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Markovian embedding of generalized Langevin equations with a nonlinear friction kernel and configuration-dependent mass

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Abstract: We consider a generalized Langevin equation (GLE) in which the deterministic force, the mass and the friction kernel are configuration-dependent, i.e. general nonlinear functions of the reaction coordinate. We introduce a projection operator that allows for a self-consistent Markovian embedding of such GLEs. Self-consistency means that trajectories generated by the Markovian embedding are described by a GLE with the same configuration-dependent deterministic force, mass and friction kernel. Using the projection operator, we derive a closed-form relation between the parameters of the Markovian embedding Langevin equations and the parameters of the GLE. This is accomplished by applying the projection operator formalism to the system of Markovian embedding stochastic equations.

Keywords: Non-Markovian processes, Markovian embedding, nonlinear friction, configuration-dependent mass

1. Introduction

Generalized Langevin equations (GLEs) have been proven to be a useful tool in the coarse-grained stochastic modeling of many-body dynamics [1–13]. One of the reasons for this is that GLEs can be derived from first principles using projection operator methods [14–20]. Although many different forms of GLEs can be derived, the general structure can be written as

$$\ddot{A}_t = \frac{F(A_t, \dot{A}_t)}{M(A_t)} - \int_0^t \mathrm{d}s\, \Gamma(A_s, \dot{A}_s, t-s) + F_R(t). \tag{1.1}$$

In Eq. (1.1), A_t denotes a general observable, e.g., the position of a tagged particle or the distance between clusters of particles. For the sake of clarity, we denote the time dependency of observables by a subscript, e.g., A_t, and derivatives with respect to (w.r.t.) time as dots, e.g., $\dot{A}_t$. The first term on the r.h.s. of Eq. (1.1) is a deterministic force F divided by the effective mass M of the observable [21, 22]. This part of the GLE depends on the values A_t and $\dot{A}_t$ at the present time t, i.e. it represents a Markovian contribution. The second term introduces a coupling to past values at time $s \leq t$, and, therefore, is referred to as the memory term. The memory kernel $\Gamma(A_s, \dot{A}_s, t-s)$ is usually maximal at $s = t$ and decreases as $t - s$ rises. The function $F_R(t)$ depends on the initial state of the entire system and is typically interpreted as a random force. The actual dependencies of the functions F, Γ and F_R on their arguments are determined by the choice of the projection operator [19, 20].

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Various data-based methods to estimate these functions from time series data have been introduced [4, 19, 20, 22–27]. In principle, the GLE in its general form of Eq. (1.1) is exact. Approximations enter when generating trajectories from the GLE. By choosing $F_R(t)$ to be a random process, the exact GLE is mapped onto a stochastic model that can be simulated [28, 29].

In future work, we will discuss GLE simulations via Markovian embedding in the presence of a nonlinear friction kernel, i.e. when $\Gamma(A_s, \dot{A}_s, t-s) \to \Gamma(A_s, t-s)\dot{A}_s$, but in which the mass M is assumed to be constant in A_t. In this paper, we consider the more general case where the effective mass may also depend on A_t. We introduce a projection operator that generates a GLE in which the deterministic force F is suitable for the purpose of simulating GLEs and contains a position dependent mass. In Section 2, we introduce the projection operator and derive the GLE. In Section 3, we present a system of coupled Markovian Langevin equations and use the projection operator to show that it can be used to simulate the GLE derived in Section 2.

2. GLE with nonlinear friction

2.1. Hamiltonian dynamics

In the following, we introduce the many-body Hamiltonian and the notation used throughout the paper. We also discuss the projection operator and the corresponding GLE.

We consider an N-particle Hamiltonian $H(\omega_t)$ system, where $\omega_t = (\mathbf{R}_t, \mathbf{P}_t) \in \mathbb{R}^{6N}$ is the phase space point at time t with positions $\mathbf{R}_t$ and momenta $\mathbf{P}_t$. The Hamiltonian is an invariant of motion and of the form

$$H(\omega) = \sum_{n=1}^{N} \frac{\mathbf{p}_n^2}{2m_n} + V(\mathbf{R}), \tag{2.1}$$

where lower case $\mathbf{p}_n$ denotes the momentum of the n-th particle, and m_n its mass. The interaction potential V is assumed to be a function of positions only such that there is no coupling between velocities and positions. Observables of phase space are denoted by $B_t = B(\omega_t) = B(\omega_0, t)$. The inner product of two observables B and C is the equilibrium average over the stationary Boltzmann distribution $\rho_{\text{eq}}(\omega_0) = \exp(-\beta H(\omega_0))/Z$, i.e.

