Stochastic geometric integration

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Woudschoten Conference, 7th October 2016

Plan of the talk

- Introduction
- Stochastic Hamiltonian systems and sympletic integrators
- Intro to molecular dynamics
- Langevin thermostats for Rigid Body Dynamics
- Quasi-symplectic integrators for Langevin equation
- Geometric integrators for Langevin thermostats for Rigid Body Dynamics
- Gradient thermostats for Rigid Body Dynamics and Geometric integrator
- Geometric integrators for stochastic Landau-Lifshitz equation
- Numerical experiments for Rigid Body Dynamics
- Langevin thermostat for systems with hydrodynamic interactions
- Conclusions

Introduction

Hamiltonian $H(p, r)$

$$
\begin{aligned}
\dot{P} &= \frac{\partial H}{\partial r}, \quad P(0) = p, \\
\dot{R} &= -\frac{\partial H}{\partial p}, \quad R(0) = r
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The map $(p, r) \to (P(t; p, r), R(t; p, r))$ preserves symplectic structure:

$$dP \wedge dR = dp \wedge dr$$

The sum of the oriented areas of projections of a two-dimensional surface onto the coordinate planes (p^1, r^1), ..., (p^n, r^n) is an integral invariant.

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A method for (2) based on the one-step approximation

$$\bar{P} = \bar{P}(t + h; t, p, r), \quad \bar{R} = \bar{R}(t + h; t, p, r)$$

preserves symplectic structure if $d\bar{P} \wedge d\bar{R} = dp \wedge dr$.
[Hairer, Lubich, Wanner; Springer, 2002]

Introduction: example of symplectic integrator

Let $H(p, r)$ be a separable Hamiltonian:

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$$\begin{aligned} \frac{d\mathbf{R}}{dt} &= \frac{\mathbf{P}}{m}, \quad \mathbf{R}(0) = \mathbf{r}, \\ \frac{d\mathbf{P}}{dt} &= \mathbf{f}(\mathbf{R}), \quad \mathbf{P}(0) = \mathbf{p}, \end{aligned} \tag{1}$$

where $\mathbf{f}(\mathbf{r}) = -\nabla_{\mathbf{r}} U(\mathbf{r})$.

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Example of splitting:

$$1/2 \text{ step } \frac{d\mathbf{P}}{dt} = \mathbf{f}(\mathbf{R}) + \text{full step of } \frac{d\mathbf{R}}{dt} = \frac{\mathbf{P}}{m} + 1/2 \text{ step } \frac{d\mathbf{P}}{dt} = \mathbf{f}(\mathbf{R})$$

Introduction: example of symplectic integrator

(the Störmer-Verlet scheme; partitioned Runge-Kutta methods)

$$\begin{aligned}
\mathcal{P}_{1,k} &= \mathbf{P}_k + \frac{h}{2}\mathbf{f}(\mathbf{R}_k), \\
\mathbf{R}_{k+1} &= \mathbf{R}_k + \frac{h}{m}\mathcal{P}_{1,k}, \\
\mathbf{P}_{k+1} &= \mathcal{P}_{1,k} + \frac{h}{2}\mathbf{f}(\mathbf{R}_{k+1})
\end{aligned}$$

symplectic, 2nd order, one evaluation of force per step
[Hairer, Lubich, Wanner; Springer, 2002]

Stochastic Hamiltonian systems

Stochastic Hamiltonian system:

$$dP = f(t,P,Q)dt + \sum_{r=1}^{m} \sigma_r(t,P,Q) \circ dw_r(t), \;\; P(t_0) = p, \qquad (2)$$

$$dQ = g(t,P,Q)dt + \sum_{r=1}^{m} \gamma_r(t,P,Q) \circ dw_r(t), \;\; Q(t_0) = q,$$

$$f^i = -\partial H/\partial q^i, \quad g^i = \partial H/\partial p^i, \qquad (3)$$

$$\sigma_r^i = -\partial H_r/\partial q^i, \quad \gamma_r^i = \partial H_r/\partial p^i, \quad i = 1,\dots,n, \quad r = 1,\dots,m.$$

The phase flow $(p,q) \mapsto (P,Q)$ of (2) preserves symplectic structure:

$$dP \wedge dQ = dp \wedge dq, \qquad (4)$$

where

$$\omega^2 = dp \wedge dq = dp^1 \wedge dq^1 + \dots + dp^n \wedge dq^n \qquad (5)$$

is the differential 2-form.

Bismut 1981; Milstein, Repin&T. SINUM 2002

Symplectic integrators

A method for (2) based on the one-step approximation

$$\bar{P} = \bar{P}(t+h;t,p,q), \quad \bar{Q} = \bar{Q}(t+h;t,p,q)$$

preserves symplectic structure if

$$d\bar{P} \wedge d\bar{Q} = dp \wedge dq \,. \tag{6}$$

Milstein, Repin&T. SINUM 2002; Milstein&T IMA JNA 2003; Milstein&T, Springer 2004

Symplectic integrators

Kubo oscillator [Kubo, Toda, Hashitsume, Springer 1985]:

$$
\begin{aligned}
dX^1 &= -aX^2dt - \sigma X^2 \circ dw(t)\,, \quad X^1(0) = x^1, \\
dX^2 &= aX^1dt + \sigma X^1 \circ dw(t)\,, \quad X^2(0) = x^2.
\end{aligned} \tag{7}
$$

$$
\mathcal{H}(X^1(t), X^2(t)) = \mathcal{H}(x^1, x^2) = \left(x^1\right)^2 + \left(x^2\right)^2 \quad \text{for } t \geq 0.
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$$\rho(x) \propto \exp(-\beta H(x)),$$

where $\beta = 1/(k_B T) > 0$ is an inverse temperature.

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Two computational tasks

- nondynamic quantities
- dynamic quantities

Milstein&T. *Physica D* 2007

Rigid Body Dynamics

Consider a system of n rigid three-dimensional molecules described by the center-of-mass coordinates $\mathbf{r} = ({r^1}^{\mathsf{T}}, \ldots, {r^n}^{\mathsf{T}})^{\mathsf{T}} \in \mathbb{R}^{3n}$, $r^j = (r^j_1, r^j_2, r^j_3)^{\mathsf{T}} \in \mathbb{R}^3$, and the rotational coordinates in the quaternion representation $\mathbf{q} = ({q^1}^{\mathsf{T}}, \ldots, {q^n}^{\mathsf{T}})^{\mathsf{T}} \in \mathbb{R}^{4n}$, $q^j = (q^j_0, q^j_1, q^j_2, q^j_3)^{\mathsf{T}} \in \mathbb{R}^4$, such that $|q^j| = 1$.

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$$H(\mathbf{r}, \mathbf{p}, \mathbf{q}, \boldsymbol{\pi}) = \frac{\mathbf{p}^\mathsf{T}\mathbf{p}}{2m} + \sum_{j=1}^{n} \sum_{k=1}^{3} V_k(q^j, \pi^j) + U(\mathbf{r}, \mathbf{q}), \tag{8}$$

where $\mathbf{p} = (p^{1^\mathsf{T}}, \dots, p^{n^\mathsf{T}})^\mathsf{T} \in \mathbb{R}^{3n}$, $p^j = (p^j_1, p^j_2, p^j_3)^\mathsf{T} \in \mathbb{R}^3$, are the center-of-mass momenta conjugate to $\mathbf{r}$; $\boldsymbol{\pi} = (\pi^{1^\mathsf{T}}, \dots, \pi^{n^\mathsf{T}})^\mathsf{T} \in \mathbb{R}^{4n}$, $\pi^j = (\pi^j_0, \pi^j_1, \pi^j_2, \pi^j_3)^\mathsf{T} \in \mathbb{R}^4$, are the angular momenta conjugate to $\mathbf{q}$;

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$$V_l(q, \pi) = \frac{1}{8I_l} \left[\pi^\mathsf{T} S_l q\right]^2, \quad q, \pi \in \mathbb{R}^4, \quad l = 1, 2, 3, \tag{9}$$

I_l – the principal moments of inertia and the constant 4-by-4 matrices S_l :

$$\begin{aligned} S_1 q &= (-q_1, q_0, q_3, -q_2)^\mathsf{T}, \; S_2 q = (-q_2, -q_3, q_0, q_1)^\mathsf{T}, \\ S_3 q &= (-q_3, q_2, -q_1, q_0)^\mathsf{T}. \end{aligned}$$

$$
\begin{aligned}
S_1 &= \begin{bmatrix} 0 & -1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & -1 & 0 \end{bmatrix}, \; S_2 = \begin{bmatrix} 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{bmatrix}, \\
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Also introduce $S_0 = \mathrm{diag}(1,1,1,1)$, $D = \mathrm{diag}(0, 1/I_1, 1/I_2, 1/I_3)$, and

$$
S(q) = [S_0 q, S_1 q, S_2 q, S_3 q] = \begin{bmatrix} q_0 & -q_1 & -q_2 & -q_3 \\ q_1 & q_0 & -q_3 & q_2 \\ q_2 & q_3 & q_0 & -q_1 \\ q_3 & -q_2 & q_1 & q_0 \end{bmatrix}.
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The rotational kinetic energy of a molecule:

$$\sum_{l=1}^{3} V_l(q, \pi) = \frac{1}{8} \pi^{\mathsf{T}} S(q) D S^{\mathsf{T}}(q) \pi \,.$$

Rigid Body Dynamics

We assume that $U(\mathbf{r}, \mathbf{q})$ is a sufficiently smooth function. Let $f^j(\mathbf{r}, \mathbf{q}) = -\nabla_{r^j} U(\mathbf{r}, \mathbf{q}) \in \mathbb{R}^3$, the net force acting on molecule j, and $F^j(\mathbf{r}, \mathbf{q}) = -\tilde{\nabla}_{q^j} U(\mathbf{r}, \mathbf{q}) \in T_{q^j}\mathbb{S}^3$, which is the rotational force. Note that, while ∇_{r^j} is the gradient in the Cartesian coordinates in $\mathbb{R}^3$, $\tilde{\nabla}_{q^j}$ is the directional derivative tangent to the three dimensional sphere $\mathbb{S}^3$ implying that

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We note

$$\begin{aligned} \sum_{l=1}^{3} \nabla_{\pi} V_l(q,\pi) &= \frac{1}{4} \sum_{l=1}^{3} \frac{1}{I_l} S_l q \left[S_l q\right]^{\mathsf{T}} \pi \qquad (11) \\ &= \frac{1}{4} S(q) D S^{\mathsf{T}}(q) \pi, \\ \sum_{l=1}^{3} \nabla_{q} V_l(q,\pi) &= -\frac{1}{4} \sum_{l=1}^{3} \frac{1}{I_l} \left[\pi^{\mathsf{T}} S_l q\right] S_l \pi. \end{aligned}$$

