cdot\Delta r_\theta(0)\rangle\\ &+\frac{\gamma_{1,\theta x}\left(e^{t\gamma_{x0}}-1\right)e^{-t(\gamma_{\theta 0}+2\gamma_{x0})}\left(\gamma_{\theta 0}e^{t\gamma_{\theta 0}}\left(e^{t\gamma_{x0}}-1\right)-\gamma_{x0}\left(e^{t\gamma_{\theta 0}}-1\right)e^{t\gamma_{x0}}\right)}{\gamma_{\theta 0}\gamma_{x0}^2\left(\gamma_{x0}-\gamma_{\theta 0}\right)}\left\langle v_x^2(0)\right\rangle\\ &+\frac{\gamma_{1,x\theta}\left(e^{t\gamma_{\theta 0}}-1\right)e^{-t(2\gamma_{\theta 0}+\gamma_{x0})}\left(\gamma_{\theta 0}e^{t\gamma_{\theta 0}}\left(e^{t\gamma_{x0}}-1\right)-\gamma_{x0}\left(e^{t\gamma_{\theta 0}}-1\right)e^{t\gamma_{x0}}\right)}{\gamma_{\theta 0}^2\gamma_{x0}\left(\gamma_{x0}-\gamma_{\theta 0}\right)}\left\langle v_\theta^2(0)\right\rangle\\ &+\frac{e^{-t(\gamma_{\theta 0}+\gamma_{x0})}}{\gamma_{\theta 0}^2\gamma_{x0}^2}\langle v_x(0)v_\theta(0)\rangle\times\\ &\quad\left[\gamma_{x0}\left(\gamma_{\theta 0}\left(\left(e^{t\gamma_{x0}}-1\right)\left(e^{t\gamma_{\theta 0}}+t\gamma_{1,\theta\theta}-1\right)+t\gamma_{1,xx}\left(e^{t\gamma_{\theta 0}}-1\right)\right)\right.\right.\\ &\quad\left.\left.-\gamma_{1,\theta\theta}\left(e^{t\gamma_{\theta 0}}-1\right)\left(e^{t\gamma_{x0}}-1\right)\right)-\gamma_{\theta 0}\gamma_{1,xx}\left(e^{t\gamma_{\theta 0}}-1\right)\left(e^{t\gamma_{x0}}-1\right)\right]\end{aligned}$$

Diffusion coefficient

As a basic parameter to describe the mobility of a given particle inside one specific environment, the diffusion coefficient D is linked with the probability density ρ of particles as a function of time t and displacement x by

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

For diffusion of spherical particles through a liquid with low Reynolds number, we recall Stokes-Einstein relation [7]:

$$D = \frac{k_\mathrm{B}T}{6\pi\eta r}$$

where η is the dynamic viscosity, r is the radius of the spherical particle. If there is no soft surface, we have diffusion coefficients at 0 order:

$$D_{z0} = \frac{k_B T}{m_z \gamma_{z0}} \quad D_{x0} = \frac{k_B T}{m_x \gamma_{x0}} \quad D_{\theta 0} = \frac{k_B T}{m_\theta \gamma_{\theta 0}}$$

In the presence of the soft wall, we can exploit Kubo's relations:

$$D_x = \int_0^\infty \langle v_x(0) v_x(t) \rangle \, \mathrm{d}t = \frac{k_B T}{\gamma_{x0}^2} \left(\frac{\gamma_{x0} - \gamma_{1,xx}}{m_x} - \frac{\gamma_{1,x\theta} \gamma_{x0}}{m_{x\theta} \gamma_{\theta 0}} \right)$$

$$D_\theta = \int_0^\infty \langle v_\theta(0) v_\theta(t) \rangle \, \mathrm{d}t = \frac{k_B T}{\gamma_{\theta 0}^2} \left(\frac{\gamma_{\theta 0} - \gamma_{1,\theta\theta}}{m_\theta} - \frac{\gamma_{\theta 0} \gamma_{1,\theta x}}{m_{x\theta} \gamma_{x0}} \right)$$

Note, D_x, D_θ are both functions of Δ. Thus D_x, D_θ are constants only if the height Δ is fixed.