$$\langle B_t, C_{t'} \rangle = \int \mathrm{d}\omega_0 \, \rho_{\text{eq}}(\omega_0) B(\omega_0, t) C(\omega_0, t'), \tag{2.2}$$

with $Z = \int \mathrm{d}\omega_0 \, e^{-\beta H(\omega_0)}$ being the partition function. The adjoint Liouville equation determines the time evolution of an observable

$$\dot{B}_t = L B_t, \tag{2.3a}$$

$$L = \sum_{n=1}^{N} \left(\frac{\partial H}{\partial \mathbf{p}_n} \cdot \frac{\partial}{\partial \mathbf{r}_n} - \frac{\partial H}{\partial \mathbf{r}_n} \cdot \frac{\partial}{\partial \mathbf{p}_n} \right), \tag{2.3b}$$

where L is the Liouville operator. The general solution of the Liouville equation in Eq. (2.3) is given by $B_t = e^{tL} B_0$. The Liouville operator L is anti-self-adjoint with respect to the inner product in Eq. (2.2), i.e.

$$\langle L B_t, C_{t'} \rangle = -\langle B_t, L C_{t'} \rangle. \tag{2.4}$$

2.2. Projection operator

Projection operators are linear, idempotent operators [30, 31], i.e. a projection operator $\mathcal{P}$ fulfills

$$\mathcal{P}^2 = \mathcal{P}. \tag{2.5}$$

We denote the projection onto the complementary subspace by $\mathcal{Q} = 1 - \mathcal{P}$, where 1 is the identity operator. From the idempotent property in Eq. (2.5), it follows

$$\mathcal{P}\mathcal{Q} = \mathcal{Q}\mathcal{P} = 0. \tag{2.6}$$

A projection operator is orthogonal w.r.t. a given inner product if it is self-adjoint w.r.t. the inner product. In case of the inner product in Eq. (2.2), this implies

$$\langle \mathcal{P}B_t, C_{t'} \rangle = \langle B_t, \mathcal{P}C_{t'} \rangle, \tag{2.7a}$$

$$\langle \mathcal{Q}B_t, C_{t'} \rangle = \langle B_t, \mathcal{Q}C_{t'} \rangle, \tag{2.7b}$$

$$\langle \mathcal{Q}B_t, \mathcal{P}C_{t'} \rangle = 0. \tag{2.7c}$$

Using projection operators, the Liouville equation (Eq. (2.3a)) can be decomposed into two terms

$$\dot{B}_t = LB_t = e^{tL}LB_0 = e^{tL}(\mathcal{P}_L + \mathcal{Q}_L)LB_0. \tag{2.8}$$

We use the subscript L to highlight that the pair $\mathcal{P}_L, \mathcal{Q}_L$ is used to decompose the Liouville equation. Using the Dyson decomposition [32, 33] of the propagation operator e^{tL}, we can further decompose Eq. (2.8) [34]. The Dyson decomposition is given by [35]

$$e^{tL} = e^{t\mathcal{Q}_D L} + \int_0^t \mathrm{d}s\, e^{(t-s)L}\mathcal{P}_D L e^{s\mathcal{Q}_D L}. \tag{2.9}$$

The subscript D denotes that we use the pair $\mathcal{P}_D, \mathcal{Q}_D$, which in general can be different from $\mathcal{P}_L, \mathcal{Q}_L$, in the Dyson decomposition. Inserting Eq. (2.9) into Eq. (2.8), we obtain an equation with a similar structure to a GLE in terms of general projection operators $\mathcal{P}_L, \mathcal{Q}_L, \mathcal{P}_D, \mathcal{Q}_D$:

$$\dot{B}_t = e^{tL}\mathcal{P}_L LB_0 + \int_0^t \mathrm{d}s\, e^{(t-s)L}\mathcal{P}_D L F_R(s) + F_R(t), \tag{2.10a}$$

$$F_R(t) = e^{t\mathcal{Q}_D L}\mathcal{Q}_L LB_0. \tag{2.10b}$$

Note that the projection $\mathcal{P}_L$ determines the functional form of the first term $e^{tL}\mathcal{P}_L LB_0$ and the initial value $F_R(0) = \mathcal{Q}_L LB_0$, while the projection $\mathcal{P}_D$ determines the functional form of the integrand $\mathcal{P}_D L F_R(s)$ and the propagation of $F_R(0)$ in time via $e^{t\mathcal{Q}_D L}$.

