MOLECULAR PHYSICS, 20 JULY 2003, VOL. 101, NO. 14, 2149–2156

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Analysis of a few numerical integration methods for the Langevin equation

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(*Received 30 June 2002; revised version accepted 15 April 2003*)

We study the position recurrence relation of several existing numerical integrators for the Langevin equation and use the modified equation approach to analyse their accuracy. We show that for the harmonic oscillator, the BBK integrator converges weakly with order 1 while the vGB82 and Langevin impulse (LÎ)‡ integrator converge weakly with order 2. We also study a restricted class of velocity definitions—those that lead to explicit starting procedures. We show that some recurrence relations exact for constant force, can achieve the exact virial relation by a proper definition of velocity, extending the result of Pastor *et al.* on the analysis of BBK integrators in 1988.

1. Introduction

The Langevin equation is a popular model for macromolecular simulations, because it is computationally less demanding than ordinary Newtonian molecular dynamics (MD). This paper is an analytical comparative study of several integrators suitable for the Langevin equation with a diagonal diffusion tensor: the 1982 scheme of van Gunsteren and Berendsen (vGB82) [1], the Brooks–Brünger–Karplus (BBK) scheme [2], and a 'Langevin impulse' (LÎ) integrator from [3]. The Langevin equation under consideration is given by

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

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

The current work is motivated by an earlier analytical study [4], which compares various Langevin integrators of a simple form involving only one set of independent random variables, with one random variable used per time step. This excludes the vGB82 integrator, which is otherwise well regarded because of its accuracy in the Brownian dynamics limit of zero inertia [5]. The 1988 study [4] was favourable to the BBK integrator and, in particular, showed that the velocity could be redefined for BBK so that the virial relation is exactly satisfied in the case of a harmonic oscillator $F(x) = -M\omega^2 x$.

The vGB82 and LÎ integrators are examined in a companion article [6] and shown to be as efficient in their use of random variables as BBK. Also, both vGB82 and LÎ are exact for constant force unlike BBK and the other integrators examined in [4].

All three methods are explicit integrators. Another set of analytical studies [7, 8] compares BBK to several implicit schemes, which are stable for larger values of the time step Δ. The article [8] also introduces additional statistical measures of accuracy.

Section 2 of the current article examines the accuracy of the three integrators for the harmonic oscillator. This is done by means of the 'method of modified equations' [9, 10] and this paper gives perhaps the first such analysis for stochastic differential equations. The idea is to find the nearby analytical problem whose solution exactly coincides with the numerical solution for the original problem. For the BBK scheme the nearby problem has coefficients that differ by $O(\Delta)$ from those of the original problem; whereas for the other two schemes this difference is only $O(\Delta^2)$. To confirm the first-order accuracy of BBK, the modified problem is solved analytically and the variance of the solution is shown to be in error by $O(\Delta)$. On the other hand, the vGB82 and LÎ integrators are shown to converge with order 2 for the harmonic oscillator.

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‡We put a hat on the I to distinguish LÎ from the abbreviation LI for 'Langevin/Implicit-Euler' used in [7] and other papers.

Molecular Physics ISSN 0026–8976 print/ISSN 1362–3028 online
http://www.tandf.co.uk/journals
DOI: 10.1080/0026897031000135825

The accuracy concept used here is known as 'weak convergence' (see Section 17.2 of [11]).

Section 3 of the current article examines the question of redefining velocity to exactly satisfy the virial relation for a harmonic oscillator. It is shown that this is possible not only for BBK but also for integrators such as vGB82 and LÎ.

2. Position recurrence relation

If we consider v in the Langevin equation as an auxiliary variable, the integrator can be developed without velocity. Consequently, an integrator can be expressed by two independent components. One is the position recurrence relation; another is the velocity definition. We want first to study an integrator in isolation from its velocity definition so that the conclusions are not contaminated by the choice of velocity definition.

Let $x^n \approx x(n\Delta)$ and define $f^n = f(x^n) = M^{-1}F(x^n)\Delta^2$. We consider a general two-step, explicit position recurrence relation†

$$x^{n+1} = \xi x^n + \zeta x^{n-1} + e f^n + d f^{n-1} + Q_c^n . \tag{2}$$

We assume ξ, ζ, d, e are dimensionless parameters, $\{Q_c^n\}$ is a set of Gaussian random variables, with $\langle Q_c^n Q_c^n\rangle = A_0$, $\langle Q_c^n Q_c^{n+1}\rangle = A_1$, $\langle Q_c^n Q_c^m\rangle = 0$ for $|m-n| > 1$. Here, $\langle\cdot\rangle$ means ensemble average. All the parameters, ξ, ζ, d e, and A_0, A_1 depend on γ, Δ, M and k_BT only. The framework considered by Pastor *et al.* [4] is a special case of the above with $\xi + \zeta = 1$, $d = 0$ and $A_1 = 0$.

