Internship report M1 – 2022

Brownian Motion near a Soft Surface

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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 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 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. Other pioneers like Einstein and Perrin provided decisive evidence for the existence of atoms.

In 1905, Albert Einstein proposed a stochastic model for Brownian motion [2], indicating clean connection with the motion of 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 great achievement, he was honored with the Nobel Prize for Physics in 1926. [3]

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 Stockes in 1850s. However, this result would lead to a zero velocity at long time limit, conflicting with the nature that particles would never stop. Based on that, Paul Langevin in 1908 furnished the formation in term of equations of motions and laws of mechanism. With a brillant idea, he introduced the concept of a random force or noise, toward the famous Langevin equation: [4]

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

where the first term refers to systematic put of the environment influence, while the second term δF refers to the very sudden effect, random impacts due to thermal fluctuation of solvent molecules. Generally, there is no correlation in time, so $\langle \delta F(t) \rangle = 0$. Also, Gaussian white noise would be exploited as $\langle \delta F(\tau_1)\delta F(\tau_2) \rangle = 2k_B T \zeta \delta(\tau_1 - \tau_2)$, which could reflect well the fluctuation dissipation theorem [5], Stokes-Einstein relation [6], and Green-Kubo relations [7].

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 microscopic biological matters towards certain targets is a paramount question of biophysics, such as: DNA replication, antibody recognition, and various self-assembly. Ideally, this problem could be simplified to mechanics through a basic combination of necessary ingredients: confined environment, elastic boundaries, thermal fluctuations, and viscous flow; as the soft contacts are ubiquitous in biology.

In soft matter, an emergent ElastoHydroDynamic (EHD) lift force was theoretically predicted for elastic bodies moving past each other in a fluid. This amazing effect has thus been explored with various deterministic models and experiments, showing its potential relevance for biological and nanoscale systems. For the sake of further understanding of EHD, the "EMetBrown" project was carried out with 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 [8], confined Brownian motion in 2021 [9, 10], rigid sphere near elastic wall in 2022 [11]

To step further on physical description of biological motility by solving a fundamental problem at the boundary between continuum and statistical mechanics, there confronts challenges about Brownian motion near soft interfaces. Exactly, the study of Brownian motion in soft-lubricated environments appears here as the canonical problems of biophysics and nanophysics. However, it is still 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 theoretical framework on 3D non-linear EHD forces coupled by Langevin problem including multiplicative noise and external potential, then derive the effective friction and modified noise correlators. Besides, numerical simulations with multi-dimensional discretisation have also been completed to verify simultaneous experiments. The core strategy is to develop perturbation at leading order in compliance of soft surface, demonstrating the effect of softness on various statistical variables.

Theoretical Analyses

Situation of the problem

Herein, we consider a 2D particle's Brownian motion near a soft surface (see Figure 1), based on the work in 2015 [12]. Below are equations of motion, with three coupled variables: X_G, Δ for parallel, vertical displacement, 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 for the soft wall deformation to describe elasticity. In our case, we focus on a rigid support plan, so $\alpha = 0$, $\sin\alpha = 0$, $\cos\alpha = 1$.

In these equations, the perpendicular height Δ plays a significant role, leading to no possible analytical expressions for each variable. Also, velocities $\dot{X}_G, \dot{\Delta}, \dot{\Theta}$ would interact with each other, at leading order of κ. Moreover, extra acceleration terms emerge with non-zero κ. Consider Brownian motion for such a system, we should describe the corresponding friction coefficient, and random force correlator as well. To simplify, we would address r_x, r_z, r_θ for three directions X_G, Δ, Θ, and v_x, v_z, v_θ for $\dot{X}_G, \dot{\Delta}, \dot{\Theta}$.

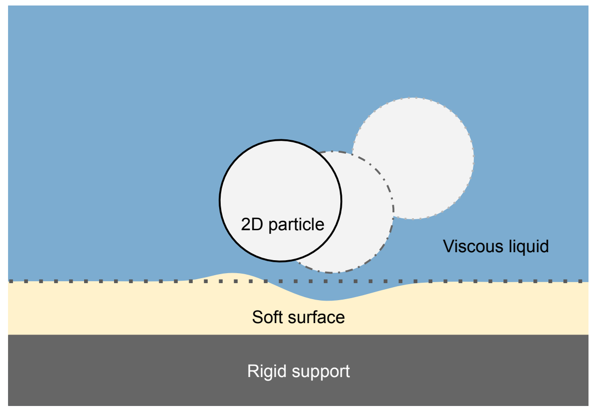


Figure 1. Schematic of the system. A negatively buoyant cylinder (grey) falls down under the influence of gravity **g**, inside a viscous fluid (blue), in the vicinity of a thin soft wall (yellow). The ensemble lies atop a infinitely rigid support (black).