2.3. Final form of the GLE

Next, we specify the projections $\mathcal{P}_L$ and $\mathcal{P}_D$ in order to obtain an explicit form of the GLE. For this, we need the conditional correlation between two observables B and C, which is defined by

$$\langle B_t, C_{t'} \rangle_{A_0} = \frac{\langle \delta(A(\hat{\omega}_0) - A(\omega_0)), B(\hat{\omega}_0, t)C(\hat{\omega}_0, t') \rangle}{\langle \delta(A(\hat{\omega}_0) - A(\omega_0)) \rangle}. \tag{2.11}$$

In Eq. (2.11), the phase space position with a hat, i.e. $\hat{\omega}_0$, is integrated over. The condition in Eq. (2.11) is that the observable A has initially the value $A_0 = A(\omega_0)$. We will refer to the observable A, which we project onto, as the observable of interest, or reaction coordinate. In the remainder, we assume that A is a function of particle positions only, i.e. $A(\omega_0) = A(\mathbf{R}_0) = A_0$. For example, A could be the center of mass of a cluster of particles, the mean distance from the native state of a protein or the dihedral angle. When A is a function of positions only, its velocity $\dot{A}_0 = (M^{-1}\mathbf{P}_0) \cdot \nabla_R A_0$ is linear in particle momenta, where M is the diagonal mass matrix $M_{ij} = m_i \delta_{ij}$. From this, and from Eq. (2.1) and Eq. (2.2), it follows that, for given position $\mathbf{R}_0$, the velocity $\dot{A}_0$ is Gaussian distributed with zero mean. Using conditional correlations, we define the first projection operator $\mathcal{P}_D$. It is a reformulation of the projection operators discussed in refs. [19, 20] and given by

$$\mathcal{P}_D B_t = \langle B_t \rangle_{A_0} + \frac{\langle \dot{A}_0, B_t \rangle_{A_0}}{\langle \dot{A}_0^2 \rangle_{A_0}} \dot{A}_0 \,. \tag{2.12}$$

The projection operator $\mathcal{P}_L$ is an extension of $\mathcal{P}_D$ and reads

$$\mathcal{P}_L = \mathcal{P}_D + \mathcal{P}_2, \tag{2.13a}$$

$$\mathcal{P}_2 B_t = \frac{\left\langle \left(\dot{A}_0^2 - \langle \dot{A}_0^2 \rangle_{A_0} \right), B_t \right\rangle_{A_0}}{\left\langle \left(\dot{A}_0^2 - \langle \dot{A}_0^2 \rangle_{A_0} \right)^2 \right\rangle_{A_0}} \left(\dot{A}_0^2 - \langle \dot{A}_0^2 \rangle_{A_0} \right). \tag{2.13b}$$

Both projections, $\mathcal{P}_L$ and $\mathcal{P}_D$, are orthogonal projections w.r.t. the inner product in Eq. (2.2). Further, we have $\mathcal{Q}_L B_t = \mathcal{Q}_D \mathcal{Q}_L B_t$. To obtain the final form of the GLE, we set $B_t = \dot{A}_t$ in Eq. (2.10) and use the projection operators defined in Eq. (2.12) and Eq. (2.13). This gives the GLE

$$\ddot{A}_t = -\frac{1}{M(A_t)} \frac{\mathrm{d}U(A_t, \dot{A}_t)}{\mathrm{d}A_t} - \int_0^t \mathrm{d}s \, \Gamma(A_s, t-s) \dot{A}_s + F_R(t), \tag{2.14a}$$

with

$$U(A, \dot{A}) = U_{\mathrm{PMF}}(A) + \frac{M(A)}{2} \dot{A}^2 + k_B T \ln \sqrt{M(A)}, \tag{2.14b}$$

$$\Gamma(A, t) = \beta U'_{\mathrm{eff}}(A) D(A, t) - D'(A, t) + \frac{\langle \ddot{A}_0, F_R(t) \rangle_A}{\langle \dot{A}_0^2 \rangle_A}, \tag{2.14c}$$

$$U_{\mathrm{eff}}(A, t) = U_{\mathrm{PMF}}(A) + k_B T \ln M(A), \tag{2.14d}$$

$$D(A, t) = \frac{\langle \dot{A}_0^2, F_R(t) \rangle_A}{\langle \dot{A}_0^2 \rangle_A}. \tag{2.14e}$$

