Novel stochastic thermostats for rigid body dynamics

M.V. Tretyakov
School of Mathematical Sciences, University of Nottingham, UK

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Davidchack, Ouldridge & T. *J Chem Phys* 142 (2015), 144114

Plan of the talk

- Introduction
- Langevin thermostat for rigid body dynamics
- Stochastic Hamiltonian systems and sympletic integrators
- Quasi-symplectic integrators for Langevin equation
- Geometric integrators for Langevin thermostat for rigid body dynamics
- Gradient thermostat for rigid body dynamics
- Geometric integrator for the gradient thermostat
- Numerical experiments

Introduction

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

where

$$\omega^2 = dp \wedge dr = dp^1 \wedge dr^1 + \cdots + dp^n \wedge dr^n \tag{1}$$

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A method for (16) based on the one-step approximation

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

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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 $\mathbf{r} = ({r^1}^\mathsf{T}, \ldots, {r^n}^\mathsf{T})^\mathsf{T} \in \mathbb{R}^{3n}$, $r^j = (r_1^j, r_2^j, r_3^j)^\mathsf{T} \in \mathbb{R}^3$, and the rotational coordinates in the quaternion representation $\mathbf{q} = ({q^1}^\mathsf{T}, \ldots, {q^n}^\mathsf{T})^\mathsf{T} \in \mathbb{R}^{4n}$, $q^j = (q_0^j, q_1^j, q_2^j, q_3^j)^\mathsf{T} \in \mathbb{R}^4$, such that $|q^j| = 1$.

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

where $\mathbf{p} = ({p^1}^\mathsf{T}, \ldots, {p^n}^\mathsf{T})^\mathsf{T} \in \mathbb{R}^{3n}$, $p^j = (p_1^j, p_2^j, p_3^j)^\mathsf{T} \in \mathbb{R}^3$, are the center-of-mass momenta conjugate to $\mathbf{r}$; $\boldsymbol{\pi} = ({\pi^1}^\mathsf{T}, \ldots, {\pi^n}^\mathsf{T})^\mathsf{T} \in \mathbb{R}^{4n}$, $\pi^j = (\pi_0^j, \pi_1^j, \pi_2^j, \pi_3^j)^\mathsf{T} \in \mathbb{R}^4$, are the angular momenta conjugate to $\mathbf{q}$;

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

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

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

$$S_1 = \begin{bmatrix} 0 & -1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & -1 & 0 \end{bmatrix}, \; S_2 = \begin{bmatrix} 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{bmatrix},$$

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Also introduce $S_0 = \text{diag}(1, 1, 1, 1)$, $D = \text{diag}(0, 1/I_1, 1/I_2, 1/I_3)$, 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

$$\mathbf{q}^{\mathsf{T}} \tilde{\nabla}_{q^j} U(\mathbf{r}, \mathbf{q}) = 0. \tag{4}$$

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We note

$$\begin{aligned} \sum_{l=1}^{3} \nabla_{\pi} V_l(q, \pi) &= \frac{1}{4} \sum_{l=1}^{3} \frac{1}{I_l} S_l q \left[S_l q\right]^{\mathsf{T}} \pi \\ &= \frac{1}{4} S(q) D S^{\mathsf{T}}(q) \pi, \\ \sum_{l=1}^{3} \nabla_{q} V_l(q, \pi) &= -\frac{1}{4} \sum_{l=1}^{3} \frac{1}{I_l} \left[\pi^{\mathsf{T}} S_l q\right] S_l \pi. \end{aligned} \tag{5}$$

Rigid Body Dynamics

The Hamilton equations of motion are

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\begin{aligned}
\frac{dR^j}{dt} &= \frac{P^j}{m}, \quad R^j(0) = r^j, \qquad (6)\\
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i.e. $\Pi^j(t) \in T_{q^j} \mathbb{S}^3$

Symplectic integrator for (6) in [Miller III et al *J. Chem. Phys.*, 2002]

Thermostats

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- Deterministic
- Stochastic

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Now we derive stochastic thermostats for the molecular system (6), 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

$$\rho(\mathbf{r}, \mathbf{p}, \mathbf{q}, \boldsymbol{\pi}) \propto \exp(-\beta H(\mathbf{r}, \mathbf{p}, \mathbf{q}, \boldsymbol{\pi})), \tag{9}$$

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

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

Langevin thermostat for Rigid Body Dynamics

$$
\begin{aligned}
dR^j &= \frac{P^j}{m}dt, \quad R^j(0) = r^j, && (10)\\
dP^j &= f^j(\mathbf{R},\mathbf{Q})dt - \gamma P^j dt + \sqrt{\frac{2m\gamma}{\beta}}dw^j(t), \quad P^j(0) = p^j,\\
dQ^j &= \frac{1}{4}S(Q^j)DS^{\mathsf{T}}(Q^j)\Pi^j dt, \;\; Q^j(0) = q^j, \;\; |q^j| = 1, && (11)\\
d\Pi^j &= \frac{1}{4}\sum_{l=1}^{3}\frac{1}{I_l}\left(\Pi^{j\,\mathsf{T}} S_l Q^j\right) S_l \Pi^j dt + F^j(\mathbf{R},\mathbf{Q})dt - \Gamma J(Q^j)\Pi^j dt\\
&\quad + \sqrt{\frac{2M\Gamma}{\beta}}\sum_{l=1}^{3} S_l Q^j dW_l^j(t), \quad \Pi^j(0) = \pi^j, \;\; q^{j\,\mathsf{T}}\pi^j = 0, \;\; j = 1,\ldots,n,
\end{aligned}
$$