We ignored the MSD along z direction, since all γs depend on the height Δ. Note that $\gamma_{z0} = \frac{\xi}{\Delta^{3/2}}$, $\gamma_{1,zz} = \frac{15\kappa\xi^2}{8\Delta^4}$. In this case, the particle will have different diffusion coefficients at different heights rather than a constant parameter, even though we could derive the expression of $\langle v_z(0) v_z(t) \rangle$ and the following calculations.

$$\langle v_z(0) v_z(t) \rangle = \langle v_z^2(0) \rangle e^{-\gamma_{z0} t} (1 - \gamma_{1,zz} t)$$

towards the vertical diffusion coefficient D_z:

$$D_z = \int_0^\infty \langle v_z(0) v_z(t) \rangle \, \mathrm{d}t = \frac{k_B T}{\gamma_{z0}^2} \left(\frac{\gamma_{z0} - \gamma_{1,zz}}{m_z} \right) = D_{z0} \left(1 - \frac{\gamma_{1,zz}}{\gamma_{z0}} \right)$$

Without considering the non-diagonal elements in the effective friction, we also have

$$D_x = D_{x0} \left(1 - \frac{\gamma_{1,xx}}{\gamma_{x0}} \right) \quad D_\theta = D_{\theta 0} \left(1 - \frac{\gamma_{1,\theta\theta}}{\gamma_{\theta 0}} \right)$$

Therefore, the presence of a soft surface will decrease diffusion coefficients, which might have important practical consequences in nanophysics and biophysics. Since $\gamma_1 \propto \frac{1}{\Delta^3}$, the closer one particle approaches the surface, the less diffusion there will be.

Numerical Simulations

Up to now, we have explored the theoretical framework, including the exact expressions of modified noise correlator amplitudes, MSD, and diffusion coefficients. Still, due to the Δ-dependent coefficients γ_{eff}, we could NOT find the analytical particle trajectory on each direction. Indeed, we could hardly fix the height Δ along the whole experiment in reality. Therefore, for the sake of better understanding this non-linear coupled systems, numerical simulations were employed.

In this section, we incorporate the modified noise correlator amplitudes found previously inside the numerical simulations, and address properties like time correlation functions and MSD. All codes are written in *Fortran90*, as the simulations will be done by the compiler *gfortran*, with figures shown by *gnuplot*.

Discretisation algorithm

Generally speaking, we could not figure out analytical functions for each velocity or position displacement, especially with the existence of thermal noises. So all variables like $v(t), r(t), \delta F(t)$ will be discretized as $v(t_i), r(t_i), \delta F(t_i)$, as we calculate all functions stepwise at each moment. If we suppose that $N_{\max}$ is the maximum number for simulation steps, we divide the continuous time $t \in [0, t_{\max}]$ as $t_i \in \{t_0 = 0, t_1, \cdots, t_N = t_{\max}\}$ with $i \in [1, N_{\max}]$, where the time gap $\Delta t = t_{\max}/N_{\max}$.

Dimensionless variables

In order to non-dimensionalize the problem, we follow the variables used in [14]:

$$\delta = \Delta \cdot r\varepsilon \quad x_G = X_G \cdot r\sqrt{2\varepsilon} \quad \theta = \Theta \cdot \sqrt{2\varepsilon}$$

Here, δ is the distance between the particle and the soft wall (see Figure 2), x_G is the parallel displacement, θ is the rotation degree. We introduce the time t as $t = T \cdot r\sqrt{2\varepsilon}/c$, where r is the particle radius. $c = \sqrt{2gr\rho^*/\rho}$, g is the gravitational acceleration, ρ^* is the density difference between the particle and the solvent, and ρ refers to the solvent density. So the velocities in reality will be replaced by those shown in our equations of motion:

$$v_\Delta = \frac{v_z}{c} \cdot \sqrt{\frac{2}{\varepsilon}} \qquad v_X = \frac{v_x}{c} \qquad v_\Theta = \frac{v_\theta r}{c}$$

Similarly, accelerations and forces will be treated in the same way.

Random number generator

In the numerical practice, we regard the white noise as a Gaussian random variable at every position and time. We follow the Box-Muller transform to generate normally distributed random variables, which uses two independent random numbers U and V distributed uniformly on $(0, 1)$. Then the two random variables X and Y given by

$$X = \sqrt{-2\ln U} \cos(2\pi V) \qquad Y = \sqrt{-2\ln U} \sin(2\pi V)$$

will both have the standard normal distribution, and will be independent with each other. If we take n-dimensional vectors U and V, then $2n$ independent random variables will be furnished.

