Molecular dynamics in systems with multiple time scales: Systems with stiff and soft degrees of freedom and with short and long range forces

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When there are high and low frequency motions in systems with long and short range forces a judicious choice of reference system leads to very large accelerations in molecular dynamic (MD) simulations. Building on our previous work where we have developed reference system methods for systems with high frequency oscillators, disparate masses, or long range forces, we present a double reference system method which leads to acceleration of as much as 20 in systems consisting of 864 molecules with Lennard-Jones (12-6) forces. Much larger savings should be achieved when this method is applied to longer range forces and larger systems.

I. INTRODUCTION

In our recent work we have addressed the problem of multiple time scales in molecular dynamics (MD) simulations.[1,2,3] The most obvious cases involve either "stiff oscillators" dissolved in "soft fluids"[1] (e.g., N_2 in Ar) or low mass solutes dissolved in high mass solvents[2] (e.g., He in Xe). In such cases, standard MD methods require very short integration time steps, δt, to guarantee stable integration of the fast degrees of freedom. Thus, to follow the relaxation of the slow degrees of freedom requires the generation of a very large number of interactions.

We have invented reference system methods such as numerical analytical propagator algorithm (NAPA)[1] and reference system propogator algorithm (RESPA)[2,3] for integrating such systems. When the systems are dilute in the fast degrees of freedoms these methods greatly accelerate the simulations largely because forces for the slow coordinates are recalculated much less frequently than in the standard algorithms. The acceleration factor for RESPA over straightforward velocity Verlet is defined to be

$$\eta(\delta t) \equiv \frac{T_{\text{Verlet}}(\delta t)}{T_{\text{RESPA}}(\delta t)}, \tag{1.1}$$

where $T_{\text{Verlet}}(\delta t)$ is the cpu time required to carry out a direct simulation using the straightforward velocity Verlet integrator[4] with a time step δt while $T_{\text{RESPA}}(\delta t)$ is the cpu time required by RESPA (or NAPA) to simulate the same amount of real time, integrating the reference system with a time step δt. We have achieved up to eightfold accelerations in systems we have simulated to date.

Intermolecular forces can be subdivided into short and long range parts. The short range component varies much more rapidly than the long range component, and thus determines the integration time step. Too large a time step will lead to an error in the new positions with a concomitantly large error in the short range force which subsequently leads to amplifying errors. Even in systems in which there is no obvious separation of time scales this leads to a *de facto* multiple time scale problem. One is forced to use small integration time steps and to recalculate the full force after every small time step. Judicious choice of a reference system (RESPA) has allowed us to reduce these force computations considerably and to thereby achieve factors as large as 6 in the acceleration of the simulations[3] for the same accuracy as measured by the energy conservation, which is measured by

$$\Delta\hat{E} = \frac{1}{N}\sum_{i=1}^{N}\left|\frac{E_i - E_0}{E_0}\right|, \tag{1.2}$$

where N is the total number of MD steps, E_i is the energy at step i, and E_0 is the initial energy of the system.

In this paper we show, for systems in which there are multiple time scales (stiff and soft degrees of freedom) and in which the forces can be subdivided into short and long components, that a double application of RESPA leads to very large accelerations of the simulation time for simple systems. For simplicity we treat the two systems already presented in our previous papers: namely (a) one stiff diatomic dissolved in 862 Lennard-Jones (LJ) (12-6) atoms[1] and (b) 40 light LJ particles ($m = 1$) dissolved in a fluid consisting of 824 heavy LJ atoms ($m = 100$) all interacting with the same LJ (12-6) potential.[2] Double RESPA solutions yield twentyfold accelerations in the cpu times required for the simulations.

We expect that for larger systems and systems with long range forces double RESPA can yield as much as a fortyfold acceleration.