The BBK, vGB82 and LÎ integrators are all within the above framework. For example, the recurrence relation of the BBK integrator is ($g = \gamma\Delta$)

$$x^{n+1} = \frac{2}{1+g/2}x^n - \frac{1-g/2}{1+g/2}x^{n-1} + \frac{1}{1+g/2}f^n + \frac{1}{1+g/2}\left(\frac{2\gamma k_B T\Delta^3}{M}\right)^{1/2} Z^n, \tag{3}$$

where $\{Z^n\}$ is a set of independent standard Gaussian random variables. The starting procedure of BBK is given by

$$x^1 = x^0 + \left(1 - \frac{g}{2}\right)v^0\Delta + \frac{1}{2}f^0 + \left(\frac{\gamma k_B T\Delta^3}{2M}\right)^{1/2} Z^0. \tag{4}$$

The vGB82 and LÎ integrators are given in section 2.2.

We give the fundamental formula for the error analysis in Section 2.1, then give a one-parameter class of position recurrence relations exact for constant force in section 2.2, of which vGB82 and LÎ integrator are two special cases. In section 2.3, we present the error analysis of these integrators for the case of a harmonic oscillator.

2.1. *Modified equation approach*

Our discussion uses the modified equation approach to analyse the weak convergence order of the numerical integrators for a model problem—the harmonic oscillator. This approach is similar to backward error analysis in that we propose a modified equation which is solved exactly by the numerical integrator applied to the original equation. The modified equation resembles the original Langevin equation, but with different values of parameters and an extra term. We examine the size of the modifications. Then, going beyond backward error analysis, we proceed and calculate the exact solution to the modified equations. Based on the exact solution, we calculate the covariance of positions at different times and make comparison with the same quantity derived from the original Langevin equations. The error term provides us with the weak convergence order of the numerical integrator for the model problem.

Since we focus on the harmonic oscillator model problem, the modified equation used in this paper takes the form of

$$\frac{\mathrm{d}}{\mathrm{d}t}\begin{bmatrix} x \\ v \end{bmatrix} = \begin{bmatrix} 0 & 1 \\ -\tilde{\omega}^2 & -\tilde{\gamma} \end{bmatrix}\begin{bmatrix} x \\ v \end{bmatrix} + \begin{bmatrix} \alpha \\ \tilde{\gamma} \\ \beta \end{bmatrix}\left(\frac{2\tilde{\gamma}k_B T}{M}\right)^{1/2}\frac{\mathrm{d}W(t)}{\mathrm{d}t} = AY(t) + B\frac{\mathrm{d}W(t)}{\mathrm{d}t}, \tag{5}$$

where $Y = [x, v]^T$, $W(t)$ is a standard Wiener process, $\tilde{\omega}$ and $\tilde{\gamma}$ are the modified frequency and friction coefficient, and α, β are dimensionless parameters. The original Langevin equation has $\tilde{\omega} = \omega$, $\tilde{\gamma} = \gamma$, $\alpha = 0$ and $\beta = 1$. We need to add a (small) random term to the first equation of the Langevin equation, which is reminiscent of the 'dynamics driver' in [13]. The article [8] studies the modified values $\tilde{\omega}$ and $\tilde{\gamma}$ only. Integrating from t^n to t^{n+1}, we have

$$Y(t^{n+1}) = \exp(\Delta A)Y(t^n) + X^n , \tag{6}$$

where

$$X^n = \int_{t^n}^{t^{n+1}} \exp\left[A(t^{n+1} - t)\right]B\,\mathrm{d}W(t) \tag{7}$$

is a pair of Gaussian random variables with mean 0 and covariances

$$\left\langle X^n X^{m\mathrm{T}}\right\rangle = \begin{cases} \displaystyle\int_0^\Delta \exp(tA)BB^{\mathrm{T}}\exp(tA^{\mathrm{T}})\mathrm{d}t & (m = n), \\ 0 & (m \neq n). \end{cases} \tag{8}$$

†To reduce the round-off error, it is recommended that this be implemented as a pair of first-order difference equations [12].

In appendix A, we derive a position recurrence relation from (6):

$$x(t^{n+1}) = 2\exp(-\tilde{g}/2)\cos\tilde{w}'x(t^n) - \exp(-\tilde{g})x(t^{n-1}) + Q^n\,, \tag{9}$$

where $\tilde{g} = \tilde{\gamma}\Delta$, $\tilde{w} = \tilde{\omega}\Delta$, $\tilde{w}' = \tilde{\omega}'\Delta$ and $\tilde{\omega}' = (\tilde{\omega}^2 - \tilde{\gamma}^2/4)^{1/2}$. Note that when $\tilde{\omega} < \tilde{\gamma}/2$, $\cos\tilde{w}'$ becomes $\cos(\tilde{g}^2/4 - \tilde{w}^2)^{1/2}$. The random terms Q^n are Gaussian random variables with covariances