Euler-Maruyama method

In Itô calculus, the Euler–Maruyama method is used for the approximate numerical solution of a stochastic differential equation (SDE). Consider the equation

$$dX_t = a(X_t, t)dt + b(X_t, t)dW_t$$

with initial condition $X_0 = x_0$, where W_t stands for the Wiener process, and suppose that we wish to solve this SDE on some interval of time $[0, T]$. Then the Euler-Maruyama method to the true solution X is the Markov chain Y defined as follows:

$$Y_{n+1} = Y_n + a(Y_n, \tau_n)\Delta t + b(Y_n, \tau_n)\Delta W_n$$

The Euler-Maruyama scheme could be applied [15], in our case as $t_{i+1} = t_i + \Delta t$

$$\mathbf{v}(t_{i+1}) = \mathbf{v}(t_i) + \left[-\gamma_{\text{eff}}(\mathbf{x},t_i)\cdot\mathbf{v}(t_i) + M^{-1}\cdot\mathbf{F}_{1\alpha}(\mathbf{x},t_i)\right]\Delta t + \sqrt{\frac{2k_{\text{B}}T\,(\gamma_0-\gamma_1)}{m}}\cdot\Delta\mathbf{W}(\Delta t)$$
$$\mathbf{r}(t_{i+1}) = \mathbf{r}(t_i) + \mathbf{v}(t_i)\Delta t$$

where $\mathbf{F}_{1\alpha}(\mathbf{x},t_i)$ contains the gravity and the spurious force.

Numerical Results

We will like to simulate the Brownian motion of polystyrene particles ($\rho_{\text{sty}} = 1.06$ g/cm^3, radius $r_{\text{p}} = 1.5\mu$m) inside water ($\rho_{\text{sol}} = 1.00$ g/cm^3) near a soft wall made by polydimethylsiloxane (PDMS). For the sake of valid perturbation practice, we pick the following parameters:

$$\kappa = 10^{-4} \qquad \varepsilon = 0.1 \qquad \xi = 0.1$$

Brownian motion simulation with fixed height

First, we simulate the Brownian motion with the fixed height $\Delta = 1.0$, following the parallel displacement (see Figure 5) and the rotation (see Figure 6). Here, we set initial conditions as $X_G(0) = \Theta(0) = 0$, $v_x(0) = v_\theta(0) = 0$ for all trajectories.

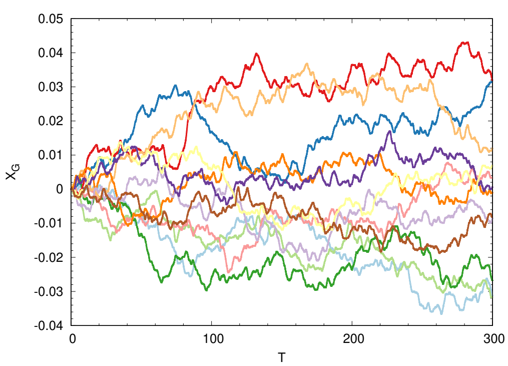

Figure 5. Brownian motion simulations of 1.5 μm polystyrene particles in water with fixed $\Delta = 1.0$, $\kappa = 10^{-4}$, $\varepsilon = \xi = 0.1$. Each line represents one trajectory of X_G coordinate, with 12 trajectories in total.

Since Δ is fixed as one constant here, all elements in the effective friction matrix depending on Δ will also be constant. Thus, it is equivalent to a classical simulation in the bulk.

Brownian motion simulation without fixed height

Next, we are interested in the simulations with unlimited Δ, rather than a constant. With the additional initial conditions $\Delta(0) = 0$ and $\dot{\Delta}(0) = 0$, we would like to trace the particle vertically. As we can see in Figure 7, the particle falls at first under the gravity. Then, it mainly moves inside a confined region around $\Delta = 0.75$, even though affected by the random force.

