Generalized Langevin Equation

Stochastic Differential Equations

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Agenda

Scope of the Project

What? Generalized Langevin Dynamics is a modeling technique that can be used to model anomalous diffusive phenomena observed in viscoelastic fluid flow and in biological systems.

Why? Anomalous diffusion problems: Langevin model fails to capture sub-diffusive and super-diffusive behavior which the GLE succeeds in capturing. But GLE is *Non-Markovian* i.e. `memory kernel` depends on the history of velocity. This issue is overcome by using Extended Variable GLE that considers a finite dimensional subspace for the `memory kernel`.

Where? Applications of GLE include but are not restricted to micro-rheology, biological systems, nuclear quantum effects and systems in which anomalous diffusion arise.

How? Study Extended Variable GLE using Prony series approximation. Accuracy of Implicit/Explicit Euler and Splitting Numerical schemes are also tested to find out the optimal scheme. Study the sensitivity of the solution to the changes in the parameters of the extended variable GLE.

Introduction

What? **Langevin Dynamics:** Large particles in a bath of small particles, motion of large particles directly integrated while the dynamics of small particles are "averaged out".

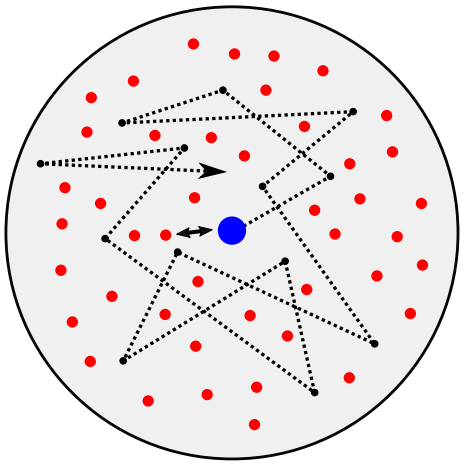
Why? *Molecular Dynamics* simulations involving all particles is computationally expensive. Langevin Equation model is computationally cheaper.

Drawback

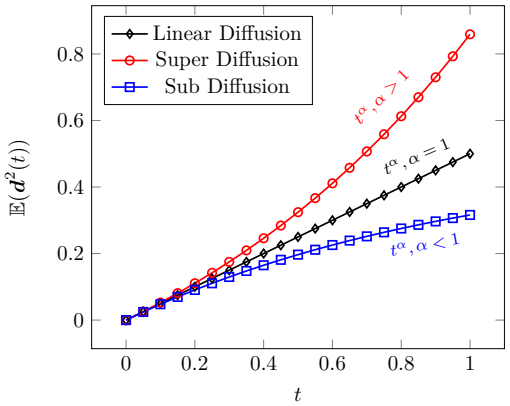
Anomalous diffusion problems arising due to *Power Law* behavior of solute-solvent systems cannot be solved.

Solution

Generalized Langevin Equation (**GLE**)



(a) Big Particles interacting with Smaller Particles



(b) Sub-diffusive and Super-diffusive behavior of solute-solvent systems

Mathematical Model

The velocity term of GLE is based on *Ornstein-Uhlenbeck* process.

GLE Equations

$$d\boldsymbol{X}(t) = \boldsymbol{V}(t)dt \tag{1}$$

$$M d\boldsymbol{V}(t) = \underbrace{\boldsymbol{F}^c(\boldsymbol{X}(t))dt}_{\substack{\text{Conservative Force due to Potential}}} \underbrace{- \int_0^t \boldsymbol{\Gamma}(t-s)\boldsymbol{V}(s)dsdt}_{\substack{\text{Temporally Non-Local Drag } \left(\boldsymbol{F}^d\right) \text{ Force}}} + \underbrace{\boldsymbol{F}^r(t)dt}_{\substack{\text{Random Correlated Force given by } FDT}} \tag{2}$$

$$\boldsymbol{X}(0) = \boldsymbol{X}_0, \quad \boldsymbol{V}(0) = \boldsymbol{V}_0 \quad \text{(Initial Conditions)} \tag{3}$$

Note:

$\boldsymbol{F}^r$ and $\boldsymbol{F}^d$ are characterized by the `memory kernel` consistent with **FDT**.