Rigid Body Dynamics

The Hamilton equations of motion are

$$\begin{aligned}
\frac{dR^j}{dt} &= \frac{P^j}{m}, \quad R^j(0) = r^j, &\quad (12)\\
\frac{dP^j}{dt} &= f^j(\mathbf{R}, \mathbf{Q}), \quad P^j(0) = p^j, \\
\frac{dQ^j}{dt} &= \frac{1}{4} S(Q^j) D S^{\mathsf{T}}(Q^j) \Pi^j, \ Q^j(0) = q^j, \ |q^j| = 1, \\
\frac{d\Pi^j}{dt} &= \frac{1}{4} \sum_{l=1}^{3} \frac{1}{I_l} \left(\Pi^{j\,\mathsf{T}} S_l Q^j \right) S_l \Pi^j + F^j(\mathbf{R}, \mathbf{Q}), \ \Pi^j(0) = \pi^j, \quad q^{j\,\mathsf{T}} \pi^j = 0, \\
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We have

$$
|Q^j(t)| = 1\,, \quad j = 1,\ldots,n\,, \quad \text{for } t \geq 0. \tag{13}
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i.e. $\Pi^j(t) \in T_{q^j}\mathbb{S}^3$

Symplectic integrator for (12) in [Miller III et al *J. Chem. Phys.*, 2002]

Symplectic integrator for rigid bodies

- 1/2 step $\frac{d\mathbf{P}}{dt} = \mathbf{f}(\mathbf{R}, \mathbf{Q})$ $+$1/2 step of $\dot{\Pi}^j = F^j(\mathbf{R}, \mathbf{Q})$
  $+$full step of $\frac{d\mathbf{R}}{dt} = \frac{\mathbf{P}}{m}$

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- full step of rotation, i.e. of

$$\frac{dQ^j}{dt} = \frac{1}{4} S(Q^j) D S^{\mathsf{T}}(Q^j) \Pi^j, \; \frac{d\Pi^j}{dt} = \frac{1}{4} \sum_{l=1}^{3} \frac{1}{I_l} \left(\Pi^{j\,\mathsf{T}} S_l Q^j \right) S_l \Pi^j,$$

  with 2nd order accuracy and so that $|Q^j(t)| = 1$ and
  $Q^{j\,\mathsf{T}}(t) \Pi^j(t) = 0$;

Symplectic integrator for rigid bodies

- 1/2 step $\dfrac{d\mathbf{P}}{dt} = \mathbf{f}(\mathbf{R},\mathbf{Q})$ +1/2 step of $\dot{\Pi}^j = F^j(\mathbf{R},\mathbf{Q})$
  +full step of $\dfrac{d\mathbf{R}}{dt} = \dfrac{\mathbf{P}}{m}$
- full step of rotation, i.e. of

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  with 2nd order accuracy and so that $|Q^j(t)| = 1$ and $Q^{j\,\mathsf{T}}(t)\Pi^j(t) = 0$;
- 1/2 step of $\dot{\Pi}^j = F^j(\mathbf{R},\mathbf{Q})$ +1/2 step $\dfrac{d\mathbf{P}}{dt} = \mathbf{f}(\mathbf{R},\mathbf{Q})$

Symplectic integrator for rigid bodies

For the 'rotation' step, we use a composite map

$$\Psi_t = \Psi_{t/2,3} \circ \Psi_{t/2,2} \circ \Psi_{t,1} \circ \Psi_{t/2,2} \circ \Psi_{t/2,3} \,, \tag{15}$$

where "$\circ$" denotes function composition, i.e., $(g \circ f)(x) = g(f(x))$ and the mapping $\Psi_{t,l}(q,\pi) : (q,\pi) \mapsto (\mathcal{Q},\Pi)$ is defined by

$$\begin{aligned} \mathcal{Q} &= \cos(\chi_l t) q + \sin(\chi_l t) S_l q \,, \\ \Pi &= \cos(\chi_l t) \pi + \sin(\chi_l t) S_l \pi \,, \end{aligned} \tag{16}$$

with

$$\chi_l = \frac{1}{4 I_l} \pi^{\mathsf{T}} S_l q \,.$$

[Miller III et al *J. Chem. Phys.*, 2002]

Symplectic integrator for rigid bodies

$$\mathbf{P}_0 = \mathbf{p},\ \mathbf{R}_0 = \mathbf{r},\ \mathbf{Q}_0 = \mathbf{q},\ |q^j| = 1,\ j = 1, \ldots, n,\ \ \Pi_0 = \boldsymbol{\pi},\ \mathbf{q}^{\mathsf{T}}\boldsymbol{\pi} = 0,$$

$$\begin{aligned}
\mathcal{P}_{1,k} &= \mathbf{P}_k + \frac{h}{2}\mathbf{f}(\mathbf{R}_k, \mathbf{Q}_k), \\
\Pi^j_{1,k} &= \Pi^j_{1,k} + \frac{h}{2}F^j(\mathbf{R}_k, \mathbf{Q}_k), \quad j = 1, \ldots, n, \\
\mathbf{R}_{k+1} &= \mathbf{R}_k + \frac{h}{m}\mathcal{P}_{1,k}, \\
(Q^j_{k+1}, \Pi^j_{2,k}) &= \Psi_h(Q^j_k, \Pi^j_{1,k}), \\
\Pi^j_{k+1} &= \Pi^j_{2,k} + \frac{h}{2}F^j(\mathbf{R}_{k+1}, \mathbf{Q}_{k+1}),\ j = 1, \ldots, n, \\
\mathbf{P}_{k+1} &= \mathcal{P}_{1,k} + \frac{h}{2}\mathbf{f}(\mathbf{R}_{k+1}, \mathbf{Q}_{k+1}), \\
k &= 0, \ldots, N-1
\end{aligned}$$

[Miller III et al *J. Chem. Phys.*, 2002]

Thermostats

Thermostats

- Deterministic
- Stochastic

Thermostats

- Deterministic
- Stochastic

Now we derive stochastic thermostats for the molecular system (12), which preserve $|Q^j(t)| = 1$ and $Q^{j\,\mathsf{T}}(t)\Pi^j(t) = 0$. They take the form of ergodic stochastic differential equations (SDEs) with the Gibbsian (canonical ensemble) invariant measure possessing the density

$$\rho(\mathbf{r}, \mathbf{p}, \mathbf{q}, \boldsymbol{\pi}) \propto \exp(-\beta H(\mathbf{r}, \mathbf{p}, \mathbf{q}, \boldsymbol{\pi})), \tag{17}$$

where $\beta = 1/(k_B T) > 0$ is an inverse temperature.

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Langevin thermostat for Rigid Body Dynamics

$$
\begin{aligned}
dR^j &= \frac{P^j}{m}dt, \quad R^j(0) = r^j, & (18)\\
dP^j &= f^j(\mathbf{R},\mathbf{Q})dt - \gamma P^j dt + \sqrt{\frac{2m\gamma}{\beta}}dw^j(t), \quad P^j(0) = p^j, \\
dQ^j &= \frac{1}{4}S(Q^j)DS^{\mathsf{T}}(Q^j)\Pi^j dt, \ \ Q^j(0) = q^j, \ |q^j| = 1, & (19)\\
d\Pi^j &= \frac{1}{4}\sum_{l=1}^{3}\frac{1}{I_l}\left(\Pi^{j\,\mathsf{T}}S_l Q^j\right)S_l\Pi^j dt + F^j(\mathbf{R},\mathbf{Q})dt - \Gamma J(Q^j)\Pi^j dt \\
&\quad + \sqrt{\frac{2M\Gamma}{\beta}}\sum_{l=1}^{3}S_l Q^j dW_l^j(t), \quad \Pi^j(0) = \pi^j, \ q^{j\,\mathsf{T}}\pi^j = 0, \ j = 1,\ldots,n,
\end{aligned}
$$

where $(\mathbf{w}^{\mathsf{T}},\mathbf{W}^{\mathsf{T}})^{\mathsf{T}} = (w^{1\,\mathsf{T}},\ldots,w^{n\,\mathsf{T}},W^{1\,\mathsf{T}},\ldots,\ W^{n\,\mathsf{T}})^{\mathsf{T}}$ is a $(3n+3n)$-dimensional standard Wiener process with $w^j = (w_1^j, w_2^j, w_3^j)^{\mathsf{T}}$ and $W^j = (W_1^j, W_2^j, W_3^j)^{\mathsf{T}}$; $\gamma \geq 0$ and $\Gamma \geq 0$ are the friction coefficients for the translational and rotational motions, $\beta = 1/(k_B T) > 0$ and

$$
J(q) = \frac{M}{4}S(q)DS^{\mathsf{T}}(q), \ \ M = \frac{4}{\sum_{l=1}^{3}\frac{1}{I_l}}. \qquad (20)
$$

Langevin thermostat for Rigid Body Dynamics

- The Ito interpretation of the SDEs (18)–(19) coincides with its Stratonovich interpretation.
- The solution of (18)–(19) preserves the quaternion length

$$|Q^j(t)| = 1, \quad j = 1, \ldots, n, \quad \text{for all } t \geq 0. \tag{21}$$

- The solution of (18)–(19) automatically preserves the constraint:

$$Q^{j\,\mathsf{T}}(t)\Pi^j(t) = 0\,, \quad j = 1, \ldots, n\,, \quad \text{for } t \geq 0 \tag{22}$$

- Assume that the solution $X(t) = (\mathbf{R}^{\mathsf{T}}(t),\, \mathbf{P}^{\mathsf{T}}(t), \mathbf{Q}^{\mathsf{T}}(t), \Pi^{\mathsf{T}}(t))^{\mathsf{T}}$ of (18)–(19) is an ergodic process on

$$\begin{aligned}\mathbb{D} \;\; = \;\; & \{x = (\mathbf{r}^{\mathsf{T}}, \mathbf{p}^{\mathsf{T}}, \mathbf{q}^{\mathsf{T}}, \boldsymbol{\pi}^{\mathsf{T}})^{\mathsf{T}} \in \mathbb{R}^{14n} : \\ & \quad |q^j| = 1, \quad q^{j\,\mathsf{T}}\pi^j = 0, \quad j = 1, \ldots, n\}.\end{aligned}$$