In Figure 8, we do not limit the height Δ along the simulations, but with different initial conditions, as $\Delta(0) = \Delta_0 =$

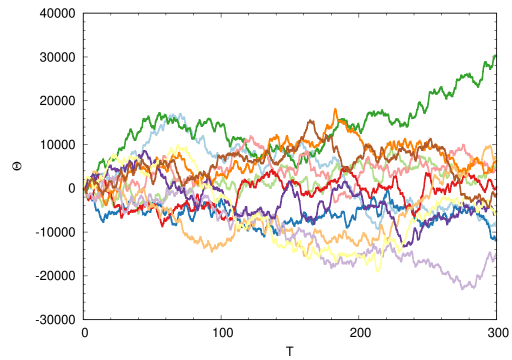

Figure 6. Brownian motion simulations of 1.5 μm polystyrene particles in water with the same condition of Figure 5, like fixed $\Delta = 1.0$ and $\kappa = 10^{-4}$. Each line represents the trajectory of Θ coordinate.

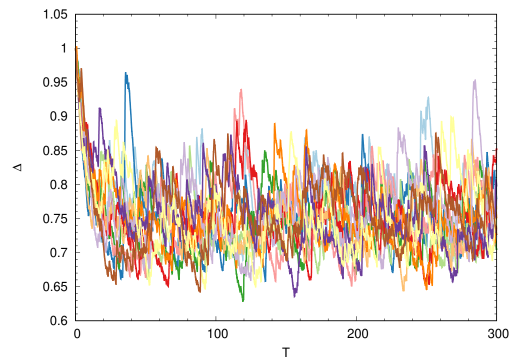

Figure 7. Brownian motion simulations with the same condition of Figure 5, but without fixed height. $\Delta(0) = 1.0$, $\dot{\Delta}(0) = 0$, $\kappa = 10^{-4}$.

$0.2, 0.3, 0.4, \cdots, 1.3$, respectively. We can recover the similar movement inside a limited range around $\Delta = 0.75$ as mentioned above. However, the numerical simulation will collapse if we choose a very small initial height such as $\Delta_0 = 0.1$, namely the particle will go into the PDMS surface.

MSD depending on height

Based on these data in Figure 7 and 8, MSD of X_G and Θ have also been calculated as a function of the time gap Δt by

$$\langle \Delta r(t)\cdot\Delta r(t+\Delta t)\rangle(\Delta t) = \frac{1}{N}\sum_{i=1}^{N}\Delta r(t_i)\cdot\Delta r(t_i+\Delta t)$$

where N refers to the total number of samples for the time average, and Δr refers to X_G or Θ.

In Figure 9 and Figure 10, we fix the height Δ, but give different initial conditions. We can see that the MSDs (and the diffusion coefficient) are influenced by the initial height Δ_0. At short time, we have MSD $\propto t^2$; while at long time, MSD $\propto t$.

In Figure 11 and Figure 12, we calculate MSDs with unlimited Δ, also with different initial heights. We recover

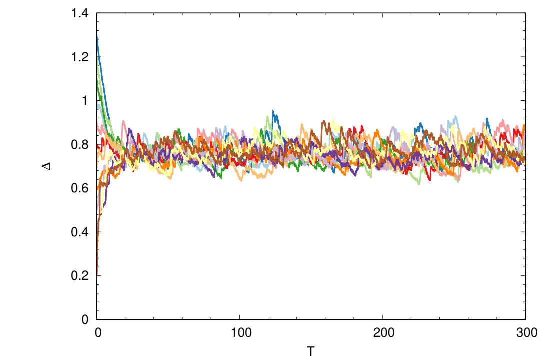

Figure 8. Brownian motion simulations with different initial heights. $\Delta(0) = 0.2, 0.3, \cdots, 1.3$, $\kappa = 10^{-4}$. Other parameters are same as 5.

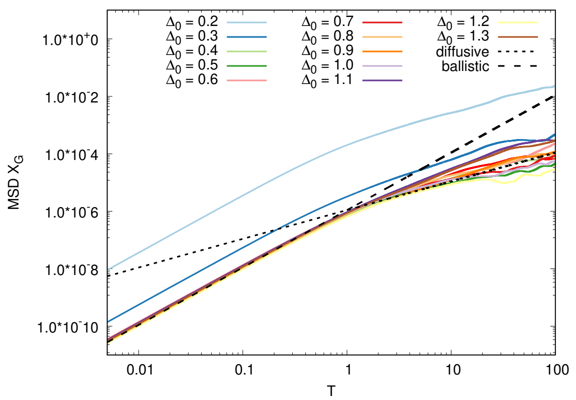

Figure 9. MSD along X_G with various fixed Δ. Same condition as 7.