Mathematical Model

Theorem

FDT (Fluctuation Dissipation Theorem) states that the equilibration to a temperature, T, requires that the two-time correlation of $\boldsymbol{F}^r(t)$ and $\boldsymbol{\Gamma}(t)$ be related as:

$$\left\langle \boldsymbol{F}_i^r(t+s), \boldsymbol{F}_j^r(t) \right\rangle = k_B T \boldsymbol{\Gamma}(s) \delta_{ij}, \qquad s \geq 0 \tag{4}$$

where k_B is the Boltzmann's Constant and δ_{ij} is the Kronecker Delta.

Note:

- $\boldsymbol{F}^d(t)$ depends on the velocity history unlike in *Langevin Equation* where it depends on the velocity at that instant.
- The random forces are not just delta correlated but are correlated by the `memory kernel`. Memory Kernel choice and approximation important based on the problem to be studied.

Model Complications and Solutions

Complications

1. Storage of subset of the time history of $\boldsymbol{V}(t)$.
2. Sequence of $\boldsymbol{F}^r(t)$ given by `FDT`.
3. Numerical SDE solution should converge in distribution.

Solution

1. Using extended variable `Prony Series` for `Memory Kernel`.

$$\boldsymbol{\Gamma}(t) \approx \sum_{k=1}^{N_k} \frac{c_k}{\tau_k} \exp\left[-\frac{t}{\tau_k}\right], \qquad t \geq 0 \tag{5}$$

   where N_k is the number of terms used in approximating the `memory kernel`.

2. Using a suitable integration scheme for the numerical method.

Model Complications and Solutions

Why use extended variable Prony Series?

- Approximation of `memory kernel` to map **Non-Markovian** GLE to **Markovian** system of N_k variables.
- Typically used for modelling *Power Law* based decay/growth as observed in sub/super diffusive systems.

Importance of choice of integration scheme?

- Conservation of moments of variables of interest such as displacement and velocity (usual variables of interest for MD simulations)
- Convergence of **GLE** to Langevin equation in the limit of small τ_k as observed in theory.

Extended Variable GLE

Main Extended Variable GLE Equations

$$m_i dV_i(t) = F_i^c(\boldsymbol{X}(t))dt + \sum_{k=1}^{N_k} S_{i,k}\,dt \tag{6}$$

$$dX_i(t) = V_i(t)dt \tag{7}$$

$$dS_{i,k}(t) = -\frac{1}{\tau_k} S_{i,k}(t)dt - \frac{c_k}{\tau_k} V_i(t)dt + \frac{1}{\tau_k}\sqrt{2k_B T c_k}\,dW_{i,k}(t) \tag{8}$$

Auxiliary Extended Variable GLE Equations

$$S_{i,k}(t) = Z_{i,k}(t) + F_{i,k}(t) \tag{9}$$

$$dZ_{i,k}(t) = -\frac{1}{\tau_k} Z_{i,k}(t)dt - \frac{c_k}{\tau_k} V_i(t)dt \qquad Z_{i,k}(t) = -\int_0^t \frac{c_k}{\tau_k}\exp\left[-\frac{(t-s)}{\tau_k}\right] V_i(s)ds \tag{10}$$

$$dF_{i,k}(t) = -\frac{1}{\tau_k} F_{i,k}(t)dt + \frac{1}{\tau_k}\sqrt{2k_B T c_k}\,dW_{i,k}(t) \qquad \left\langle F_{i,k}(t+s), F_{i,k}(t)\right\rangle = k_B T \frac{c_k}{\tau_k}\exp\left[-\frac{s}{\tau_k}\right] \tag{11}$$

$$F_i^r(t) = \sum_{k=1}^{N_k} F_{i,k}(t) \tag{12}$$

Numerical Schemes

Numerical Schemes:

- Explicit Euler Scheme.
- Splitting Scheme.

Which numerical scheme to choose for solving the problem?

Scheme that is able to conserve the first and second moments of quantities of interest i.e. $\boldsymbol{V}(t)$ and $\boldsymbol{X}(t)$.

Reason: General observables/physical quantities that are measured to understand the behavior of a system. For example, *Mean Square Displacement*(`MSD`) in microrheology simulations.

Implementation Details:

- Uniform time-step size, Δt, where $N_t \Delta t = T_{\text{tot}}$ (T_{tot} represents the total time of the simulation and N_t represents the # of time-steps.)
- All N_p particles are seeded with the same constant $\boldsymbol{X}(0)$ and $\boldsymbol{V}(0)$ (**Note:** We could also seed the initial conditions based on the p.d.f if known.)
- The composite variable $S_{i,k}(t)$ is assumed to be zero initially.

