Numerical methods for the Extended Variable Generalized Langevin Equation

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Acknowledgments and Literature

People

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- "Physics-Based Multiscale Stochastic Methods for Computational Mechanics of Heterogeneous Materials" (LDRD; J. Lechman)

Publication

- A. D. Baczewski, S. D. Bond, "Numerical Integration of the Extended Variable Generalized Langevin Equation with a Positive Prony Representable Memory Kernel", J. Chem. Phys., **139** (2013) 044107.

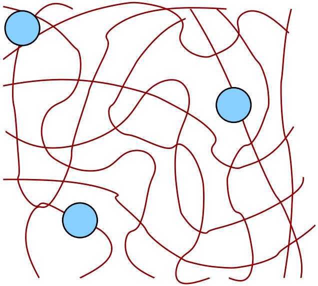
LAMMPS module

- `fix gld` (http://lammps.sandia.gov/doc/fix_gld.html)

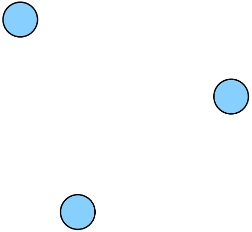
Motivation

Anomalous Diffusion

Heterogeneous environments



Reduced model



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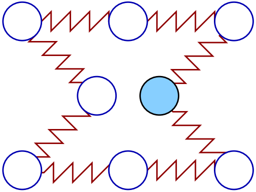
Anomalous Diffusion

Bead in a polymer ring



Reduced model

Langevin Equation

- Langevin Equation

$$\underbrace{M\ddot{X}(t)}_{\text{inertia}} = \underbrace{F\left(X(t)\right)}_{\text{deterministic}} + \underbrace{-\gamma\dot{X}(s)}_{\text{drag}} + \underbrace{\sigma R(t)}_{\text{random}}$$

- Gaussian process

$$\langle R_n(t)R_m(s)\rangle = \begin{cases} \delta(t-s), & n = m, \\ 0, & n \neq m \end{cases}$$

- Balance between random and drag forces

$$\sigma^2 = 2\,\gamma\,k_B\,T$$

- Small mass limit $\rightarrow$ Brownian dynamics

$$\gamma\dot{X}(t) = F\left(X(t)\right) + \sigma R(t)$$

Generalized Langevin Equation

- Generalized Langevin Equation

$$\underbrace{M\ddot{X}(t)}_{\text{inertia}} = \underbrace{F\left(X(t)\right)}_{\text{deterministic}} + \underbrace{-\int_{-\infty}^{t} \Gamma\left(t-s\right)\dot{X}(s)\,ds}_{\text{drag}} + \underbrace{\sigma R(t)}_{\text{random}}$$

- Balance between random and drag forces

$$\sigma^2 \langle R_n(t) R_n(s) \rangle = k_B T\,\Gamma\left(|t-s|\right)$$

- Memory kernel

Delta function	$\longrightarrow$	Langevin equation
General function	$\longrightarrow$	Generalized Langevin

Memory Kernel

- Connection with the velocity auto-correlation function

$$\Gamma(t) = \mathcal{L}^{-1}\left\{\frac{k_B T}{\langle \hat{V}(s) V(0)\rangle} - ms\right\}(t)$$

$$\langle \hat{V}(s) V(0)\rangle = \mathcal{L}\left\{\langle V(t) V(0)\rangle\right\}$$

- Power law

$$\Gamma(t) = c\left(\frac{\tau}{t}\right)^{\alpha}$$

- Prony series

$$\Gamma(t) = \sum_{k=0}^{N_k} \frac{c_k}{\tau_k} e^{-t/\tau_k}$$

Extended variable transformation

- Positive Prony series

$$m_i dV_i(t) = F_i^c\left(X(t)\right)\,dt - \int_{-\infty}^{t} \sum_{k=0}^{N_k} \frac{c_k}{\tau_k} e^{-(t-s)/\tau_k} V_i(s)\,ds\,dt + dF_i^{\mathrm{rand}}(t)$$

$$dX_i(t) = V_i(t)\,dt$$

- "Memoryless" extended variable transformation

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

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

$$dX_i(t) = V_i(t)\,dt$$

Numerical method

Algorithm:

$$
\begin{aligned}
V_i^{n+1/2} &= V_i^n + \frac{\Delta t}{2m_i}\left(F_i^c(X^n) + \sum_{k=1}^{N_k} S_{i,k}^n\right) \\
X_i^{n+1} &= X_i^n + \Delta t V_i^{n+1/2} \\
S_{i,k}^{n+1} &= \theta_k S_{i,k}^n + (1-\theta_k) c_k V_i^{n+1/2} + \alpha_k \sqrt{2k_B T c_k} B_{i,k}^n \\
V_i^{n+1} &= V_i^{n+1/2} + \frac{\Delta t}{2m_i}\left(F_i^c(X^{n+1}) + \sum_{k=1}^{N_k} S_{i,k}^{n+1}\right)
\end{aligned}
$$

where

$$\theta_k = e^{-\Delta t/\tau_k} \qquad \text{and} \qquad \alpha_k = \frac{1-\theta_k}{\Delta t}$$

Features:

- Uses $N_k \times 3N$ additional memory ($N_k \approx 1$ to 8)
- Stable Langevin limit as $\tau_k \to 0$
- Verlet limit as $c_k \to 0$
- Exact preservation of first and second moments of V_i

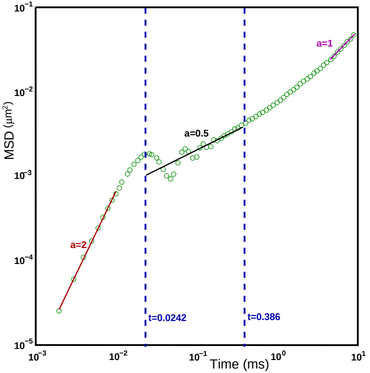
```
fix ID group-ID gld Tstart Tstop Nk seed series c_1 tau_1
...  c_Nk tau_Nk keyword values ...
```

- Syntax
  - Tstart, Tstop = Temperature at start/end
  - Nk = Number of terms in the series
  - seed = Positive integer seed for the random number generator
  - series = pprony
  - c_k = weight for the kth term
  - tau_k = time constant for the kth term
- Keywords (yes or no)
  - frozen = zero (yes) or equilibrate (no) extended variables
  - zero = set total GLD force to zero
- Notes
  - GLD fix can be combined with `fix langevin`
  - GLD fix steps in time (no need to combine with `fix nve`)

Examples

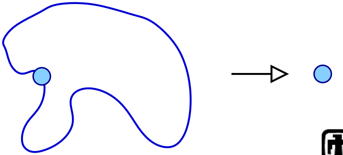
Rouse chain

```
fix 3 rouse gld 7.355 7.355 4 48823 pprony 107.1 0.02415 186.0 0.04294 428.6 0.09661 1714 0.38643
```

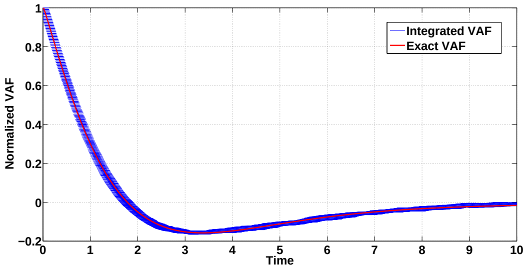


Anomalous diffusion as measured by mean-square displacement

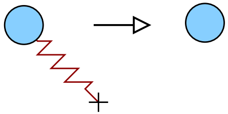
- Four term Prony series
- Early time:
  → Ballistic motion
- Intermediate time:
  → Anomalous diffusion
- Late time:
  → Diffusive motion



Harmonically confined particle

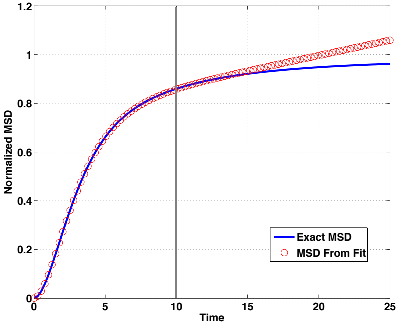


- Confined particle → memory kernel
- GLD system has no conservative force
- Particle is confined only by drag forces

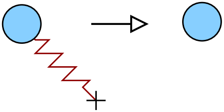


Examples

Caution with extrapolation



- Prony series is asymptotically diffusive
- Particle is confined for finite time
- Asymptotic confinement not possible with exponentially decaying memory kernel!



Future work

- Complex Prony series memory kernel (Fourier series)
- Combine with Boltzmann inversion (Potential of mean force)
- Inference tools
- Models for anomalous heat conduction