The Targeted Shadowing Hybrid Monte Carlo (TSHMC) Method

Elena Akhmatskaya[1] and Sebastian Reich[2]

[1] Fujitsu Laboratories of Europe Ltd (FLE), Hayes Park Central, Hayes End Road, Hayes UB4 8FE, United Kingdom,
Elena.Akhmatskaya@uk.fujitsu.com

[2] Institut für Mathematik, Universität Potsdam, Postfach 60 15 53, D-14415 Potsdam, Germany
sreich@math.uni-potsdam.de

Abstract. Following IZAGUIRRE & HAMPTON [14], HOROWITZ [13], and ATTARD [1] as well as work of one of the authors on dissipative particle dynamics [4] and modified equations [23], we suggest a modified Metropolis criterion and a more flexible momentum update to improve the acceptance rate and the flexibility of the thermal coupling in standard hybrid Monte Carlo simulations.

1 Introduction

The starting point of any (classical) molecular simulation is a system of N particles, which interact through both long and short range forces through Newton's second law:

$$\dot{\mathbf{r}}_i = \mathbf{p}_i/m_i, \tag{1}$$

$$\dot{\mathbf{p}}_i = \mathbf{F}_i, \qquad i = 1, \ldots, N \tag{2}$$

where m_i is the mass of particle i with position vector $\mathbf{r}_i = (x_i, y_i, z_i)^T \in \mathbb{R}^3$ and momentum $\mathbf{p}_i = m_i\dot{\mathbf{r}}_i \in \mathbb{R}^3$. It is also assumed that the force acting on the i^{th} particle is conservative, i.e., there is a potential energy function $V(\mathbf{r}_1, \ldots, \mathbf{r}_N)$ such that

$$\mathbf{F}_i = -\nabla_{\mathbf{r}_i} V.$$

Molecular dynamics can be performed under various ensembles. The most popular ensembles are (i) constant number of particles, constant energy, and constant volume (NVE) ensemble, (ii) constant number of particles, constant pressure, and constant temperature (NPT) ensemble, and (iii) constant number of particles, constant volume, and constant temperature (NVT) ensemble. For the purpose of this paper we will restrict ourselves to NVT ensemble simulations using the hybrid Monte

Carlo (HMC) method of DUANE, KENNEDY, PENDLETON & ROWETH [6]. However, NVE simulation techniques play an important role in the design of the HMC method.

The main contribution of this paper is the development of a new HMC method that allows for (i) a modified momentum update and (ii) leads to a much improved acceptance rate. That part of the report relies on theoretical results for symplectic time-stepping methods (see, for example, BENETTIN & GIORGILLI [2]), the recently introduced shadow hybrid Monte Carlo (SHMC) method of IZAGUIRRE & HAMPTON [14], the modified Monte-Carlo method suggested by HOROWITZ [13] (see also ATTARD [1]), and work of one of the authors on dissipative particle dynamics (DPD) (see, for example, [4]) and modified equations [23].

2 Description of the Basic HMC Method

The HMC method offers an elegant and efficient way to turn an NVE simulation into a sampling method for the NVT ensemble. Let us assume that we have a numerical method that time-steps the equations (1)-(2). We first randomly sample all momenta $\mathbf{p}_i$ according to the Boltzmann distribution

$$\rho_{\text{Boltzmann}} \sim e^{-\beta\|\mathbf{p}_i\|^2/2m_i}.$$

Here $\beta = 1/k_B T$ denotes the inverse temperature.

We next apply a MD simulation for a fixed number of time-steps and denote the resulting update from the current positions and momenta $(\mathbf{r}_i, \mathbf{p}_i)$, $i = 1, \ldots, N$, to a new configuration $(\mathbf{r}_i', \mathbf{p}_i')$, $i = 1, \ldots, N$, by

$$\Psi : (\mathbf{r}, \mathbf{p}) \to (\mathbf{r}', \mathbf{p}'),$$

where $\mathbf{r}$ is the collection of the N particle position vectors $\mathbf{r}_i$ and $\mathbf{p}$ is the associated momentum vector.