  Then it can be shown that the invariant measure of $X(t)$ is Gibbsian with the density $\rho(\mathbf{r}, \mathbf{p}, \mathbf{q}, \boldsymbol{\pi})$ on $\mathbb{D}$:

$$\rho(\mathbf{r}, \mathbf{p}, \mathbf{q}, \boldsymbol{\pi}) \propto \exp(-\beta H(\mathbf{r}, \mathbf{p}, \mathbf{q}, \boldsymbol{\pi})) \tag{23}$$

Langevin equations and quasi-symplectic integrators

$$
\begin{aligned}
dR^j &= \frac{P^j}{m}dt, \quad R^j(0) = r^j, && (9)\\
dP^j &= f^j(\mathbf{R},\mathbf{Q})dt - \gamma P^j dt + \sqrt{\frac{2m\gamma}{\beta}}dw^j(t), \quad P^j(0) = p^j, &&\\
dQ^j &= \frac{1}{4}S(Q^j)DS^{\mathsf{T}}(Q^j)\Pi^j dt, \ Q^j(0) = q^j, \ |q^j| = 1, && (10)\\
d\Pi^j &= \frac{1}{4}\sum_{l=1}^{3}\frac{1}{I_l}\left(\Pi^{j\,\mathsf{T}}S_l Q^j\right)S_l\Pi^j dt + F^j(\mathbf{R},\mathbf{Q})dt - \Gamma J(Q^j)\Pi^j dt &&\\
&\quad + \sqrt{\frac{2M\Gamma}{\beta}}\sum_{l=1}^{3}S_l Q^j dW_l^j(t), \quad \Pi^j(0) = \pi^j, \ q^{j\,\mathsf{T}}\pi^j = 0, \ j = 1,\ldots,n, &&
\end{aligned}
$$

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dQ^j &= \frac{1}{4} S(Q^j) D S^\mathsf{T}(Q^j) \Pi^j dt, \ Q^j(0) = q^j, \ |q^j| = 1, && (10)\\
d\Pi^j &= \frac{1}{4} \sum_{l=1}^{3} \frac{1}{I_l} \left(\Pi^{j\,\mathsf{T}} S_l Q^j \right) S_l \Pi^j dt + F^j(\mathbf{R}, \mathbf{Q})dt - \Gamma J(Q^j) \Pi^j dt \\
&\quad + \sqrt{\frac{2M\Gamma}{\beta}} \sum_{l=1}^{3} S_l Q^j dW_l^j(t), \quad \Pi^j(0) = \pi^j, \ q^{j\,\mathsf{T}} \pi^j = 0, \ j = 1, \ldots, n,
\end{aligned}$$

Let $D_0 \in \mathbb{R}^d$, $d = 14n$, be a domain with finite volume. The transformation
$x = (\mathbf{r}, \mathbf{p}, \mathbf{q}, \boldsymbol{\pi}) \mapsto X(t) = X(t; x) = (\mathbf{R}(t; x), \mathbf{P}(t; x), \mathbf{Q}(t; x), \Pi(t; x))$
maps D_0 into the domain D_t.

$$\begin{aligned} V_t &= \int\limits_{D_t} dX^1 \dots dX^d \qquad (24)\\ &= \int\limits_{D_0} \left| \frac{D(X^1,\dots,X^d)}{D(x^1,\dots,x^d)} \right| dx^1 \dots dx^d. \end{aligned}$$

The Jacobian $\mathbb{J}$ is equal to

$$\mathbb{J} = \frac{D(X^1,\dots,X^d)}{D(x^1,\dots,x^d)} = \exp\left(-n(3\gamma + \Gamma)\cdot t\right). \qquad (25)$$

Quasi-symplectic integrators

It is natural to expect that making use of numerical methods, which are close, in a sense, to symplectic ones, has advantages when applying to stochastic systems close to Hamiltonian ones. In [Milstein&T. *IMA J. Numer. Anal.* 2003 (also Springer 2004)] numerical methods (they are called **quasi-symplectic**) for Langevin equations were proposed, which satisfy the two structural conditions:

Quasi-symplectic integrators

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RL1. *The method applied to Langevin equations degenerates to a symplectic method when the Langevin system degenerates to a Hamiltonian one.*

RL2. *The Jacobian* $\bar{\mathbb{J}} = D\bar{X}/Dx$ *does not depend on* x.

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RL1. *The method applied to Langevin equations degenerates to a symplectic method when the Langevin system degenerates to a Hamiltonian one.*

RL2. *The Jacobian* $\bar{\mathbb{J}} = D\bar{X}/Dx$ *does not depend on* x.

The requirement RL2 is natural since the Jacobian $\mathbb{J}$ of the original system (18)–(19) does not depend on x. RL2 reflects the structural properties of the system which are connected with the law of phase volume contractivity. It is often possible to reach a stronger property consisting in the equality $\bar{\mathbb{J}} = \mathbb{J}$.

Langevin integrators

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For simplicity we use a uniform time discretization of a time interval $[0, T]$ with the step $h = T/N$.

Langevin integrators

Davidchack, Ouldridge&T. *J Chem Phys* 2015

For simplicity we use a uniform time discretization of a time interval $[0, T]$ with the step $h = T/N$.
Goal: to construct integrators

- quasi-symplectic
- preserve $|\bar{Q}^j(t_k)| = 1, \ \ j = 1, \dots, n\,,$ for all $t \geq 0$ automatically
- preserve $\bar{Q}^{j\,\mathsf{T}}(t_k)\bar{\Pi}^j(t_k) = 0\,, \ \ j = 1, \dots, n\,,$ for $t \geq 0$ automatically
- of weak order 2 with one evaluation of force per step

To this end:

- stochastic numerics+splitting techniques [see e.g. Milstein&T, Springer 2004]
- the deterministic symplectic integrator from [Miller III et al *J. Chem. Phys.*, 2002]

‘Langevin A’ integrator

Splitting the Langevin system:

$$
\begin{aligned}
dR^j &= \frac{P^j}{m}dt, \quad R^j(0) = r^j, && (26)\\
dP^j &= f^j(\mathbf{R},\mathbf{Q})dt + \sqrt{\frac{2m\gamma}{\beta}}dw^j(t), \\
dQ^j &= \frac{1}{4}S(Q^j)DS^{\mathsf{T}}(Q^j)\Pi^j dt, && (27)\\
d\Pi^j &= \frac{1}{4}\sum_{l=1}^{3}\frac{1}{I_l}\left(\Pi^{j\,\mathsf{T}}S_l Q^j\right)S_l\Pi^j dt + F^j(\mathbf{R},\mathbf{Q})dt \\
&\quad + \sqrt{\frac{2M\Gamma}{\beta}}\sum_{l=1}^{3}S_l Q^j dW_l^j(t), \; j = 1,\ldots,n,
\end{aligned}
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and the deterministic system of linear differential equations

$$\dot{p} = -\gamma p, \quad \dot{\pi}^j = -\Gamma J(q^j)\pi^j,\ j = 1,\ldots,n\,.$$

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d\Pi^j &= \frac{1}{4}\sum_{l=1}^{3}\frac{1}{I_l}\left(\Pi^{j\,\mathsf{T}}S_lQ^j\right)S_l\Pi^j dt + F^j(\mathbf{R},\mathbf{Q})dt \\
&\quad + \sqrt{\frac{2M\Gamma}{\beta}}\sum_{l=1}^{3}S_lQ^j dW_l^j(t),\ j = 1,\dots,n,
\end{aligned}
$$

and the deterministic system of linear differential equations

$$\dot{p} = -\gamma p, \quad \dot{\pi}^j = -\Gamma J(q^j)\pi^j,\ j = 1,\dots,n\,. \tag{28}$$

1/2 of (28) + step of a method for (26)-(27) + 1/2 of (28)

'Langevin A' integrator

$$\begin{aligned}
\mathbf{P}_0 &= \mathbf{p}, \quad \mathbf{R}_0 = \mathbf{r}, \; \mathbf{Q}_0 = \mathbf{q} \text{ with } |q^j| = 1, \; j = 1, \ldots, n, \\
\Pi_0 &= \boldsymbol{\pi} \text{ with } \mathbf{q}^{\mathsf{T}} \boldsymbol{\pi} = \mathbf{0}, \\
\mathcal{P}_{1,k} &= \mathrm{e}^{-\gamma \frac{h}{2}} \mathbf{P}_k \,, \; \Pi^j_{1,k} = \mathrm{e}^{-\Gamma J(Q^j_k) \frac{h}{2}} \Pi^j_k, \quad j = 1, \ldots, n,
\end{aligned} \tag{29}$$

$$\begin{aligned}
\mathcal{P}_{2,k} &= \mathcal{P}_{1,k} + \frac{h}{2} \mathbf{f}(\mathbf{R}_k, \mathbf{Q}_k) + \frac{\sqrt{h}}{2} \sqrt{\frac{2m\gamma}{\beta}} \boldsymbol{\xi}_k \\
\Pi^j_{2,k} &= \Pi^j_{1,k} + \frac{h}{2} F^j(\mathbf{R}_k, \mathbf{Q}_k) + \frac{\sqrt{h}}{2} \sqrt{\frac{2M\Gamma}{\beta}} \sum_{l=1}^{3} S_l \mathbf{Q}_k \eta_k^{j,l}, \; j = 1, \ldots, n, \\
\mathbf{R}_{k+1} &= \mathbf{R}_k + \frac{h}{m} \mathcal{P}_{2,k}, \\
(Q^j_{k+1}, \Pi^j_{3,k}) &= \Psi_h(Q^j_k, \Pi^j_{2,k}), \quad j = 1, \ldots, n,
\end{aligned}$$

$$\begin{aligned}
\Pi^j_{4,k} &= \Pi^j_{3,k} + \frac{h}{2} F^j(\mathbf{R}_{k+1}, \mathbf{Q}_{k+1}) + \frac{\sqrt{h}}{2} \sqrt{\frac{2M\Gamma}{\beta}} \sum_{l=1}^{3} S_l \mathbf{Q}_{k+1} \eta_k^{j,l}, \; j = 1, \ldots, n, \\
\mathcal{P}_{3,k} &= \mathcal{P}_{2,k} + \frac{h}{2} \mathbf{f}(\mathbf{R}_{k+1}, \mathbf{Q}_{k+1}) + \frac{\sqrt{h}}{2} \sqrt{\frac{2m\gamma}{\beta}} \boldsymbol{\xi}_k, \\
\mathbf{P}_{k+1} &= \mathrm{e}^{-\gamma \frac{h}{2}} \mathcal{P}_{3,k} \,, \; \Pi^j_{k+1} = \mathrm{e}^{-\Gamma J(Q^j_{k+1}) \frac{h}{2}} \; \Pi^j_{4,k}, \; j = 1, \ldots, n, \\
k &= 0, \ldots, N-1,
\end{aligned}$$