Numerical Schemes

Explicit Euler Scheme

Input: $\boldsymbol{X}(0), \boldsymbol{V}(0), \boldsymbol{S}(0)$
Output: $\boldsymbol{X}(t), \boldsymbol{V}(t)$

for $n = 0$ to N_t **do**

$V_i^{n+1} = V_i^n + \frac{\Delta t}{m_i} F_i^c\left(\boldsymbol{X}^n\right) + \frac{\Delta t}{m_i} \sum_{k=1}^{N_k} S_{i,k}^n$ ▷ Advance $\boldsymbol{V}(t)$ by a full step

$X_i^{n+1} = X_i^n + \Delta t V_i^n$ ▷ Advance $\boldsymbol{X}(t)$ by a full step

$S_{i,k}^{n+1} = \left(1 - \frac{\Delta t}{\tau_k}\right) S_{i,k}^n - \frac{c_k \Delta t}{\tau_k} V_i^n + \frac{1}{\tau_k} \sqrt{2 \mathrm{k_B} T c_k} \Delta W_{i,k}$ ▷ Advance $\boldsymbol{S}(t)$ by a full step

end for

Splitting Scheme

Input: $\boldsymbol{X}(0), \boldsymbol{V}(0), \boldsymbol{S}(0)$
Output: $\boldsymbol{X}(t), \boldsymbol{V}(t)$

for $n = 0$ to N_t **do**

$V_i^{n+1/2} = V_i^n + \frac{\Delta t}{2m_i} F_i^c\left(\boldsymbol{X}^n\right) + \frac{\Delta t}{2m_i} \sum_{k=1}^{N_k} S_{i,k}^n$ ▷ Advance $\boldsymbol{V}(t)$ by a half step

$X_i^{n+1} = X_i^n + \Delta t V_i^{n+1/2}$ ▷ Advance $\boldsymbol{X}(t)$ by a full step

$S_{i,k}^{n+1} = \theta_k S_{i,k}^n - \left(1 - \theta_k\right) c_k V_i^{n+1/2} + \alpha_k \sqrt{2 \mathrm{k_B} T c_k} \Delta W_{i,k}$ ▷ Advance $\boldsymbol{S}(t)$ by a full step

$V_i^{n+1} = V_i^{n+1/2} + \frac{\Delta t}{2m_i} F_i^c\left(\boldsymbol{X}^{n+1}\right) + \frac{\Delta t}{2m_i} \sum_{k=1}^{N_k} S_{i,k}^{n+1}$ ▷ Advance $\boldsymbol{V}(t)$ by a half step

end for

Comparison of Numerical Schemes

Case Study:

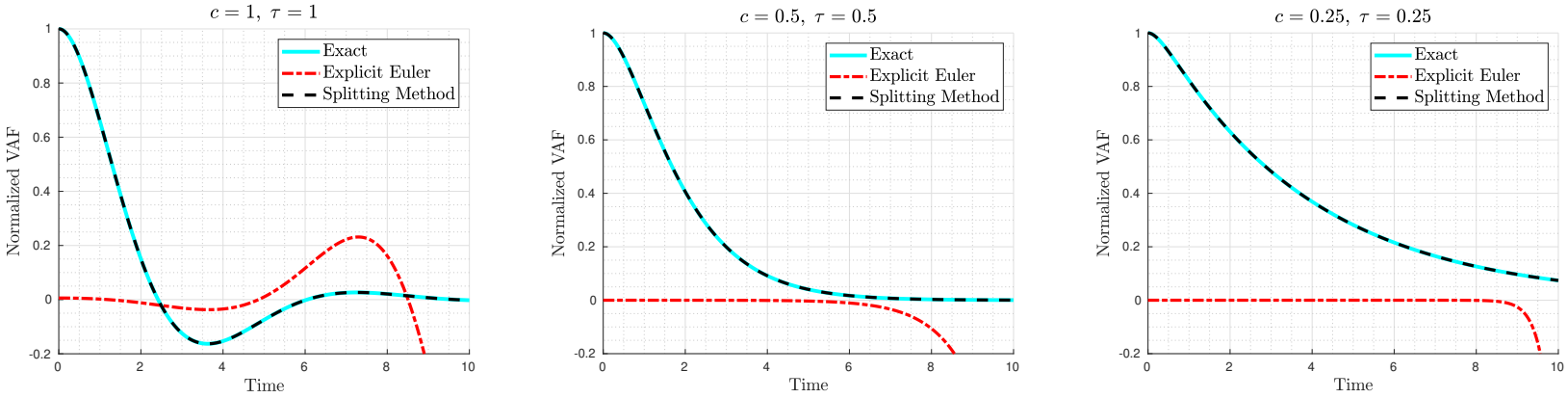
- One dimensional problem, $d = 1$
- Single mode in the Prony series approximation, $N_k = 1$
- Zero conservative force acting on the particles, $\boldsymbol{F}^c\left(\boldsymbol{X}(t)\right) = 0$