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

Langevin equation

$\downarrow$

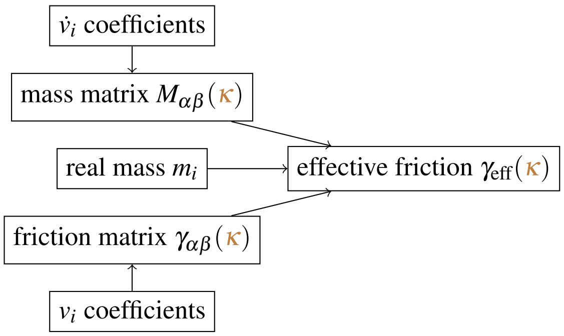
$\boxed{v(t)} \longrightarrow \boxed{\langle v^2(t)\rangle} \longrightarrow$ noise amplitudes

$\downarrow$

$\boxed{\langle v(0)v(t)\rangle} \longrightarrow$ MSD, diffusion coefficients

Effective friction matrix

In Langevin equation, the parameter γ plays a paramount role to reflect the friction property of a given environment. This parameter would result in several important variables mentioned above. Therefore, in this subsection, we would derive effective friction matrix according to equations of motion, considering parameters before velocities as friction and those before accelerations as the effective mass.



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 before velocities. For z, x components, the mass $m_\alpha = m = \pi r^2 \rho$, namely the mass of the column (per unit length); while $m_\theta = mr^2/2$ refers to the moment of inertia.

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

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

and its inverse matrix at first-order approximation of κ:

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

Fokker-Planck equation for friction matrix

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

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

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

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

The last two terms would vanish, so we have

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

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

$$U_\alpha = \gamma_{\alpha\beta} v_\beta$$

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

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

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

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

Consequently, we have $\Gamma_{\alpha\beta\gamma}(\mathbf{x}) v_\beta v_\gamma = \Lambda_{\alpha\beta\gamma}(\mathbf{x}) v_\beta v_\gamma$. 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 $\Gamma_{\alpha\beta\gamma}$.

Using the Itô convention, the Langevin equation would be shown as below, corresponding to the case without taking the mass into account,

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

which could be written as

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

where the first term refers to the friction, $-\frac{\partial\phi}{\partial x_\alpha} + k_B T \Gamma_{\alpha\beta\beta}$ the external potentials, and δF_α the random force. Note, we only have non-zero $\Gamma_{\alpha\beta\beta}$ along the vertical direction, which could also be addressed as the spurious force. To be exact, we have $\Gamma_{z\beta\beta}$ shown below

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

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

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

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

Effective friction matrix

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

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

Thus we find the effective friction matrix as

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

with elements below, still at 1-order of κ:

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

Modified noise correlator amplitude

After the effective friction matrix γ_{eff}, we consider the random forces and their correlator amplitudes. For the 1D case in the bulk, we only need the square root of friction coefficient. Similarly, we could suppose that $\gamma_{\text{eff}} \approx \Psi + \kappa\Phi$, as well as $\gamma_{\text{eff}}^{1/2} \approx \psi + \kappa\chi$, then we have

$$\gamma_{\text{eff}} = \gamma_{\text{eff}}^{1/2}\gamma_{\text{eff}}^{1/2} = (\psi + \kappa\chi)(\psi + \kappa\chi) \approx \psi\psi + \kappa(\psi\chi + \chi\psi)$$

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

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

The results seem plausible and enough with the first-order correction of κ. However, as for γ_{eff}, several velocities have been included. In 1D case, we make Laplace and the its inverse transform for solutions, while here we have to consider that as a matrix equation

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

Note, γ_{eff} is not a constant matrix, which should be included inside the Laplace transform.

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

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

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

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

Hence we could separate the transform as

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

Since γ_0 is a diagonal matrix, we write $\gamma_{i0} = \gamma_{i0}$ 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 $g_{12x} = -\frac{\kappa\xi v_x}{4\Delta^{7/2}}$. A symmetric γ_{eff} results in symmetric γ_0 and γ_1, so is $g_{ij\alpha}$.

It would be raisonnable to consider the perturbation on κ, for this elastic compliance parameter $\kappa \ll 1$, about $10^{-4} \sim 10^{-3}$. We write $\mathbf{v} = \mathbf{v}_0 + \mathbf{v}_1$, where the former is on 0 order while the latter 1 order. Similarly, the mass matrix and random forces would be treated in the same way.