‘Langevin A’ integrator

$\xi_k = (\xi_{1,k}, \ldots, \xi_{3n,k})^\mathsf{T}$ and $\eta_k^j = (\eta_{1,k}^j, \ldots, \eta_{3,k}^j)^\mathsf{T}$, $j = 1, \ldots, n$, with their components being i.i.d. with the same law

$$P(\theta = 0) = 2/3, \quad P(\theta = \pm\sqrt{3}) = 1/6. \tag{30}$$

'Langevin A' integrator

$\xi_k = (\xi_{1,k}, \dots, \xi_{3n,k})^\mathsf{T}$ and $\eta_k^j = (\eta_{1,k}^j, \dots, \eta_{3,k}^j)^\mathsf{T}$, $j = 1, \dots, n$, with their components being i.i.d. with the same law

$$P(\theta = 0) = 2/3, \quad P(\theta = \pm\sqrt{3}) = 1/6. \tag{30}$$

Proposition 1. *The numerical scheme* (29)–(30) *for* (18)–(19) *is quasi-symplectic, it preserves the structural properties* (21) *and* (22) *and it is of weak order two.*

'Langevin B' integrator

$$\begin{aligned} d\mathbf{P}_I &= -\gamma \mathbf{P}_I\, dt + \sqrt{\frac{2m\gamma}{\beta}}\, d\mathbf{w}(t), \\ d\Pi_I^j &= -\Gamma J(q)\Pi_I^j dt + \sqrt{\frac{2M\Gamma}{\beta}} \sum_{l=1}^{3} S_l q dW_l^j(t); \end{aligned} \tag{31}$$

$$\begin{aligned} d\mathbf{R}_{II} &= \frac{\mathbf{P}_{II}}{m}\, dt,\ d\mathbf{P}_{II} = \mathbf{f}(\mathbf{R}_{II}, \mathbf{Q}_{II})dt,\ dQ_{II}^j = \frac{1}{4} S(Q_{II}^j) D S^{\mathsf{T}}(Q_{II}^j)\Pi_{II}^j dt\,, \quad (32) \\ d\Pi_{II}^j &= F^j(\mathbf{R}_{II}, \mathbf{Q}_{II})dt + \frac{1}{4}\sum_{l=1}^{3} \frac{1}{I_l}\left[(\Pi_{II}^j)^{\mathsf{T}} S_l Q_{II}^j\right] S_l \Pi_{II}^j dt\,,\ j = 1, \dots, n. \end{aligned}$$

'Langevin B' integrator

$$
\begin{aligned}
d\mathbf{P}_I &= -\gamma \mathbf{P}_I \, dt + \sqrt{\frac{2m\gamma}{\beta}} d\mathbf{w}(t), \\
d\Pi_I^j &= -\Gamma J(q) \Pi_I^j dt + \sqrt{\frac{2M\Gamma}{\beta}} \sum_{l=1}^{3} S_l q dW_l^j(t);
\end{aligned}
\tag{31}
$$

$$
\begin{aligned}
d\mathbf{R}_{II} &= \frac{\mathbf{P}_{II}}{m} \, dt, \;\; d\mathbf{P}_{II} = \mathbf{f}(\mathbf{R}_{II}, \mathbf{Q}_{II}) dt, \;\; dQ_{II}^j = \frac{1}{4} S(Q_{II}^j) D S^{\mathsf{T}}(Q_{II}^j) \Pi_{II}^j dt \,, & (32) \\
d\Pi_{II}^j &= F^j(\mathbf{R}_{II}, \mathbf{Q}_{II}) dt + \frac{1}{4} \sum_{l=1}^{3} \frac{1}{I_l} \left[(\Pi_{II}^j)^{\mathsf{T}} S_l Q_{II}^j \right] S_l \Pi_{II}^j dt \,, \; j = 1, \ldots, n.
\end{aligned}
$$

The SDEs (31) have the exact solution:

$$
\begin{aligned}
\mathbf{P}_I(t) &= \mathbf{P}_I(0) \exp(-\gamma t) + \sqrt{\frac{2m\gamma}{\beta}} \int_0^t \exp(-\gamma(t-s)) d\mathbf{w}(s), & (33) \\
\Pi_I^j(t) &= \exp(-\Gamma J(q) t) \Pi_I^j(0) + \sqrt{\frac{2M\Gamma}{\beta}} \sum_{l=1}^{3} \int_0^t \exp(-\Gamma J(q)(t-s)) dW_l^j(s).
\end{aligned}
$$

'Langevin B' integrator

$$d\mathbf{P}_I = -\gamma \mathbf{P}_I \, dt + \sqrt{\frac{2m\gamma}{\beta}} d\mathbf{w}(t),$$
$$d\Pi_I^j = -\Gamma J(q)\Pi_I^j dt + \sqrt{\frac{2M\Gamma}{\beta}} \sum_{l=1}^{3} S_l q dW_l^j(t); \tag{31}$$

$$\begin{aligned} d\mathbf{R}_{II} &= \frac{\mathbf{P}_{II}}{m}\, dt,\ d\mathbf{P}_{II} = \mathbf{f}(\mathbf{R}_{II}, \mathbf{Q}_{II})dt,\ dQ_{II}^j = \frac{1}{4} S(Q_{II}^j) D S^{\mathsf{T}}(Q_{II}^j)\Pi_{II}^j dt\,, \quad (32) \\ d\Pi_{II}^j &= F^j(\mathbf{R}_{II}, \mathbf{Q}_{II})dt + \frac{1}{4}\sum_{l=1}^{3} \frac{1}{I_l}\left[(\Pi_{II}^j)^{\mathsf{T}} S_l Q_{II}^j\right] S_l \Pi_{II}^j dt\,,\ j = 1, \ldots, n. \end{aligned}$$

The SDEs (31) have the exact solution:

$$\begin{aligned} \mathbf{P}_I(t) &= \mathbf{P}_I(0)\exp(-\gamma t) + \sqrt{\frac{2m\gamma}{\beta}} \int_0^t \exp(-\gamma(t-s))d\mathbf{w}(s), \quad (33) \\ \Pi_I^j(t) &= \exp(-\Gamma J(q)t)\Pi_I^j(0) + \sqrt{\frac{2M\Gamma}{\beta}} \sum_{l=1}^{3} \int_0^t \exp(-\Gamma J(q)(t-s))dW_l^j(s). \end{aligned}$$

1/2 step (33) + step of the symplectic method for (32) + 1/2 step (33).

'Langevin B' integrator

The vectors $\int_0^t e^{-\Gamma J(q)(t-s)} S_l q dW_l^j(s)$ in (33) are Gaussian with zero mean and covariance $C_l(t;q) = \int_0^t e^{-\Gamma J(q)(t-s)} S_l q (S_l q)^\mathsf{T} e^{-\Gamma J(q)(t-s)} ds$.

$$C(t;q) = \sum_{l=1}^{3} C_l(t;q) = \frac{2}{M\Gamma} S(q) \Lambda_C(t;\Gamma) S^\mathsf{T}(q),$$

where

$$\begin{aligned}\Lambda_C(t;\Gamma) =& \mathrm{diag}(0, I_1(1-\exp(-M\Gamma t/(2I_1))), I_2(1-\exp(-M\Gamma t/(2I_2))),\\ & I_3(1-\exp(-M\Gamma t/(2I_3)))).\end{aligned}$$

Let $\sigma(t;q)\sigma^\mathsf{T}(t;q) = C(t;q)$, e.g., $\sigma(t;q)$ with the columns

$$\sigma_l(t;q) = \sqrt{\frac{2}{M\Gamma} I_l \left(1 - \exp(-\frac{M\Gamma t}{2I_l})\right)} S_l q, \;\; l = 1, 2, 3,$$

then $\Pi_l^j(t)$ in (33) can be written as

$$\Pi_l^j(t) = e^{-\Gamma J(q) t} \Pi_l^j(0) + \sqrt{\frac{2M\Gamma}{\beta}} \sum_{l=1}^{3} \sigma_l(t;q) \chi_l^j, \quad \chi_l^j \text{ are i.i.d. } \mathcal{N}(0,1).$$

'Langevin B' integrator

$$\mathbf{P}_0 = \mathbf{p},\ \mathbf{R}_0 = \mathbf{r},\ \mathbf{Q}_0 = \mathbf{q},\ |q^j| = 1,\ j = 1,\ldots,n,\ \ \Pi_0 = \boldsymbol{\pi},\ \mathbf{q}^\mathsf{T}\boldsymbol{\pi} = 0, \tag{34}$$

$$\mathcal{P}_{1,k} = \mathbf{P}_k \mathrm{e}^{-\gamma h/2} + \sqrt{\frac{m}{\beta}(1-\mathrm{e}^{-\gamma h})}\boldsymbol{\xi}_k,$$

$$\Pi^j_{1,k} = \mathrm{e}^{-\Gamma J(Q^j_k)\frac{h}{2}}\Pi^j_k + \sqrt{\frac{4}{\beta}}\sum_{l=1}^{3}\sqrt{I_l\left(1-\mathrm{e}^{-\frac{M\Gamma h}{4I_l}}\right)}S_l Q^j_k \eta^{j,l}_k,\ j = 1,\ldots,n,$$

$$\begin{aligned}
\mathcal{P}_{2,k} &= \mathcal{P}_{1,k} + \frac{h}{2}\mathbf{f}(\mathbf{R}_k,\mathbf{Q}_k), \\
\Pi^j_{2,k} &= \Pi^j_{1,k} + \frac{h}{2}F^j(\mathbf{R}_k,\mathbf{Q}_k), \quad j = 1,\ldots,n, \\
\mathbf{R}_{k+1} &= \mathbf{R}_k + \frac{h}{m}\mathcal{P}_{2,k}, \\
(Q^j_{k+1},\Pi^j_{3,k}) &= \Psi_h(Q^j_k,\Pi^j_{2,k}), \quad \Pi^j_{4,k} = \Pi^j_{3,k} + \frac{h}{2}F^j(\mathbf{R}_{k+1},\mathbf{Q}_{k+1}),\ j = 1,\ldots,n, \\
\mathcal{P}_{3,k} &= \mathcal{P}_{2,k} + \frac{h}{2}\mathbf{f}(\mathbf{R}_{k+1},\mathbf{Q}_{k+1}), \\
\mathbf{P}_{k+1} &= \mathcal{P}_{3,k}\mathrm{e}^{-\gamma h/2} + \sqrt{\frac{m}{\beta}(1-\mathrm{e}^{-\gamma h})}\boldsymbol{\zeta}_k, \\
\Pi^j_{k+1} &= \mathrm{e}^{-\Gamma J(Q^j_{k+1})\frac{h}{2}}\Pi^j_{4,k} + \sqrt{\frac{4}{\beta}}\sum_{l=1}^{3}\sqrt{I_l\left(1-\mathrm{e}^{-\frac{M\Gamma h}{4I_l}}\right)}S_l Q^j_{k+1}\varsigma^{j,l}_k, \\
j &= 1,\ldots,n,\ k = 0,\ldots,N-1,
\end{aligned}$$