II. SUBDIVISION OF FORCES

The starting point for combining reference systems in the separation of the interatomic forces into short and long range components according to

$$F(x) = F_s(x) + F_l(x). \tag{2.1}$$

The separation can be achieved by means of a WCA subdivision or by using a switching function.[3] We have shown that by choosing a reference system based on $F_s(x)$, factors of between 2 and 4 savings in cpu time can be achieved for simple LJ (12-6) systems, and factors exceeding 5 can be reached for (12-1) systems when Ewald summation is used.[3] The RESPA algorithm is implemented by writing the trajectory $x(t)$ as a sum of a reference trajectory $x_s(t)$ and a correction $x_l(t)$ which satisfy the equations of motion

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$$m\ddot{x}_s = F_s(x_s) + F_l(0), \tag{2.2}$$

$$m\ddot{x}_l = F_s(x_s + x_l) - F_s(x_s) + F_l(x_s + x_l) - F_l(0), \tag{2.3}$$

where $F_l(0)$ is the value of the long range force at the beginning of the time step. The initial conditions are taken to be

$$x_s(0) = x(0), \qquad \dot{x}_s(0) = \dot{x}(0), \tag{2.4}$$

$$x_l(0) = \dot{x}_l(0) = 0. \tag{2.5}$$

Equation (2.2) is integrated for n little time steps δt subject to the initial conditions, Eq. (2.4) and then the correction x_l is computed using a big time step $\Delta t = n\delta t$ subject to the initial conditions, Eq. (2.5). The true trajectory is then given by $x(\Delta t) = x_s(\Delta t) + x_l(\Delta t)$. The initial conditions are reset so that

$$x_s(0) = x(\Delta t), \quad \dot{x}_s(0) = \dot{x}(\Delta t), \tag{2.6}$$

$$x_l(0) = \dot{x}_l(0) = 0, \tag{2.7}$$

and the procedure is repeated for each step determining the initial conditions for the next step.

III. DISPARATE MASS SYSTEMS

In dilute fluid mixtures consisting of light solute atoms and heavy solvent atoms, there is a separation of time scales: the light atoms move much more quickly than the solvent atoms. A simple example of this is that of 864 LJ(12-6) atoms consisting of 40 light spheres with $m = 1$ and 824 spheres with $m = 100$ all with the same diameter σ and the same well depth ϵ. In this system, the time scale for the heavy particle is 10 times longer than that for the light particles. We have already shown how this system can be integrated using RESPA resulting in a sevenfold speedup of the simulation over standard results using the velocity Verlet integrator.[2] Here we wish to combine this with another version of RESPA based on the subdivision of the forces into long and short range components.

Consider a system consisting of a mixture of 40 light LJ particles with $m = 1$ and 824 heavy LJ particles with $M = 100$. Denoting the set of light particle coordinates as x and the heavy particle coordinates as y, the equations of motion take the form

$$\ddot{x} = \frac{1}{m} F_x(x,y),$$

$$\ddot{y} = \frac{1}{M} F_y(x,y). \tag{3.1}$$

As before, the forces and coordinates are broken up into short and long range components giving equations for the reference system trajectories and corrections

$$\ddot{x}_s = \frac{1}{m}\,[F_{xs}(x_s,y_s) + F_{xl}(0)], \tag{3.2}$$

$$\ddot{y}_s = \frac{1}{M}\,[F_{ys}(x_s,y_s) + F_{yl}(0)], \tag{3.3}$$

$$\ddot{x}_l = \frac{1}{m}\,[F_{xs}(x_s + x_l,y_s + y_l) - F_{xs}(x_s,y_s)] + \frac{1}{m}\,[F_{xl}(x_s + x_l,y_s + y_l) - F_{xl}(0)], \tag{3.4}$$

$$\ddot{y}_l = \frac{1}{M}\,[F_{ys}(x_s + x_l,y_s + y_l) - F_{ys}(x_s,y_s)] + \frac{1}{m}\,[F_{yl}(x_s + x_l,y_s + y_l) - F_{yl}(0)]. \tag{3.5}$$

The initial conditions on x_s, y_s, x_l, and y_l are given by Eqs. (2.4) and (2.5). To handle the mass disparity, we make a further subdivision of x_s and x_l according to

$$x_s = x_s^{(0)} + \delta_s, \qquad x_l = x_l^{(0)} + \delta_l, \tag{3.6}$$

where $x_s^{(0)}$ and δ_s are chosen to satisfy the equations of motion

$$\ddot{x}_s^{(0)} = \frac{1}{m}\,\{F_{xs}[x_s^{(0)},\bar{y}_s] + F_{xl}(0)\}, \tag{3.7}$$

$$\ddot{\delta}_s = \frac{1}{m}\,\{F_{xs}[x_s^{(0)} + \delta_s,y_s] - F_{xs}[x_s^{(0)},\bar{y}_s]\}, \tag{3.8}$$