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

$$
J(q) = \frac{M}{4}S(q)DS^{\mathsf{T}}(q), \;\; M = \frac{4}{\sum_{l=1}^{3}\frac{1}{I_l}}. \qquad (12)
$$

Langevin thermostat for Rigid Body Dynamics

- The Ito interpretation of the SDEs (10)–(11) coincides with its Stratonovich interpretation.
- The solution of (10)–(11) preserves the quaternion length

$$|Q^j(t)| = 1, \quad j = 1, \ldots, n, \quad \text{for all } t \geq 0. \tag{13}$$

- The solution of (10)–(11) automatically preserves the constraint:

$$Q^{j\,\mathsf{T}}(t)\Pi^j(t) = 0\,, \quad j = 1, \ldots, n, \quad \text{for } t \geq 0 \tag{14}$$

- 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 (10)–(11) is an ergodic process on

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

  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 $\mathbb{D}$:

$$\rho(\mathbf{r}, \mathbf{p}, \mathbf{q}, \boldsymbol{\pi}) \propto \exp(-\beta H(\mathbf{r}, \mathbf{p}, \mathbf{q}, \boldsymbol{\pi})) \tag{15}$$

Stochastic Hamiltonian systems

Stochastic Hamiltonian system:

$$dP = f(t,P,R)dt + \sum_{l=1}^{m} \sigma_l(t,P,R) \star dw_l(t),\ P(t_0) = p, \tag{16}$$

$$dR = g(t,P,R)dt + \sum_{r=1}^{m} \gamma_l(t,P,R) \star dw_l(t),\ R(t_0) = r,$$

$$f^i = -\partial H/\partial r^i, \quad g^i = \partial H/\partial p^i, \tag{17}$$

$$\sigma_l^i = -\partial H_l/\partial r^i, \quad \gamma_l^i = \partial H_l/\partial p^i, \quad i = 1,\dots,n, \quad l = 1,\dots,m.$$

The phase flow $(p,r) \mapsto (P,R)$ of (16) preserves symplectic structure:

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Bismut 1981; Milstein, Repin&T. SINUM 2002

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A method for (16) based on the one-step approximation

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preserves symplectic structure if

$$d\bar{P} \wedge d\bar{R} = dp \wedge dr\,. \tag{19}$$

Milstein, Repin&T. SINUM 2002; Milstein&T, Springer 2004

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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)\\
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&\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.

$$
\begin{aligned}
V_t &= \int_{D_t} dX^1 \dots dX^d \qquad (20)\\
&= \int_{D_0} \left| \frac{D(X^1, \dots, X^d)}{D(x^1, \dots, x^d)} \right| dx^1 \dots dx^d .
\end{aligned}
$$

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

$$
\mathbb{J} = \frac{D(X^1, \dots, X^d)}{D(x^1, \dots, x^d)} = \exp\left(-n(3\gamma + \Gamma) \cdot t\right). \qquad (21)
$$

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:

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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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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 (10)–(11) 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 $\bar{\mathbb{J}} = \mathbb{J}$.

Weak-sense numerical integration

We usually consider two types of numerical methods for SDEs: mean-square and weak [Milstein&T. Springer 2004]. Mean-square methods are useful for direct simulation of stochastic trajectories while weak methods are sufficient for evaluation of averages and are simpler than mean-square ones.

A method $\bar{X}$ is **weakly convergent** with order $p > 0$ if

$$|E\varphi(\bar{X}(T)) - E\varphi(X(T))| \leq Ch^p, \tag{22}$$

where h is a time discretization step and φ is a sufficiently smooth function with growth at infinity not faster than polynomial. The constant C does not depend on h, it depends on the coefficients of a simulated stochastic system, on φ, and T.

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 $h = T/N$.

Langevin integrators

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

- quasi-symplectic
- preserve $|\bar{Q}^j(t_k)| = 1, \quad j = 1, \ldots, n, \quad$ for all $t \geq 0$ automatically
- preserve $\bar{Q}^{j\,\mathsf{T}}(t_k)\bar{\Pi}^j(t_k) = 0\,, \quad j = 1, \ldots, n, \quad$ for $t \geq 0$ automatically
- of weak order 2

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 integrators

We use the mapping $\Psi_{t,I}(q,\pi) : (q,\pi) \mapsto (\mathcal{Q},\Pi)$ defined by

$$\begin{aligned} \mathcal{Q} &= \cos(\chi_I t) q + \sin(\chi_I t) S_I q \,, \\ \Pi &= \cos(\chi_I t) \pi + \sin(\chi_I t) S_I \pi \,, \end{aligned} \tag{23}$$

where

$$\chi_I = \frac{1}{4 I_I} \pi^{\mathsf{T}} S_I q \,.$$

We also introduce a composite map

$$\Psi_t = \Psi_{t/2,3} \circ \Psi_{t/2,2} \circ \Psi_{t,1} \circ \Psi_{t/2,2} \circ \Psi_{t/2,3} \,, \tag{24}$$

where "$\circ$" denotes function composition, i.e., $(g \circ f)(x) = g(f(x))$.