'Langevin B' integrator

$\boldsymbol{\xi}_k = (\xi_{1,k}, \ldots, \xi_{3n,k})^T$, $\boldsymbol{\zeta}_k = (\zeta_{1,k}, \ldots, \zeta_{3n,k})^T$, $\eta_k^j = (\eta_{1,k}^j, \ldots, \eta_{3,k}^j)^T$, $j = 1, \ldots, n$, with their components being i.i.d. with the same law (30):

$$P(\theta = 0) = 2/3, \quad P(\theta = \pm\sqrt{3}) = 1/6.$$

Proposition 2. *The numerical scheme* (34), (30) *for* (18)–(19) *is quasi-symplectic, it preserves* (21) *and* (22) *and it is of weak order two.*

'Langevin C' integrator

Based on the same spliting (31) and (32) as Langevin B, i.e., the determinisitic Hamiltonian system + OU.

To construct the method:

- $1/2$ step of the symplectic method for (32)
- step of OU (33)
- $1/2$ step of the symplectic method for (32)

‘Langevin C’ integrator

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Various splittings are compared for a translational Langevin thermostat in [Leimkuhler&Matthews 2013]

'Langevin C' integrator

$$\mathbf{P}_0 = \mathbf{p}, \quad \mathbf{R}_0 = \mathbf{r}, \;\; \mathbf{Q}_0 = \mathbf{q}, \;\; |q^j| = 1, \;\; j = 1, \dots, n, \;\; \Pi_0 = \boldsymbol{\pi}, \quad \mathbf{q}^\mathsf{T}\boldsymbol{\pi} = 0, \tag{35}$$

$$\mathcal{P}_{1,k} = \mathbf{P}_k + \frac{h}{2}\mathbf{f}(\mathbf{R}_k, \mathbf{Q}_k),$$

$$\Pi^j_{1,k} = \Pi^j_k + \frac{h}{2}F^j(\mathbf{R}_k, \mathbf{Q}_k), \quad j = 1, \dots, n,$$

$$R_{1,k} = \mathbf{R}_k + \frac{h}{2m}\mathcal{P}_{1,k},$$

$$(\mathcal{Q}^j_{1,k}, \Pi^j_{2,k}) = \Psi_{h/2}(Q^j_k, \Pi^j_{1,k}), \;\; j = 1, \dots, n,$$

$$\mathcal{P}_{2,k} = \mathcal{P}_{1,k}\mathrm{e}^{-\gamma h} + \sqrt{\frac{m}{\beta}(1 - \mathrm{e}^{-2\gamma h})}\boldsymbol{\xi}_k$$

$$\Pi^j_{3,k} = \mathrm{e}^{-\Gamma J(\mathcal{Q}^j_{1,k})h}\;\Pi^j_{2,k} + \sqrt{\frac{4}{\beta}}\sum_{l=1}^{3}\sqrt{I_l\left(1 - \mathrm{e}^{-\frac{M\Gamma h}{2I_l}}\right)}S_l\mathcal{Q}^j_{1,k}\eta^{j,l}_k, j = 1, \dots, n,$$

$$\begin{aligned}
\mathbf{R}_{k+1} &= R_{1,k} + \frac{h}{2m}\mathcal{P}_{2,k}, \\
(Q^j_{k+1}, \Pi^j_{4,k}) &= \Psi_{h/2}(\mathcal{Q}^j_{1,k}, \Pi^j_{3,k}), \quad j = 1, \dots, n, \\
\mathbf{P}_{k+1} &= \mathcal{P}_{2,k} + \frac{h}{2}\mathbf{f}(\mathbf{R}_{k+1}, \mathbf{Q}_{k+1}), \\
\Pi^j_{k+1} &= \Pi^j_{4,k} + \frac{h}{2}F^j(\mathbf{R}_{k+1}, \mathbf{Q}_{k+1}), \quad j = 1, \dots, n,
\end{aligned}$$

'Langevin C' integrator

where $\boldsymbol{\xi}_k = (\xi_{1,k}, \ldots, \xi_{3n,k})^\mathsf{T}$ and $\eta_k^j = (\eta_{1,k}^j, \ldots, \eta_{3,k}^j)^\mathsf{T}$, $j = 1, \ldots, n$, with their components being i.i.d. random variables with the same law (30).

Proposition 3. *The numerical scheme* (35), (30) *for* (18)–(19) *is quasi-symplectic, it preserves* (21) *and* (22) *and it is of weak order two.*

Included in LAMMPS

The gradient thermostat for rigid body dynamics

It is easy to verify that

$$\int_{\mathbb{D}_{\mathrm{mom}}} \exp(-\beta H(\mathbf{r},\mathbf{p},\mathbf{q},\boldsymbol{\pi}))d\mathbf{p}d\boldsymbol{\pi} \propto \exp(-\beta U(\mathbf{r},\mathbf{q})) =: \tilde{\rho}(\mathbf{r},\mathbf{q}), \quad (36)$$

where $(\mathbf{r}^{\mathsf{T}},\mathbf{q}^{\mathsf{T}})^{\mathsf{T}} \in \mathbb{D}' = \{(\mathbf{r}^{\mathsf{T}},\mathbf{q}^{\mathsf{T}})^{\mathsf{T}} \in \mathbb{R}^{7n} : \ \ |q^j| = 1\}$ and the domain of conjugate momenta $\mathbb{D}_{\mathrm{mom}} = \{(\mathbf{p}^{\mathsf{T}},\boldsymbol{\pi}^{\mathsf{T}})^{\mathsf{T}} \in \mathbb{R}^{7n} : \mathbf{q}^{\mathsf{T}}\boldsymbol{\pi} = 0\}$.

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We introduce the gradient system in the form of Stratonovich SDEs:

$$d\mathbf{R} = \frac{\upsilon}{m}\mathbf{f}(\mathbf{R},\mathbf{Q})dt + \sqrt{\frac{2\upsilon}{m\beta}}d\mathbf{w}(t), \quad \mathbf{R}(0) = \mathbf{r}, \quad (37)$$

$$dQ^j = \frac{\Upsilon}{M}F^j(\mathbf{R},\mathbf{Q})dt + \sqrt{\frac{2\Upsilon}{M\beta}}\sum_{l=1}^{3} S_l Q^j \circ dW_l^j(t), \quad (38)$$

$$Q^j(0) = q^j, \quad |q^j| = 1, \quad j = 1,\dots,n,$$

where the parameters $\upsilon > 0$ and $\Upsilon > 0$ control the speed of evolution of the gradient system (37)–(38), $\mathbf{f} = (f^{1\,\mathsf{T}},\dots,f^{n\,\mathsf{T}})^{\mathsf{T}}$ and the rest of the notation is as in (18)–(19).
[Davidchack, Ouldridge&T. *J Chem Phys* 2015]

The gradient thermostat for rigid body dynamics

This new gradient thermostat possesses the following properties.

- As in the case of (18)–(19), the solution of (37)–(38) preserves the quaternion length (21).
- Assume that the solution $X(t) = (\mathbf{R}^\mathsf{T}(t), \mathbf{Q}^\mathsf{T}(t))^\mathsf{T} \in \mathbb{D}'$ of (37)–(38) is an ergodic process. Then, by the usual means of the stationary Fokker-Planck equation, one can show that its invariant measure is Gibbsian with the density $\tilde{\rho}(\mathbf{r}, \mathbf{q})$ from (36).

Geometric integrator for the gradient thermostat

The main idea is to rewrite the components Q^j of the solution to (37)–(38) in the form $Q^j(t) = \exp(Y^j(t))Q^j(0)$ and then solve numerically the SDEs for the 4×4-matrices $Y^j(t)$. To this end, we introduce the 4×4 skew-symmetric matrices:

$$\mathbb{F}_j(\mathbf{r}, \mathbf{q}) = F^j(\mathbf{r}, \mathbf{q}) q^{j\,\mathsf{T}} - q^j (F^j(\mathbf{r}, \mathbf{q}))^{\mathsf{T}}, j = 1, \ldots, n.$$

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Note that $\mathbb{F}_j(\mathbf{r}, \mathbf{q}) q^j = F^j(\mathbf{r}, \mathbf{q})$ under $|q^j| = 1$ and the equations (38) can be written as

$$dQ^j = \frac{\Upsilon}{M} \mathbb{F}_j(\mathbf{R}, \mathbf{Q}) Q^j dt + \sqrt{\frac{2\Upsilon}{M\beta}} \sum_{l=1}^{3} S_l Q^j \circ dW_l^j(t), \; Q^j(0) = q^j, \;\; |q^j| = 1. \tag{39}$$

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One can show that

$$\begin{aligned} Y^j(t+h) = h\frac{\Upsilon}{M} \mathbb{F}_j(\mathbf{R}(t), \mathbf{Q}(t)) \quad &+ \quad \sqrt{\frac{2\Upsilon}{M\beta}} \sum_{l=1}^{3} \left(W_l^j(t+h) - W_l^j(t) \right) S_l \\ &+ \quad \text{terms of higher order.} \end{aligned}$$