where $\bar{y}_s$ indicates that the heavy particle reference system is held fixed while $x_s^{(0)}$ is integrated. A simple choice is to fix y_s at its initial value. The initial conditions are taken to be the same as in Eqs. (4.5) and (4.10). Similarly, $x_l^{(0)}$ and δ_l satisfy the equations of motion

$$\ddot{x}_l^{(0)} = \frac{1}{m}\,\{F_{xs}[x_s + x_l^{(0)},y_s + \bar{y}_l] - F_{xs}(x_s,y_s)\} + \frac{1}{m}\,\{F_{xl}[x_s + x_l^{(0)},y_s + \bar{y}_l] - F_{xl}(0)\}, \tag{3.9}$$

$$\begin{aligned}\ddot{\delta}_l = {} & \frac{1}{m}\,\{F_{xs}[x_s + x_l^{(0)} + \delta_l,y_s + y_l] - F_{xs}[x_s + x_l^{(0)},y_s + \bar{y}_l]\} \\ & + \frac{1}{m}\,\{F_{xl}[x_s + x_l^{(0)} + \delta_l,y_s + y_l] - F_{xl}[x_s + x_l^{(0)},y_s + \bar{y}_l]\}.\end{aligned} \tag{3.10}$$

Because of the initial conditions on x_l, $x_l^{(0)}(0)$, $\dot{x}_l^{(0)}(0)$, $\delta_l(0)$, and $\dot{\delta}_l(0)$ are all 0. The procedure is to integrate Eq. (3.7) for n_1 time steps δt_1 and then to correct according to Eq. (3.8) while simultaneously integrating Eqs. (3.9) and (3.3) with a time step δt_2. The initial conditions are reset and the procedure is repeated n_2 times. Finally the corrections δ_l and y_l are computed from Eqs. (3.10) and (3.5), respectively using a big time step $\Delta t = n_2\delta t_2 = n_1 n_2 \delta t_1$. We have already shown how to adopt the velocity Verlet algorithm for use with RESPA,[3] and the extension to double RESPA follows straightforward from this treatment. Let η_1 be the acceleration from the light particle reference systems and η_2 be the acceleration from the short range reference system. We expect the overall acceleration to be $\eta_1\eta_2$.

The test is carried out on two systems. One is at temperature 0.67 and density 0.86 which corresponds to the triple point. The energy conservation is set at $\Delta\hat{E} = 2\times10^{-6}$ which requires the Verlet time step to be chosen as $\delta t_1 = 2\times10^{-3}$. For RESPA, we choose $n_1 = 10$ and

$n_2 = 5$. This gives an overall cpu saving factor of $\eta = 13$. Direct measurements of η_1 and η_2 yield values of 7 and 2, respectively so that the prediction is $\eta_1 \eta_2 = 14$. The second system is at temperature 1.0 and density 0.86. Keeping the same Verlet time step gives an energy conservation of $\Delta\hat{E} = 3\times10^{-6}$. For RESPA we choose $n_1 = 7$ and $n_2 = 6$ which gives an overall saving of $\eta = 20$. The direct measurement of η_2 gives 3.3 so that the prediction is $\eta_1 \eta_2 = 23$.

IV. A STIFF OSCILLATOR DISSOLVED IN A SOFT FLUID

Consider a fluid mixture consisting of one very stiff diatomic molecule dissolved in 862 LJ atoms where the molecular atoms interact with the solvent atoms and the solvent atoms interact with each other through the same LJ(12-6) potential. We have already shown how NAPA and RESPA can be used to treat the multiple time scale problem.[1] These studies yield up to eightfold accelerations over standard methods for the same energy conservation. Here we show how to improve upon this by including the breakup of the force into short and long range components.

The equation of motion for the relative coordinate r of the oscillator takes the form

$$\mu\ddot{r} = f(r) + F(r), \tag{4.1}$$

where μ is the reduced mass, $f(r)$ is the oscillatory force, and $F(r)$ is the force due to the surrounding solvent atoms. We have shown that choosing a reference system based solely on $f(r)$ can lead to a factor of 8 acceleration in cpu time when a frequency of 300 is used for the oscillator.