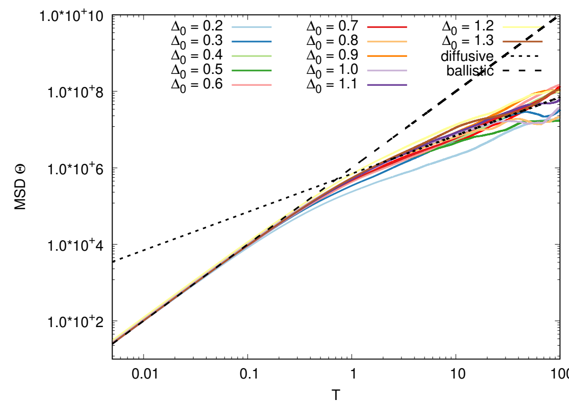

Figure 10. MSD along Θ with various fixed Δ. Same condition as 7.

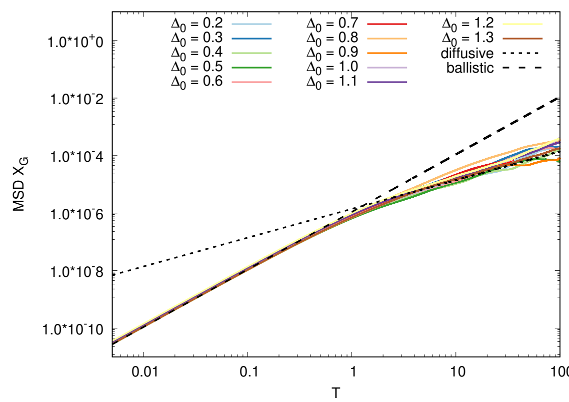

Figure 11. MSD along X_G with unfixed Δ. Same condition as 8.

the similar results. Since the height Δ is not limited, the particle will enter the confined region quickly, which is almost equivalent to the case with a fixed height around Δ. Thus, there is no outliers for $\Delta_0 = 0.2, 0.3$ in Figure 11. And all lines get closer in the diffusive region.

Finally, we concentrate on the effect of κ, the dimensionless compliance parameter. With the initial conditions as $\Delta = 1.0$, $\dot{\Delta} = 0$, we do not fix the height for the simulations. See Figure 13, we can see distinct MSDs under different values of κ. Ballistic regions can be see clearly; however, with the increase of κ, more time is needed to reach the diffusive region.

Conclusion and Perspectives

During this long internship from the beginning of February to the end of July, a rather complete work has been done at LOMA on the "Brownian motion near a Soft Surface". Both the theoretical framework and numerical simulations have been figured out. Given a non-linear coupled system of known deterministic elastohydrodynamic equations, we extract an effective friction matrix γ_{eff} at first, then acquire modified noise correlator amplitudes, which play the significant role for statistical aspects and numerical simulations. MSD and diffusion coefficients have also been computed. We always neglect the correlation between velocities and forces, the velocities of different directions, and higher odd-power correlations. Further research would be continued.

Personally, I have learned quite a lot during my internship, such as Langevin equation with Fokker-Planck equation, the perturbation theory, ordinary differential equations, integral transforms, etc. Besides, I revised skills for numerical simulations by *Fortran* and *Python*. To step further, the subsequent research will perhaps be concentrated on a 3D spherical particle rather than a 2D one, or even that with an irregular conformation. As for the soft surface, there exist numerous examples in the nature of such biological membranes. As a matter of fact, important applications may be found like the transportation towards specific targets in the blood vessel or other membranes with curvature.

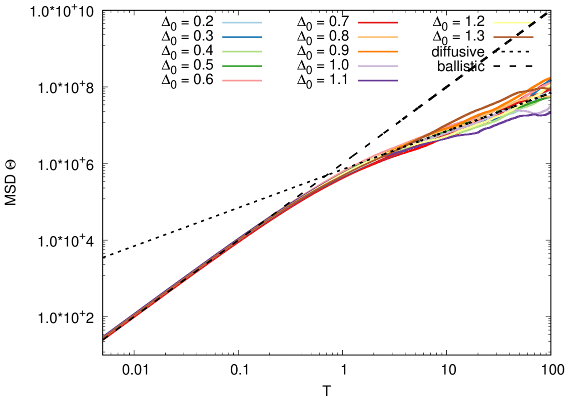

Figure 12. MSD along Θ with unfixed Δ. Same condition as 8.