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

We only keep terms of 0 and 1 order of 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 $\mathscr{L}_t\left[\int_0^t f(\tau)g(t-\tau)\,d\tau\right](s) = \left(\mathscr{L}_t[f(t)](s)\right)\left(\mathscr{L}_t[g(t)](s)\right)$, 0-order solutions are rather simple:

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

Follow the same process we have done previously, we get the amplitude of noise correlator:

$$\left\langle \delta F_{i0}(\tau_1)\delta F_{j0}(\tau_2)\right\rangle = 2k_BTm_i\gamma_{i0}\delta_{ij}\delta(\tau_1-\tau_2)$$

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

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

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

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

with

$$\widetilde{v_{i,gv}} = \frac{1}{s+\gamma_{i0}}\left(-\sum_j \gamma_{1,ij}\widetilde{v_{j0}}\right)$$

$$\widetilde{v_{i,vv}} + \widetilde{v_{i,vf}} + \widetilde{v_{i,fv}} + \widetilde{v_{i,ff}} = \frac{1}{s+\gamma_{i0}}\left[-\sum_j\sum_k g_{ijk}\left(\widetilde{v_{j0}\cdot v_{k0}}\right)\right]$$

$$\widetilde{v_{i,fm}} = \frac{1}{s+\gamma_{i0}}\left(M_{0i}^{-1}\widetilde{\delta F_{i1}}\right)$$

$$\widetilde{v_{i,mf}} = \frac{1}{s+\gamma_{i0}}\left(\sum_j M_{1,ij}^{-1}\widetilde{\delta F_{j0}}\right)$$

Higher order correlation functions would be introduced due to $v_{vv}, v_{fv}, v_{vf}, v_{ff}$ while calculating noise correlator amplitudes and diffusion coefficients, such as $\left\langle v_iv_jv_k\right\rangle$, $\left\langle v_iv_j\delta F_{k0}\right\rangle$, $\left\langle v_i\delta F_{j0}\delta F_{k0}\right\rangle$, $\left\langle \delta F_{i0}\delta F_{j0}\delta F_{k0}\right\rangle$. In fact, 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 $\left\langle \delta F_{i0}\right\rangle = 0$. Thus 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.

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

Still, we consider the velocity square average up to 1-order κ:

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

Suppose there exists the correlation between 0-order and 1-order random force, $\left\langle\delta F_{z0}(\tau_1)\delta F_{z1}(\tau_2)\right\rangle = K_z\cdot\delta(\tau_1-\tau_2)$. So at long time limit $t\to\infty$, $\left\langle v_z^2(t)\right\rangle$ would converge to

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

Since $\left\langle v_z^2(t)\right\rangle = \frac{k_BT}{m_z}$, we obtain the amplitude K_z

$$K_z = k_BTm_z\left(\gamma_{1,zz} - 2\gamma_{z0}m_zM_{1,zz}^{-1}\right)$$

Hence, up to 1-order correction, the modified noise amplitude of z turns to:

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

Note $M_{1,zz}^{-1} = \frac{15\kappa\xi}{8\Delta^{5/2}m_z}$, $\gamma_{z0}+\gamma_{1,zz} = \frac{\xi}{\Delta^{3/2}} + \frac{15\kappa\xi^2}{8\Delta^4}$, 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 an amazingly concise result:

$$\left\langle\delta F_z(\tau_1)\delta F_z(\tau_2)\right\rangle = 2k_BTm_z\delta(\tau_1-\tau_2)\cdot(\gamma_{z0}-\gamma_{1,zz})$$

which is always valid at 1-order correction.

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. As for non-diagonal elements in γ_1, $\gamma_{1,x\theta}$ and $\gamma_{1,\theta x}$ are non-zero. So we get additional terms shown below:

$$v_{x1}(t) = -v_x(0)\gamma_{1,xx}te^{-\gamma_{x0}t} + \frac{v_\theta(0)\gamma_{1,x\theta}}{\gamma_{x0}-\gamma_{\theta0}}\left(e^{-\gamma_{x0}t}-e^{-\gamma_{\theta0}t}\right) - \gamma_{1,xx}\int_0^t \mathrm{d}\tau(t-\tau)e^{-\gamma_{x0}(t-\tau)}\frac{\delta F_{x0}(\tau)}{m_x} + \frac{\gamma_{1,x\theta}}{\gamma_{\theta0}-\gamma_{x0}}\int_0^t \mathrm{d}\tau\left(e^{-\gamma_{\theta0}(t-\tau)}-e^{-\gamma_{x0}(t-\tau)}\right)\frac{\delta F_{\theta0}(\tau)}{m_\theta} + \int_0^t \mathrm{d}\tau e^{-\gamma_{x0}(t-\tau)}\left[M_{1,xx}^{-1}\delta F_{x0}(\tau) + M_{1,x\theta}^{-1}\delta F_{\theta0}(\tau) + \frac{\delta F_{x1}(\tau)}{m_x}\right]$$

