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Second-order integrators for Langevin equations with holonomic constraints

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Abstract

We propose a numerical scheme for the integration of the Langevin equation which is second-order accurate. More importantly, we indicate how to generalize this scheme to situations where holonomic constraints are added and show that the resulting scheme remains second-order accurate.

1. Introduction

The evolution of a system of interacting particles in the presence of a thermal bath at temperature T can be described by the Langevin equation

$$M\ddot{x}(t) = F(x(t)) - \gamma M\dot{x}(t) + \sqrt{2k_B T\gamma}M^{1/2}\eta(t) \tag{1}$$

where $x(t) \in \mathbb{R}^{3N}$ denotes the position of the N particles, M the diagonal mass tensor, $F(x)$ the force, $\gamma > 0$ the friction coefficient and $\eta(t) = \dot{W}(t)$ is a white-noise ($W(t)$ being a Wiener process). As a result, the Langevin Eq. (1) is an useful tool to sample the Boltzmann–Gibbs distribution $\rho(x,v) = Z^{-1}\mathrm{e}^{-\beta H(x,v)}$ where $Z = \int_{\mathbb{R}^{3N}\times\mathbb{R}^{3N}} e^{-\beta H(x,v)}\mathrm{d}x\mathrm{d}v$ is the partition function and $H(x,v) = \frac{1}{2}\langle v, Mv\rangle + V(x)$ is the Hamiltonian (here we assumed that $F = -\nabla V$).

The question that we investigate here is how to generate an accurate approximation of a trajectory $(x(t), v(t))$ via time-discretization of (2). This question has been addressed by many authors. Among the most popular integrators are the one of van Gunsteren and Berendsen (vGB) proposed in [1], the one of Brooks–Brünger–Karplus (BBK) proposed in [2] and the Langevin impulse ($\widehat{\mathrm{LI}}$) integrator proposed in [3]. These various integrators have been recently reviewed and compared in [4], and it has been shown that BBK is first-order accurate, whereas both vGB and $\widehat{\mathrm{LI}}$ are second-order accurate. More recently, a class of integrators which are up to third-order accurate and also have some additional nice properties have been proposed in [5]. While all of these integrators have been derived for Langevin equations subject to no constraints, they have been often used to integrate systems in which holonomic constraints are present: this is usually done by simply applying an extra step of SHAKE [6] at every time-step. To the best of our knowledge, however, nobody has ever addressed the question of whether such a generalization of these integrators to simulate systems with constraints affect their numerical accuracy. This question is pertinent since higher-order accurate integrators allow for bigger time-steps and thereby permit to simulate the systems over longer time-intervals. In the deterministic context, because SHAKE does not affect the general structure of second-order integrators such as Verlet, one can easily show that it must preserve the order of accuracy of the integrator. The situation is more complex for Langevin integrators, however, because the structure of these integrators is more complicated and there is a nontrivial interplay between the force and the random noise at every time-step.

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In this Letter, we investigate the issue of the accuracy of a Langevin integrator used with SHAKE. Our main results are: (i) the integrator (21) and its quasi-symplectic version (23) in Section 2, which give simple and, to the best of our knowledge, new second-order accurate integrators for Langevin equations without constraints and (ii) the integrators (34) and (39) in Section 3, which show that SHAKE can be applied to (21) and (23) to impose holonomic constraints without loosing the second-order accuracy of the integrator. While we do not do so here, the method used in Section 3 can in principle be applied to prove (or disprove) that the popular integrators such as vGB, BBK or LĨ keep their order of accuracy when applied in conjunction with SHAKE.

2. Basic algorithms

Written componentwise as a stochastic differential equation, (1) becomes

$$\begin{cases} \mathrm{d}x_i(t) = v_i(t)\mathrm{d}t \\ \mathrm{d}v_i(t) = (m_i^{-1}F_i(x(t)) - \gamma_i v_i(t))\mathrm{d}t + \sqrt{2k_\mathrm{B}T\gamma_i m_i^{-1}}\mathrm{d}W_i(t) \end{cases} \tag{2}$$

where (x_1, x_2, x_3) are the x, y and z components of particle 1 (v_1, v_2, v_3) are the components of its velocity, $m_1 = m_2 = m_3 > 0$ is its mass and $\gamma_1 = \gamma_2 = \gamma_3 > 0$ is the friction coefficient it is subject to, and similarly for (x_4, x_5, x_6), etc. To simplify the formula, it will be convenient to write (2) as

$$\begin{cases} \mathrm{d}x_i(t) = v_i(t)\mathrm{d}t \\ \mathrm{d}v_i(t) = (f_i(x(t)) - \gamma_i v_i(t))\mathrm{d}t + \sigma_i \mathrm{d}W_i(t), \end{cases} \tag{3}$$

where we defined $f_i(x) = m_i^{-1}F_i(x)$ and $\sigma_i = \sqrt{2k_\mathrm{B}T\gamma_i m_i^{-1}}$. Going back to vectorial notations, this equation can be written as the system of integral equations

$$\begin{cases} x(t+h) = x(t) + \int_t^{t+h} v(s)\mathrm{d}s \\ v(t+h) = v(t) + \int_t^{t+h} f(x(s))\mathrm{d}s - \gamma\int_t^{t+h} v(s)\mathrm{d}s \\ \qquad\quad +\sigma(W(t+h) - W(h)) \end{cases} \tag{4}$$