The new configuration is accepted with a probability of

$$\min\left(1, \exp\left[-\beta\left\{(\mathbf{p}')^T\mathbf{M}^{-1}\mathbf{p}'/2 + V(\mathbf{r}') - \mathbf{p}^T\mathbf{M}^{-1}\mathbf{p}/2 - V(\mathbf{r})\right\}\right]\right). \qquad (3)$$

The sequence of steps:

1. randomly re-sample momenta from the Boltzmann distribution,
2. generate a new configuration $(\mathbf{r}', \mathbf{p}')$,
3. accept the new configuration according to the Metropolis criterion (3),

is now repeated as often as necessary to sample properly from an NVT ensemble. As shown by MEHLIG, HEERMANN & FORREST [21], it is essential for the method to work properly that the map Ψ is time-reversible and volume preserving.

A number of modifications to Step 1 and Step 3 have been suggested. In particular, IZAGUIRRE & HAMPTON [14] implemented a modified Metropolis criterion (3) to further increase the acceptance rate of HMC. Their approach relies on

recent advances for symplectic integration methods and their theoretical understanding. Furthermore, HOROWITZ [13] (see also [1]) pointed out that it is not necessary to completely re-sample the momenta under Step 1 of a HMC scheme. However, the scheme is not widely used due to its frequent reversal of momenta in case of non-negligible rejection rates.

Combining these two specific modifications with work of one of the authors (see, e.g., [4]) on dissipative particle dynamics (DPD) [7, 11], we will derive yet another class of HMC methods, which we will describe in §4 and which we wish to promote for further use in NVT simulations.

The results of the paper can be easily extended to Hamiltonian systems with holonomic constraints by using the SHAKE extension [26] of the standard Störmer-Verlet time-stepping method [9, 18].

3 Störmer-Verlet Time-Stepping Method and Modified Hamiltonian

The most widely used numerical method for MD of type (1)-(2) is the Störmer-Verlet/leapfrog method, which is written here in the velocity/momentum formulation:

$$\mathbf{p}^{n+1/2} = \mathbf{p}^n - \frac{\Delta t}{2}\nabla_{\mathbf{r}} V(\mathbf{r}^n), \tag{4}$$

$$\mathbf{r}^{n+1} = \mathbf{r}^n + \Delta t \mathbf{M}^{-1}\mathbf{p}^{n+1/2}, \tag{5}$$

$$\mathbf{p}^{n+1} = \mathbf{p}^{n+1/2} - \frac{\Delta t}{2}\nabla_{\mathbf{r}} V(\mathbf{r}^{n+1}), \tag{6}$$

where Δt is the step-size.

The popularity of the Störmer-Verlet method is due to its simplicity and its remarkable conservation properties. We next outline a particular implication of its conservation of symplecticity [9, 18]. Namely, one can find a time-dependent Hamiltonian function $\tilde{\mathcal{H}}(\mathbf{r}, \mathbf{p}, 2\pi\, t/\Delta t)$, which is 2π-periodic in its third argument such that the solution of

$$\dot{\mathbf{r}} = +\nabla_{\mathbf{p}}\tilde{\mathcal{H}}(\mathbf{r}, \mathbf{p}, 2\pi\, t/\Delta t),$$
$$\dot{\mathbf{p}} = -\nabla_{\mathbf{r}}\tilde{\mathcal{H}}(\mathbf{r}, \mathbf{p}, 2\pi\, t/\Delta t),$$

with initial conditions $\mathbf{r}(0) = \mathbf{r}^n$ and $\mathbf{p}(0) = \mathbf{p}^n$ is exactly equivalent to $(\mathbf{r}^{n+1}, \mathbf{p}^{n+1})$ at $t = \Delta t$. (See the papers by KUKSIN & PÖSCHEL [17] and MOAN [22] for the mathematical details.)

