Molecular dynamics algorithm for condensed systems with multiple time scales

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A frequently encountered problem in molecular dynamics simulations is the long runs required to study condensed systems consisting of both high frequency and low frequency degrees of freedom. Standard integrators require the choice of time step sufficiently small to guarantee stable solution of the highest frequency motion with the consequence that simulations require a very large number of central processing unit (CPU) cycles. In this note we present a new integrator that allows one to use a time step appropriate for the low frequency degrees of freedom without making any approximations related to the separation of time scales. This method is based on a choice of an analytically solvable reference system for the high frequency motion. We show how the analytical solution can be incorporated into a numerical integrator. The method is applied to two cases which are paradigms for this problem and it is shown that this approach and suitable generalizations should be very useful for future simulations of quantum and classical condensed matter systems.

I. INTRODUCTION

A problem often encountered in computer simulations is that of multiple time scale motion.[1] The separation of time scales occurs when some subset of the forces present in a system is large compared to the rest of the forces. In the simulation of polyatomic liquids with flexible bonds, for example, the bond vibrations usually occur on a time scale which is short compared to that of the translations and rotations. In path integral simulations of electron solvation, the vibrational force constants arising from the kinetic energy operator increase linearly with the size of the chain (or the discretization). Hence, the vibrations of the chain are often fast compared with any other motion in the system. In such problems the configuration space can be subdivided into fast and slow degrees of freedom. If one wishes to simulate such systems using the standard integrators of molecular dynamics, then the maximum time step that can be used to integrate the equations of motion must be chosen to insure accurate integration of the highest frequency motion in the system, with the consequence that a very small time step may be needed. When a large disparity in time scales exists, a very large number of central processing unit (CPU) cycles will be required to allow the slow degrees of freedom to fluctuate enough to obtain converged time averages for the whole system. Swindoll and Haile[2] and Teleman and Jönsson[3] have proposed multiple time-step (MTS) methods in which the force is separated into its slow and fast components. This separation yields a set of coupled equations of motion for the evolution of the slow and fast degrees of freedom which is larger than the original set.[3] Instead of solving this set of equations simultaneously, MTS integration uses a small time step δt to advance the fast degrees of freedom n steps hold-

ing the slow variables fixed. The slow degrees of freedom are then updated using a time step $n\delta t$. Teleman and Jönsson[3] have found that n could be chosen typically between 5 and 10 in molecular simulations. We have found that the disadvantage of the MTS methods lie in the loss of accuracy due to the approximation of holding the slow variables fixed while integrating the equations for the fast variables. In addition, a non-negligible amount of CPU time is spent in the n-step integration of the fast forces. Ideally, one would like an exact integrator which utilizes a time step appropriate for the slow forces without spending too much additional CPU time.

It often happens that high frequency motion can be approximated by an analytically integrable reference system. In this note we show that if such an analytic solution can be found, this solution can be incorporated into an integration scheme for the whole system such that a time step characteristic of the slow degrees of freedom can be used and the system can be simulated effectively with a much smaller number of cycles. The algorithm makes no approximations related to the separation of time scales and is, therefore, an exact algorithm. In addition, the CPU time required to advance the system by one time step using this new integrator is almost exactly the same as for any standard integrator.

For illustrative purposes we study two dynamical systems. First we discuss two bilinearly coupled harmonic degrees of freedom, one with a very high frequency and the other with very low frequency. We show that straightforward use of the common integrators forces one to choose a very small time step. On the other hand, the integrator we propose in this paper, called numerical analytical propagator algorithm (NAPA), allows numerical integration of this system using a time step more appropriate for the

lower frequency. Comparisons of NAPA, and the standard integrators with the analytical solution show that NAPA is far superior for the treatment of such problems. A more realistic illustration is the application of NAPA to the simulation of a high frequency diatomic molecule dissolved in a Lennard-Jones fluid. We show that NAPA leads to a great reduction in the time required for the study of this system. These systems are paradigms for the many systems encountered in statistical mechanics. Although both of these systems make use of harmonic reference systems, the method is easily applied to other reference systems.