However, if we now combine this oscillatory reference system with short range force reference system, a substantial improvement can be achieved. All the solvent–solvent and solvent–solute forces are subdivided according to Eq. (2.1). The equation of motion for the oscillator now takes the form

$$\mu\ddot{r} = f(r) + F_s(r) + F_l(r). \tag{4.2}$$

The relative coordinate r is written as the sum of a reference system trajectory r_s and a correction r_l. r_s and r_l satisfy the equations of motion

$$\mu\ddot{r}_s = f(r_s) + F_s(r_s) + F_l(0), \tag{4.3}$$

$$\begin{aligned}\mu\ddot{r}_l = {} & f(r_s + r_l) - f(r_s) + F_s(r_s + r_l) \\ & - F_s(r_s) + F_l(r_s + r_l) - F_l(0),\end{aligned} \tag{4.4}$$

where $F_l(0)$ denotes the value of the long range part of the force at the beginning of a time step. The initial conditions are chosen to be

$$r_s(0) = r(0), \qquad \dot{r}_s(0) = \dot{r}(0), \tag{4.5}$$

$$\dot{r}_l(0) = \dot{r}(0) = 0. \tag{4.6}$$

The reference system trajectory r_s is further subdivided according to $r_s(t) = r_s^{(0)}(t) + \delta_s(t)$, where $r_s^{(0)}$ and δ_s satisfy

$$\mu\ddot{r}_s^{(0)} = f[r_s^{(0)}], \tag{4.7}$$

$$\begin{aligned}\mu\ddot{\delta}_s = {} & f[r_s^{(0)} + \delta_s] - f[r_s^{(0)}] \\ & + F_s[r_s^{(0)} + \delta_s] - F_l(0)\end{aligned} \tag{4.8}$$

with initial conditions

$$r_s^{(0)}(0) = r_s(0), \qquad \dot{r}_s^{(0)}(0) = \dot{r}_s(0), \tag{4.9}$$

$$\delta_s(0) = \dot{\delta}_s(0) = 0. \tag{4.10}$$

The procedure is to integrate Eq. (4.7) for n_1 time steps δt_1 subject to the initial conditions, Eq. (4.9) and then simultaneously to correct for $r_s^{(0)}$ using Eq. (4.8) and evolve the reference system, Eq. (2.2) for the solvent atoms using a time step δt_2. The initial conditions on $r_s^{(0)}$ are reset, and the procedure is repeated n_2 times to generate the full reference system trajectory $r_s(t)$ and $x_s(t)$ for the oscillator and solvent atoms, respectively. Then the corrections are computed according to Eqs. (4.4) and (2.3) for one big time step $\Delta t = n_2 \delta t_2 = n_1 n_2 \delta t_1$. If η_1 is the cpu acceleration factor for the oscillator reference system alone and η_2 is the cpu acceleration factor for the short range force reference system alone, then we expect the overall speedup to be the product $\eta_1 \eta_2$.

We have tested this prediction on an oscillator for which $f(r) = -\mu\omega^2(r-a)$ with $\mu = \frac{1}{2}$, $\omega = 300$, and $a = 1.25$ in a bath of 864 LJ atoms at temperature 1.0 and density 0.9. The energy conservation is set at $\Delta\hat{E} = 2\times10^{-5}$ which requires a Verlet time step of 2.5×10^{-4}. In the RESPA simulation, we use $n_1 = 8$ and $n_2 = 6$ and a large time step $\Delta t = 1.39\times10^{-2}$. These parameters give a cpu saving factor of $\eta = 22$. From previous work, we have determined that $\eta_1 = 7.9$ while $\eta_2 = 3.2$ which gives a prediction of the saving factor of $\eta_1 \eta_2 = 25$ in close agreement with our finding.

V. CONCLUSION

The reference system methods (RESPA) lead to a dramatic acceleration of molecular dynamics for systems with multiple time scales and short and long range forces. These methods are simple to use and are capable of generalization to more complicated systems. The underlying equations of motion used in RESPA are exact and can be solved using any of the standard numerical integrators. The work presented here uses the velocity Verlet integrator,[4] but we are presently trying to apply RESPA to dynamical systems with bond length and bond angle constraints using SHAKE.[5] We are also presently trying to extend these methods to treat large molecules with many stiff coupled internal degrees of freedom.

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