$$\begin{aligned}\langle Q^n Q^n\rangle = \frac{2k_\mathrm{B}T\Delta^2}{M}\Bigg\{&\frac{(\alpha+\beta)^2}{\tilde{w}^2}\\ &\times\left[\frac{1-\exp(-2\tilde{g})}{2} - \tilde{g}\exp(-\tilde{g})\frac{\sin 2\tilde{w}'}{2\tilde{w}'}\right]\\ &+\frac{\alpha^2}{\tilde{g}^2}\left[\frac{1-\exp(-2\tilde{g})}{2} + \tilde{g}\exp(-\tilde{g})\frac{\sin 2\tilde{w}'}{2\tilde{w}'}\right]\Bigg\},\end{aligned} \tag{10}$$

$$\begin{aligned}&\langle Q^n Q^{n+1}\rangle\\ &= \frac{2k_\mathrm{B}T\Delta^2}{M}\frac{1}{4}\exp(-\tilde{g}/2)\Bigg\{\frac{(\alpha+\beta)^2}{\tilde{w}^2}\\ &\times\left[\tilde{g}[1+\exp(-\tilde{g})]\frac{\sin\tilde{w}'}{\tilde{w}'} - 2[1-\exp(-\tilde{g})]\cos\tilde{w}'\right]\\ &-\frac{\alpha^2}{\tilde{g}^2}\left[\tilde{g}[1+\exp(-\tilde{g})]\frac{\sin\tilde{w}'}{\tilde{w}'} + 2[1-\exp(-\tilde{g})]\cos\tilde{w}'\right]\Bigg\}.\end{aligned} \tag{11}$$

Other covariances are zero.

2.2. *Position recurrence relations exact for constant force*

Computations similar to (9) give the exact recurrence relation of the Langevin equations for constant force:

$$\begin{aligned}x(t^{n+1}) = (1+\exp(-g))x(t^n) - \exp(-g)x(t^{n-1})\\ +\frac{1-\exp(-g)}{g}f + R^n\end{aligned} \tag{12}$$

with

$$R_+^n = \left(\frac{2\gamma k_\mathrm{B}T}{M}\right)^{1/2}\int_{t^n}^{t^{n+1}}\frac{1-\exp[-\gamma(t^{n+1}-t)]}{\gamma}\,\mathrm{d}W(t)\,, \tag{13}$$

$$R_-^n = \left(\frac{2\gamma k_\mathrm{B}T}{M}\right)^{1/2}\int_{t^{n-1}}^{t^n}\frac{\exp[\gamma(t-t^n)] - \exp(-\gamma\Delta)}{\gamma}\mathrm{d}W(t), \tag{14}$$

$$R^n = R_+^n + R_-^n. \tag{15}$$

By requiring (2) to be exact for constant force, it becomes

$$\begin{aligned}x^{n+1} = (1+\exp(-g))x^n - \exp(-g)x^{n-1}\\ +\left(\frac{1-\exp(-g)}{g} - d\right)f^n + df^{n-1} + Q_\mathrm{c}^n\end{aligned} \tag{16}$$

with

$$\langle Q_\mathrm{c}^n Q_\mathrm{c}^{n+k}\rangle = \begin{cases} a+c & (k=0)\,,\\ b & (k=\pm1)\,,\\ 0 & (\text{otherwise})\,,\end{cases} \tag{17}$$

where

$$a \equiv \langle R_+^n R_+^n\rangle = \frac{2k_\mathrm{B}T}{\gamma^2 M}\left(-\frac{3}{2} + g + 2\exp(-g) - \frac{1}{2}\exp(-2g)\right), \tag{18}$$

$$b \equiv \langle R_+^n R_-^n\rangle = \frac{2k_\mathrm{B}T}{\gamma^2 M}\left(\frac{1}{2} - g\exp(-g) - \frac{1}{2}\exp(-2g)\right), \tag{19}$$

$$\begin{aligned}c &\equiv \langle R_-^n R_-^n\rangle\\ &= \frac{2k_\mathrm{B}T}{\gamma^2 M}\left(\frac{1}{2} - 2\exp(-g) + \frac{3}{2}\exp(-2g) + g\exp(-2g)\right).\end{aligned} \tag{20}$$

Note that equation (16) contains one free parameter d. The position recurrence relation used in L$\hat{\mathrm{I}}$ and vGB82 integrator are two special cases of (16) with

$$d_{\mathrm{L}\hat{\mathrm{I}}} = 0\,, \tag{21}$$

$$d_{\mathrm{vGB82}} = \frac{1-g/2-(1+g/2)\exp(-g)}{g^2}\,. \tag{22}$$

Another special case is the method introduced in [14] on p. 263, for which

$$d = \frac{(1-\exp(-g))^2 - g^2\exp(-g)}{g^3}\,. \tag{23}$$

The starting procedure of L$\hat{\mathrm{I}}$ and vGB82 integrators is

$$\begin{aligned}x^1 = x^0 + \frac{1-\exp(-g)}{g}v^0\Delta\\ +\frac{\exp(-g)-1+g}{g^2}f^0 + R_+^0.\end{aligned} \tag{24}$$

The BBK integrator is not exact for constant force.