Here, $M(A) = k_B T / \langle \dot{A}_0^2 \rangle_A$ denotes the position-dependent effective mass of the reaction coordinate and $U_{\mathrm{PMF}}(a) = -k_B T \ln \mathbb{P}(a)$ is the potential of mean force (PMF) with $\mathbb{P}(a) = \langle \delta(A(\hat{\omega}_0) - a) \rangle$ being the positional distribution. An algorithm to extract GLE parameters from time series data by explicitly computing the random force $F_R(t)$ was introduced in refs. [25, 36] and extended to GLE's in

the presence of finite, in general nonlinear, potentials and nonlinear friction in ref. [19]. The random force (and simultaneously the memory kernel) is computed by discretizing the iterative equation

$$F_R(\omega_0, t+\Delta t) = F_R(\omega_{\Delta t}, t) + \int_0^{\Delta t} \mathrm{d}s\, \Gamma(A_{\Delta t - s}, t+s)\dot{A}_{\Delta t - s}\,, \tag{2.15}$$

where $\omega_{\Delta t}$ corresponds to the configuration obtained by propagating ω_0 with the Liouville propagator $e^{\Delta t L}$, while the explicit time dependency of $F_R(\omega, t)$ results from an orthogonal propagation with e^{tQL}. Alternatively, one can also use the Volterra scheme discussed in ref. [20].

3. Markovian embedding of a GLE with configuration-dependent mass and nonlinear friction

In this section, we will present a system of Markovian Langevin equations that allows for a self-consistent Markovian embedding of a GLE with a configuration-dependent mass and nonlinear friction. But first, we need to clarify in what sense the Markovian embedding is *self-consistent*.

3.1. The concept of self-consistent Markovian embedding

The goal of Markovian embedding is to find a map of a low-dimensional non-Markovian GLE onto a higher-dimensional Markovian system of equations that can be used to perform efficient and accurate computer simulations of the non-Markovian system. One simple example of such a Markovian embedding can be given for a GLE with constant mass M and single-exponential memory,

$$\ddot{x}_t = -\frac{1}{M}U'(x_t) - \int_0^t \mathrm{d}s\, \Gamma_0 e^{-(t-s)/\tau}\dot{x}_s + F_R(t), \tag{3.1}$$

$$\langle F_R(t)\rangle = 0, \qquad \langle F_R(t), F_R(0)\rangle = \frac{k_B T}{M}\,\Gamma_0 e^{-t/\tau}. \tag{3.2}$$

Eq. (3.1) can be generated from the following coupled system of Markovian Langevin equations

$$\dot{x}_t = v_t, \tag{3.3a}$$

$$\dot{v}_t = -\frac{1}{M}U'(x_t) + \gamma_1\, u_t, \tag{3.3b}$$

$$\dot{u}_t = -\gamma_2\, u_t - \gamma_1\, v_t + \sqrt{2k_B T\gamma_2}\,\eta(t), \tag{3.3c}$$

$$\mathbb{E}[\eta(t)] = 0, \qquad \mathbb{E}[\eta(t)\eta(t')] = \delta(t-t'), \tag{3.3d}$$

if one chooses the input parameters γ_1, γ_2 to be

$$\gamma_1 = \sqrt{\Gamma_0}, \qquad\qquad \gamma_2 = \frac{1}{\tau}. \tag{3.4}$$

In Eq. (3.3), $\eta(t)$ is white noise and $\mathbb{E}[\cdot]$ denotes an average over the noise. When it comes to numerical simulations, Eq. (3.3) is preferable over Eq. (3.1) because Eq. (3.1) is an integro-differential equation and thus, numerically much more demanding. Suppose the memory kernel $\Gamma(t) = \Gamma_0 e^{-t/\tau}$ is known, e.g., the parameters Γ_0 and τ have been estimated from data. Then, Eq. (3.4) determines