The case study is simulated using both numerical schemes, *Explicit Euler* and *Splitting Method*, for three different τ and c values in the `Prony Series` approximation (Table 1)

Type of System	c	τ
Under-damped	1	1
Critically-damped	0.5	0.5
Over-damped	0.25	0.25

Table: c and τ values used for the case study

Comparison of Numerical Schemes - Results



(a) Under-damped **(b)** Critically-damped **(c)** Over-damped

Figure: Comparison of different numerical schemes w.r.t. Normalized VAF

Normalized VAF (*Velocity Autocorrelation Function*)

$$\frac{\langle \boldsymbol{V}(t), \boldsymbol{V}(0) \rangle}{\langle \boldsymbol{V}(0), \boldsymbol{V}(0) \rangle} = \begin{cases} \exp\left[-\frac{t}{2\tau}\right] \left(\cos\left(\Omega t\right) + \frac{1}{2\tau\Omega} \sin\left(\Omega t\right)\right) & \text{for } \Omega \neq 0 \\ \exp\left[-\frac{t}{2\tau}\right] \left(1 + \frac{t}{2\tau}\right) & \text{for } \Omega = 0 \end{cases} \tag{13}$$

$$\Omega = \sqrt{c/\tau - 1/4\tau^2}$$

Note: VAF is for one mode Prony series approx. without any conservative force terms.

Comparison of Numerical Schemes - Results

Observation: Explicit Euler scheme produces wrong results for the `Normalized VAF` as when compared to the Splitting scheme (***Reason:*** *Independent updates for* $\boldsymbol{X}(t)$ *and* $\boldsymbol{V}(t)$ *when using Explicit Euler scheme.*)

Solution: Using the Splitting scheme as the preferred integration scheme for all proceeding cases.

Harmonic Potential Well

Harmonic Potential Well GLE

$$d\boldsymbol{V}(t) = \underbrace{-\omega_0^2 \boldsymbol{X}(t)}_{\text{Conservative Force arising from Harmonic Potential}} dt - \underbrace{\int_0^t \frac{\gamma_\lambda}{\Gamma_0\,(1-\lambda)}\,(t-s)^{-\lambda}}_{\text{Power Law decay memory kernel function}} \boldsymbol{V}(s)dsdt + \boldsymbol{M}^{-1}\boldsymbol{F}^r(t)dt \tag{14}$$

Question?

Approximation of the `memory kernel` in Equation (14) using Prony series

Answer:

log-spaced values for τ_k from $\Delta t/10$ to $10N_t\Delta t$ and then linearly fitting c_k using *least squares regression* i.e.

$$\min_{\boldsymbol{x}} ||\boldsymbol{A}\cdot\boldsymbol{x} - \boldsymbol{b}||^2, \quad \boldsymbol{x} = \{c_k\} \quad \forall k = 1, \cdots, N_k$$