2.3. *Error analysis*

The fact that the backward error is $O(\Delta^2)$ generally implies that the (forward) error is $O(\Delta^2)$. However, due

to cancellation, it is possible that the forward error is of higher order. To make sure that our analysis gives the precise order of the forward error, it is wise to compute both errors.

For a harmonic oscillator, the force is linear: $F(x) = -M\omega^2 x$. The BBK integrator gives the following recurrence relation ($w = \omega\Delta$):

$$x^{n+1} = \frac{2-w^2}{1+g/2}x^n - \frac{1-g/2}{1+g/2}x^{n-1} + \left(\frac{2\gamma k_B T \Delta^3}{M}\right)^{1/2} Z^n. \tag{25}$$

We assume the modified equation is (5), which has recurrence relation (9). Comparing equation (9) with (25) and equating the two coefficients and two non-zero covariances of the random terms, we obtain

$$\tilde{\gamma} = \gamma\left(1 + \frac{1}{12}\gamma^2\Delta^2 + O(\Delta^4)\right), \tag{26}$$

$$\tilde{\omega} = \omega\left(1 - \frac{1}{24}(\gamma^2 + \omega^2)\Delta^2 + O(\Delta^4)\right), \tag{27}$$

$$\alpha = \frac{1}{6^{1/2}}\gamma\Delta + O(\Delta^2), \tag{28}$$

$$\beta = 1 - \frac{1}{6^{1/2}}\gamma\Delta + O(\Delta^2). \tag{29}$$

The computation is performed using Maple [15]. The values given here for $\tilde{\gamma}$ and $\tilde{\omega}$ are consistent with the values $\gamma_{\text{eff}}(\Delta t)$ and $[\omega_{\text{eff}}^2(\Delta t) + \gamma_{\text{eff}}^2(\Delta t)/4]^{1/2}$ from table II of [8]†. Note that the error in the parameters is first order in Δ.

In appendix B, we solve equation (5) analytically and derive the position covariance error. The result for $\omega = 0$ (zero force) is

$$\begin{aligned}&\text{cov}(x(t_1)x(t_2))_{\text{BBK}} - \text{cov}(x(t_1)x(t_2))_{\text{exact}} \\ &= \frac{2k_B T}{6M\gamma}(1 - \exp(-\gamma t_1))(1 - \exp(-\gamma t_2))\Delta + O(\Delta^2).\end{aligned} \tag{30}$$

This error is first order in Δ, meaning that the BBK integrator converges weakly with order 1 even if the force is 0. For $\omega \neq 0$, we also obtain a first-order error:

$$\begin{aligned}&\text{cov}(x(t_1)x(t_2))_{\text{BBK}} - \text{cov}(x(t_1)x(t_2))_{\text{exact}} \\ &= \frac{2k_B T}{M}\frac{\gamma}{6\omega'^2}\left[\exp\left(-\frac{\gamma(t_1+t_2)}{2}\right)\sin\omega' t_1 \sin\omega' t_2\right]\Delta \\ &\quad + O(\Delta^2).\end{aligned} \tag{31}$$

†Note that there is a typo in paper [8], namely, for the BBK method, $\omega_{\text{eff}}(\Delta t) = (1/\Delta t)\cos^{-1}[(2-\epsilon^2)/(4-\delta^2)^{1/2}]$.

The same analysis is carried out for equation (16), which is exact for constant force and includes both the vGB82 integrator and the L$\hat{\text{I}}$ integrator. This time, the parameters in the modified equations (5) are [15]

$$\tilde{\gamma} = \gamma - d\omega^2\Delta + O(\Delta^2), \tag{32}$$

$$\tilde{\omega} = \omega - \frac{1}{24}(6d-1)\omega^3\Delta^2 + O(\Delta^3), \tag{33}$$

$$\alpha = \frac{1}{3(10^{1/2})}\omega\gamma\Delta^2 + O(\Delta^3), \tag{34}$$

$$\beta = 1 + d\frac{\omega^2}{2\gamma}\Delta + O(\Delta^2). \tag{35}$$

As long as $d = O(\Delta)$, the errors are $O(\Delta^2)$. The L$\hat{\text{I}}$ integrator sets $d = 0$, while the vGB82 integrator sets $d = -((1+g/2)\exp(-g) - 1 + g/2)/g^2 = -\frac{1}{12}\gamma\Delta + O(\Delta^2)$, so both integrators introduce second-order error into the parameters.

The position covariance errors for the vGB82 and L$\hat{\text{I}}$ integrators are complicated, but the leading term is $O(\Delta^2)$. This means both vGB82 and L$\hat{\text{I}}$ integrators converge weakly with order 2 for the harmonic oscillator problem.