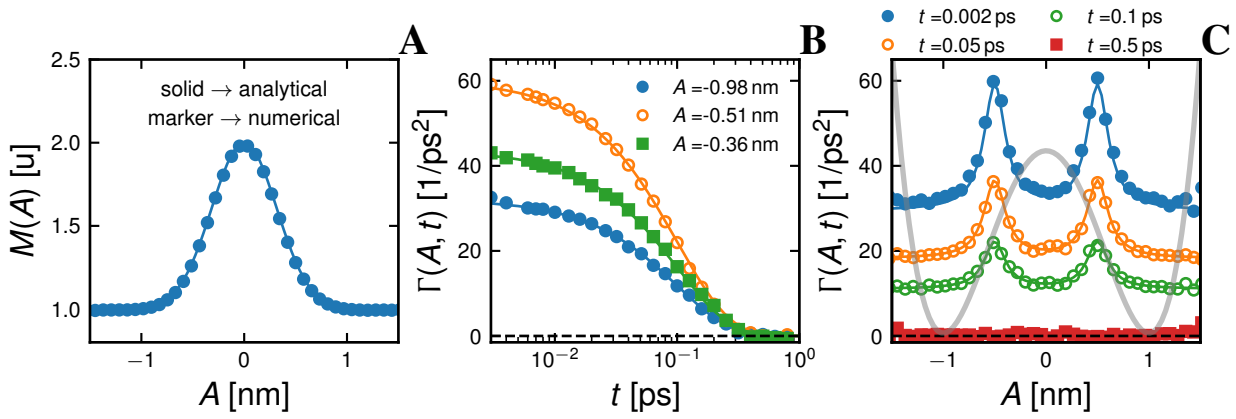

Figure 1. Comparison of the numerically extracted GLE parameters (markers) with the input values (solid lines). In **A**, we show the position dependent mass $M(A)$, where we compare the numerically computed conditional average in Eq. (3.10b) (markers) with the input function in Eq. (3.21) (solid line). In **B** and **C**, we compare the numerically extracted memory kernel defined in Eq. (2.14c) (markers) with the input memory kernel given in Eq. (3.13c) and Eq. (3.22) (solid lines). In **B**, $\Gamma(A,t)$ is shown as a function of time at different positions A, and in **C**, as a function of the position A at different times t. We show the shape of the PMF $U(A)$ in the background in **C** as a thick gray line. The underlying trajectory was generated via simulations of Eq. (3.5) with U given in Eq. (3.20) and $\gamma_{21}(A)$ given by Eq. (3.22). The memory function $\Gamma(A,t)$ is extracted using Eq. (2.15) (cf. ref. [19]).

how to choose the parameters of Eq. (3.3) in order to simulate the GLE in Eq. (3.1). Self-consistency then means that, after performing computer simulations of the system in Eq. (3.3) and numerically extracting GLE parameters from the simulated trajectory using the same method employed to estimate Γ_0 and τ from data, one obtains values of Γ_0 and τ that are identical to the values used in the simulations. This means that the numerical extraction of GLE parameters and the simulation procedure are consistent.

3.2. Markovian embedding

We next show that the following system of Markovian Langevin equations

$$\dot{x}_t = v_t, \tag{3.5a}$$

$$\dot{v}_t = -\frac{1}{M(x_t)}\left(U'(x_t) + \frac{k_B T}{2}\frac{M'(x_t)}{M(x_t)} + \frac{M'(x_t)}{2}v_t^2 - \sum_{n=1}^{N+1}\gamma_{1n}\,\nu_n(t) + \sum_{n=1}^{2N}\sigma_{1n}(x_t)\,\eta_n(t)\right), \tag{3.5b}$$

$$\dot{u}_n(t) = \frac{1}{m_n}\left(-\sum_{j=1}^{N+1}\gamma_{n+1,j}(x_t)\,\nu_j(t) + \sum_{j=1}^{2N}\sigma_{n+1,j}(x_t)\,\eta_j(t)\right), \qquad \text{for } n = 1,2,\ldots,N \tag{3.5c}$$

$$\mathbb{E}[\eta_i(t)] = 0, \quad \mathbb{E}[\eta_i(t)\eta_j(t')] = \delta_{ij}\delta(t-t') \tag{3.5d}$$

can be used to perform a self-consistent Markovian embedding of the GLE in Eq. (2.14). In Eq. (3.5), we introduce a velocity vector $\boldsymbol{\nu}(t) = (v_t, u_1(t), u_2(t), \ldots, u_N(t))^T \in \mathbb{R}^{N+1}$ and the white noise

vector $\boldsymbol{\eta}(t) \in \mathbb{R}^{2N}$. The $u_n(t)$ denote the N auxiliary velocity variables. The friction matrix $\hat{\boldsymbol{\gamma}} \in \mathbb{R}^{(N+1)\times(N+1)}$ is only nonzero in the first row, the first column and in the diagonal, i.e. it is given by

$$\hat{\boldsymbol{\gamma}}(x_t) = \begin{pmatrix} \gamma_{11}(x_t) & \gamma_{12}(x_t) & \gamma_{13}(x_t) & \cdots \\ \gamma_{21}(x_t) & \gamma_{22} & 0 & \\ \gamma_{31}(x_t) & 0 & \gamma_{33} & \\ \vdots & & & \ddots \end{pmatrix} = \begin{pmatrix} M(x_t)\sum_{n=1}^{N} g_n & M(x_t)h_1 & M(x_t)h_2 & \cdots \\ \gamma_{21}(x_t) & \gamma_{22} & 0 & \\ \gamma_{31}(x_t) & 0 & \gamma_{33} & \\ \vdots & & & \ddots \end{pmatrix}. \tag{3.6}$$