$$v_{\theta1}(t) = -v_\theta(0)\gamma_{1,\theta\theta}te^{-\gamma_{\theta0}t} + \frac{v_x(0)\gamma_{1,\theta x}}{\gamma_{x0}-\gamma_{\theta0}}\left(e^{-\gamma_{x0}t}-e^{-\gamma_{\theta0}t}\right)$$
$$+\frac{\gamma_{1,\theta x}}{\gamma_{\theta0}-\gamma_{x0}}\int_0^t \mathrm{d}\tau\left(e^{-\gamma_{\theta0}(t-\tau)}-e^{-\gamma_{x0}(t-\tau)}\right)\frac{\delta F_{x0}(\tau)}{m_x}$$
$$-\gamma_{1,\theta\theta}\int_0^t \mathrm{d}\tau(t-\tau)e^{-\gamma_{\theta0}(t-\tau)}\frac{\delta F_{\theta0}(\tau)}{m_\theta}$$
$$+\int_0^t \mathrm{d}\tau e^{-\gamma_{\theta0}(t-\tau)}\left[M^{-1}_{1,\theta x}\delta F_{x0}(\tau)+M^{-1}_{1,\theta\theta}\delta F_{\theta0}(\tau)+\frac{\delta F_{\theta1}(\tau)}{m_\theta}\right]$$

Again, we suppose $\langle\delta F_{x0}(\tau_1)\delta F_{x1}(\tau_2)\rangle = K_x\cdot\delta(\tau_1-\tau_2)$, and $\langle\delta F_{\theta0}(\tau_1)\delta F_{\theta1}(\tau_2)\rangle = K_\theta\cdot\delta(\tau_1-\tau_2)$ for the calculations towards $\left\langle v_x^2\right\rangle$ and $\left\langle v_\theta^2\right\rangle$. At long time limit, they converge to:

$$\left\langle v_x^2(t)\right\rangle = k_BT\left[\frac{1}{m_x}+2\left(M^{-1}_{1,xx}-\frac{\gamma_{1,xx}}{2m_x\gamma_{x0}}\right)\right]+\frac{K}{m_x^2\gamma_{x0}}$$
$$\left\langle v_\theta^2(t)\right\rangle = k_BT\left[\frac{1}{m_\theta}+2\left(M^{-1}_{1,\theta\theta}-\frac{\gamma_{1,\theta\theta}}{2m_\theta\gamma_{x0}}\right)\right]+\frac{K}{m_\theta^2\gamma_{\theta0}}$$

Since they should be equal to $\frac{k_BT}{m_x}$, $\frac{k_BT}{m_\theta}$, respectively, we get:

$$K_x = k_BTm_x\left(\gamma_{1,xx}-2m_xM^{-1}_{1,xx}\gamma_{x0}\right)$$
$$K_\theta = k_BTm_\theta\left(\gamma_{1,\theta\theta}-2m_\theta M^{-1}_{1,\theta\theta}\gamma_{\theta0}\right)$$

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

$$\langle\delta F_x(\tau_1)\delta F_x(\tau_2)\rangle = 2k_BTm_x\delta(\tau_1-\tau_2)\cdot(\gamma_{x0}-\gamma_{1,xx})$$
$$\langle\delta F_\theta(\tau_1)\delta F_\theta(\tau_2)\rangle = 2k_BTm_\theta\delta(\tau_1-\tau_2)\cdot(\gamma_{\theta0}-\gamma_{1,\theta\theta})$$

Mean square displacement

We have already obtained noise correlator amplitudes by $\left\langle v^2(t)\right\rangle$. At the same time, we could also derive the mean square displacement (MSD) by $\langle v(0)v(t)\rangle$. Reminder, there is no correlation between $v_i(t)$ and $\delta F_j(t)$, $\left\langle v_i(t_1)\delta F_j(t_2)\right\rangle = 0$. But we assume that $\langle v_x(0)v_\theta(0)\rangle = \langle v_\theta(0)v_x(0)\rangle = k_BT/m_{x\theta}$. And note $m_x\left\langle v_x^2(0)\right\rangle/2 = k_BT/2$, $m_\theta\left\langle v_\theta^2(0)\right\rangle/2 = k_BT/2$.

$$\langle v_x(0)v_x(t)\rangle = \langle v_x(0)v_{x0}(t)\rangle + \langle v_x(0)v_{x1}(t)\rangle$$
$$=\frac{k_BT}{m_x}e^{-\gamma_{x0}t}\left(1-\gamma_{1,xx}t\right)+\frac{k_BT}{m_{x\theta}}\frac{\gamma_{1,x\theta}}{\gamma_{x0}-\gamma_{\theta0}}\left(e^{-\gamma_{x0}t}-e^{-\gamma_{\theta0}t}\right)$$

$$\langle v_\theta(0)v_\theta(t)\rangle = \langle v_\theta(0)v_{\theta0}(t)\rangle + \langle v_\theta(0)v_{\theta1}(t)\rangle$$
$$=\frac{k_BT}{m_\theta}e^{-\gamma_{\theta0}t}\left(1-\gamma_{1,\theta\theta}t\right)+\frac{k_BT}{m_{x\theta}}\frac{\gamma_{1,\theta x}}{\gamma_{x0}-\gamma_{\theta0}}\left(e^{-\gamma_{x0}t}-e^{-\gamma_{\theta0}t}\right)$$