The fact that the BBK integrator has lower weak convergence order than L$\hat{\text{I}}$ and vGB82 may not be as significant as it may seem. This is because for zero force, the leading term of the position covariance is proportional to t_1, which increases linearly as t_1 increases, but the error expressed in equation (30) for the BBK integrator does not; for the harmonic oscillator case, the error decays exponentially with time, as can be seen from (31).

3. Velocity definition

Sometimes, an approximation to velocity is needed during the molecular dynamics simulation. There are several ways to define velocity in the numerical integrator. One way is to use the starting procedure, as is done by the BBK and the L$\hat{\text{I}}$ integrator [6]. They simply extend equation (4) for BBK, and (24) for L$\hat{\text{I}}$, by changing the upper indices 0 to n, and 1 to $n+1$. Consequently, these methods are 'restartable', meaning that a restart after step N would be equivalent to one more use of the position recurrence relation without the restart. Notice that although vGB82 uses the same starting procedure as L$\hat{\text{I}}$ does, its velocity definition is not consistent with its starting procedure [1]. Another way to define velocity is to impose some requirement, such as exact virial relation. It is shown in [4] that a proper re-definition of velocity can give the exact virial relation for the case of a harmonic oscillator. In this section, we explore whether the position recurrence relation (16), which is exact for constant force, can be

augmented with a proper velocity definition to give the exact virial relation.

3.1. *Virial theorem*

For a thermodynamic system, the virial theorem states, see [14] p. 46,

$$\langle p_k \partial H/\partial p_k \rangle = k_B T \,, \tag{36}$$

$$\langle q_k \partial H/\partial q_k \rangle = k_B T \,, \tag{37}$$

where H is the Hamiltonian of the system, and q_k and p_k are generalized position coordinates and corresponding momenta, respectively, and where $\langle\cdot\rangle$ means ensemble average. In our discussion, the 'virial relation' means the following relation derived from the above equation:

$$\langle p_k \partial H/\partial p_k \rangle = \langle q_k \partial H/\partial q_k \rangle \,. \tag{38}$$

For the simple case of a particle moving under the linear force $F(x) = -M\omega^2 x$ in one-dimensional space, the virial relation simplifies to

$$\langle v^2 \rangle - \omega^2 \langle x^2 \rangle = 0 \,. \tag{39}$$

In this paper, reference to 'exact virial relation' means exact virial relation for the harmonic oscillator.

In [4], it is shown that by changing the velocity definition to $v^n = (x^n - x^{n-1})/\Delta$, the virial relation for a harmonic oscillator is observed for BBK:

$$\lim_{n\to\infty} (\langle v^n v^n \rangle - \omega^2 \langle x^n x^n \rangle) = 0 \,. \tag{40}$$

This property is not held either by the vGB82 or by the $\hat{\text{LI}}$ integrator. So the question is, can equation (16) achieve exact virial relation with a proper definition of velocity?

3.2. *Exact virial relation*

We start with

$$\begin{cases} x^{n+1} = (1+\exp(-g))x^n - \exp(-g)x^{n-1} \\ \qquad\quad +((1-\exp(-g))/g - d)f^n + df^{n-1} + Q_c^n, \\ v^n \Delta = px^n + qx^{n-1} + sf^n + rf^{n-1} + \rho Q_c^n \,, \end{cases} \tag{41}$$

with $\langle Q_c^n Q_c^n \rangle = A_0 = a + c$, $\langle Q_c^n Q_c^{n+1} \rangle = A_1 = b$ and $\langle Q_c^n Q_c^{n+k} \rangle = 0$ for $k > 1$. The first equation is (16), which is exact for constant force. The second equation is the definition of velocity v^n. Here d, p, q, s and u are dimensionless parameters depending on γ, Δ, M and $k_B T$.

For the linear force case, the first equation of (41) gives

$$x^{n+1} = a_1 x^n + a_2 x^{n-1} + Q_c^n \,, \tag{42}$$

with $a_1 = 1 + \exp(-g) - ((1-\exp(-g))/g - d)w^2$ and $a_2 = -\exp(-g) - dw^2$. The recurrence relation has the solution

$$x^{n+1} = Q_c^n + a_1 Q_c^{n-1} + \text{linear combination of } Q_c^{n-2}, \ldots, Q_c^1 \text{ and } x^0, x^1. \tag{43}$$

Define

$$Y_i = \lim_{n\to\infty} \langle x^n x^{n+i} \rangle \,, \quad \text{for } i = 0, 1, 2. \tag{44}$$

Equations (42) and (43) give

$$\begin{cases} Y_0 = a_1 Y_1 + a_2 Y_2 + A_0 + a_1 A_1, \\ Y_1 = a_1 Y_0 + a_2 Y_1 + A_1, \\ Y_2 = a_1 Y_1 + a_2 Y_0. \end{cases} \tag{45}$$

