Research Note

Comment on the Accuracy of Numerical Integration Methods for the Langevin Equation

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March 23, 2004

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Abstract

The accuracy of numerical integrators for the Langevin equation is analyzed in a recent article by the authors. There, the accuracy of transient solutions is studied for a class of simple integrators that are exact for constant force. This note considers the accuracy of steady state solutions. The position squared ensemble average for the Langevin equation is presented for the harmonic oscillator model problem, as an indication of the accuracy order of the steady state distribution function generated by numerical integrators. Surprisingly, the 1982 scheme of van Gunsteren and Berendsen integrator is 4th order accurate, achieving the best accuracy order within the class.

Perhaps the most important criterion for assessing the accuracy of an integrator for molecular dynamics is the accuracy with which the steady state distribution function is approximated. For systems at constant temperature, the most important quantity is the position distribution function, from which all thermodynamic quantities can be computed [1, chapter 2]. Reference [4] studies the Brooks-Brünger-Karplus (BBK) scheme [2] and its variants, while [3] compares BBK scheme with several implicit schemes applicable to diagonal diffusion tensors and introduces additional statistical measures of accuracy.

A new one-parameter class of integrators is discussed in [5, 7]. These integrators have a three-term recurrence relation and are exact for constant force. They include the 1982 scheme of van Gunsteren and Berendsen (vGB82) [6], the "Langevin impulse" (L$\hat{\mathrm{I}}$) method [5], and the "Velocity-Verlet" method proposed in the classic book by Allen and Tildesley (AT-vv) [1, page 263]. The previous work [7] focuses on the short time trajectory accuracy and shows that these integrators are generally second order accurate for practical values of the free parameter. In contrast, the BBK method is only first order accurate. This research note determines the accuracy order of the steady-state distribution function for this class of integrators.

The Langevin equation considered here assumes Gaussian white noise and position-independent diffusion coefficients [1, chapter 9]:

$$\begin{cases} \mathrm{d}x &= v\mathrm{d}t, \\ \mathrm{d}v &= M^{-1}F(x)\mathrm{d}t - \gamma v\mathrm{d}t + (2\gamma k_{\mathrm{B}}T)^{1/2}M^{-1/2}\mathrm{d}W(t). \end{cases} \tag{1}$$

where x is the displacement vector, v is the velocity vector, t is time, M is a diagonal matrix of masses, $F(x)$ is the collective force vector, γ is a diagonal matrix of friction coefficients, k_{B} is the Boltzmann constant, T is temperature, and $W(t)$ is a collection of independent standard Wiener processes.

The 1-parameter class of integrators have the following position recurrence relation [5, 7]:

$$x^{n+1} = (1+e^{-\gamma\Delta})x^n - e^{-\gamma\Delta}x^{n-1} + (\frac{1-e^{-\gamma\Delta}}{\gamma\Delta} - d)M^{-1}F(x^n)\Delta^2 + dM^{-1}F(x^{n-1})\Delta^2 + Q_{\mathrm{c}}^n. \tag{2}$$

where Δ is the timestep, $\{Q_{\mathrm{c}}^n\}$ is a set of Gaussian random variables whose correlations are nonzero only if the superscript difference is 0 or 1, with precise values given in [5, 7], d is the free parameter, depending on friction coefficients γ.

For the harmonic oscillator model problem, the force is linear in x: $-M\omega^2 x$, where ω is the oscillator frequency. For the exact solution, the position obeys the Boltzmann distribution, which is proportional to $\exp(-M\omega^2x^2/(2k_{\mathrm{B}}T))$. For numerical methods, we see immediately from equation (2) that the position x^n has a Gaussian distribution since it is a linear combination of (correlated) Gaussians, and the initial conditions decay exponentially to zero if $\omega \neq 0$ and the integration timestep is not too large. This is clearly seen from equation (B8) of reference [7]. A Gaussian distribution is fully specified by its first and second moment. Taking the average of equation (2), we see $\langle x^n \rangle \to 0$ as $n \to \infty$. The averages of position squared computed from position recurrence relations are summarized in the following, in units of the exact value $k_{\mathrm{B}}T/M\omega^2$:

$$\lim_{n\to\infty}\langle x^n x^n\rangle_{\mathrm{AT-vv}} = 1+\frac{1}{6}\omega^2\Delta^2-\frac{1}{24}\gamma\omega^2\Delta^3+O(\Delta^4), \tag{3}$$

$$\lim_{n\to\infty}\langle x^n x^n\rangle_{\mathrm{LI}} = 1+\frac{1}{12}\omega^2\Delta^2+O(\Delta^4), \tag{4}$$

$$\lim_{n\to\infty}\langle x^n x^n\rangle_{\mathrm{vGB82}} = 1+\frac{1}{48}\omega^4\Delta^4+\frac{1}{288}\gamma\omega^4\Delta^5+O(\Delta^6), \tag{5}$$

$$\lim_{n\to\infty}\langle x^n x^n\rangle_{\mathrm{BBK}} = 1+\frac{1}{4}\omega^2\Delta^2+O(\Delta^4). \tag{6}$$

Equation (4)–(6) appear in [7, equation (48)–(50)]; equation (3) is obtained from [7, equation(23)]. Equation (6) is also computed in [4, 3], and is put here for comparison purpose. In general, an observable physical quantity $A(x)$ has ensemble average

$$\langle A(x)\rangle_{\mathrm{numerical}} = \langle A(x)\rangle_{\mathrm{exact}}+O(\Delta^p). \tag{7}$$

For the harmonic oscillator problem, p is same as the accuracy order of $\lim_{n\to\infty}\langle x^n x^n\rangle$.

With respect to the steady-state averages for the harmonic oscillator, the accuracy of vGB82 integrator is fourth order in timestep, while those of the other three integrators are second order. In contrast to this is the transient accuracy order, for which BBK is only first order accurate while LÎ , vGB82, and AT-vv are second order [7].

Because the parameter d is independent of force, the best order of accuracy with respect to the steady-state distribution of the 1-parameter class integrators is 4. This means the vGB82 integrator gives the best accuracy in the class.

This material is based upon work supported by the National Science Foundation under Grant No. 020442 and by NIH Grant P41RR05969.

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