The multiplicative noise matrix $\hat{\boldsymbol{\sigma}}(x_t) \in \mathbb{R}^{(N+1)\times 2N}$ is given by

$$\hat{\boldsymbol{\sigma}}(x_t) = \begin{pmatrix} s_{11}(x_t) & 0 & s_{21}(x_t) & 0 & s_{31}(x_t) & 0 & \cdots \\ s_{12}(x_t) & s_{13}(x_t) & 0 & 0 & 0 & 0 & \\ 0 & 0 & s_{22}(x_t) & s_{23}(x_t) & 0 & 0 & \\ 0 & 0 & 0 & 0 & s_{32}(x_t) & s_{33}(x_t) & \cdots \\ \vdots & & & & & \vdots & \end{pmatrix}. \tag{3.7}$$

If the system in Eq. (3.5) fulfills the following fluctuation-dissipation relation [38]

$$\left(\hat{\boldsymbol{\gamma}}(x_t) + \hat{\boldsymbol{\gamma}}^T(x_t)\right)/\beta = \hat{\boldsymbol{\sigma}}(x_t) \cdot \hat{\boldsymbol{\sigma}}^T(x_t), \tag{3.8}$$

it has the stationary probability distribution

$$\rho_{\mathrm{st}}(x, v, \mathbf{u}) \propto \sqrt{M(x)} e^{-\beta U(x)} e^{-\beta \frac{M(x)}{2} v^2} e^{-\beta \sum_n \frac{m_n}{2}(u_n)^2}, \tag{3.9}$$

with the desired properties

$$U(x) = -k_B T \ln \rho_{\mathrm{st}}(x), \tag{3.10a}$$

$$\langle v^2 \rangle_x = \frac{k_B T}{M(x)}, \tag{3.10b}$$

where $\rho_{\mathrm{st}}(x) = \int \mathrm{d}v \int \mathrm{d}^N u\, \rho_{\mathrm{st}}(x, v, \mathbf{u})$ is the marginal distribution in x. The fluctuation-dissipation in Eq. (3.8) holds when the entries s_{ij} of the multiplicative noise matrix $\hat{\boldsymbol{\sigma}}(x_t)$ are given by

$$2\frac{g_n M(x_t)}{\beta} = s_{n1}^2(x_t) \qquad \Rightarrow \qquad s_{n1}(x_t) = \sqrt{2k_B T g_n M(x_t)}, \tag{3.11a}$$

$$\frac{h_n M(x_t) + \gamma_{n+1,1}}{\beta} = s_{n1}(x_t) s_{n2}(x_t) \qquad \Rightarrow \qquad s_{n2}(x_t) = k_B T \frac{h_n M(x_t) + \gamma_{n+1,1}}{s_{n1}(x_t)}, \tag{3.11b}$$

$$2\frac{\gamma_{n+1,n+1}}{\beta} = s_{n2}^2(x_t) + s_{n3}^2(x_t) \qquad \Rightarrow \qquad s_{n3}(x_t) = \sqrt{2k_B T \gamma_{n+1,n+1} - s_{n2}^2(x_t)} \tag{3.11c}$$

where g_n and h_n are defined in Eq. (3.6). In order to get finite, real valued multiplicative noise factors, Eq. (3.11) requires the following inequalities to hold

$$g_n > 0, \tag{3.12a}$$

$$4\gamma_{n+1,n+1}\, g_n M(x_t) \geq \left(h_n M(x_t) + \gamma_{n+1,1}\right)^2, \tag{3.12b}$$

for all $n = 1, 2, \ldots, N$. Eq. (3.12) puts a lower bound on each g_n for given $M(x_t), h_n, \gamma_{n+1,1}(x_t)$ and $\gamma_{n+1,n+1}$. Consequently, the presence of a delta contribution in the memory kernel is required. Solving Eq. (3.5c) for $u_n(t)$ and inserting the result into Eq. (3.5b) yields the GLE

$$\dot{v}_t = -\frac{1}{M(x_t)}\frac{\mathrm{d}\tilde{U}(x_t, v_t)}{\mathrm{d}x_t} - \int_0^t \mathrm{d}s\, \Gamma(x_s, t-s)v_s + \xi(t), \tag{3.13a}$$