We obtain Y_0 and Y_1 by solving the above set of equations:

$$Y_0 = \frac{(1-a_2)A_0 + 2a_1 A_1}{(1+a_2)[(1-a_2)^2 - a_1^2]} \,, \tag{46}$$

$$Y_1 = \frac{a_1 A_0 + (1 + a_1^2 - a_2^2)A_1}{(1+a_2)[(1-a_2)^2 - a_1^2]} \,. \tag{47}$$

We do not write down Y_2 explicitly since we do not need it in the following discussions. In particular we obtain

$$\langle x^n x^n \rangle_{\hat{\text{LI}}} = \frac{k_B T}{m\omega^2}\left(1 + \frac{1}{12}\omega^2\Delta^2 + O(\Delta^3)\right), \tag{48}$$

$$\langle x^n x^n \rangle_{\text{vGB82}} = \frac{k_B T}{m\omega^2}\left(1 + \frac{1}{48}\omega^4\Delta^4 + O(\Delta^5)\right). \tag{49}$$

The above result can be used to compare with

$$\langle x^n x^n \rangle_{\text{BBK}} = \frac{k_B T}{m\omega^2}\frac{1}{1 - \omega^2\Delta^2/4} = \frac{k_B T}{m\omega^2}\left(1 + \frac{1}{4}\omega^2\Delta^2 + O(\Delta^3)\right), \tag{50}$$

which is given in [4] as well as in [8]. From the second equation of (41), we can write v^n in terms of x^n and x^{n-1}, square both sides, and obtain

$$\lim_{n\to\infty} \langle v^n v^n \rangle \Delta^2 = [(p - sw^2)^2 + (q - rw^2)^2]Y_0 + \rho^2 A_0 + 2(p - sw^2)(q - rw^2)Y_1 + 2(p - sw^2)\rho A_1. \tag{51}$$

The exact virial relation requires

$$w^2 Y_0 - \lim_{n\to\infty} \langle v^n v^n \rangle \Delta^2 = 0. \tag{52}$$

With a common denominator, the numerator in the above equation is a polynomial in w^2 of degree 4. Requiring all the coefficients to be zero, we obtain five conditions. The unknowns in the equation are p, q, s, r and ρ. The five conditions determine the five unknowns. Solving equation (52) gives the corresponding parameters for defining velocity to give an exact virial relation. If $d = 0$ (the choice of the $\hat{\text{LI}}$ integrator), we have

$$r = 0\,, \tag{53}$$

$$s = 0\,, \tag{54}$$

$$p = -q = \left[\frac{g(1+\exp(-g))}{2(1-\exp(-g))}\right]^{1/2}, \tag{55}$$

$$\rho = \frac{1}{A_0[1-\exp(-g)]^{1/2}} \times \left(-A_1[1+\exp(-g)]^{1/2} + [A_1(2A_0 + A_1 + A_1\exp(-g))]\right)^{1/2}\left(\frac{g}{2}\right)^{1/2}. \tag{56}$$

As long as $g = \gamma\Delta > 0$, we have $A_0 > 0$ and $A_1 > 0$. So the above solution is real. For the vGB82 integrator, the equations are too complicated to solve although solutions can be shown to exist for small g.

4. Summary

Theoretical evidence given here and in [6] strongly suggests that the $\hat{\text{LI}}$ and vGB82 [1] schemes are no worse than and often much better than the BBK [2] scheme in situations where it is practical to compute the exponential of the friction tensor, such as in the common case of a diagonal tensor. It is recommended that for such situations $\hat{\text{LI}}$ and vGB82 be implemented and tested.

The research is supported in part by NSF Grants DMS-9971830, DBI-9974555 and DBI-9807882.

Appendix A: Modified equation analysis

Here, we give details of the derivation of the position recurrence relation (9) from the modified equation (5).

For matrix A defined in equation (5), we have

$$\exp(At) = \exp(-\tilde{\gamma}t/2)\cos\tilde{\omega}'t\begin{bmatrix}1 & 0\\ 0 & 1\end{bmatrix} + \exp(-\tilde{\gamma}t/2)\frac{\sin\tilde{\omega}'t}{\tilde{\omega}'}\begin{bmatrix}\tilde{\gamma}/2 & 1\\ -\tilde{\omega}^2 & -\tilde{\gamma}/2\end{bmatrix}. \tag{A1}$$