This statement is not entirely satisfactory as it is well known that energy is *not* conserved for time-dependent Hamiltonian problems. However, as first pointed out by NEISHTADT [24], the time-dependence in $\tilde{\mathcal{H}}$ averages itself out up to negligible terms of size $\mathcal{O}(e^{-c/\Delta t})$ for sufficiently small step-sizes Δt (here $c > 0$ is a constant which depends on the particular problem). Hence the Störmer-Verlet method is the

nearly exact solution [2] of a Hamiltonian problem with *time-independent* Hamiltonian $\hat{\mathcal{H}}_{\Delta t}(\mathbf{r}, \mathbf{p})$. This time-independent Hamiltonian possesses an asymptotic expansion in the step-size Δt of the form

$$\hat{\mathcal{H}}_{\Delta t} = \mathcal{H} + \Delta t^2 \delta\mathcal{H}_2 + \Delta t^4 \delta\mathcal{H}_4 + \Delta t^6 \delta\mathcal{H}_6 + \ldots, \tag{7}$$

with

$$\mathcal{H}_2 = \frac{1}{12}\mathbf{p}^T\mathbf{M}^{-1}[D_{\mathbf{rr}}V(\mathbf{r})]\mathbf{M}^{-1}\mathbf{p} + \frac{1}{24}[\nabla_{\mathbf{r}}V(\mathbf{r})]^T\mathbf{M}^{-1}\nabla_{\mathbf{r}}V(\mathbf{r}),$$

where $D_{\mathbf{rr}}V(\mathbf{r})$ denotes the Hessian matrix of the potential energy V. Expressions for the higher-order correction terms $\delta\mathcal{H}_i$, $i = 4, 6, \ldots$, can be found using the Baker-Campbell-Hausdorff (BCH) formula (see, e.g., [9, 18]).

A practical algorithm for assessing energy conservation with respect to a modified Hamiltonian has been proposed by SKEEL & HARDY [27]. We will follow the modified equation approach of MOORE & REICH [23], which is particularly suited to the Störmer-Verlet method.

The fact that the modified energy $\hat{\mathcal{H}}_{\Delta t}$ is essentially preserved exactly under the Störmer-Verlet method has implications for HMC simulations. Namely, the quasi-exact conservation of $\hat{\mathcal{H}}_{\Delta t}$ under the Störmer-Verlet method allows one to accept almost all candidate moves with regard to a modified canonical ensemble (see IZAGUIRRE & HAMPTON [14]). We outline the details in the following section.

4 A New Method: Targeted Shadowing Hybrid Monte Carlo (TSHMC)

A high acceptance rate is a desirable property of any Monte Carlo scheme. In fact, one of the reasons for the introduction of the HMC method was its vastly superior acceptance rate over standard Monte Carlo methods. However the acceptance rate of HMC degrades with the size of the simulated molecular system. Furthermore, in light of the modified Hamiltonian, it would appear that essentially no rejections are necessary at all for a symplectic integration method such as Störmer-Verlet. In fact, that is indeed the case up to a small rejection rate caused by the truncation of (7) after a finite number of terms. A practical HMC algorithm based on modified Hamiltonians was first proposed by IZAGUIRRE & HAMPTON [14]. We will describe below a variant of their SHMC method with two important modifications:

(i) a simplified evaluation of the modified energy (Hamiltonian),
(ii) a modified and more flexible momentum update.

Note that time averages need to include the factor

$$w^m = e^{\beta(\hat{E}^m_{\Delta t} - E^m)}, \tag{8}$$

where E^m is the value of the given energy after completion of the m^{th} SHMC/TSHMC step and $\hat{E}^m$ is the modified energy, respectively, i.e., averages of an observable A are computed according to the formula:

$$\langle A \rangle = \frac{\frac{1}{M}\sum_{m=1}^{M} A(\mathbf{r}^m, \mathbf{p}^m)\, w^m}{\frac{1}{M}\sum_{m=1}^{M} w^m}.$$

This is a standard re-weighting procedure for simulations in modified ensembles.