‘Langevin A’ integrator

The first integrator is based on splitting the Langevin system in

$$
\begin{aligned}
dR^j &= \frac{P^j}{m}dt, \quad R^j(0) = r^j, && (25)\\
dP^j &= f^j(\mathbf{R},\mathbf{Q})dt + \sqrt{\frac{2m\gamma}{\beta}}dw^j(t),\\
dQ^j &= \frac{1}{4}S(Q^j)DS^{\mathsf{T}}(Q^j)\Pi^j dt, && (26)\\
d\Pi^j &= \frac{1}{4}\sum_{l=1}^{3}\frac{1}{I_l}\left(\Pi^{j\,\mathsf{T}}S_l Q^j\right)S_l\Pi^j dt + F^j(\mathbf{R},\mathbf{Q})dt\\
&\quad + \sqrt{\frac{2M\Gamma}{\beta}}\sum_{l=1}^{3}S_l Q^j dW_l^j(t),\ j = 1,\ldots,n,
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&\quad + \sqrt{\frac{2M\Gamma}{\beta}}\sum_{l=1}^{3}S_l Q^j dW_l^j(t),\ j=1,\ldots,n,
\end{aligned}
$$

and the deterministic system of linear differential equations

$$
\dot{p} = -\gamma p, \quad \dot{\pi}^j = -\Gamma J(q^j)\pi^j,\ j=1,\ldots,n\,. \qquad (27)
$$

‘Langevin A’ integrator

$$
\begin{aligned}
\mathbf{P}_0 &= \mathbf{p}, \quad \mathbf{R}_0 = \mathbf{r}, \ \mathbf{Q}_0 = \mathbf{q} \text{ with } |q^j| = 1, \ j = 1, \ldots, n, \\
\Pi_0 &= \boldsymbol{\pi} \text{ with } \mathbf{q}^{\mathsf{T}} \boldsymbol{\pi} = \mathbf{0}, \\
\mathcal{P}_{1,k} &= \mathrm{e}^{-\gamma \frac{h}{2}} \mathbf{P}_k \ , \ \Pi^j_{1,k} = \mathrm{e}^{-\Gamma J(Q^j_k) \frac{h}{2}} \Pi^j_k, \quad j = 1, \ldots, n,
\end{aligned}
\tag{28}
$$

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

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

‘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

$$P(\theta = 0) = 2/3, \quad P(\theta = \pm\sqrt{3}) = 1/6. \tag{29}$$

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$$P(\theta = 0) = 2/3, \quad P(\theta = \pm\sqrt{3}) = 1/6. \tag{29}$$

Proposition 1. *The numerical scheme* (28)–(29) *for* (10)–(11) *is quasi-symplectic, it preserves the structural properties* (13) *and* (14) *and it is of weak order two*.

‘Langevin B’ integrator

$$
\begin{aligned}
d\mathbf{P}_I &= -\gamma \mathbf{P}_I \, dt + \sqrt{\frac{2m\gamma}{\beta}} d\mathbf{w}(t), \\
d\Pi_I^j &= -\Gamma J(q) \Pi_I^j dt + \sqrt{\frac{2M\Gamma}{\beta}} \sum_{l=1}^{3} S_l q dW_l^j(t);
\end{aligned}
\tag{30}
$$

$$
d\mathbf{R}_{II} = \frac{\mathbf{P}_{II}}{m} \, dt, \; d\mathbf{P}_{II} = \mathbf{f}(\mathbf{R}_{II}, \mathbf{Q}_{II}) dt, \; dQ_{II}^j = \frac{1}{4} S(Q_{II}^j) D S^{\mathsf{T}}(Q_{II}^j) \Pi_{II}^j dt \,, \tag{31}
$$

$$
d\Pi_{II}^j = F^j(\mathbf{R}_{II}, \mathbf{Q}_{II}) dt + \frac{1}{4} \sum_{l=1}^{3} \frac{1}{I_l} \left[(\Pi_{II}^j)^{\mathsf{T}} S_l Q_{II}^j \right] S_l \Pi_{II}^j dt \,, \; j = 1, \ldots, n.
$$

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\end{aligned}
\tag{30}
$$

$$
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$$

$$
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$$

The SDEs (30) have the exact solution:

$$
\begin{aligned}
\mathbf{P}_I(t) &= \mathbf{P}_I(0) \exp(-\gamma t) + \sqrt{\frac{2m\gamma}{\beta}} \int_0^t \exp(-\gamma(t-s)) d\mathbf{w}(s), \qquad (32) \\
\Pi_I^j(t) &= \exp(-\Gamma J(q) t) \Pi_I^j(0) + \sqrt{\frac{2M\Gamma}{\beta}} \sum_{l=1}^{3} \int_0^t \exp(-\Gamma J(q)(t-s)) dW_l^j(s).
\end{aligned}
$$

To construct the method: half a step of (32) + one step of a symplectic method for (31) + half a step of (32).

‘Langevin B’ integrator

The vectors $\int_0^t \mathrm{e}^{-\Gamma J(q)(t-s)} S_l q dW_l^j(s)$ in (32) are Gaussian with zero mean and covariance $C_l(t;q) = \int_0^t \mathrm{e}^{-\Gamma J(q)(t-s)} S_l q (S_l q)^{\mathsf{T}} \mathrm{e}^{-\Gamma J(q)(t-s)} ds$.

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

where

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

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

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

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then $\Pi_l^j(t)$ in (32) can be written as

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

'Langevin B' integrator

$$\mathbf{P}_0 = \mathbf{p},\ \mathbf{R}_0 = \mathbf{r},\ \mathbf{Q}_0 = \mathbf{q},\ |q^j| = 1,\ j = 1, \ldots, n,\ \Pi_0 = \boldsymbol{\pi},\ \mathbf{q}^{\mathsf{T}}\boldsymbol{\pi} = 0, \tag{33}$$

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

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

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

‘Langevin B’ integrator

$\boldsymbol{\xi}_k = (\xi_{1,k}, \ldots, \xi_{3n,k})^T$, $\boldsymbol{\zeta}_k = (\zeta_{1,k}, \ldots, \zeta_{3n,k})^T$, $\boldsymbol{\eta}_k^j = (\eta_{1,k}^j, \ldots, \eta_{3,k}^j)^T$, $j = 1, \ldots, n$, with their components being i.i.d. with the same law (29):

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

Proposition 2. *The numerical scheme* (33), (29) *for* (10)–(11) *is quasi-symplectic, it preserves* (13) *and* (14) *and it is of weak order two*.