Harmonic Potential Well - Parameter Fitting

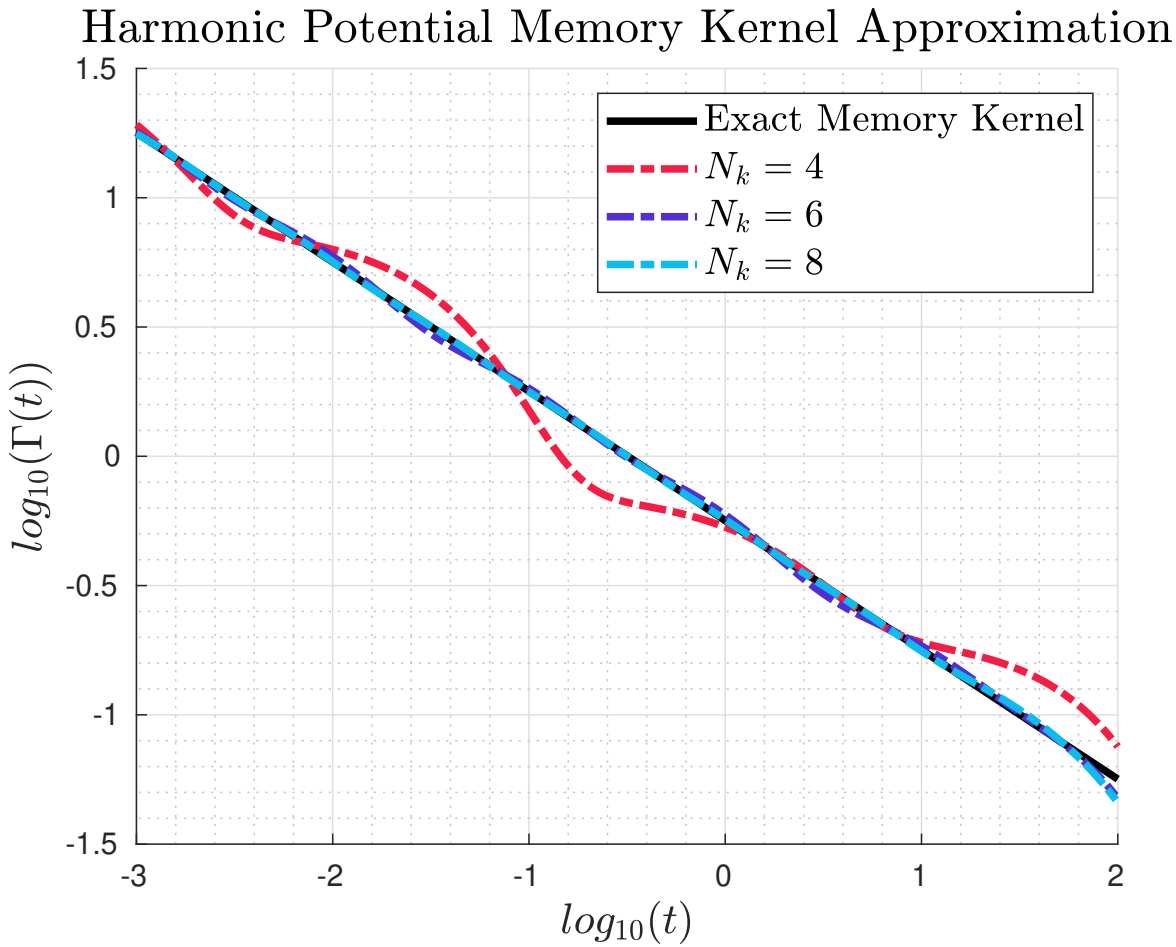
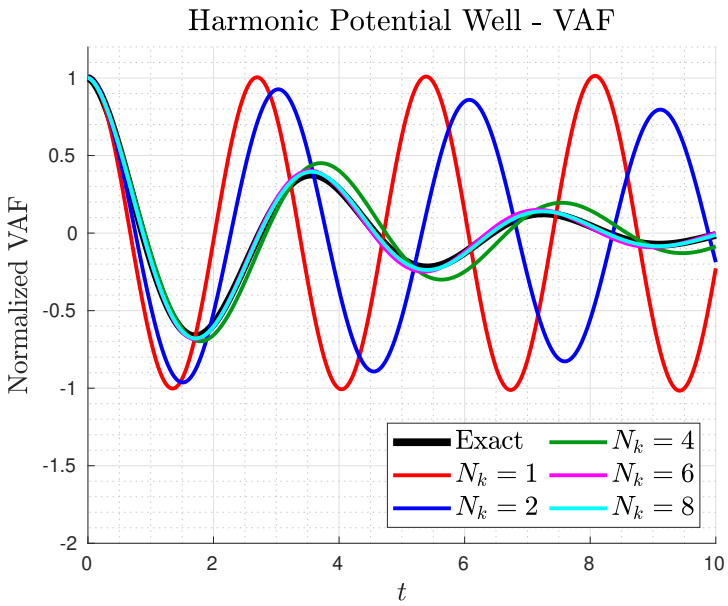
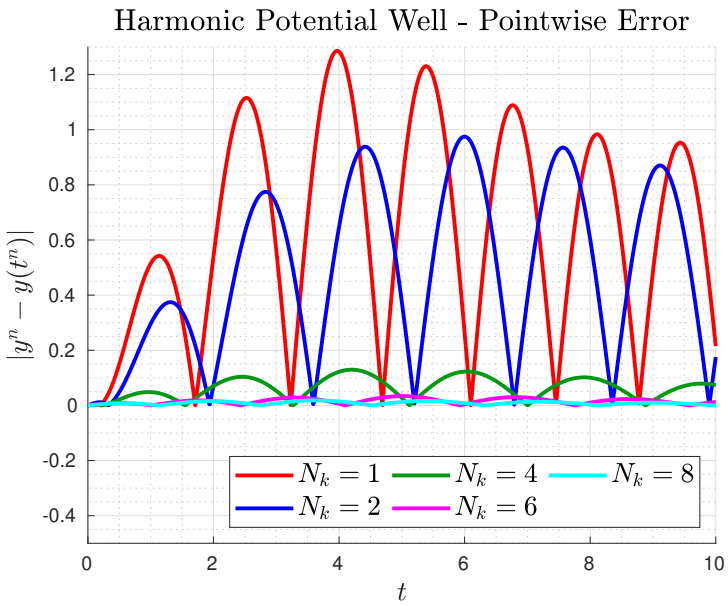