with

$$\tilde{U}(x, v) = U(x) + \frac{M(x)}{2}v^2 + k_B T \ln\sqrt{M(x)}, \tag{3.13b}$$

$$\Gamma(x_s, t-s) = \sum_{n=1}^{N}\left(g_n\delta(t-s) - h_n e^{-\frac{\gamma_{n+1,n+1}}{m_n}(t-s)}\frac{\gamma_{n+1,1}(x_s)}{m_n}\right), \tag{3.13c}$$

$$\xi(t) = \sum_{n=1}^{N}\left(-\frac{h_n}{m_n}e^{-\frac{\gamma_{n+1,n+1}}{m_n}t}u_n(0) + \sum_{j=1}^{2N}\left[\sigma_{nj}(x_t)\eta_j(t) - \int_0^t \mathrm{d}s\,\frac{h_n}{m_n}e^{-\frac{\gamma_{n+1,n+1}}{m_n}(t-s)}\sigma_{n+1,j}(x_s)\eta_j(s)\right]\right). \tag{3.13d}$$

To show that the system of Markovian Langevin equations in Eq. (3.5) can be used to perform a self-consistent Markovian embdedding of the GLE in Eq. (2.14) in combination with the extraction scheme in Eq. (2.15), we consider the mean dynamics of v_t in Eq. (3.5). The mean dynamics can be obtained by writing Eq.(3.5) as a general Ito diffusion process [37]

$$d\zeta_t = a(\zeta_t)\,\mathrm{d}t + b(\zeta_t)\,\mathrm{d}W_t, \tag{3.14}$$

where the variables $x_t, v_t, u_n(t)$ are components of the state vector $\zeta_t = (x_t, v_t, u_1(t), u_2(t), \ldots, u_N(t)) \in \mathbb{R}^{N+2}$ and $\mathrm{d}W_t$ is the increment of a $2N+1$ dimensional Wiener process. Ito's lemma gives an equation for the differential $\mathrm{d}f(\zeta_t)$ of a function $f(\zeta_t)$, e.g., the chain rule for an Ito diffusion process [37]. Averaging the differential equation for $\mathrm{d}f(\zeta_t)$ over the noise gives the mean dynamics. By setting $f(\zeta_t) = v_t$, one obtains the mean dynamics of v_t in Eq. (3.5)

$$\dot{v}_t = L^{\dagger}_{\mathrm{FP}} v_t, \tag{3.15}$$

where $L^{\dagger}_{\mathrm{FP}}$ is the infinitesimal generator of the system of stochastic differential equations in Eq. (3.5) [38]

$$\begin{aligned} L^{\dagger}_{\mathrm{FP}} = {} & v\frac{\partial}{\partial x} - \left(\frac{1}{M(x)}\frac{\mathrm{d}\tilde{U}(x, v)}{\mathrm{d}x} + \sum_{n=1}^{N}(g_n v + h_n u_n)\right)\frac{\partial}{\partial v} \\ & - \sum_{n=1}^{N}\frac{1}{m_n}\left(\gamma_{n+1,1}(x)v + \gamma_{n+1,n+1}u_n\right)\frac{\partial}{\partial u_n} \\ & + \frac{1}{2}\sum_{i,j=1}^{N+1}\left(\hat{\boldsymbol{\sigma}}(x)\cdot\hat{\boldsymbol{\sigma}}^T(x)\right)_{ij}\frac{\partial^2}{\partial\nu_i\partial\nu_j}. \end{aligned} \tag{3.16}$$

The L_2-adjoint of $L_{\mathrm{FP}}^\dagger$ is the Fokker-Planck operator, i.e. $L_{\mathrm{FP}}\rho_{st}(x,v,\mathbf{u})=0$, where the stationary distribution is given in Eq. (3.9). Starting from Eq. (3.15), we can derive the GLE using the projection operators $\mathcal{P}_D$ and $\mathcal{P}_L$ in Eq. (2.12) and Eq. (2.13), respectively. The inner product in Eq. (2.2) is obtained by replacing ρ_{eq} by the stationary distribution in Eq. (3.9). First, we calculate the Markovian contribution generated by the projection. According to Eq. (2.10) and the adjoint Fokker-Planck operator $L_{\mathrm{FP}}^\dagger$ in Eq. (3.16), the Markovian contribution is given by

$$e^{tL_{\mathrm{FP}}^\dagger}\mathcal{P}_L L_{\mathrm{FP}}^\dagger v = -\frac{1}{M(x)}\frac{\mathrm{d}\tilde{U}(x_t,v_t)}{\mathrm{d}x_t} - \sum_{n=1}^{N} g_n v_t. \tag{3.17}$$