‘Langevin C’ integrator

Based on the same spliting (30) and (31) as Langevin B, i.e., the determinisitic Hamiltonian system + OU.

To construct the method: half a step of a symplectic method for (31) + step of (32) + half a step of a symplectic method for (31).

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

'Langevin C' integrator

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

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

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

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

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

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

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

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

‘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 (29).

Proposition 3. *The numerical scheme* (34), (29) *for* (10)–(11) *is quasi-symplectic, it preserves* (13) *and* (14) *and* it *is of weak order two*.

The gradient thermostat for rigid body dynamics

It is easy to verify that

$$\int_{\mathbb{D}_{\mathrm{mom}}} \exp \qquad (-\beta H(\mathbf{r},\mathbf{p},\mathbf{q},\boldsymbol{\pi}))d\mathbf{p}d\boldsymbol{\pi} \tag{35}$$
$$\propto \quad \exp(-\beta U(\mathbf{r},\mathbf{q})) =: \tilde{\rho}(\mathbf{r},\mathbf{q}),$$

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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$$\int_{\mathbb{D}_{\mathrm{mom}}} \exp \quad (-\beta H(\mathbf{r},\mathbf{p},\mathbf{q},\boldsymbol{\pi}))d\mathbf{p}d\boldsymbol{\pi} \tag{35}$$
$$\propto \quad \exp(-\beta U(\mathbf{r},\mathbf{q})) =: \tilde{\rho}(\mathbf{r},\mathbf{q}),$$

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 $\mathbb{D}_{\mathrm{mom}} = \{(\mathbf{p}^{\mathsf{T}},\boldsymbol{\pi}^{\mathsf{T}})^{\mathsf{T}} \in \mathbb{R}^{7n} : \mathbf{q}^{\mathsf{T}}\boldsymbol{\pi} = 0\}$.
We introduce the gradient system in the form of Stratonovich SDEs:

$$d\mathbf{R} = \frac{\upsilon}{m}\mathbf{f}(\mathbf{R},\mathbf{Q})dt + \sqrt{\frac{2\upsilon}{m\beta}}d\mathbf{w}(t), \quad \mathbf{R}(0) = \mathbf{r}, \tag{36}$$

$$dQ^j = \frac{\Upsilon}{M}F^j(\mathbf{R},\mathbf{Q})dt + \sqrt{\frac{2\Upsilon}{M\beta}}\sum_{l=1}^{3} S_l Q^j \star dW_l^j(t), \tag{37}$$

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

where "$\star$" indicates the Stratonovich form of the SDEs, parameters $\upsilon > 0$ and $\Upsilon > 0$ control the speed of evolution of the gradient system (36)–(37), $\mathbf{f} = (f^{1\,\mathsf{T}},\ldots,f^{n\,\mathsf{T}})^{\mathsf{T}}$ and the rest of the notation is as in (10)–(11). [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 (10)–(11), the solution of (36)–(37) preserves the quaternion length (13).
- Assume that the solution $X(t) = (\mathbf{R}^{\mathsf{T}}(t), \mathbf{Q}^{\mathsf{T}}(t))^{\mathsf{T}} \in \mathbb{D}'$ of (36)–(37) 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 (35).

Geometric integrator for the gradient thermostat

The main idea is to rewrite the components Q^j of the solution to (36)–(37) 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 (37) can be written as

$$dQ^j = \frac{\Upsilon}{M} \mathbb{F}_j(\mathbf{R}, \mathbf{Q}) Q^j dt + \sqrt{\frac{2\Upsilon}{M\beta}} \sum_{l=1}^{3} S_l Q^j \star dW_l^j(t),\ Q^j(0) = q^j,\ |q^j| = 1. \tag{38}$$

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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

$$\mathbf{R}_0 = \mathbf{r},\ \mathbf{Q}_0 = \mathbf{q},\ |q^j| = 1,\ j = 1, \ldots, n, \tag{39}$$

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

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

$$Q_{k+1}^j = \exp(Y_k^j)Q_k^j,\quad j = 1, \ldots, n,$$

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

$$P(\theta = \pm 1) = 1/2. \tag{40}$$

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$$P(\theta = \pm 1) = 1/2. \tag{40}$$

Proposition 4. *The numerical scheme* (39)–(40) *for* (36)–(37) *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