It is essential for the SHMC/TSHMC method that the modified energy can be evaluated inexpensively. This rules out a direct evaluation according to the asymptotic expansion (7), since it would require the evaluation of higher-order derivatives of the potential energy function V. However, it turns out that one can approximate the modified energy to any order *without* any evaluation of higher-order derivatives of V. We will outline the basic idea in the following subsection.

4.1 Evaluation of the Modified Energy

We now describe the approach of MOORE & REICH [23] for approximating modified Hamiltonians. The Störmer-Verlet method is first expressed in its positions only leapfrog formulation

$$\mathbf{M}\frac{\mathbf{r}^{n+1} - 2\mathbf{r}^n + \mathbf{r}^{n-1}}{\Delta t^2} = -\nabla_{\mathbf{r}} V(\mathbf{r}^n).$$

We next assume that there is a smooth function $\mathbf{r}(t)$ such that $\mathbf{r}(t_n) = \mathbf{r}^n$ for all time-steps t_n of interest. Taylor expansion of $\mathbf{r}(t)$ about t_n readily yields the following well-known expression for the local truncation error formula for the second-order central difference approximation:

$$\frac{\mathbf{r}^{n+1} - 2\mathbf{r}^n + \mathbf{r}^{n-1}}{\Delta t^2} = \ddot{\mathbf{r}}(t_n) + \frac{\Delta t^2}{12}\mathbf{r}^{(4)}(t_n) + \mathcal{O}(\Delta t^4).$$

Since, by assumption, $\mathbf{r}(t_n) = \mathbf{r}^n$, we find that the smooth function $\mathbf{r}(t)$ has to satisfy the (in second-order) modified equation

$$\mathbf{M}\ddot{\mathbf{r}} + \frac{\Delta t^2}{12}\mathbf{M}\mathbf{r}^{(4)} = -\nabla_{\mathbf{r}} V(\mathbf{r}) \tag{9}$$

up to terms of order Δt^4. Higher-order modified equations can be easily found. We restrict the discussion to the second-order modification for simplicity.

We now multiply the whole equation (9) by $\dot{\mathbf{r}}^T$ from the left to obtain, after a rearrangement of term, the scalar equation

$$\frac{d}{dt}\left[\frac{1}{2}\dot{\mathbf{r}}^T\mathbf{M}\dot{\mathbf{r}} + V(\mathbf{r})\right] = -\frac{\Delta t^2}{12}\dot{\mathbf{r}}^T\mathbf{M}\mathbf{r}^{(4)}.$$

A remarkable observation is that the term on the right hand side of the last equation can also be written as a total time derivative, i.e.

$$\frac{\Delta t^2}{12}\dot{\mathbf{r}}^T\mathbf{M}\mathbf{r}^{(4)} = \frac{\Delta t^2}{12}\frac{d}{dt}\left[\dot{\mathbf{r}}^T\mathbf{M}\mathbf{r}^{(3)} - \frac{1}{2}\ddot{\mathbf{r}}^T\mathbf{M}\ddot{\mathbf{r}}\right].$$

We may conclude that the modified energy

$$\hat{E}_{\Delta t} = \frac{1}{2}\dot{\mathbf{r}}^T \mathbf{M}\dot{\mathbf{r}} + V(\mathbf{r}) + \frac{\Delta t^2}{12}\left[\dot{\mathbf{r}}^T \mathbf{M}\mathbf{r}^{(3)} - \frac{1}{2}\ddot{\mathbf{r}}^T \mathbf{M}\ddot{\mathbf{r}}\right] \tag{10}$$

is preserved to fourth-order in the step-size Δt along numerical solutions computed by the Störmer-Verlet/leapfrog method.