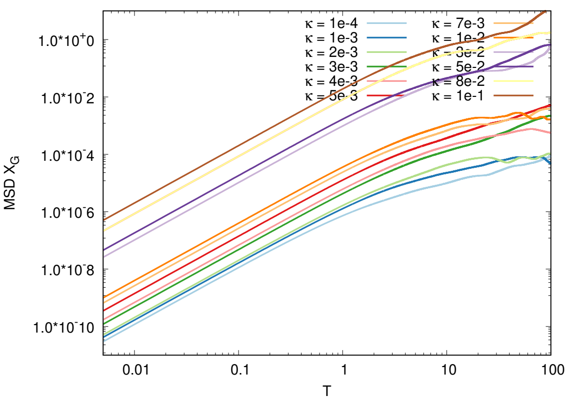

Figure 13. MSD along X_G with different κs. $\Delta_0 = 1.0$.

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References

[1] R. Brown, *Philosophical Magazine* **1828**, *4(21)*, 161-173, **A brief account of microscopical observations made in the months of June, July and August, 1827, on the particles contained in the pollen of plants; and on the general existence of active molecules in organic and inorganic bodies**.

[2] A. Einstein, in *Investigations on the Theory of the Brownian Movement*, Courier Corporation, **1956**.

[3] J. Perrin, *J. Phys. Theor. Appl.* **1910**, *9(1)*, 5-39, **Mouvement brownien et molécules**.

[4] J. Perrin, in *Atoms*, London: Constable **1914**, pp. 115.

[5] P. Langevin, *Compt. Rendus* **1908**, *146*, 530-533, **Sur la théorie du mouvement brownien**.

[6] H. B. Callen, T. A. Welton, *Physical Review* **1951**, *83(1)*, 34, **Irreversibility and generalized noise**.

[7] A. Einstein, *Annalen der physik* **1905**, *322(8)*, 549-560, **Über die von der molekularkinetischen Theorie der Wärme geforderte Bewegung von in ruhenden Flüssigkeiten suspendierten Teilchen**.

[8] M. Green, *The Journal of Chemical Physics* **1954**, *22(3)*, 398-413, **Markoff Random Processes and the Statistical Mechanics of Time-Dependent Phenomena. II. Irreversible Processes in Fluids**.
R. Kubo, *Journal of the Physical Society of Japan* **1957**, *12(6)*, 570-586, **Statistical-Mechanical Theory of Irreversible Processes. I. General Theory and Simple Applications to Magnetic and Conduction Problems**.

[9] K. Sekimoto, L. Leibler, *EPL* **1993**, *23(2)*, 113, **A mechanism for shear thickening of polymer-bearing surfaces: elasto-hydrodynamic coupling**.

[10] Z. Zhang, V. Bertin, M. Arshad, E. Raphael, T. Salez, and A. Maali, *Phys. Rev. Lett.* **2020**, *124(5)*, 054502, **Direct measurement of the elastohydrodynamic lift force at the nanoscale**.

[11] M. Lavaud, T. Salez, Y. Louyer, and Y. Amarouchene, *Phys. Rev. Research* **2021**, *3(3)*, L032011, **Stochastic inference of surface-induced effects using Brownian motion**.

[12] M. Lavaud, PhD thesis, *Université de Bordeaux*, nov. **2021**, **Confined Brownian Motion**.

[13] V. Bertin, Y. Amarouchene, E. Raphael, and T. Salez, *J. Fluid Mech.* **2022**, *933*, A23, **Soft-lubrication interactions between a rigid sphere and an elastic wall**.

[14] T. Salez, L. Mahadevan, *J. Fluid Mech.* **2015**, *779*, 181-196, **Elastohydrodynamics of a sliding, spinning and sedimenting cylinder near a soft wall**.

[15] M. D. Graham, in *Microhydrodynamics, Brownian motion, and complex fluids*, Vol.58, Cambridge University Press, Cambridge **2018**.