Figure: A Prony series fit of the *power law* memory kernel in eq. (14) for $\gamma_\lambda = 1$, $\lambda = 0.5$ for different N_k

Harmonic Potential Well - Normalized VAF & Pointwise Error



(a) Normalized VAF at different times for different no. of modes used in Prony series approximation



(b) Pointwise error in VAF at different times for different no. of modes used in Prony series approximation

Figure: Approximation of the Harmonic Potential Well problem for $\gamma_\lambda = 1$, $\lambda = 0.5$ and $\omega_0 = 1.4$ using Prony series approximation

Harmonic Potential Well - Normalized VAF & Pointwise Error

Normalized VAF - Exact Solution

$$\underbrace{C_V(t)}_{\text{Normalized VACF}} = \sum_{k=0}^{\infty} \frac{(-1)^k}{k!} (\omega_0 t)^{2k} \, \mathscr{E}^{(k)}_{2-\lambda,1+\lambda k}\left(-\gamma_\lambda t^{2-\lambda}\right)$$

where $\mathscr{E}^{(k)}_{\alpha,\beta}(y)$ represents the k$^{\text{th}}$ derivative of the *Generalized Mittag-Leffler* function given by:

$$\mathscr{E}^{(k)}_{\alpha,\beta}(y) = \sum_{j=0}^{\infty} \frac{(j+k)!\, y^j}{j!\, \Gamma_0\left(\alpha(j+k)+\beta\right)}$$