For a numerical verification of the modified energy $\hat{E}_{\Delta t}$, we need to approximate the time derivatives by finite difference approximations of sufficiently high order. For the given modified energy (10), this requires that the first-order time derivative in $\dot{\mathbf{r}}^T \mathbf{M}\dot{\mathbf{r}}/2$ needs to be discretized to fourth-order in Δt while the remaining time derivatives need only be approximated to second-order (due to the prefactor of $\Delta t^2/12$). We use the fourth-order finite difference formula

$$\dot{\mathbf{r}}(t_n) \approx \frac{\mathbf{r}^{n+1} - \mathbf{r}^{n-1}}{2\Delta t} - \frac{\mathbf{r}^{n+2} - 2\mathbf{r}^{n+1} + \mathbf{r}^{n-1} - \mathbf{r}^{n-2}}{12\Delta t}$$

as well as the second-order formulas

$$\ddot{\mathbf{r}}(t_n) \approx \frac{\mathbf{r}^{n+1} - 2\mathbf{r}^n + \mathbf{r}^{n-1}}{\Delta t^2}$$

and

$$\mathbf{r}^{(3)}(t_n) \approx \frac{\mathbf{r}^{n+2} - 2\mathbf{r}^{n+1} + \mathbf{r}^{n-1} - \mathbf{r}^{n-2}}{12\Delta t^3}.$$

It follows that we require the five coordinate approximations $\{\mathbf{r}^{n+i}\}_{i=-2,-1,0,1,2}$ to evaluate the modified energy (10) at time t_n to the desired fourth-order accuracy. Given $\mathbf{r}^0$ and $\dot{\mathbf{r}}^0$ at the start of a MD simulation, this implies the additional computation of "past" positions $\mathbf{r}^{-1}$ and $\mathbf{r}^{-2}$. Making use of the time-reversibility of the Newtonian equations of motion, those positions can be computed by integrating the equations forward in time over two time-steps with initial values $\mathbf{r}^0$ and $-\dot{\mathbf{r}}^0$. In summary, given any pair of initial conditions $(\mathbf{r}^0, \dot{\mathbf{r}}^0)$, the Störmer-Verlet/leapfrog method assigns a modified energy $\hat{E}^0_{\Delta t}$ by the procedure just described. For all later times t_n, the modified energy $\hat{E}^n_{\Delta t}$ is computed "on the fly". (At the end of the simulation interval we have to take two additional time-steps.)

The standard Metropolis criterion (3) is now replaced by

$$\min\left(1, \exp\left[-\beta\{\hat{E}_{\Delta t}(\mathbf{r}', \mathbf{v}') - \hat{E}_{\Delta t}(\mathbf{r}, \mathbf{v})\}\right]\right), \tag{11}$$

where $(\mathbf{r}, \mathbf{v}) = (\mathbf{r}^0, \mathbf{v}^0)$ and $(\mathbf{r}', \mathbf{v}')$ is the numerical solution obtained at a given time t_N (i.e., after N Störmer-Verlet integration steps with step-size Δt). Here we used the notation $\mathbf{v} = \dot{\mathbf{r}} = \mathbf{M}^{-1}\mathbf{p}$, $\mathbf{v}' = \dot{\mathbf{r}}' = \mathbf{M}^{-1}\mathbf{p}'$. If the proposed move is rejected, then the simulation is continued with $\mathbf{r}$ and negated momenta $-\mathbf{p}$ [13].

Following the HMC analysis of MEHLIG, HEERMANN & FORREST and HOROWITZ [13, 21], it follows that the Störmer-Verlet method combined with the Metropolis criterion (11) satisfies detailed balance and preserves the canonical ensemble for the modified energy $\hat{E}_{\Delta t}$.

The negation of the momenta in case of rejection is needed to satisfy detailed balance. Contrary to the guided Monte Carlo method [13] such a reversal of momenta is very infrequent under the TSHMC method and should not impact on the sampling efficiency of the method. At the same time, the same argument leads to the expectation that ignoring momentum negation after a rejected step will not alter the simulation results significantly. In fact, the simulations carried out in §5 used no such momentum negation.

