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.

Generalized Langevin Equation

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".

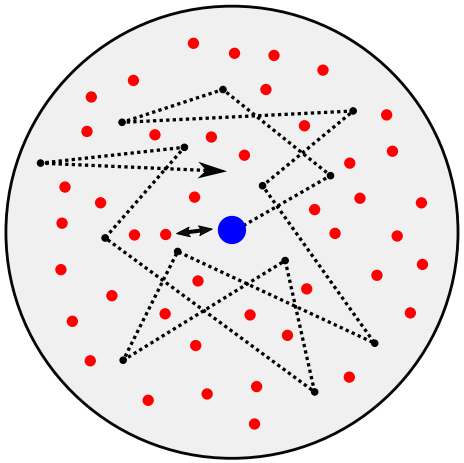
Why? *Molecular Dynamics* simulations involving all particles is computationally expensive. Langevin Equation model is computationally cheaper.

Drawback

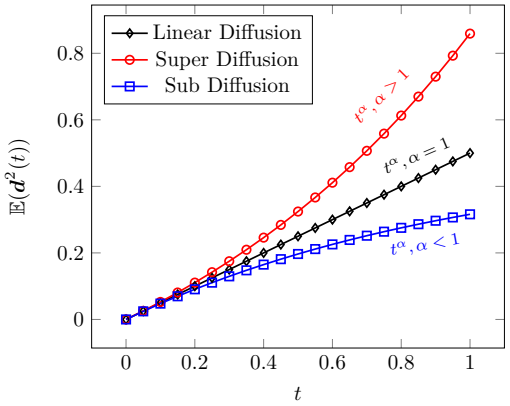
Anomalous diffusion problems arising due to *Power Law* behavior of solute-solvent systems cannot be solved.

Solution

Generalized Langevin Equation (**GLE**)



(a) Big Particles interacting with Smaller Particles



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

Generalized Langevin Equation

Mathematical Model

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

GLE Equations

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

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

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

Note:

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

Generalized Langevin Equation

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.

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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.

Generalized Langevin Equation

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.

Generalized Langevin Equation

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

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

$$dZ_{i,k}(t) = -\frac{1}{\tau_k}Z_{i,k}(t)dt - \frac{c_k}{\tau_k}V_i(t)dt$$

$$dF_{i,k}(t) = -\frac{1}{\tau_k}F_{i,k}(t)dt + \frac{1}{\tau_k}\sqrt{2k_B T c_k}dW_{i,k}(t)$$

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

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

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

Generalized Langevin Equation

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 $\boldsymbol{X}(t)$.

Implementation Det

- 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.

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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

$S_{i,k}^{n+1} = \left(1 - \frac{\Delta t}{\tau_k}\right) S_{i,k}^n - \frac{c_k \Delta t}{\tau_k} V_i^n + \frac{1}{\tau_k} \sqrt{2 k_B T c_k} \Delta W_{i,k}$ ▷ 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**

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

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

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

end for

Generalized Langevin Equation

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	$\boldsymbol{c}$	$\boldsymbol{\tau}$
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

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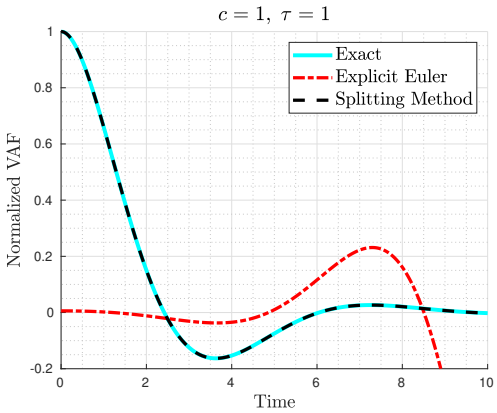
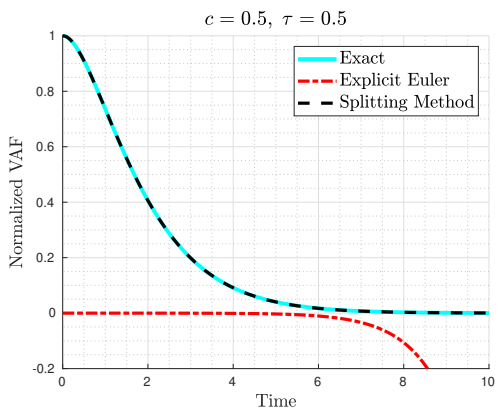
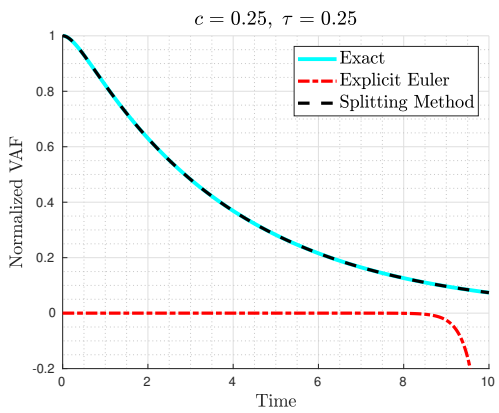
Comparison of Numerical Schemes - Results



(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*)

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

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

Generalized Langevin Equation

Comparison of Numerical Schemes - Results

Observation: Explicit Euler scheme produces wrong results for the `Normalized VAF` as when compared to the Splitting scheme.