Numerical experiments

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

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

rotational temperature

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

and potential energy per molecule

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

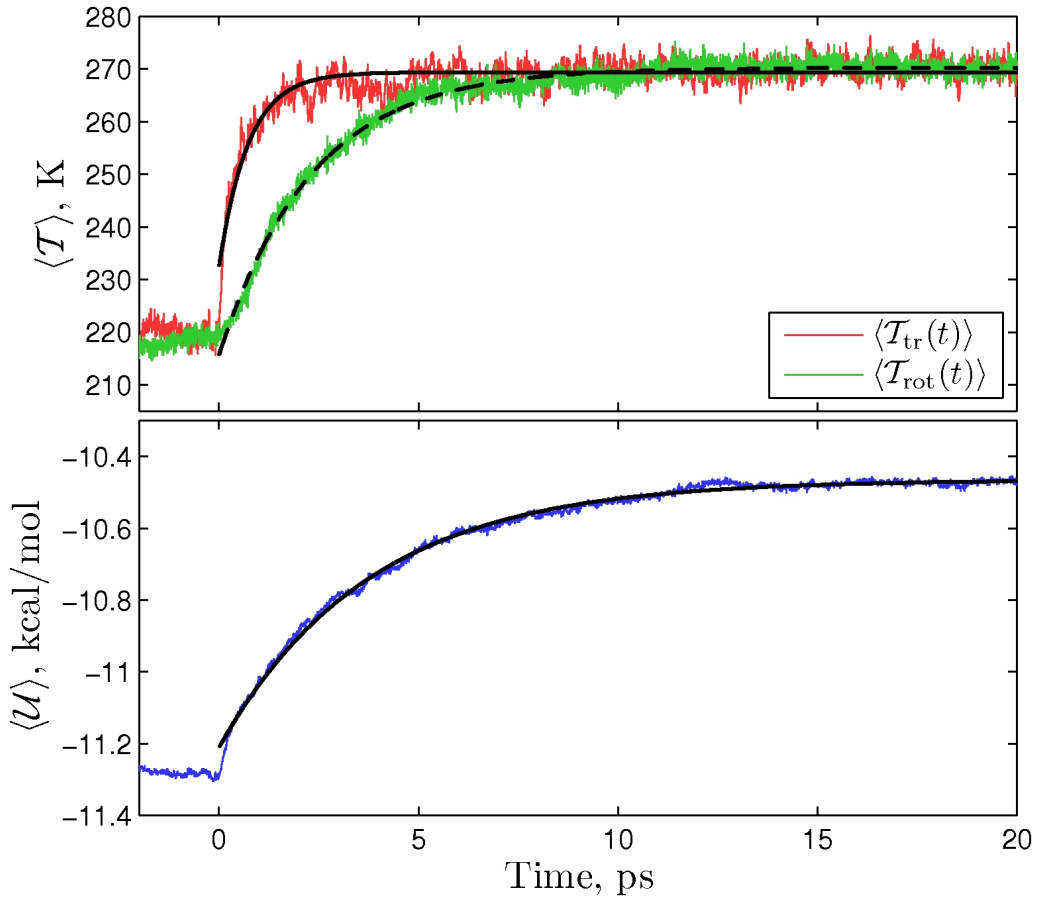

Figure: Langevin thermostat: $\gamma = 4\,\mathrm{ps}^{-1}$, $\Gamma = 0$.

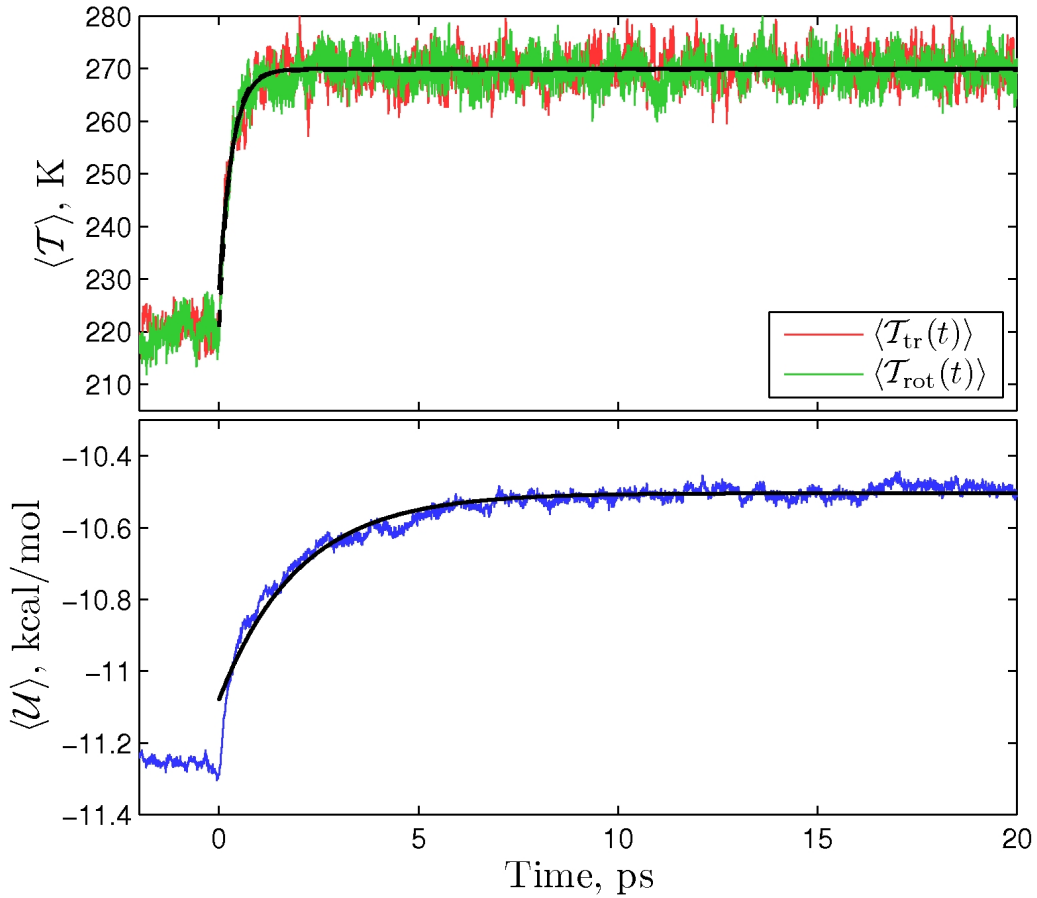

Figure: Langevin thermostat: $\gamma = 4\,\mathrm{ps}^{-1}$, $\Gamma = 10\,\mathrm{ps}^{-1}$.