II. METHOD

To illustrate the method, consider a differential equation of the form

$$\ddot{x} = f(x) + g(x). \tag{2.1}$$

We write the solution to Eq. (2.1) in the form

$$x(t) = x_0(t) + \delta(t), \tag{2.2}$$

where $x_0(t)$ is chosen to satisfy the "reference system" equation of motion,

$$\ddot{x}_0 = f(x_0), \tag{2.3}$$

subject to the initial conditions

$$x_0(0) = x(0),$$

$$\dot{x}_0(0) = \dot{x}(0). \tag{2.4}$$

The analytical solution to Eq. (2.3) subject to the initial conditions is then of the form,

$$x_0(t) = x_0[t; x(0), \dot{x}(0)]. \tag{2.5}$$

Substituting Eq. (2.2) and Eq. (2.5) into Eq. (2.1) then gives an equation for $\delta(t)$:

$$\ddot{\delta}(t) = \{ f[x_0(t) + \delta(t)] - f[x_0(t)] \}$$

$$+ g[x_0(t) + \delta(t)], \tag{2.6}$$

with initial conditions

$$\delta(0) = \dot{\delta}(0) = 0. \tag{2.7}$$

Because the analytical solution of Eq. (2.3) is used directly, Eq. (2.6) has an explicit time dependence.

To solve Eq. (2.1) we propose the following scheme:

1. Substitute the analytical solution for $x_0(t)$, Eq. (2.5), into Eq. (2.6).

2. Solve Eq. (2.6) subject to the initial conditions, Eq. (2.7), for one time step Δt using a suitable integrator to obtain $\delta(\Delta t)$ and $\dot{\delta}(\Delta t)$.

3. Calculate

$$x(\Delta t) = x_0(\Delta t) + \delta(\Delta t),$$

$$\dot{x}(\Delta t) = \dot{x}_0(\Delta t) + \dot{\delta}(\Delta t). \tag{2.8}$$

This process is repeated using $x(\Delta t)$ and $\dot{x}(\Delta t)$ as initial conditions. That is, we solve the combined problem Eq.

(2.3) and Eq. (2.6) with initial conditions Eq. (2.7), but with initial conditions Eq. (2.4) replaced by

$$x_0(0) = x(\Delta t),$$

$$\dot{x}_0(0) = \dot{x}(\Delta t). \tag{2.9}$$

In general, at each step, the output of the previous step is used as the initial conditions for x_0 and $\dot{x}_0$ in the next step. The key point of this method lies in the resetting of the initial conditions on $\delta(t)$ and $\dot{\delta}(t)$ to 0 at every step. Since δ and $\dot{\delta}$ never deviate much from 0 in a given step, the force term $f(x_0 + \delta) - f(x_0)$ in Eq. (2.6) is prevented from becoming too large, thus allowing the use of a larger time step in the numerical integration than could be used in the standard integration schemes.

The integration of Eq. (2.6) can be performed by any integrator suitable for equations with explicit time dependence. The Runge–Kutta and Gear predictor-corrector methods are such integrators. In some cases, a suitable integrator can be obtained from only a minor modification of the standard integrators. In particular, the velocity Verlet[4,5] integrator can be adapted for Eq. (2.6) by a straightforward extension of the usual derivation with the result

$$x(\Delta t) = x_0(\Delta t) + \tfrac{1}{2}(\Delta t)^2 g[x_0(0)],$$

$$\dot{x}(\Delta t) = \dot{x}_0(\Delta t) + \frac{\Delta t}{2} \{ g[x_0(0)]$$

$$+ g[x_0(\Delta t) + \delta(\Delta t)] \} + \frac{\Delta t}{2} \{ f[x_0(\Delta t)$$

$$+ \delta(\Delta t)] - f[x_0(\Delta t)] \}. \tag{2.10}$$

III. RESULTS

To assess the accuracy of the different integrators we plot some or all of the following quantities in the figures:

1. The quantity,

$$\Delta \widehat{E}(\Delta t) = \frac{1}{T} \int_0^T dt \left| \frac{E(t) - E(0)}{E(0)} \right|, \tag{3.1}$$

where T is the total time of the run, gives a measure of the average deviation of the total energy from its initial value as a function of the time step Δt used in the integrator. This gives a measure of how well the integrator conserves energy.