Next, we compute the random force term using Eq. (2.10b)

$$F_R(t) = e^{t\mathcal{Q}_D L_{\mathrm{FP}}^\dagger}\mathcal{Q}_L L_{\mathrm{FP}}^\dagger v = \sum_{n=0}^{\infty}\frac{t^n}{n!}(\mathcal{Q}_D L_{\mathrm{FP}}^\dagger)^n \mathcal{Q}_L L_{\mathrm{FP}}^\dagger v = -\sum_{n=1}^{N} h_n e^{-\frac{\gamma_{n+1,n+1}}{m_n}t}u_n(0), \tag{3.18}$$

from which we obtain

$$\int_0^t \mathrm{d}s\, e^{(t-s)L_{\mathrm{FP}}^\dagger}\mathcal{P}_D L_{\mathrm{FP}}^\dagger F_R(s) = -\int_0^t \mathrm{d}s \sum_{n=1}^{N} h_n e^{-\frac{\gamma_{n+1,n+1}}{m_n}t}\frac{\gamma_{n+1,1}(x_{t-s})}{m_n}v_{t-s}. \tag{3.19}$$

The results in Eq. (3.17) and Eq. (3.19) coincide with the deterministic part of the GLE in Eq. (3.13). Note that Eq. (3.18) reproduces the noise term in Eq. (3.13d) averaged over the noise terms η_j. This means that we recover the GLE in Eq. (3.13), when averaged over the white noise $\boldsymbol{\eta}(t)$. Thus, the memory kernel $\Gamma(A,t)$, obtained from the Markovian embedding in Eq. (3.5) by applying the projection operators in Eq. (2.12) and Eq. (2.13), can be computed in closed-form and is equal to the one in Eq. (3.13c), which was obtained by solving the Langevin equation in Eq. (3.5c).

We numerically demonstrate the Markovian embedding of a nonlinear GLE with position dependent mass in Figure. 1. Here, we take $k_BT = 2.494$ kJ/mol, i.e. we use molecular dynamics (MD) units. Based on Eq. (3.5) and the relations in Eq. (3.11), we generate a trajectory x_t in a double well potential

$$U(x) = U_0(x^2-1)^2, \tag{3.20}$$

with $U_0 = 2\,k_BT$. The position dependent mass is taken to be

$$M(x) = M_0(1+e^{-5x^2}), \tag{3.21}$$

with $M_0 = 1$ u, which is shown as a solid line in Figure 1A. We simulate $N=2$ auxiliary variables with equal masses $m_n = 1$ u. The friction constants are set to $g_n = 1\ \mathrm{ps}^{-1}$, $h_n = -5\ \mathrm{ps}^{-1}$ and $\gamma_{n+1,n+1} = 10$ u/ps for $n=1,2$ and for the friction profile, we take

$$\gamma_{n+1,1}(x) = \frac{\gamma_0}{1+(\frac{x-x_n}{l_n})^2}, \tag{3.22}$$

with $\gamma_0 = 3$ u/ps, $l_n = 0.125$ nm and the values $x_n = \pm 0.5$ nm for the two auxiliary variables. In other words, we simulate the case where the friction kernel increases at the inflection points of the potential. Such a friction behavior is motivated by our numerical results for the memory function of the dihedral angle in butane from fully atomistic MD simulations [19]. In Figure 1, we compare the input functions given in Eq. (3.21) and Eq. (3.13c) (solid lines) with the numerically extracted ones (markers). The position dependent mass is numerically computed from the simulated trajectories using Eq. (3.10b), the friction kernel is numerically computed using the extraction scheme in Eq. (2.15). In Figure 1, we observe perfect agreement between the input and extracted functions. This constitutes a numerical validation of the embedding method and the extraction/simulation techniques used by us.

4. Conclusion

We introduce a method to simulate a generalized Langevin equation with position-dependent mass and friction functions by Markovian embedding. Such GLEs were numerically extracted in ref. [19] from molecular dynamics simulation trajectories of the dihedral angle of butane in water. For the Markovian embedding, we introduce a projection operator that allows for a self-consistent extraction/simulation procedure. The method we introduce in this paper will be useful for simulating general non-Markovian systems. In future work, it will be interesting to study the relative effects of position-dependent mass and memory on the kinetics of such systems.

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