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

Parameters of the Langevin thermostat

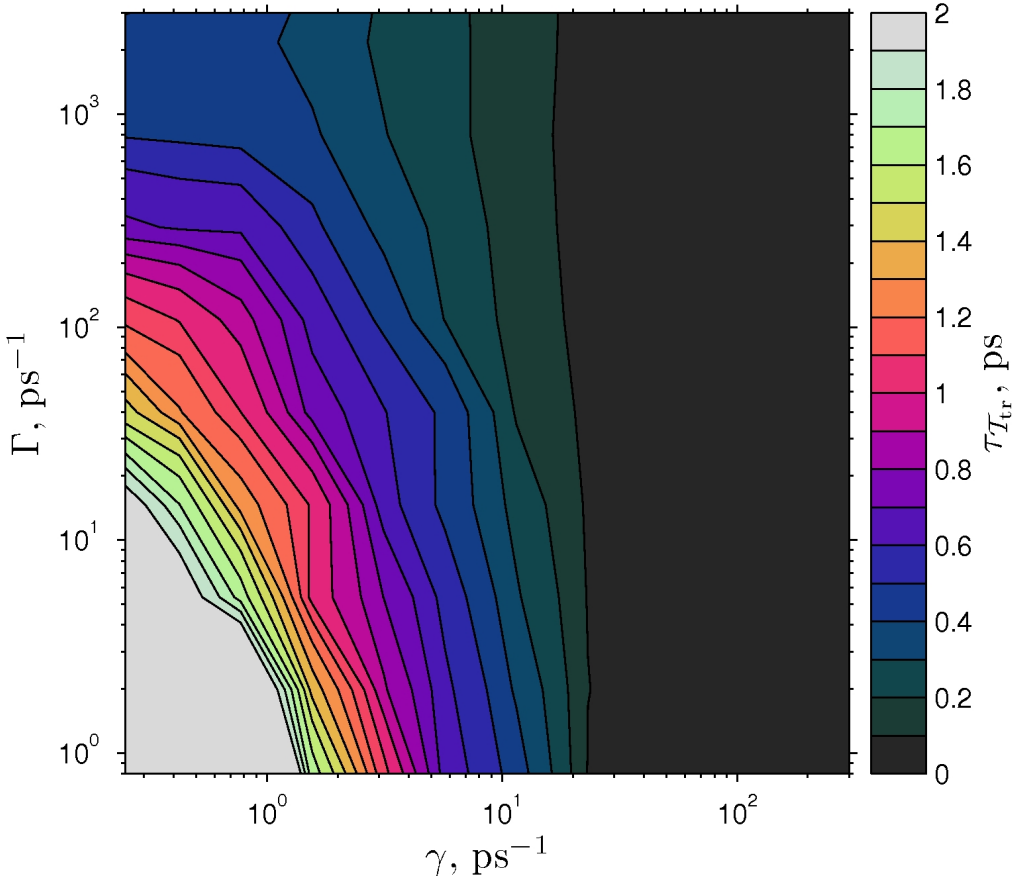

Figure: Langevin thermostat. Dependence of relaxation time of the translational temperature on γ and Γ.

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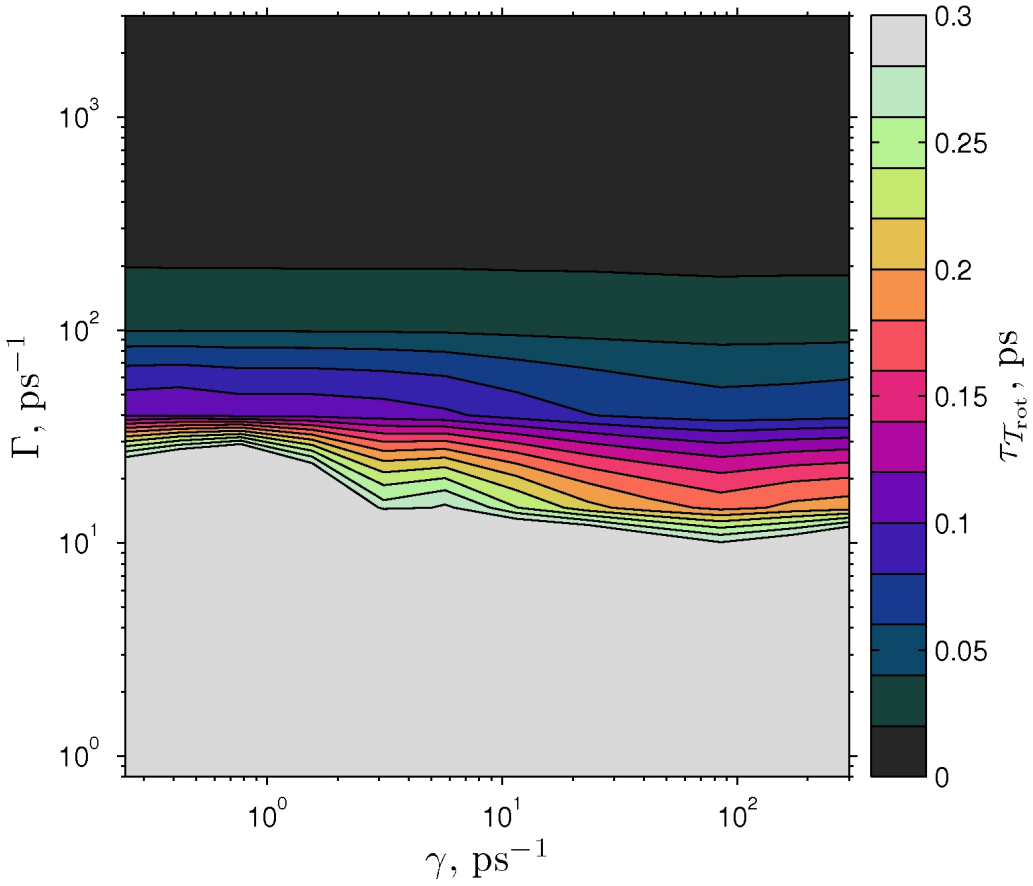


Figure: Langevin thermostat. Dependence of relaxation time of the rotational temperature on γ and Γ.