Define MSD as $\left\langle\Delta r_i^2(t)\right\rangle = \left\langle\int_0^t \mathrm{d}\tau_1\int_0^t \mathrm{d}\tau_2 v_i(\tau_1)v_i(\tau_2)\right\rangle$. We compute this value by its derivative as a function of $\langle v_i(0)v_i(t)\rangle$, since

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

After two integrations, we have $\left\langle\Delta r_i^2(t)\right\rangle$

$$\left\langle\Delta r_x^2(t)\right\rangle = \left\langle\Delta r_x^2(0)\right\rangle + k_BT\times$$
$$\left(\frac{\frac{e^{-t\gamma_{x0}}-1}{\gamma_{x0}}+t}{m_x\gamma_{x0}}+\frac{\gamma_{1,x\theta}\left(\frac{e^{-t\gamma_{x0}}-1}{\gamma_{x0}}+t\right)}{\gamma_{x0}m_{x\theta}\left(\gamma_{x0}-\gamma_{\theta0}\right)}\right.$$
$$\left.-\frac{\gamma_{1,x\theta}\left(\frac{e^{-t\gamma_{\theta0}}-1}{\gamma_{\theta0}}+t\right)}{\gamma_{\theta0}m_{x\theta}\left(\gamma_{x0}-\gamma_{\theta0}\right)}-\frac{\gamma_{1,xx}\left(t-\frac{2-e^{-t\gamma_{x0}}(t\gamma_{x0}+2)}{\gamma_{x0}}\right)}{m_x\gamma_{x0}^2}\right)$$

$$\left\langle\Delta r_\theta^2(t)\right\rangle = \left\langle\Delta r_\theta^2(0)\right\rangle + k_BT\times$$
$$\left(\frac{\frac{e^{-t\gamma_{\theta0}}-1}{\gamma_{\theta0}}+t}{m_\theta\gamma_{\theta0}}+\frac{\gamma_{1,\theta x}\left(\frac{e^{-t\gamma_{x0}}-1}{\gamma_{x0}}+t\right)}{\gamma_{x0}m_{x\theta}\left(\gamma_{x0}-\gamma_{\theta0}\right)}\right.$$
$$\left.-\frac{\gamma_{1,\theta x}\left(\frac{e^{-t\gamma_{\theta0}}-1}{\gamma_{\theta0}}+t\right)}{\gamma_{\theta0}m_{x\theta}\left(\gamma_{x0}-\gamma_{\theta0}\right)}-\frac{\gamma_{1,\theta\theta}\left(t-\frac{2-e^{-t\gamma_{\theta0}}(t\gamma_{\theta0}+2)}{\gamma_{\theta0}}\right)}{m_\theta\gamma_{\theta0}^2}\right)$$

Additionally, cross mean "square" 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

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

Consider cross velocity product average up to 1-order of κ:

$$\langle v_x(\tau_1)v_\theta(\tau_2)\rangle\approx$$
$$\langle v_{x0}(\tau_1)v_{\theta0}(\tau_2)\rangle+\langle v_{x0}(\tau_1)v_{\theta1}(\tau_2)\rangle+\langle v_{x1}(\tau_1)v_{\theta0}(\tau_2)\rangle$$

Only taking $\left\langle v_x^2(0)\right\rangle$, $\left\langle v_\theta^2(0)\right\rangle$, $\langle v_x(0)v_\theta(0)\rangle = \frac{k_BT}{m_{x\theta}}$ mentioned previously into account, we insist that $\langle\delta F_x(\tau_1)\delta F_\theta(\tau_2)\rangle = 0$, and $\left\langle v_i(\tau_1)\delta F_j(\tau_2)\right\rangle = 0$. Therefore, we could easily calculate each term:

$$\langle v_{x0}(\tau_1)v_{\theta0}(\tau_2)\rangle = \langle v_x(0)v_\theta(0)\rangle e^{-\gamma_{0x}\tau_1}e^{-\gamma_{0\theta}\tau_2}$$

$$\langle v_{x0}(\tau_1)v_{\theta1}(\tau_2)\rangle = \left\langle v_x^2(0)\right\rangle\frac{e^{-\gamma_{0x}\tau_1}\gamma_{1,\theta x}}{\gamma_{0x}-\gamma_{0\theta}}\left(e^{-\gamma_{0x}\tau_2}-e^{-\gamma_{0\theta}\tau_2}\right)$$
$$-\langle v_x(0)v_\theta(0)\rangle\gamma_{1,\theta\theta}\tau_2e^{-\gamma_{0x}\tau_1}e^{-\gamma_{0\theta}\tau_2}$$

$$\langle v_{x1}(\tau_1)v_{\theta0}(\tau_2)\rangle = \left\langle v_\theta^2(0)\right\rangle\frac{e^{-\gamma_{0\theta}\tau_2}\gamma_{1,x\theta}}{\gamma_{0x}-\gamma_{0\theta}}\left(e^{-\gamma_{0x}\tau_1}-e^{-\gamma_{0\theta}\tau_1}\right)$$
$$-\langle v_x(0)v_\theta(0)\rangle\gamma_{1,xx}\tau_1e^{-\gamma_{0x}\tau_1}e^{-\gamma_{0\theta}\tau_2}$$