Applying equation (6) twice, we get $Y(t^{n+1}) = D^2 Y(t^{n-1}) + DX^{n-1} + X^n$, where $D = \exp(\Delta A)$. By Cayley's theorem, any 2×2 matrix D satisfies $D^2 = \operatorname{tr}(D)D - \det(D)I$. Combining the two equations and using (6) again, we have

$$Y(t^{n+1}) = \operatorname{tr}(D)Y(t^n) - \det(D)Y(t^{n-1}) - \operatorname{tr}(D)X^{n-1} + DX^{n-1} + X^n; \tag{A2}$$

we obtain the position recurrence relation by multiplying both sides by vector [1 0]:

$$x(t^{n+1}) = \operatorname{tr}(D)x(t^n) - \det(D)x(t^{n-1}) + Q^n\,, \tag{A3}$$

where

$$Q^n = [1 \quad 0](X^n + (D - \operatorname{tr}(D)I)X^{n-1}). \tag{A4}$$

Since $D = \exp(A\Delta)$, equation (A 1) gives $\det(D) = \exp(-\tilde{g})$ and $\operatorname{tr}(D) = 2\exp(-\tilde{g}/2)\cos\tilde{w}'$, from which equation (9) follows. From equations (A 4) and (8), we use Maple to calculate the covariances between the Q^ns. The non-zero covariances are as given in equations (10) and (11).

Appendix B: Error analysis

Here, we give details of the derivation of equations (30) and (31). For zero force, we assume the modified equation is (5) with $\tilde{\omega} = 0$. Taking the limit $\omega \to 0$ in equations (9), (10) and (11), we obtain the recurrence relation for equation (5) ($\tilde{g} = \tilde{\gamma}\Delta$):

$$x^{n+1} = (1+\exp(-\tilde{g}))x^n - \exp(-\tilde{g})x^{n-1} + Q^n \tag{B 1}$$

with

$$\langle Q^n Q^n\rangle = \frac{2k_{\mathrm{B}}T\Delta^2}{M}\frac{1}{\tilde{g}^2}\left[\tilde{g}(\alpha+\beta)^2(1+\exp(-2\tilde{g})) - \beta(2\alpha+\beta)(1-\exp(-2\tilde{g}))\right], \tag{B2}$$

$$\langle Q^n Q^{n+1}\rangle = \frac{2k_{\mathrm{B}}T\Delta^2}{M}\frac{1}{2\tilde{g}^2}\left[\beta(2\alpha+\beta)(1-\exp(-2\tilde{g})) - 2\tilde{g}\exp(-\tilde{g})(\alpha+\beta)^2\right]. \tag{B3}$$

For zero force, the BBK integrator gives

$$x^{n+1} = \frac{2}{1+g/2}x^n - \frac{1-g/2}{1+g/2}x^{n-1} + \frac{1}{1+g/2}\left(\frac{2\gamma k_{\mathrm{B}}T\Delta^3}{M}\right)^{1/2}Z^n. \tag{B4}$$

Comparing equations (B1)–(B3) with (B4) and solving for α, β and $\tilde{g}$, we have

$$\tilde{g} = \ln\frac{1+g/2}{1-g/2} = g\left(1 + \frac{1}{12}\gamma^2\Delta^2 + O(\Delta^4)\right), \tag{B5}$$

$$\alpha = \left\{\left[1 - \left(1 - \frac{g^2}{4}\right)\frac{\tilde{g}}{g}\right]\frac{\tilde{g}}{g}\right\}^{1/2} = \frac{1}{6^{1/2}}\gamma\Delta + +O(\Delta^3), \tag{B6}$$

$$\beta = \left(\frac{\tilde{g}}{g}\right)^{1/2} - \alpha = 1 - \frac{1}{6^{1/2}}\gamma\Delta + O(\Delta^2). \tag{B7}$$

Note the error is of first order in Δ.

If $t^n = 0$ and $t^{n+1} = t$, equation (6) gives the analytical solution to the modified equation:

$$\begin{aligned} x(t) = {} & \exp\left(-\frac{1}{2}\tilde{\gamma}t\right)\left(\cos\tilde{\omega}'t + \frac{\tilde{\gamma}}{2\tilde{\omega}'}\sin\tilde{\omega}'t\right)x(0) \\ & + \exp\left(-\frac{1}{2}\tilde{\gamma}t\right)\frac{\sin\tilde{\omega}'t}{\tilde{\omega}'}v(0) \\ & + \left(\frac{2\tilde{\gamma}k_{\mathrm{B}}T}{M}\right)^{1/2}\int_0^t \exp\left[-\frac{1}{2}\tilde{\gamma}(t-s)\right] \\ & \times\left[\frac{\alpha}{\tilde{\gamma}}\left(\cos\tilde{\omega}'(t-s) + \frac{\tilde{\gamma}}{2\tilde{\omega}'}\sin\tilde{\omega}'(t-s)\right)\right. \\ & \left. + \beta\frac{\sin\tilde{\omega}'(t-s)}{\tilde{\omega}'}\right]\mathrm{d}W(s). \end{aligned} \tag{B8}$$

For zero force, $\tilde{\omega} = 0$, the solution simplifies to

$$\begin{aligned} x(t) = {} & x(0) + \frac{1-\exp(-\tilde{\gamma}t)}{\tilde{\gamma}}v(0) + \left(\frac{2\tilde{\gamma}k_{\mathrm{B}}T}{M}\right)^{1/2} \\ & \times\int_0^t \frac{\alpha+\beta-\beta\exp[-\tilde{\gamma}(t-s)]}{\tilde{\gamma}}\,\mathrm{d}W(s)\,. \end{aligned} \tag{B9}$$