Parameters of the Langevin thermostat

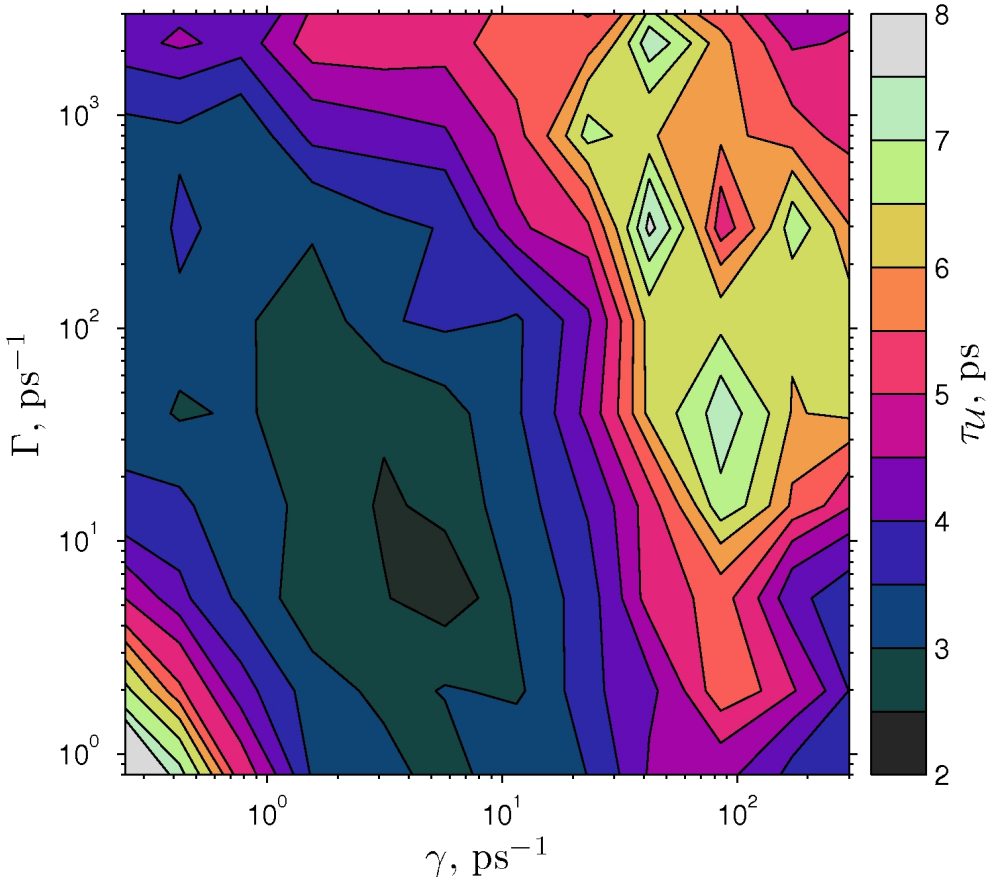


Figure: Langevin thermostat. Dependence of relaxation time of the potential energy on γ and Γ.

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

Accuracy of integrators

- Translational kinetic temperature

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

- Rotational kinetic temperature

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

- 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.