Geometric integrator for the gradient thermostat

$$\begin{aligned}
\mathbf{R}_0 &= \mathbf{r},\ \mathbf{Q}_0 = \mathbf{q},\ |q^j| = 1,\ j = 1, \ldots, n, \qquad (40) \\
\mathbf{R}_{k+1} &= \mathbf{R}_k + h\frac{\upsilon}{m}\mathbf{f}(\mathbf{R}_k, \mathbf{Q}_k) + \sqrt{h}\sqrt{\frac{2\upsilon}{m\beta}}\boldsymbol{\xi}_k, \\
Y_k^j &= h\frac{\Upsilon}{M}\mathbb{F}_j(\mathbf{R}_k, \mathbf{Q}_k) + \sqrt{h}\sqrt{\frac{2\Upsilon}{M\beta}}\sum_{l=1}^{3}\eta_k^{j,l}S_l, \\
Q_{k+1}^j &= \exp(Y_k^j)Q_k^j,\quad j = 1, \ldots, n,
\end{aligned}$$

where $\boldsymbol{\xi}_k = (\xi_{1,k}, \ldots, \xi_{3n,k})^\mathsf{T}$ and $\xi_{i,k}$, $i = 1, \ldots, 3n$, $\eta_k^{j,l}$, $l = 1, 2, 3$, $j = 1, \ldots, n$, are i.i.d. random variables with the same law

$$P(\theta = \pm 1) = 1/2. \qquad (41)$$

Geometric integrator for the gradient thermostat

$$\mathbf{R}_0 = \mathbf{r},\ \mathbf{Q}_0 = \mathbf{q},\ |q^j| = 1,\ j = 1, \ldots, n, \tag{40}$$

$$\mathbf{R}_{k+1} = \mathbf{R}_k + h\frac{\upsilon}{m}\mathbf{f}(\mathbf{R}_k, \mathbf{Q}_k) + \sqrt{h}\sqrt{\frac{2\upsilon}{m\beta}}\boldsymbol{\xi}_k,$$

$$Y_k^j = h\frac{\Upsilon}{M}\mathbb{F}_j(\mathbf{R}_k, \mathbf{Q}_k) + \sqrt{h}\sqrt{\frac{2\Upsilon}{M\beta}}\sum_{l=1}^{3}\eta_k^{j,l}S_l,$$

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$$P(\theta = \pm 1) = 1/2. \tag{41}$$

Proposition 4. *The numerical scheme* (40)–(41) *for* (37)–(38) *preserves the length of quaternions, i.e.,* $|Q_k^j| = 1,\ \ j = 1, \ldots, n$, *for all* k, *and it is of weak order one.*

Davidchack, Ouldridge&T. *J Chem Phys* 2015

Stochastic Landau-Lifshitz equation

Consider a system of n spins. Let B^i be the effective field acting on spin i

$$B^i(\mathbf{x}) = -\nabla_i H(\mathbf{x}),$$

where ∇_i is the gradient with respect to the Cartesian components of the effective magnetic field acting on spin i and H is the Hamiltonian.

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$$\begin{aligned} dX^i &= X^i \times a_i(\mathbf{X})dt + X^i \times \sigma(X^i) \circ dW^i(t), \\ X^i(0) &= x_0^i, \;\; |x_0^i| = 1, \; i = 1, \ldots, n, \end{aligned} \tag{42}$$

where $X^i = (X_x^i, X_y^i, X_z^i)^\top$ are three-dimensional unit spin vectors and $\mathbf{X} = ({X^1}^\top, \ldots, {X^n}^\top)^\top$ is a $3n$-dimensional vector; $W^i(t) = (W_x^i(t), W_y^i(t), W_z^i(t))^\top$, $W_x^i(t)$, $W_y^i(t)$, $W_z^i(t)$, $i = 1, \ldots, n$, are independent standard Wiener processes;

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$$a_i(\mathbf{x}) = -B^i(\mathbf{x}) - \alpha x^i \times B^i(\mathbf{x}) \ , \tag{43}$$

$\alpha \geq 0$ is the damping parameter; $\sigma(x)$, $x \in \mathbb{R}^3$, is a 3×3-matrix:

$$\sigma(x)y = -\sqrt{2D}y - \alpha\sqrt{2D}x \times y, \quad D = \frac{\alpha}{(1+\alpha^2)} \frac{k_b T}{\hat{X}\hat{B}} \ , \tag{44}$$

$\hat{X}$ is the magnetization of each spin and $\hat{B}$ is a reference magnetic field strength.

Properties of SSL:

Stochastic Landau-Lifshitz equation

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- The length of each individual spin is a constant of motion, i.e.,

$$|X^i(t)| = 1, \; i = 1, \dots, n, \quad t \geq 0.$$

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- Ergodic, the Gibbsian invariant measure with the density

$$\rho(\mathbf{x}) \propto \exp(-\beta H(\mathbf{x})) \; , \tag{46}$$

where $\beta = \hat{X}\hat{B}/(k_B T) > 0$ is the inverse temperature.

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  where $\beta = \hat{X}\hat{B}/(k_B T) > 0$ is the inverse temperature.
- Stratonovich form of the SDE

Numerics for SLLE

- **Mid-point method** - preserves spin length, has good long time simulation properties but very expensive for large spin systems since it is fully implicit:

$$X_{k+1}^i = X_k^i + h\frac{X_k^i + X_{k+1}^i}{2} \times a_i\left(\frac{\mathbf{X}_k + \mathbf{X}_{k+1}}{2}\right) \tag{47}$$

$$+h^{1/2}\frac{X_k^i + X_{k+1}^i}{2} \times \sigma\left(\frac{X_k^i + X_{k+1}^i}{2}\right)\xi_{k+1}^i\ , \quad i = 1, \dots, n,\ \ k = 1, \dots, N,$$

where $\xi_{k+1}^i = \left(\xi_{k+1}^{i,1}, \xi_{k+1}^{i,2}, \xi_{k+1}^{i,3}\right)^\top$; $\xi_k^{i,j}$, $j = 1, 2, 3$, $i = 1, \dots, n$, $k = 1, \dots, N$, are i.i.d. random variables which can be distributed according to, e.g. $P(\xi_k^{i,j} = \pm 1) = 1/2$. Alternatively, we can choose $\xi_k^{i,j}$ being distributed as

$$\xi_h = \begin{cases} \zeta,\ |\zeta| \le A_h, \\ A_h,\ \zeta > A_h, \\ -A_h,\ \zeta < -A_h, \end{cases} \tag{48}$$

where $A_h = \sqrt{2|\ln h|}$ and $\zeta \sim \mathcal{N}(0, 1)$ [Milstein, Repin, T. SINUM 2002]

Numerics for SLLE

- **Heun method** - a projection is required to preserve spin length, has poor long time simulation properties but low cost per step since it is explicit

$$
\begin{aligned}
\mathcal{X}_k^i &= X_k^i + hX_k^i \times a_i(\mathbf{X}_k) + h^{1/2} X_k^i \times \sigma(X_k^i)\xi_{k+1}^i, \\
& \quad i = 1, \dots, n, \\
{X^*}_{k+1}^i &= X_k^i + \frac{h}{2}\left[X_k^i \times a_i(\mathbf{X}_k) + \mathcal{X}_k^i \times a_i(\mathcal{X}_k)\right] \\
& \quad + \frac{h^{1/2}}{2}\left[X_k^i \times \sigma(X_k^i)\xi_{k+1}^i + \mathcal{X}_k^i \times \sigma(\mathcal{X}_k^i)\xi_{k+1}^i\right], \\
X_{k+1}^i &= {X^*}_{k+1}^i / |{X^*}_{k+1}^i|, \ i = 1, \dots, n, \\
& \quad k = 1, \dots, N,
\end{aligned} \tag{49}
$$

where $\mathcal{X}_k = (\mathcal{X}_k^{1^\top}, \dots, \mathcal{X}_k^{n^\top})^\top$; $\xi_{k+1}^i = \left(\xi_{k+1}^{i,1}, \xi_{k+1}^{i,2}, \xi_{k+1}^{i,3}\right)^\top$; $\xi_k^{i,j}$, $j = 1, 2, 3$, $i = 1, \dots, n$, $k = 1, \dots, N$, are independent identically distributed (i.i.d.) random variables which can be distributed, e.g., as $P(\xi_k^{i,j} = \pm 1) = 1/2$ or $\xi_l^{i,j} \sim \mathcal{N}(0, 1)$.

Numerics for SLLE

New semi-implicit methods [Mentink, T., Fasolino, Katsnelson, Rasing 2010]
Semi-implicit scheme A (SIA)

$$
\begin{aligned}
\mathcal{X}_k^i &= X_k^i + hX_k^i \times a_i(\mathbf{X}_k) + h^{1/2} X_k^i \times \sigma(X_k^i)\xi_{k+1}^i, \\
&\quad i = 1, \dots, n, \\
X_{k+1}^i &= X_k^i + h\frac{X_k^i + X_{k+1}^i}{2} \times a_i\left(\frac{\mathbf{X}_k + \mathcal{X}_k}{2}\right) \\
&\qquad + h^{1/2}\frac{X_k^i + X_{k+1}^i}{2} \times \sigma\left(\frac{X_k^i + \mathcal{X}_k^i}{2}\right)\xi_{k+1}^i, \;\; i = 1, \dots, n, \\
&\quad k = 1, \dots, N,
\end{aligned}
\tag{50}
$$

where $\xi_{k+1}^i = \left(\xi_{k+1}^{i,1}, \xi_{k+1}^{i,2}, \xi_{k+1}^{i,3}\right)^\top$; $\xi_l^{i,j}$ are i.i.d. random variables distributed as, e.g. $P(\xi_k^{i,j} = \pm 1) = 1/2$.

Semi-implicit scheme B (SIB)

$$\mathcal{X}_k^i = X_k^i + h\frac{X_k^i + \mathcal{X}_k^i}{2} \times a_i(\mathbf{X}_k) + h^{1/2}\frac{X_k^i + \mathcal{X}_k^i}{2} \times \sigma(X_k^i)\xi_{k+1}^i, \qquad (51)$$

$$i = 1, \ldots, n,$$

$$X_{k+1}^i = X_k^i + h\frac{X_k^i + X_{k+1}^i}{2} \times a_i\left(\frac{\mathbf{X}_k + \mathcal{X}_k}{2}\right)$$

$$+ h^{1/2}\frac{X_k^i + X_{k+1}^i}{2} \times \sigma\left(\frac{X_k^i + \mathcal{X}_k^i}{2}\right)\xi_{k+1}^i \ , \ i = 1, \ldots, n,$$

$$k = 1, \ldots, N.$$

Numerics for SLLE

Semi-implicit scheme B (SIB)

$$\mathcal{X}_k^i = X_k^i + h\frac{X_k^i + \mathcal{X}_k^i}{2} \times a_i(\mathbf{X}_k) + h^{1/2}\frac{X_k^i + \mathcal{X}_k^i}{2} \times \sigma(X_k^i)\xi_{k+1}^i, \quad (51)$$
$$i = 1, \dots, n,$$
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$$+ h^{1/2}\frac{X_k^i + X_{k+1}^i}{2} \times \sigma\left(\frac{X_k^i + \mathcal{X}_k^i}{2}\right)\xi_{k+1}^i\ , \ i = 1, \dots, n,$$
$$k = 1, \dots, N.$$

Proposition 5. *The numerical schemes SIA and SIB for SSLE preserve the length of each spin and are of weak order one.*

SIA and SIB are included in UppASD library

Numerical experiments: rigid body thermostats

Davidchack, Handel&T. *J Chem Phys* 2009
and Davidchack, Ouldridge&T. *J Chem Phys* 2015

Two objectives for the experiments:

- the dependence of the thermostat properties on the choice of parameters γ and Γ for the Langevin thermostat
- errors of the numerical schemes.