Harmonic Potential Well - Normalized MSD

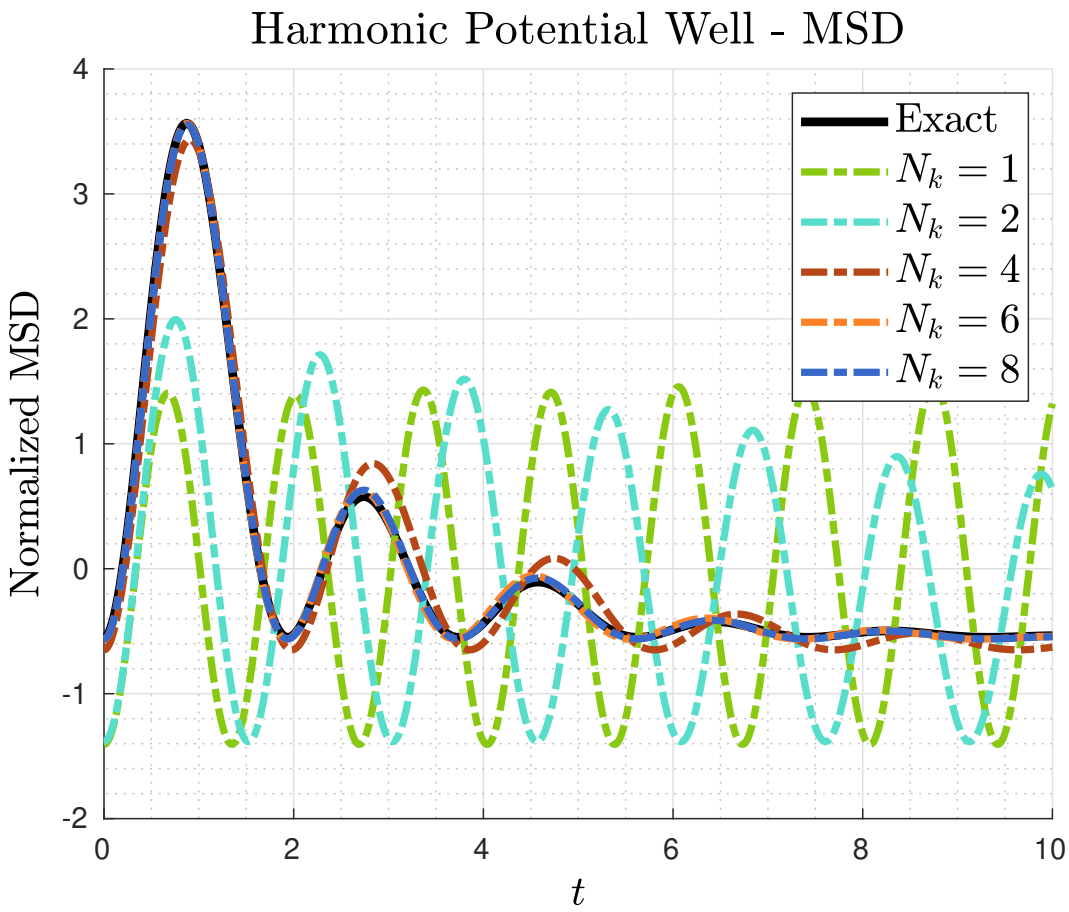


Figure: Normalized MSD at different times for different no. of modes used in Prony series approximation. ($\gamma_\lambda = 1$, $\lambda = 0.5$ and $\omega_0 = 1.4$)

Harmonic Potential Well - Normalized MSD

Normalized MSD - Exact Solution

$$\underbrace{\left\langle [\boldsymbol{X}(t+\tau)-\boldsymbol{X}(t)]^2 \right\rangle}_{\text{Normalized MSD}} = \frac{2\mathsf{k}_\mathsf{B}T}{m} I(\tau) - 2x_0 v_0 \omega_0^2 \left[G(t+\tau)-G(t)\right]\left[I(t+\tau)-I(t)\right]$$
$$+ \left(v_0^2 - \frac{\mathsf{k}_\mathsf{B}T}{m}\right)\left[G(t+\tau)-G(t)\right]^2$$
$$+ \omega_0^2 \left(x_0^2\omega_0^2 - \frac{\mathsf{k}_\mathsf{B}T}{m}\right)\left[I(t+\tau)-I(t)\right]^2$$

$$I(t) = \sum_{k=0}^{\infty} \frac{(-1)^k}{k!} \omega_0^{2k} t^{2(k+1)} \mathscr{E}^{(k)}_{2-\lambda,3+\lambda k}\left(-\gamma_\lambda t^{2-\lambda}\right) \qquad \text{(Kernel integral)}$$

$$G(t) = \sum_{k=0}^{\infty} \frac{(-1)^k}{k!} \omega_0^{2k} t^{2k+1} \mathscr{E}^{k}_{2-\lambda,2+\lambda k}\left(-\gamma_\lambda t^{2-\lambda}\right) \qquad \text{(Relaxation function)}$$

where v_0,x_0 represent the velocity and position of the particles at time $t = 0$.

Sensitivity Analysis

Inference:

- Devised an integration scheme that is able to conserve first and second moments of $\boldsymbol{V}(t)$ and $\boldsymbol{X}(t)$ (Observables for understanding the behavior of physical systems.)
- Adequately able to approximate exact memory kernel using finite no. of modes of Prony series.

Question?

Need for performing sensitivity analysis

Answer:

- Extended variable GLE fitted by matching `MSD` or `VAF` obtained from experimental data $\Rightarrow$ Prony series parameters c_k, τ_k, N_k sensitive to experimental data i.e. to errors in measurement or lack of data.
- *Ergodicity breaking:* Time averaged statistics such as `MSD` do not converge to ensemble averages.

Sensitivity Analysis

Sensitivity Analysis

Let $\mathcal{S}(t, \theta; f)$ denote the sensitivity of the stochastic process $\boldsymbol{X}_t(\theta)$ where θ is a parameter that affects the stochastic process and f is the given observable. We are interested in calculating:

$$\mathcal{S}(t, \theta; f) = \frac{\partial \mathbb{E}\left[f\left(\boldsymbol{X}_t(\theta)\right)\right]}{\partial \theta}$$

Methods of Calculation:

- *Finite Difference Stencils:* Approximating derivative by a finite difference stencil and obtain the required moments by Monte Carlo.
- *Likelihood Ratio:* Expressing sensitivity as an expectation of f under a change of measure.
- *Malliavin Calculus:* Extension of calculus of variations to stochastic processes.