In a position recurrence relation, we know $x(0)$ and $x(\Delta)$ instead of $x(0)$ and $v(0)$. We assume that $x(\Delta) - x(0) = O(\Delta)$. This is because the original Langevin equation has a continuously differentiable solution $x(t)$. Using equation (B9) for $t = \Delta$, we obtain

$$\begin{aligned} v(0) = {} & \frac{\tilde{\gamma}}{1-\exp(-\tilde{\gamma}\Delta)}\left[x(\Delta) - x(0) - \left(\frac{2\tilde{\gamma}k_{\mathrm{B}}T}{M}\right)^{1/2}\right. \\ & \left.\times\int_0^{\Delta}\frac{\alpha+\beta-\beta\exp[-\tilde{\gamma}(\Delta-s)]}{\tilde{\gamma}}\,\mathrm{d}W(s)\right]. \end{aligned} \tag{B10}$$

This gives

$$\begin{aligned} x(t) = {} & x(0) + \frac{1-\exp(-\tilde{\gamma}t)}{1-\exp(-\tilde{\gamma}\Delta)}(x(\Delta) - x(0)) \\ & - \frac{1-\exp(-\tilde{\gamma}t)}{1-\exp(-\tilde{\gamma}\Delta)}\left(\frac{2\tilde{\gamma}k_{\mathrm{B}}T}{M}\right)^{1/2} \\ & \times\int_0^{\Delta}\frac{\alpha+\beta-\beta\exp[-\tilde{\gamma}(\Delta-s)]}{\tilde{\gamma}}\,\mathrm{d}W(s) + \left(\frac{2\tilde{\gamma}k_{\mathrm{B}}T}{M}\right)^{1/2} \\ & \times\int_0^t\frac{\alpha+\beta-\beta\exp[-\tilde{\gamma}(t-s)]}{\tilde{\gamma}}\,\mathrm{d}W(s). \end{aligned} \tag{B11}$$

For the BBK integrator, α, β and $\tilde{\gamma}$ are given in (B 6), (B 7) and (B 5), respectively. For the original Langevin equation, $\alpha_{\mathrm{exact}} = 0$, $\beta_{\mathrm{exact}} = 1$ and $\tilde{\gamma}_{\mathrm{exact}} = \gamma$. From equation (B 11), we use Maple to compute the covariance of positions at two different times (assume $0 < t_1 \le t_2$):

$$\begin{aligned} & \mathrm{cov}(x(t_1)x(t_2)) \\ & = \langle[x(t_1) - \langle x(t_1)\rangle][x(t_2) - \langle x(t_2)\rangle]\rangle \\ & = \frac{2\tilde{\gamma}k_{\mathrm{B}}T}{M} \\ & \times\left\{\frac{(\exp(-\tilde{\gamma}\Delta) - \exp(-\tilde{\gamma}t_1))(\exp(-\tilde{\gamma}\Delta) - \exp(-\tilde{\gamma}t_2))}{\tilde{\gamma}^2(1-\exp(-\tilde{\gamma}\Delta))^2}\right. \\ & \times\left[(\alpha+\beta)^2\Delta - 2\beta(\alpha+\beta)\frac{\exp(\tilde{\gamma}\Delta)-1}{\tilde{\gamma}} + \beta^2\frac{\exp(2\tilde{\gamma}\Delta)-1}{2\tilde{\gamma}}\right] \\ & + \frac{1}{\tilde{\gamma}^2}\left[(\alpha+\beta)^2(t_1-\Delta) - \beta(\alpha+\beta)(\exp(-\tilde{\gamma}t_1)\right. \\ & + \exp(-\tilde{\gamma}t_2))\frac{\exp(\tilde{\gamma}t_1) - \exp(\tilde{\gamma}\Delta)}{\tilde{\gamma}} \\ & \left.\left. + \beta^2\exp[-\tilde{\gamma}(t_1+t_2)]\frac{\exp(2\tilde{\gamma}t_1) - \exp(2\tilde{\gamma}\Delta)}{2\tilde{\gamma}}\right]\right\}. \end{aligned} \tag{B12}$$

Note equation (B 12) implies

$$\lim_{t\to\infty}\frac{\langle x^2(t)\rangle_{\mathrm{BBK}}}{t} = \frac{2k_{\mathrm{B}}T}{\gamma M} = \lim_{t\to\infty}\frac{\langle x^2(t)\rangle_{\mathrm{exact}}}{t}. \tag{B13}$$

From equation (B 12), we obtain the error of the BBK integrator, which is given by equation (30).

Carrying out similar computations for $\tilde{\omega} \neq 0$, we obtain equation (31) [15].

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