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

$$\langle\Delta r_x(t)\cdot\Delta r_\theta(t)\rangle = \langle\Delta r_x(0)\cdot\Delta r_\theta(0)\rangle$$
$$+\frac{\gamma_{1,\theta x}\left(e^{t\gamma_{x0}}-1\right)e^{-t(\gamma_{\theta0}+2\gamma_{x0})}\left(\gamma_{\theta0}e^{t\gamma_{\theta0}}\left(e^{t\gamma_{x0}}-1\right)-\gamma_{x0}\left(e^{t\gamma_{\theta0}}-1\right)e^{t\gamma_{x0}}\right)}{\gamma_{\theta0}\gamma_{x0}^2\left(\gamma_{x0}-\gamma_{\theta0}\right)}\left\langle v_x^2(0)\right\rangle$$
$$+\frac{\gamma_{1,x\theta}\left(e^{t\gamma_{\theta0}}-1\right)e^{-t(2\gamma_{\theta0}+\gamma_{x0})}\left(\gamma_{\theta0}e^{t\gamma_{\theta0}}\left(e^{t\gamma_{x0}}-1\right)-\gamma_{x0}\left(e^{t\gamma_{\theta0}}-1\right)e^{t\gamma_{x0}}\right)}{\gamma_{\theta0}^2\gamma_{x0}\left(\gamma_{x0}-\gamma_{\theta0}\right)}\left\langle v_\theta^2(0)\right\rangle$$
$$+\frac{e^{-t(\gamma_{\theta0}+\gamma_{x0})}}{\gamma_{\theta0}^2\gamma_{x0}^2}\langle v_x(0)v_\theta(0)\rangle\times$$
$$\left[\gamma_{x0}\left(\gamma_{\theta0}\left(\left(e^{t\gamma_{x0}}-1\right)\left(e^{t\gamma_{\theta0}}+t\gamma_{1,\theta\theta}-1\right)+t\gamma_{1,xx}\left(e^{t\gamma_{\theta0}}-1\right)\right)\right.\right.$$
$$\left.\left.-\gamma_{1,\theta\theta}\left(e^{t\gamma_{\theta0}}-1\right)\left(e^{t\gamma_{x0}}-1\right)\right)-\gamma_{\theta0}\gamma_{1,xx}\left(e^{t\gamma_{\theta0}}-1\right)\left(e^{t\gamma_{x0}}-1\right)\right]$$

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

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

If there is no soft surface, we have diffusion coefficients at 0 order:

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

We could exploit Kubo's relation toward the diffusion coefficient D_x, D_θ:

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

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

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 $\gamma_{z0} = \frac{\xi}{\Delta^{3/2}}$, $\gamma_{1,zz} = \frac{15\kappa\xi^2}{8\Delta^4}$. In this case, the particle would furnish different diffusion coefficient at different height 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.

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

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

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

Therefore, the existence of soft surface would decrease diffusion coefficients. Since $\gamma_1 \propto \frac{1}{\Delta^3}$, the closer one particle approaches the surface, the less diffusion coefficients there would be.

Numerical Simulations

Up to now, we have already fully 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 functions to follow the 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 toward this non-linear coupled systems, numerical simulations would be highly needed in the following research.

In this section, we apply the modified noise correlator amplitudes found previously inside the numerical simulations, verifying properties like time correlation functions and MSD. All codes are stored in *Fortran90* files, as the simulations would 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 $v(t), r(t), \delta F(t)$ would 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, so 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 [12]:

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

Introduce $t = T \cdot r\sqrt{2\varepsilon}/c$, where c is the maximum velocity for free fall particles. So the velocities in reality would 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, related to velocities, accelerations and forces would be treated in the same way.

Random number generator

In the numerical practice, we regard the white noise as the Gaussian random variable. 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 vector U and V, then $2n$ independent random variables would 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:

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

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

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

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

Numerical Results

We would like to simulate the Brownian motion of polystyrene particles ($\rho_{sty} = 1.06$ g/cm^3, radius $r_p = 1.5\mu$m) inside water ($\rho_{sol} = 1.00$ 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 2) and the rotation (see Figure 3). Here, we set initial conditions as $X_G(0) = \Theta(0) = 0$, $v_x(0) = v_\theta(0) = 0$ for all trajectories.