TIP4P rigid model of water (Jorgensen et. al *J. Chem. Phys.* 1983)

The quantities we measure include the translational temperature

$$\mathcal{T}_{\mathrm{tr}} = \frac{\mathbf{p}^{\mathsf{T}}\mathbf{p}}{3nk_B m}\,,$$

rotational temperature

$$\mathcal{T}_{\mathrm{rot}} = \frac{2}{3nk_B}\sum_{j=1}^{n}\sum_{l=1}^{3} V_l(q^j,\pi^j)\,,$$

and potential energy per molecule

$$\mathcal{U} = \frac{1}{n}U(\mathbf{r},\mathbf{q})\,.$$

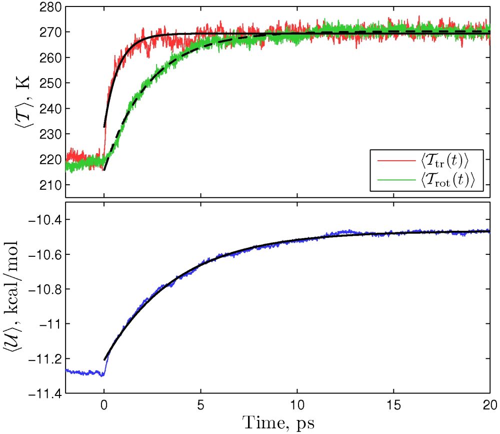


Figure: Langevin thermostat: $\gamma = 4\,\mathrm{ps}^{-1}$, $\Gamma = 0$.

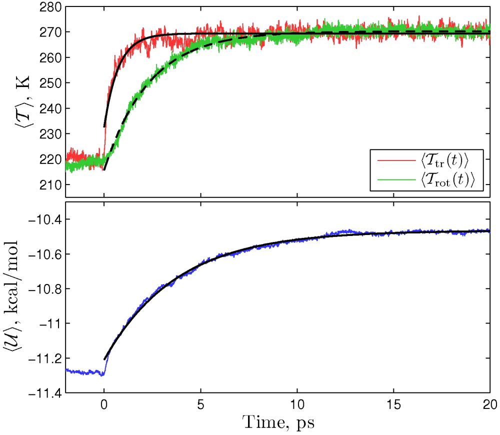


Figure: Langevin thermostat: $\gamma = 4\,\text{ps}^{-1}$, $\Gamma = 0$.

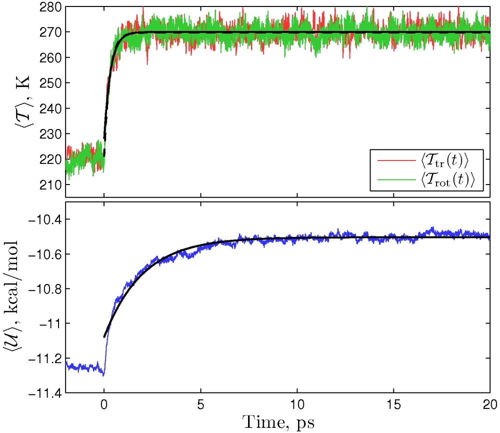


Figure: Langevin thermostat: $\gamma = 4\,\text{ps}^{-1}$, $\Gamma = 10\,\text{ps}^{-1}$.

$\tau_{\mathcal{T}_{\rm tr}} = 0.28\,\text{ps}$, $\tau_{\mathcal{T}_{\rm rot}} = 0.26\,\text{ps}$, and $\tau_{\mathcal{U}} = 2.0\,\text{ps}$

Parameters of the Langevin thermostat

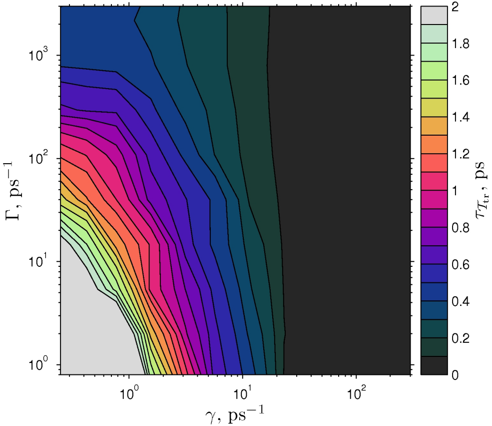


Figure: Langevin thermostat. Dependence of relaxation time of the translational temperature on γ and Γ.

Parameters of the Langevin thermostat

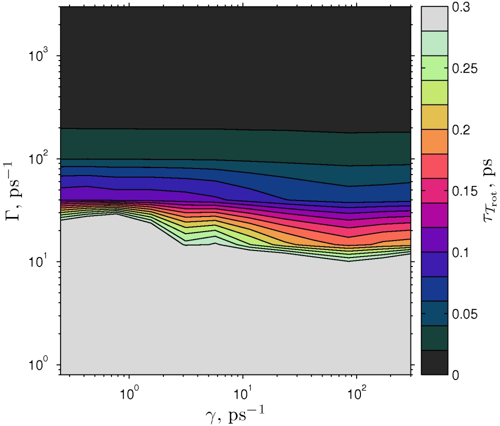


Figure: Langevin thermostat. Dependence of relaxation time of the rotational temperature on γ and Γ.

Parameters of the Langevin thermostat

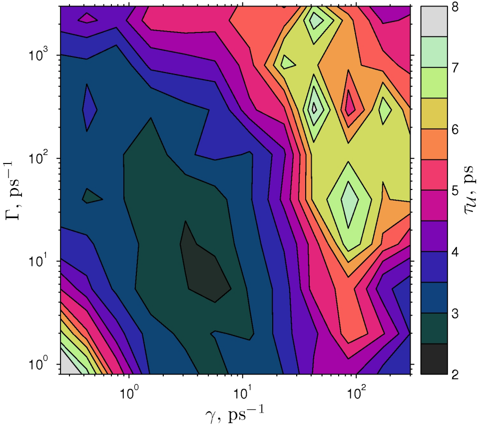


Figure: Langevin thermostat. Dependence of relaxation time of the potential energy on γ and Γ.

Parameters of the Langevin thermostat

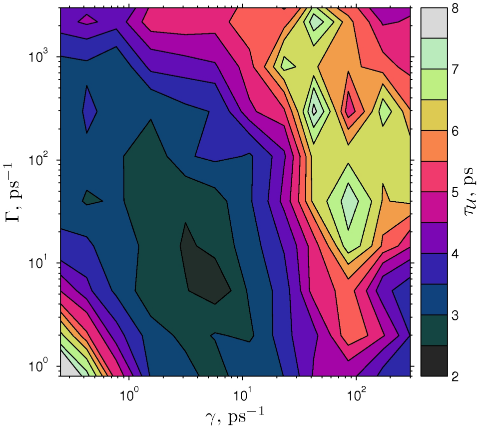


Figure: Langevin thermostat. Dependence of relaxation time of the potential energy on γ and Γ.

$\gamma = 2 - 8\,\text{ps}^{-1}$ and $\Gamma = 3 - 40\,\text{ps}^{-1}$

Accuracy of integrators

- Translational kinetic temperature

$$\langle \mathcal{T}_{\mathrm{tk}} \rangle_h = \frac{\langle \mathbf{p}^{\mathsf{T}} \mathbf{p} \rangle_h}{3 m k_B n};$$

- Rotational kinetic temperature

$$\langle \mathcal{T}_{\mathrm{rk}} \rangle_h = \frac{2 \left\langle \sum_{j=1}^{n} \sum_{l=1}^{3} V_l(q^j, \pi^j) \right\rangle_h}{3 k_B n};$$

- Translational configurational temperature

$$\langle \mathcal{T}_{\mathrm{tc}} \rangle_h = \frac{\left\langle \sum_{j=1}^{n} |\nabla_{r^j} U|^2 \right\rangle_h}{k_B \left\langle \sum_{j=1}^{n} \nabla_{r^j}^2 U \right\rangle_h};$$

- Rotational configurational temperature

$$\langle \mathcal{T}_{\mathrm{rc}} \rangle_h = \frac{\left\langle \sum_{j=1}^{n} |\nabla_{\omega^j} U|^2 \right\rangle_h}{k_B \left\langle \sum_{j=1}^{n} \nabla_{\omega^j}^2 U \right\rangle_h},$$

where ∇_{ω^j} is the angular gradient operator for molecule j;

Accuracy of integrators

- Potential energy per molecule

$$\langle \mathcal{U} \rangle_h = \frac{1}{n} \langle U \rangle_h ;$$

- Excess pressure

$$\langle \mathcal{P}_{\mathrm{ex}} \rangle_h = -\frac{\left\langle \sum_{j=1}^{n} r^{j\,\mathsf{T}} f^{j} \right\rangle_h}{3V},$$

  where V is the system volume;

- Radial distribution functions (RDFs) between oxygen (O) and hydrogen (H) interaction sites

$$\langle g_{\alpha\beta}(r) \rangle_h \,,$$

  where $\alpha\beta =$ OO, OH, and HH.

Angle brackets with subscript h represent the average over a simulation run with time step h.