2. The quantity,

$$\Delta x(t) = \sqrt{[x_1(t) - x_1^{\text{Exact}}(t)]^2 + [x_2(t) - x_2^{\text{Exact}}(t)]^2}, \tag{3.2}$$

gives the Cartesian distance between the position in configuration space of the numerical trajectory and that of the exact trajectory as a function of time (in units of the period T_2 of the fast coordinate).

3. The quantity,

$$\Delta p(t) = \sqrt{[p_1(t) - p_1^{\text{Exact}}(t)]^2 + [p_2(t) - p_2^{\text{Exact}}(t)]^2}, \tag{3.3}$$

gives the Cartesian distance between the position in momentum space of the numerical trajectory and that of the exact trajectory as a function of time (in units of the period T_2 of the fast coordinate).

Consider the case of two bilinearly coupled harmonic degrees of freedom with Hamiltonian

$$H = \frac{p_1^2}{2m_1} + \frac{p_2^2}{2m_2} + \frac{1}{2}m_1\omega_1^2 x_1^2 + \frac{1}{2}m_2\omega_2^2 x_2^2 + gx_1x_2,$$

(3.4)

where m_i and ω_i are, respectively, the masses and frequencies of the two oscillators and g is the coupling strength. By convention we take ω_2 as the higher of the two frequencies. Of course this dynamical system can be solved analytically. In this case NAPA is based on choosing the high frequency oscillatory coordinate $x_{2,0}$ to satisfy

$$\ddot{x}_{2,0} = -\omega_2^2 x_{2,0}.$$

(3.5)

The solution of Eq. (3.5) subject to the boundary conditions (as outlined in the previous section) for $n\Delta t \leqslant t \leqslant (n+1)\Delta t$ is

$$x_{2,0}(t) = x_2(n\Delta t)\cos[\omega_2(t-n\Delta t)]$$

$$+ \frac{\dot{x}_2(n\Delta t)}{\omega_2}\sin[\omega_2(t-n\Delta t)],$$

(3.6)

and the resulting equation of motion for $\delta(t)$ is then

$$\ddot{\delta}(t) = -\omega_2^2\delta(t) + F[x_{2,0}(t) + \delta],$$

(3.7)

where $F(y) = -m_2\omega_2^2 y - gx_1$. Note that in Eq. (3.6), since $x_{2,0}$ is only required at $t = (n+1)\Delta t$, repeated calls of special functions are not necessary; one need only calculate $\cos(\omega_2\Delta t)$ and $\sin(\omega_2\Delta t)$ once.