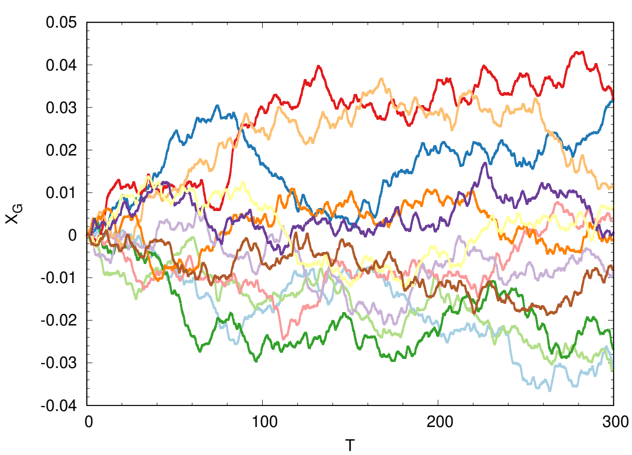


Figure 2. Brownian motion simulations of 1.5 μm polystyrene particles in water with fixed $\Delta = 1.0$. Each line represents one trajectory of X_G coordinate, with 12 trajectories in total.

Since Δ is fixed as one constant here, all elements in the effective friction matrix depending on Δ would also keep constant. Thus, it seems a classical simulation in the bulk.

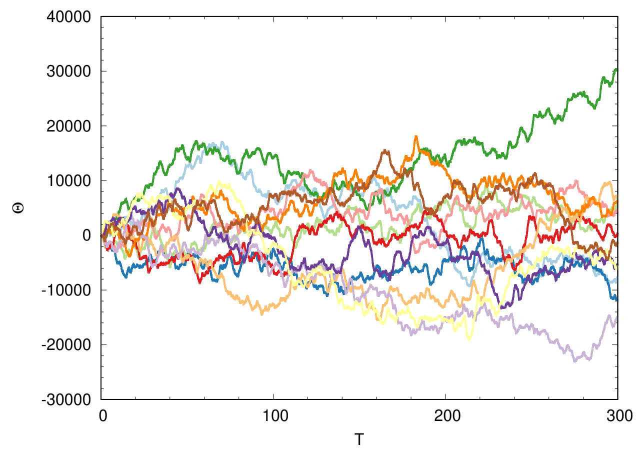


Figure 3. Brownian motion simulations of 1.5 μm polystyrene particles in water with fixed $\Delta = 1.0$. Each line represents the trajectory of Θ coordinate.

Brownian motion simulation without fixed height

Next, we are interested in the simulations with unlimited Δ, with the initial condition $\Delta(0) = 0$ and $v_z(0) = 0$. In Figure 4, as we could see, the particle would mainly move inside a converged region around $\Delta = 0.75$, even though affected by the random force.

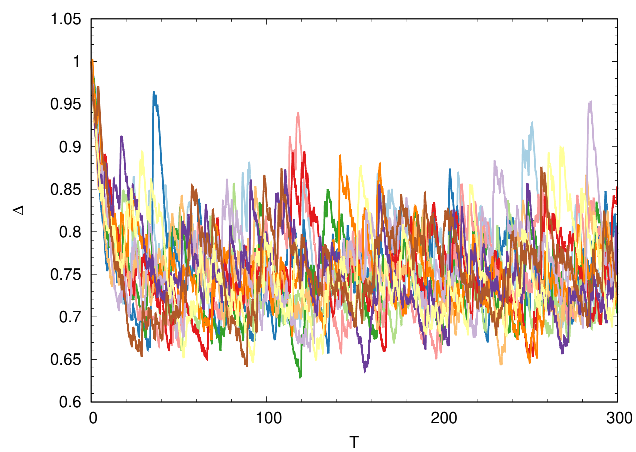


Figure 4. Brownian motion simulations with different initial height Δ.

MSD depending on height

Then, we simulate the case with different initial height, still with fixed height during the simulation. Presented in Figure 5, we recover the similar movement inside a limited range around $\Delta = 0.75$ as we mentioned above. Indeed, we select the initial condition as $\Delta(0) = \Delta_0 = 0.2, 0.3, 0.4, \cdots, 1.3$. However, the numerical simulation would collapse if we choose a very small initial height such as $\Delta_0 = 0.1$, namely the particle would drop into the PDMS surface.