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

Generalized Langevin Equation

Harmonic Potential Well

Harmonic Potential Well GLE

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

Question?

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

Answer:

log-spaced values for τ_k from $\Delta t/10$ to $10 N_t \Delta t$ and then linearly fitting c_k i.e. $\min_{\boldsymbol{x}} ||\boldsymbol{A} \cdot \boldsymbol{x} - \boldsymbol{b}||^2, \quad \boldsymbol{x} = \{c_k\} \quad \forall k = 1, \cdots, N_k$

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Harmonic Potential Well - Parameter Fitting

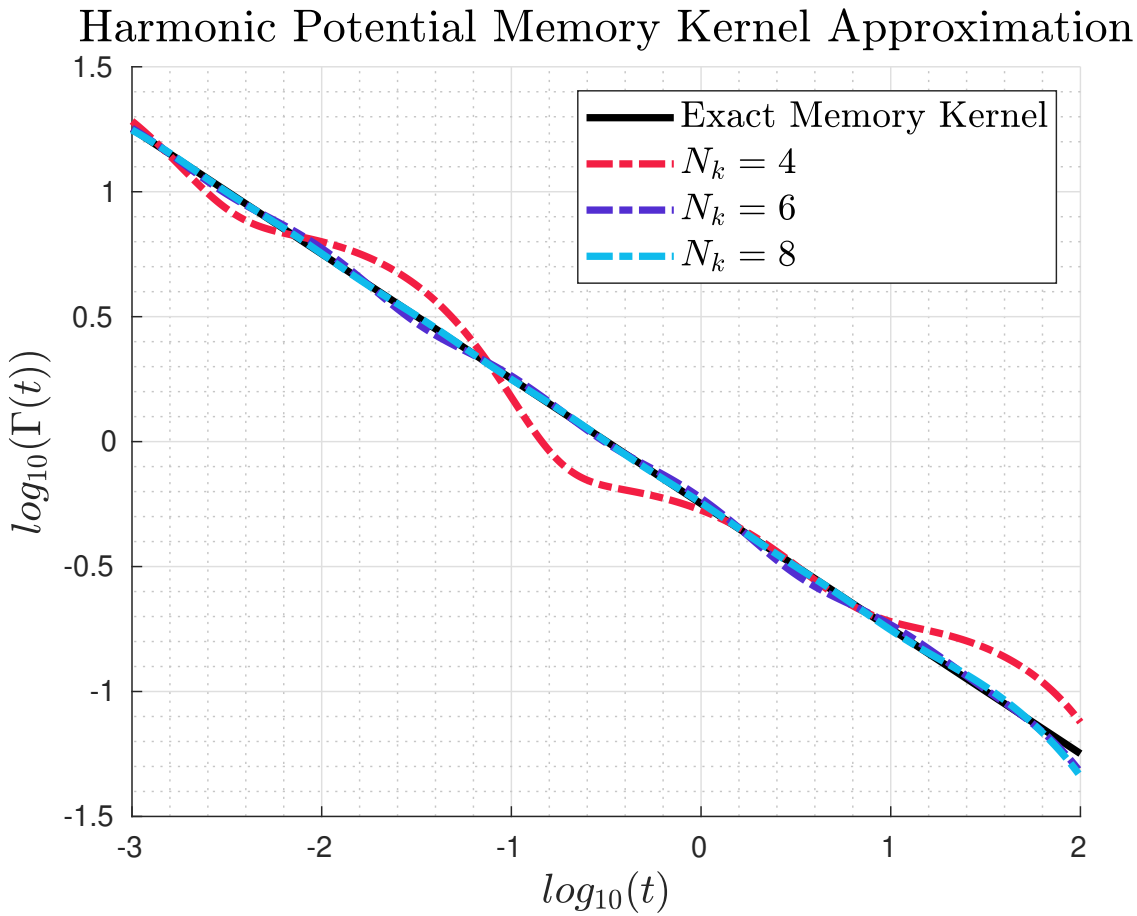

Figure: A Prony series fit of the *power law* memory kernel in eq. (14) for $\gamma_\lambda = 1$, $\lambda = 0.5$ for different N_k