For illustrative purposes consider the case where the high frequency mode has a frequency that is a factor of 100 larger than that of the low frequency mode; that is, $m_i = 1$, $\omega_1 = 3$, $\omega_2 = 300$, and $g=2$. In Fig. 1 we see that $\widehat{\Delta E}(\Delta t)$ for the velocity Verlet integrator (solid curve) increases much faster than for the NAPA integrator (dashed curve). From this curve we see that to achieve an accuracy of $\Delta\widehat{E}(\Delta t) = 1 \times 10^{-5}$ the time steps required are $\Delta t_{\text{Verlet}} = 5\times 10^{-5}$ and $\Delta t_{\text{NAPA}} = 1\times 10^{-3}$. This clearly illustrates a major advantage of NAPA which is that it can be run with a much larger time step, in this case $\Delta t_{\text{NAPA}}/\Delta t_{\text{Verlet}} = 20$. Figure 2 shows that for these time steps both algorithms are stable. Interestingly, despite the fact that the two time steps are chosen to give the same energy conservation, NAPA generates trajectories much closer to the exact trajectory than does Verlet. In particular, Verlet gives a much less accurate evolution of the momenta than NAPA. Although it is not shown in the figure, when the two integrators are compared for equal time steps of $\Delta t = 5 \times 10^{-5}$, $\Delta\widehat{E}_{\text{NAPA}} = 4 \times 10^{-8}$, and $\Delta\widehat{E}_{\text{Verlet}} = 1\times 10^{-5}$. In general, for a given time step, NAPA is more accurate than Verlet. More importantly, NAPA allows one to set the time step according to the low frequency vibration and still generate a relatively accurate trajectory. To get the same accuracy in energy converva-
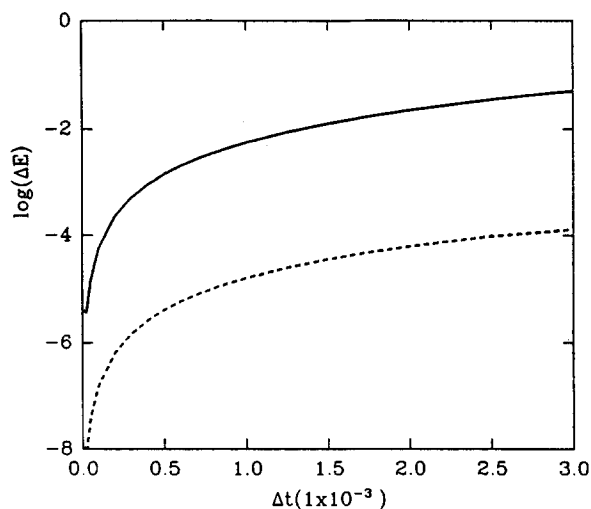

FIG. 1. The normalized energy deviation, defined in Eq. (3.1), as a function of time step for the coupled harmonic oscillator system defined by Eq. (3.4) ($\omega_1 = 3.0$, $\omega_2 = 300$, $g=2$, and averaging time $T=3000$ periods of oscillator 2), for the NAPA integrator (dashed), and for the pure velocity Verlet integrator (solid line).

tion using the standard Verlet, a time step 20 times smaller would be required. Of course, different choices of the parameters will have correspondingly different time steps associated with the two integrators. As an additional test, we measure the CPU time required to carry out one step of Verlet and one step of NAPA for this system. Expressed in CPU seconds per 10^5 steps, the results are 1.42 for Verlet and 1.6 for NAPA. Thus, NAPA gives a significant increase in accuracy without requiring significantly more CPU time.

In the foregoing we based NAPA on the harmonic trajectory of the uncoupled high frequency oscillator. Of course it is a simple matter to base it on harmonic trajectories of the uncoupled low and high frequency oscillators. It is worth noting that this doesn't work as well. This follows from the fact that for moderate coupling strength the higher normal mode frequency is relatively unchanged from ω_2 whereas the lower normal mode frequency exhibits a relatively large shift from the uncoupled ω_1. In this case the uncoupled low frequency reference trajectory is a poor approximation to the exact trajectory and thereby requires a much shorter time step when used in NAPA. From this, we conclude that NAPA should be used only on those degrees of freedom weakly coupled to the rest of the system. These are often characterized by frequencies incommensurately large compared to the other degrees of freedom in the system.