4.2 Alternative Momentum Updates

HOROWITZ pointed out in [13] that it is not necessary to completely re-sample the momenta under Step 1 of a standard HMC scheme. Instead one takes the set of given momenta $\mathbf{p}$ and modifies it by a vector $\boldsymbol{\xi} \in \mathbb{R}^{3N}$ to obtain a new set given by

$$\mathbf{p}' = \mathbf{p} + \sigma\boldsymbol{\xi}. \tag{12}$$

Here $\sigma > 0$ is a free parameter and $\boldsymbol{\xi}$ is sampled from the Boltzmann distribution $\rho_{\mathrm{Boltzmann}}$, i.e., $\boldsymbol{\xi}$ is a vector of independent Gaussian random variables with mean zero and variance k_BT. Smaller values of σ lead to smaller perturbations in the momenta. The new set of momentum vectors $\mathbf{p}'$ is accepted with a probability of

$$\min\left(1, \exp\left[-\beta\left\{(\mathbf{p}')^T\mathbf{M}^{-1}\mathbf{p}'/2 - \mathbf{p}^T\mathbf{M}^{-1}\mathbf{p}/2\right\}\right]\right).$$

This momentum update replaces the above Step 1 in a standard HMC method. Step 2 is then started from the given position vector $\mathbf{q}$ and the accepted momentum vector, which we denote again by $\mathbf{p}$.

Following COTTER & REICH [4], we suggest a further generalization of the update (12):

$$\mathbf{p}' = \mathbf{p} + \sigma\sum_{k=1}^{K}\nabla_{\mathbf{r}}h_k(\mathbf{r})\xi_k, \tag{13}$$

where σ and $\boldsymbol{\xi} = (\xi_1, \ldots, \xi_K)^T \in \mathbb{R}^K$ are defined as before, and the functions $h_k(\mathbf{r})$, $k = 1, \ldots, K$, can be chosen quite arbitrarily. The particular choice

$$h_k(\mathbf{r}) = \phi(r_{ij}), \qquad r_{ij} = \|\mathbf{r}_i - \mathbf{r}_j\|,$$

$k = 1, \ldots, (N-1)N/2$, ϕ a given function of inter-particle distances r_{ij}, transforms (13) into an update very similar to what is used in dissipative particle dynamics (DPD) [7, 11] (see also MA & IZAGUIRRE [20] for another application to MD). One attractive feature of such an update is its conservation of linear and angular momenta:

$$\sum_{i=1}^{N}\mathbf{p}_i = \sum_{i=1}^{N}\mathbf{p}'_i, \qquad \sum_{i=1}^{N}\mathbf{r}_i \times \mathbf{p}_i = \sum_{i=1}^{N}\mathbf{r}'_i \times \mathbf{p}'_i.$$

One can also set $K = 3N$ and

$$h_i(\mathbf{r}) = x_i, \qquad h_{i+N}(\mathbf{r}) = y_i, \qquad h_{i+2N}(\mathbf{r}) = z_i,$$

$i = 1, \ldots, N$, in (13), which leads back to (12). Many more choices are feasible and of potential use. For example, one could apply the update only to particles near the boundary of the simulation domain or to certain subunits of the molecular system. Again, the strength of the coupling is controlled by the parameter σ.

Given a new set of momenta $\mathbf{p}'$, we need to evaluate the corresponding modified energy $\hat{E}_{\Delta t}(\mathbf{r}, \mathbf{v}')$, $\mathbf{v}' = \mathbf{M}^{-1}\mathbf{p}'$. This step requires time-stepping the equations of motion two steps forward and backward in time and, hence, two additional force field evaluations are needed. We then apply (11) in its slightly modified form:

$$\min\left(1, \exp\left[-\beta\{\hat{E}_{\Delta t}(\mathbf{r}, \mathbf{v}') - \hat{E}_{\Delta t}(\mathbf{r}, \mathbf{v})\}\right]\right). \tag{14}$$

It is again easily verified that the momentum update (13) combined with the Metropolis criterion (14) satisfies detailed balance and preserves the canonical density corresponding to $\hat{E}_{\Delta t}$. Hence we may conclude that the TSHMC method (without reweighting) constitutes a Markov chain Monte Carlo method which samples from the canonical density $\rho_{\text{canonical}} \sim \exp(-\beta \hat{E}_{\Delta t})$.