Using $x(s) = x(t) + O(h)$ and $v(s) = v(t) + O(\sqrt{h})$ (recall that $W(t+h) - W(h) = O(\sqrt{h})$) under the integrals and neglecting the corrections of order $h^{3/2}$ and higher, we arrive at the Euler–Maruyama scheme [7,8]:

$$\begin{cases} x^{n+1} = x^n + hv^n \\ v^{n+1} = v^n + hf(x^n) - h\gamma v^n + \sqrt{h}\sigma\xi^n. \end{cases} \tag{5}$$

where x^n is the numerical approximation of $x(nh)$, v^n that of $v(nh)$ and ξ^n are independent (for different n) Gaussian variables with mean zero and covariance $\mathbb{E}(\xi_i^n\xi_j^n) = \delta_{ij}$ (here we used $W(t+h) - W(t) \overset{d}{=} \sqrt{h}\xi^n$, where $\overset{d}{=}$ denotes equality in law or distribution). It can be shown [7,8] that the scheme (5) is first-order accurate, meaning that, given any suitable observable ϕ,

$$\sup_{0\leqslant n\leqslant T/h} |\mathbb{E}\phi(x(nh), v(nh)) - \mathbb{E}\phi(x^n, v^n)| \leqslant Ch \tag{6}$$

where $(x(nh), v(nh))$ is the (exact) solution of (2) evaluated at $t = nh$, (x^n, v^n) is its numerical approximation by (5) and it is assumed that $(x(0), v(0)) = (x^0, v^0)$; $\mathbb{E}$ denotes expectation with respect to the noises in (2) and (5), and the constant C depends on $T < \infty$ and the observable $\phi(x, v)$ but not on h. Note that (6) is a finite-time error estimate, hence it says little about the error in computing equilibrium averages, but it indicates that it may be necessary to use (5) with a very small time-step h when the force field is stiff. Hence (5) may be insufficient in applications (Fig. 1).

To do better than (5), go back to (4), and for $v(s)$ in the integral $\int_t^{t+h} v(s)\mathrm{d}s$ use

$$v(s) = v(t) + \int_t^s f(x(u))\mathrm{d}u - \gamma\int_t^s v(u)\mathrm{d}u + \sigma(W(s) - W(t)) \tag{7}$$

Using $x(u) = x(t) + O(h)$ and $v(u) = v(t) + O(\sqrt{h})$ at this level we deduce that (recall that $s \in [t, t+h]$ and hence $s - t = O(h)$)

$$\begin{aligned} v(s) = v(t) &+ (s-t)(f(x(t)) - \gamma v(t)) \\ &+ \sigma(W(s) - W(t)) + O(h^{3/2}) \end{aligned} \tag{8}$$

and hence

$$\begin{aligned} \int_t^{t+h} v(s)\mathrm{d}s = hv(t) &+ \tfrac{1}{2}h^2(f(x(t)) - \gamma v(t)) \\ &+ \sigma\int_t^{t+h}(W(s) - W(t))\mathrm{d}s + O(h^{5/2}) \end{aligned} \tag{9}$$

Similarly, for $f(x(s))$ in the integral $\int_t^{t+h} f(x(s))\mathrm{d}s$, use

$$f(x(s)) = f(x(t)) + \int_t^s v(u)\cdot\nabla f(x(u))\mathrm{d}u \tag{10}$$

then $x(u) = x(t) + O(h)$ and $v(u) = v(t) + O(\sqrt{h})$ to arrive at

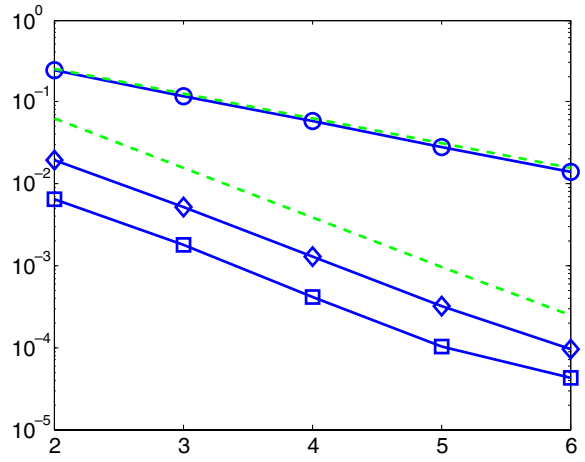

Fig. 1. Numerical errors of the integrators (5), (21) and (23) on the example of $\dot{x}(t) = v(t)$, $\dot{v}(t) = -x(t) - v(t) + \sqrt{2}\eta(t)$, $x(0) = v(0) = 0$. The times steps are $h = 2^{-n}$ for $n = 2,3,4,5,6$. The quantity monitored for the error is the estimate of $\mathbb{E}(x^2(1) + v^2(1)) = 0.9796111900\ldots$ computed by ensemble averaging over 10^8 independent realizations. The dashed curves are the graphs of the functions $2^{-n}(=h)$ and $2^{-2n}(=h^2)$ versus n. The circles are the errors obtained using the first-order integrator (5) and they are consistent with the error estimate (6); the diamonds are the errors obtained using the second-order integrator (21) and they are consistent with the error estimate (18); the squares are the errors obtained using the quasi-symplectic second-order integrator (23).