As a second example, we consider the problem of a flexible diatomic with harmonic potential buried in a Lennard-Jones fluid. If r_1 and r_2 denote the coordinates of the two atoms, and if all masses in the problem are set equal to 1, then we may transform to center of mass,
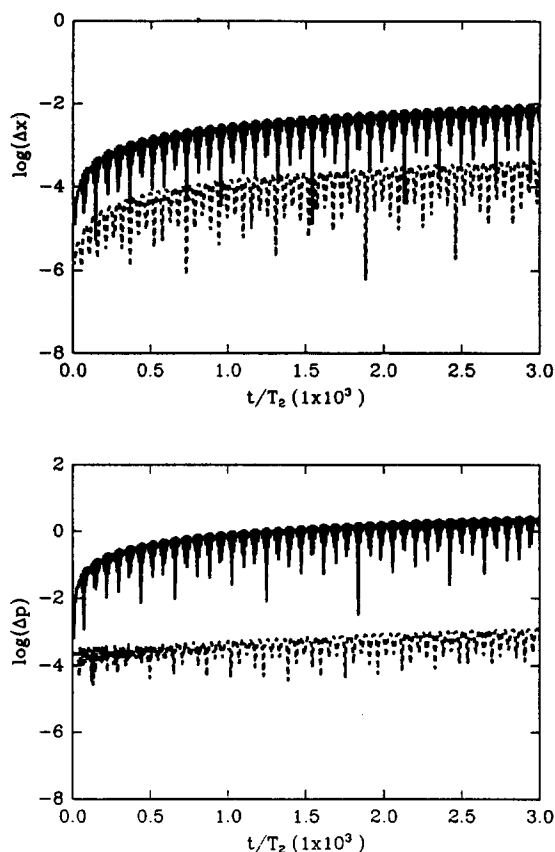
FIG. 2. The configurational and momentum deviations from the exact trajectory as defined in Eq. (3.2) and Eq. (3.3) for the coupled harmonic oscillator system defined in Eq. (3.4) for the NAPA integrator (dashed), and for the pure velocity Verlet integrator (solid line).

$\mathbf{R} = (\mathbf{r}_1 + \mathbf{r}_2)/2$, and relative, $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$, coordinates in the usual way. If the relative position is transformed to normal coordinates there will be two zero frequency modes corresponding to the rotations and one corresponding to the molecular vibration. This reference system can be integrated exactly and can be used directly in NAPA. However for illustrative purposes we simplify the problem by constraining the diatomic to be at a fixed spatial orientation. This is equivalent to writing the relative position vector in the form $\mathbf{r} = \mathbf{u}r$ where $\mathbf{u}$ is a unit vector specifying the fixed orientation of the molecular axis. Then only the relative distance r evolves with time according to the equation of motion

$$\ddot{r} = -\omega^2(r-a) + F(r), \tag{3.8}$$

where $F(r)$ is the total force on the relative coordinate due to the presence of the fluid. To integrate Eq. (3.8), we choose $r_0(t)$ to satisfy

$$\ddot{r}_0 = -\omega^2(r_0 - a), \tag{3.9}$$

where a is the equilibrium bond length. The solution of Eq. (3.9) subject to the conditions of NAPA for $n\Delta t \leqslant t \leqslant (n+1)\Delta t$ is

$$r_0(t) = [r(n\Delta t) - a]\cos[\omega(t - n\Delta t)]$$

$$+ \frac{\dot{r}(n\Delta t)}{\omega} \sin[\omega(t - n\Delta t)] + a$$

$$\tag{3.10}$$

and the resulting equation of motion for $\delta(t)$ is then

$$\ddot{\delta} = -\omega^2\delta + F(r_0 + \delta). \tag{3.11}$$

The system simulated consists of a single homonuclear diatomic molecule A_2 dissolved in a solvent consisting of 62 A atoms. The solute–solvent interaction potential is taken to be a site–site LJ(12-6) potential and the solvent–solvent potential is taken to be pairwise additive with atom–atom interactions also given by the same LJ(12-6) potential; that is an LJ potential with the same ϵ and σ. (All quantities are expressed in Lennard-Jones units so that $\epsilon = \sigma = 1$.) The intramolecular potential is taken to be harmonic with bare frequency $\omega_0 = 300$ {in LJ units $[(\epsilon/m\sigma^2)^{1/2}]$} and equilibrium bond length $x_0 = 1.25$}. The system is solved subject to cubic periodic boundary conditions using the NAPA integrator for the harmonic potential. $\mathbf{u}$ is chosen to be the vector $(1/\sqrt{3}, 1/\sqrt{3}, 1/\sqrt{3})$. The simulation is performed for a reduced temperature of $\widehat{T} = k_B T/\epsilon = 2.5$ and a reduced density of $\widehat{n} = \rho\sigma^3 = 1.05$. At this temperature and density, the peak of the spectral density of the neat fluid is around $\omega_{\text{peak}} = 20$, a value small compared to the oscillator frequency ω_0 (300 in this case). Hence, this is a good test of NAPA under extreme conditions. Equation (3.8) was integrated by straightforward velocity Verlet while Eq. (3.11) was integrated using the velocity Verlet modified for NAPA in Eq. (2.10). All the other equations of motion were integrated with velocity Verlet. For straightforward integration of Eq. (3.8), we find that under these conditions a time step of 1×10^{-4} is required to insure stability. But when the NAPA method is used with Eq. (3.11) the same stability can be obtained with a time step of 8×10^{-4}. In Fig. 3 the energy deviation defined in Eq. (3.1) is plotted versus time step for the NAPA (dashed line) integrator and for the velocity Verlet integrator (solid line). The curves are not as smooth as for the coupled harmonic oscillators because the averaging time used there was 3000 periods of the fast oscillator whereas here it is 150 periods of the fast oscillator. Nevertheless the curves are similar and the conclusions are the same. NAPA allows one to use a much larger time step than does Verlet integrator (and presumably the other standard integrators).