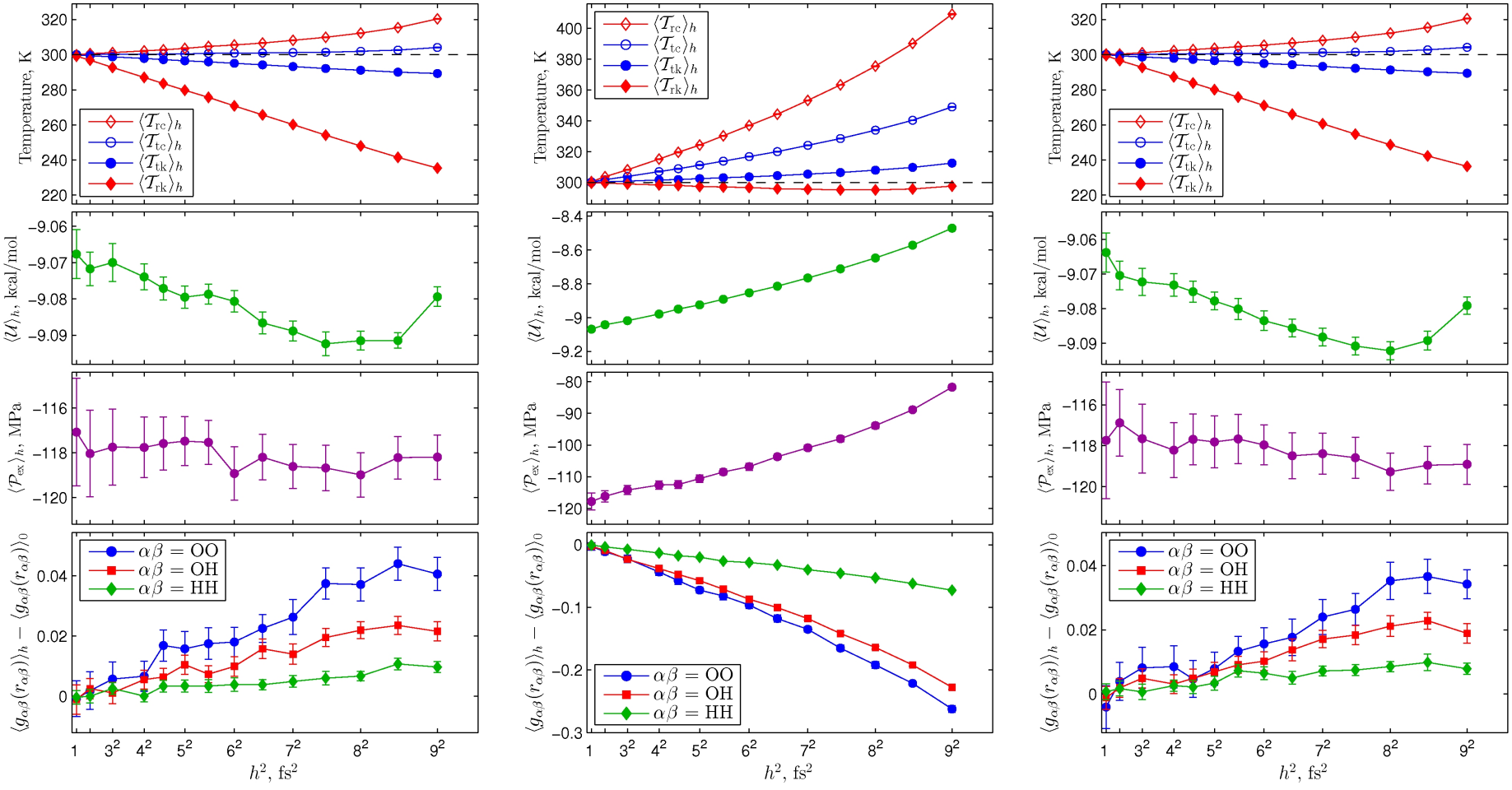
Accuracy of integrators

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

$p = 2$ 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.

Gradient thermostat

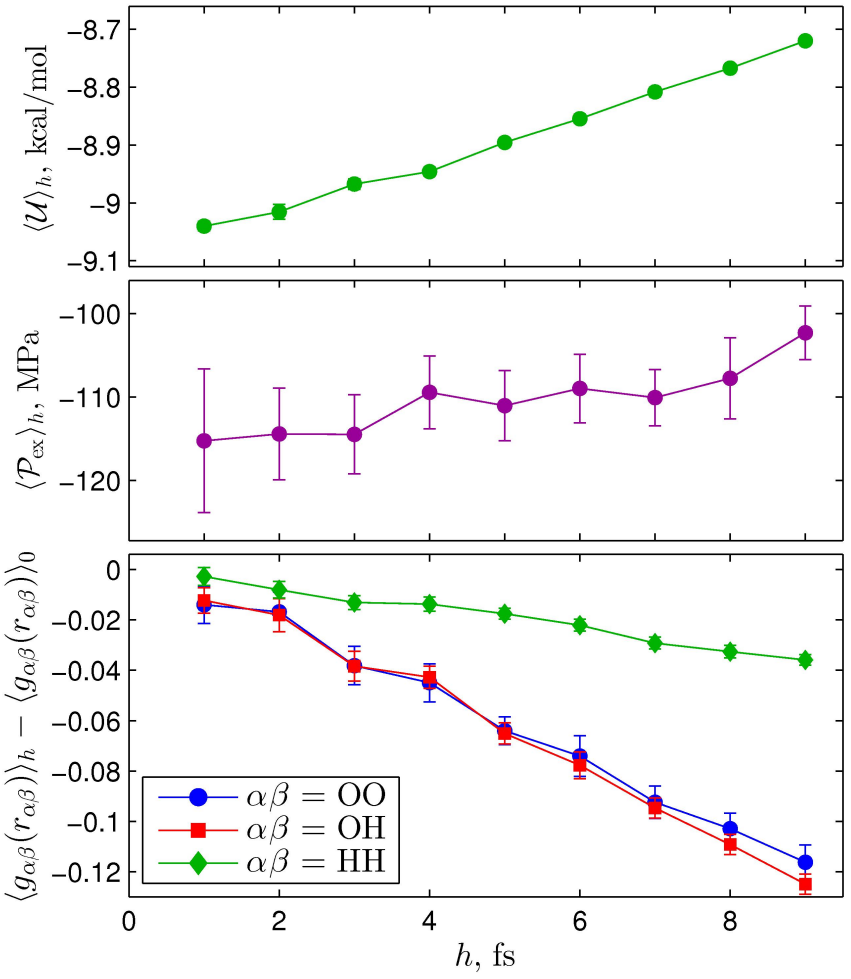


Figure: Gradient thermostat with $\upsilon = 4\,\mathrm{fs}$ and $\Upsilon = 1\,\mathrm{fs}$. Error bars denote estimated 95% confidence intervals in the measured quantities. The bottom plot illustrates numerical integration error in the evaluation of the RDFs near the first maximum.

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 $h \leq 6\,\mathrm{fs}$ for Langevin integrators and for $h \leq 4\,\mathrm{fs}$ 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.

Conclusions

- Two new thermostats, one of Langevin type and one of gradient (Brownian) type, for rigid body dynamics are introduced.
- As in the deterministic case, it is important to preserve structural properties of stochastic systems for accurate long term simulations.
- Geometric integrators for the stochastic thermostats were constructed.
- Testing of thermostats and numerical integrators were done.

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THANK YOU!

The University of Nottingham
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