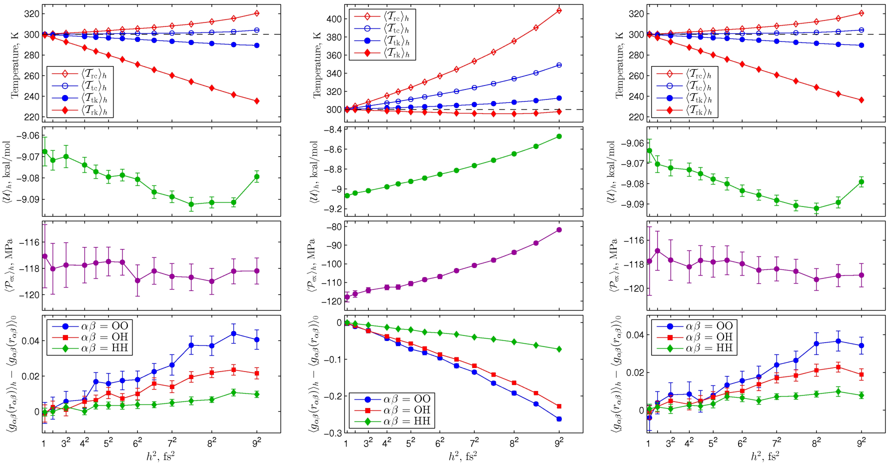
Accuracy of integrators

$$EA(\bar{X}) = EA(X) + C_A h^p + O(h^{p+1})$$

$p = 2$ for Langevin integrators and $p = 1$ for the gradient thermostat integrator

Talay&Tubaro *Stoch.Anal.Appl.* 1990

Accuracy of integrators



Langevin A (left), Langevin B (centre), and Langevin C (right) with $\gamma = 5\,\mathrm{ps}^{-1}$ and $\Gamma = 10\,\mathrm{ps}^{-1}$. Error bars denote estimated 95% confidence intervals.

Accuracy of integrators

Results for Langevin A, B, and C thermostats with $\gamma = 5\,\mathrm{ps}^{-1}$ and $\Gamma = 10\,\mathrm{ps}^{-1}$ and gradient thermostat with $\upsilon = 4\,\mathrm{fs}$ and $\Upsilon = 1\,\mathrm{fs}$.

	Langevin A		Langevin B		Langevin C		Gradient	
A, unit	$\langle A\rangle_0$	E_A	$\langle A\rangle_0$	E_A	$\langle A\rangle_0$	E_A	$\langle A\rangle_0$	E_A
$\mathcal{T}_{\mathrm{tk}}$, K	300.0(2)	−0.136(8)	299.9(2)	0.100(13)	300.0(2)	−0.135(7)	–	–
$\mathcal{T}_{\mathrm{rk}}$, K	299.9(2)	−0.808(8)	299.8(3)	−0.092(13)	300.1(2)	−0.803(8)	–	–
$\mathcal{T}_{\mathrm{tc}}$, K	300.1(3)	0.022(13)	299.9(4)	0.45(2)	300.1(3)	0.021(13)	299.6(1.0)	3.6(5)
$\mathcal{T}_{\mathrm{rc}}$, K	299.8(3)	0.158(11)	299.6(4)	0.99(2)	299.9(3)	0.152(11)	298.6(1.6)	9.9(4)
$\mathcal{U}$, kcal/mol	−9.068(4)	−0.0004(2)	−9.071(4)	0.0059(2)	−9.066(3)	−0.0005(2)	−9.075(11)	0.033(4)
$\mathcal{P}_{\mathrm{ex}}$, MPa	−117.4(1.3)	−0.02(5)	−117.4(1.6)	0.27(9)	−117.5(1.4)	−0.01(5)	−118(11)	1.7(2.8)
$g_{\mathrm{OO}}(r_{\mathrm{OO}})$	3.007(4)	0.0006(2)	3.009(4)	−0.0027(2)	3.009(4)	0.0004(2)	3.012(9)	−0.011(4)
$g_{\mathrm{OH}}(r_{\mathrm{OH}})$	1.490(3)	0.0003(2)	1.492(2)	−0.0024(2)	1.490(2)	0.00028(9)	1.491(7)	−0.011(2)
$g_{\mathrm{HH}}(r_{\mathrm{HH}})$	1.283(2)	0.00012(7)	1.284(2)	−0.00082(6)	1.282(2)	0.00018(7)	1.284(4)	−0.004(2)

Values of $\langle A\rangle_0$ and E_A were obtained by linear regression from $\langle A\rangle_h$ for $h \le 6\,\mathrm{fs}$ for Langevin integrators and for $h \le 4\,\mathrm{fs}$ for the gradient integrator. Quantities E_A are measured in the units of the corresponding quantity A per fs^p, where $p = 2$ for Langevin integrators and $p = 1$ for the gradient integrator.

Langevin systems with hydrodynamic interactions

In modelling colloidal suspensions, DNA, proteins and other macromolecules in solutions, solvent-mediated interactions between the particles should be included. Particles moving in a viscous fluid induce a flow field which affects other particles. These long-range interactions, which are only present if particles are moving, are called **hydrodynamic interactions**.

Langevin systems with hydrodynamic interactions

In modelling colloidal suspensions, DNA, proteins and other macromolecules in solutions, solvent-mediated interactions between the particles should be included. Particles moving in a viscous fluid induce a flow field which affects other particles. These long-range interactions, which are only present if particles are moving, are called **hydrodynamic interactions**.

For a system of spherical particles, forces and torques due to hydrodynamic interactions depend linearly on the linear and angular velocities of the spheres through a position-dependent friction matrix $\xi(\mathbf{r})$.

[Davidchack, Ouldridge&T. work in progress]

Langevin systems with hydrodynamic interactions

$$
\begin{aligned}
dR^i &= \frac{P^i}{m^i}dt, \quad R^i(0) = r^i, && (52) \\
dP^i &= f^i(\mathbf{R},\mathbf{Q})dt - \sum_{j=1}^{n} \frac{{}^{\mathrm{tt}}\xi^{(i,j)}(\mathbf{R})}{m^j} P^j dt \\
&\quad - \frac{1}{2}\sum_{j=1}^{n} {}^{\mathrm{tr}}\xi^{(i,j)}(\mathbf{R}) A^{\mathsf{T}}(Q^j)\hat{D}^j \hat{S}^{\mathsf{T}}(Q^j)\Pi^j dt \\
&\quad + \sum_{j=1}^{n} {}^{\mathrm{tt}}b^{(i,j)}(\mathbf{R})dw^j(t) + \sum_{j=1}^{n} {}^{\mathrm{tr}}b^{(i,j)}(\mathbf{R})dW^j(t), \quad P^i(0) = p^i,
\end{aligned}
$$

Langevin systems with hydrodynamic interactions

$$
\begin{aligned}
dQ^i &= \frac{1}{4}\hat{S}(Q^i)\hat{D}^i\hat{S}^\mathsf{T}(Q^i)\Pi^i dt, \quad Q^i(0)=q^i, \quad |q^i|=1, && (53)\\
d\Pi^i &= \frac{1}{4}\hat{S}(\Pi^i)\hat{D}^i\hat{S}^\mathsf{T}(Q^i)\Pi^i dt + F^i(\mathbf{R},\mathbf{Q})dt \\
&\quad -\sum_{j=1}^{n}\check{S}(Q^i)\ {}^{\mathrm{rr}}\xi^{(i,j)}(\mathbf{R})A^\mathsf{T}(Q^j)\hat{D}^j\hat{S}^\mathsf{T}(Q^j)\Pi^j dt \\
&\quad -2\sum_{j=1}^{n}\frac{1}{m^j}\check{S}(Q^i)\ {}^{\mathrm{rt}}\xi^{(i,j)}(\mathbf{R})P^j dt \\
&\quad +2\sum_{j=1}^{n}\check{S}(Q^i)\ {}^{\mathrm{rr}}b^{(i,j)}(\mathbf{R})dW^j(t) \\
&\quad +2\sum_{j=1}^{n}\check{S}(Q^i)\ {}^{\mathrm{rt}}b^{(i,j)}(\mathbf{R})dw^j(t), \quad \Pi^i(0)=\pi^i, \quad {q^i}^\mathsf{T}\pi^i=0, \\
&\qquad\qquad i=1,\dots,n,
\end{aligned}
$$

where ${}^{\mathrm{tt}}b^{(i,j)}(\mathbf{r})$, ${}^{\mathrm{tr}}b^{(i,j)}(\mathbf{r})$, ${}^{\mathrm{rr}}b^{(i,j)}(\mathbf{r})$, and ${}^{\mathrm{rt}}b^{(i,j)}(\mathbf{r})$, $i,j=1,\dots,n$, are 3×3-matrices.

Langevin systems with hydrodynamic interactions

The matrices ${}^{\mathrm{tt}}b^{(i,j)}(\mathbf{r})$, ${}^{\mathrm{tr}}b^{(i,j)}(\mathbf{r},\mathbf{q})$, ${}^{\mathrm{rr}}b^{(i,j)}(\mathbf{r},\mathbf{q})$, and ${}^{\mathrm{rt}}b^{(i,j)}(\mathbf{r},\mathbf{q})$ are so that the invariant measure of $X(t)$ is Gibbsian with the density $\rho(\mathbf{r},\mathbf{p},\mathbf{q},\boldsymbol{\pi})$:

$$\rho(\mathbf{r},\mathbf{p},\mathbf{q},\boldsymbol{\pi}) \propto \exp(-\beta H(\mathbf{r},\mathbf{p},\mathbf{q},\boldsymbol{\pi})).$$

$$\begin{bmatrix} {}^{\mathrm{tt}}b(\mathbf{r}) & {}^{\mathrm{tr}}b(\mathbf{r}) \\ {}^{\mathrm{rt}}b(\mathbf{r}) & {}^{\mathrm{rr}}b(\mathbf{r}) \end{bmatrix} \begin{bmatrix} {}^{\mathrm{tt}}b^{\mathsf{T}}(\mathbf{r}) & {}^{\mathrm{rt}}b^{\mathsf{T}}(\mathbf{r}) \\ {}^{\mathrm{tr}}b^{\mathsf{T}}(\mathbf{r}) & {}^{\mathrm{rr}}b^{\mathsf{T}}(\mathbf{r}) \end{bmatrix} = \frac{2}{\beta} \begin{bmatrix} {}^{\mathrm{tt}}\xi(\mathbf{r}) & {}^{\mathrm{tr}}\xi(\mathbf{r}) \\ {}^{\mathrm{rt}}\xi(\mathbf{r}) & {}^{\mathrm{rr}}\xi(\mathbf{r}) \end{bmatrix} := \frac{2}{\beta}\xi(\mathbf{r}).$$

[Davidchack, Ouldridge&T. work in progress]

Conclusions

- As in the deterministic case, it is important to preserve structural properties of stochastic systems for accurate long term simulations
- Geometric integrators for stochastic Hamiltonian systems, for various Langevin-type equations, for stochastic Landau-Lifshitz equation were constructed
- Testing of thermostats and numerical integrators.
- Current work includes stochastic rigid body dynamics with hydrodynamic interactions.
- Development of more efficient methods for stochastic gradient systems.

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