IV. CONCLUSION

The NAPA method can be most efficiently used when part of the force is analytically solvable and weakly coupled to the rest of the system. We have seen that NAPA gives rise to a significant increase in integration efficiency when stiff oscillators are involved. This should allow one greater ease in simulating liquids with polyatomic molecules using flexible bonds. In general, for such simulations,
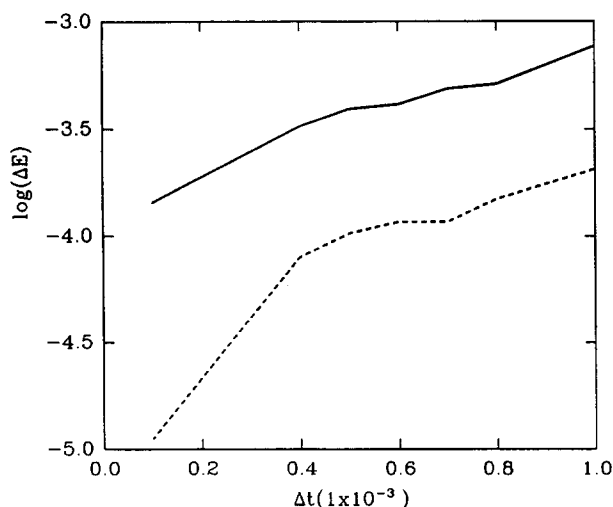
FIG. 3. The normalized energy deviation (averaged over 150 periods of the high frequency oscillator), defined in Eq. (3.1), as a function of time step for a harmonic diatomic molecule with frequency $\omega_0 = 300$ and bond length $x_0 = 1.25$ dissolved in a LJ fluid at reduced density 1.05 and reduced temperature 2.5 for the NAPA integrator (dashed) and for the pure velocity Verlet integrator (solid line) defined by Eq. (3.4).

one would need to find a suitable set of coordinates (e.g., normal modes) to specify the reference system. We expect the NAPA method to be especially useful in simulation of quantum mechanical systems by path integral molecular dynamics techniques.

In a subsequent paper we have applied NAPA to the determination of the phase relaxation of a high frequency diatomic molecule in solution and to the determination of the dynamic friction on intramolecular bonds.[6]

ACKNOWLEDGMENT

[1] J. U. Brackbill and B. I. Cohen, *Multiple Time Scales* (Academic, Orlando, 1985).
[2] R. D. Swindoll and J. M. Haile, J. Comp. Phys. **53**, 289 (1984).
[3] Olle Teleman and Bo Jönsson, J. Comp. Chem. **7**, 58 (1986).
[4] M. P. Allen and D. J. Tildesley, *Computer Simulation of Liquids* (Oxford University, Oxford, 1989).
[5] W. C. Swope, H. C. Andersen, P. H. Berens, and K. R. Wilson, J. Chem. Phys. **76**, 637 (1982).
[6] B. J. Berne, M. Tuckerman, J. Straub, and A. Bug (unpublished).