Methods for calculating sensitivity

`Finite Difference Stencil`

$$\mathcal{S}_{\varepsilon}\left(t,\theta;f\right)=\frac{\mathbb{E}\left[f\left(\boldsymbol{X}_{t}\left(\theta+\varepsilon\right)\right)\right]-\mathbb{E}\left[f\left(\boldsymbol{X}_{t}\left(\theta\right)\right)\right]}{\varepsilon}$$

`Likelihood Estimator`

$$\begin{aligned}\mathcal{S}_{LR}\left(t,\theta;f\right)=\frac{\mathbb{E}\left[f\left(\boldsymbol{X}_{t}\left(\theta\right)\right)\right]}{\partial\theta}&=\int f\left(x_{t}\right)\left[\partial_{\theta}\log g\left(\theta,x_{t}\right)\right]g\left(\theta,x_{t}\right)dx_{t}\\&=\mathbb{E}\left[f\left(\boldsymbol{X}_{t}\left(\theta\right)\right)\partial_{\theta}\log g\left(\theta,\boldsymbol{X}_{t}\right)\right]\end{aligned}$$

where g represents the change in measure by a p.d.f.

`Malliavin Calculus`

$$\mathcal{S}_{M}\left(t,\theta;f\right)=\mathbb{E}\left[f\left(\boldsymbol{X}_{T}\right)h\left(\left\{\boldsymbol{X}_{s}\right\}_{0\leq s\leq T}\right)\right]$$

where $h\left(.\right)$ represents the Malliavin weights.

Sensitivity Estimators using Finite Difference Stencils

Objective: To calculate the sensitivity of the stochastic process efficiently using finite difference stencils $\Rightarrow$ right sampling strategy to reduce variance.

Methodology: Let $\hat{\phi}(\theta)$ represent the expected value of the observable $f(\boldsymbol{X}_t(\theta))$. Then we can write,

$$\hat{\phi}(\theta) = M^{-1}\sum_{i=1}^{M} f(X_{i,t}(\theta)) \Rightarrow \mathcal{S}_\varepsilon\left(t,\theta;\hat{\phi}\right) \approx \Delta_c(M,\varepsilon) = \frac{\hat{\phi}(\theta+\varepsilon)-\hat{\phi}(\theta-\varepsilon)}{2\varepsilon}$$

where each random variable is sampled independently of each other.

$$\Rightarrow \mathrm{Var}[\Delta_c] = \varepsilon^{-2}\mathrm{Var}\left[\hat{\phi}(\theta+\varepsilon)-\hat{\phi}(\theta-\varepsilon)\right]$$

$$= \varepsilon^{-2}M^{-1}\mathrm{Var}\left[\underbrace{f(\boldsymbol{X}_t(\theta+\varepsilon))}_{R_1} - \underbrace{f(\boldsymbol{X}_t(\theta-\varepsilon))}_{R_2}\right]$$

where the variance can be rewritten as

$$\mathrm{Var}[\Delta_c] = \varepsilon^{-2}M^{-1}\left(\mathrm{Var}[R_1]+\mathrm{Var}[R_2]-2\mathrm{Cov}[R_1,R_2]\right)$$

Sensitivity Estimators using Finite Difference Stencils

Statistical Error is given by $\epsilon_M = \frac{C_\alpha \sigma}{\sqrt{M}}$ where $\sigma = \sqrt{\text{Var}\left[\Delta_c\right]}$ and C_α is a constant based on the confidence level of the solution

Coupled vs. Decoupled Noise:

- If R_1 and R_2 are not correlated, then $\text{Var}\left[\Delta_c\right] = \mathcal{O}\left(\varepsilon^{-2} M^{-1}\right)$
- If R_1 and R_2 are positively correlated, then $\text{Var}\left[\Delta_c\right] = \mathcal{O}\left(M^{-1}\right)$

Observation:

Let $\varepsilon = 0.1$. In order to reduce the error by a factor of 10.

- *Coupled Noise:* $M = 10^4$ samples
- *Decoupled Noise:* $M = 10^2$ samples

Hence the statistical error becomes independent of the perturbation parameter on using a common random path coupling i.e. R_1 and R_2 use the same Wiener process dW.

Sensitivity Analysis - Results

Conclusion