Based on these data, MSD of X_G and Θ have also been

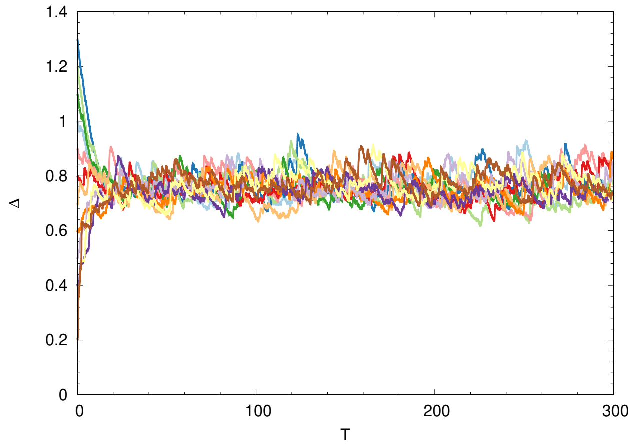


Figure 5. Brownian motion simulations with different initial height Δ.

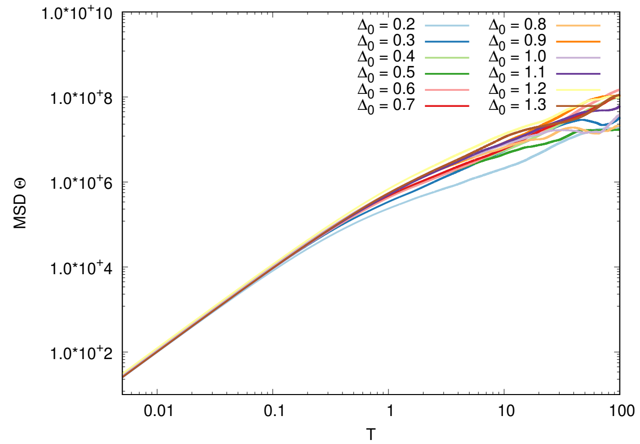


Figure 7. MSD along Θ with various Δ.

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. We could see much clear that the MSDs (and the the diffusion coefficient) would be influenced by the initial height Δ_0, shown in Figure 6 and Figure 7. At the short time limit, we have MSD $\propto t^2$; while at the long time limit MSD $\propto t$.

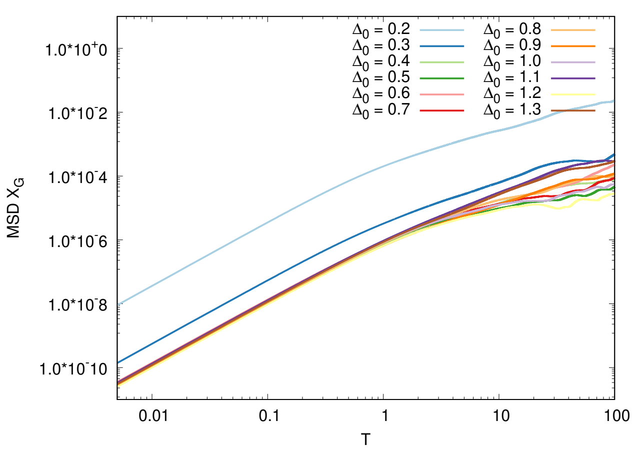


Figure 6. MSD along X_G with various Δ.

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 based on the "Brownian motion near a Soft Surface". Both the theoretical framework and numerical simulations have been figured out. Given a non-linear coupling system of equations, we extract an effective friction matrix γ_{eff} at first, then acquire modified noise correlator amplitudes, which play the significant role for numerical simulations. What's more, MSD and diffusion coefficients have also been verified. We always neglect the correlation between velocities and forces, velocities of different directions, and higher odd-power correlations. Therefore, the complicated system could be reduced to a rather simple case. Velocities and accelerations from other directions would only contribute to the discrete values in the numerical simulations, which would converge to zero while considering time-average properties.

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 would 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 such biological membranes. As a matter of fact, potential applications would be found like the transportation towards specific targets in the blood vessel or other membranes with curvature beyond the plan support in our case.

Acknowledgments

I would like to thank my supervisor Thomas SALEZ at first for his precise advice and patient instruction during my whole internship. Also, I thank Yacine AMAROUCHENE for his great insight on experimental details, as well as David DEAN for his concise pedagogy at each inspiring discussion.

From February to present, I am quite immersed in LOMA, especially the warm EMetBrown group. Thank Maxime LAVAUD and Elodie MILLAN for their explicit suggestions on my presentations. Thank Nicolas FARES for his incisive explanation on lubrification. Thank Zaicheng ZHANG and Hao ZHANG for their kind help in my daily life. Thank Ludovic BRIVADY and Quentin FERREIRA for diverse talks.

Furthermore, thank Josiane PARZYCH, Benjamin MASSET of LOMA, Univ. Bordeaux; as well as Elza MACUDZINSKI, Marie LABEYE and Jérôme DELACOTTE of ENS for their generous help on administrative issues.

In addition, we acknowledge the financial supports from the Agence Nationale de la Recherche (ANR-21-ERCC- 0010-01 EMetBrown), as well as European Research Council (ERC-EMetBrown).

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