The targeted shadowing hybrid Monte Carlo (TSHMC) method may now be summarized as follows. One alternates between constant energy MD steps, which are accepted according to the Metropolis criterion (11) with modified energy (10), and a partial DPD-type velocity resampling according to (13) and Metropolis criterion (14). The concatenation of two Markov processes with identical invariant probability density functions produces another Markov process with the same invariant probability density function. It should be noted that the computation of averages in the original ensemble requires the weight factors (8).

5 Computer Experiment

The suggested approach was implemented and tested on a Linux cluster for an alanin side chain analog. This system contains 900 water molecules with a total of 2705 atoms. We apply the OPLS-AA [16] forcefield parameters for alanin and the original TIP3P model [15] for water molecules. Electrostatic interactions were treated using a particle-mesh Ewald summation (PME) method [5, 8] and periodic boundary conditions for a truncated octahedron box were applied.

We performed the simulation using three different techniques: TSHMC, standard HMC and traditional MD. All three approaches used GROMACS 3.2.1 [19] to perform the necessary molecular dynamics simulation steps. The system was initially equilibrated for 200 ps and then run for 1 ns at a temperature of 298 K. In the traditional MD approach the temperature was coupled to a heat bath of 298 K with a coupling time constant of 0.1 ps using the Nosé-Hoover procedure [12, 25]. Integration of the equations of motion was performed using the Störmer-Verlet algorithm and all bonds were constrained using the LINCS [10] algorithm with a distance constraint of 10e-6 Å. We used a step-size of Δt = 2 fs in the traditional MD method.

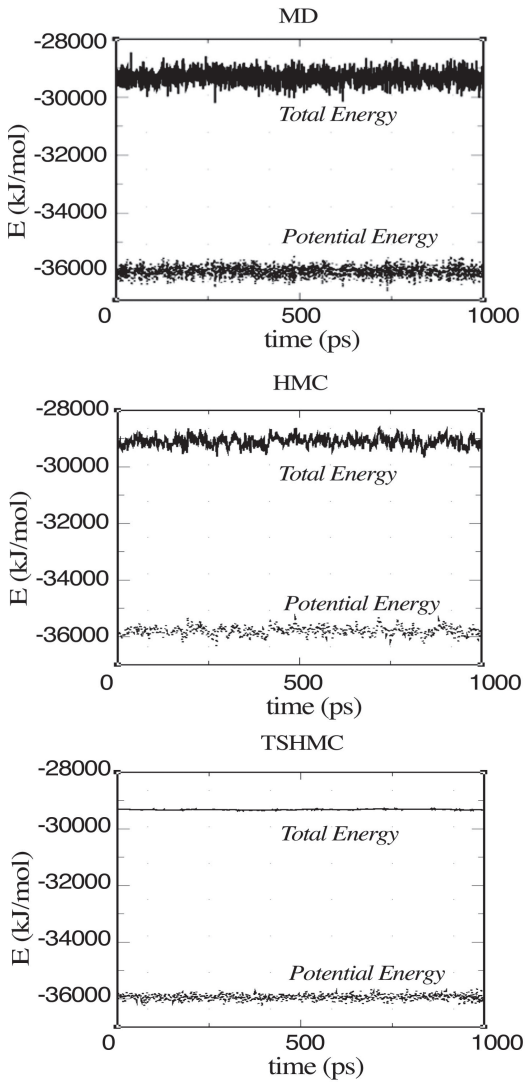

Figure 1. Total and potential energies for MD, HMC, and TSHMC

To investigate the effect of step-size and length of MD simulations per HMC step on sampling efficiency of HMC and TSHMC, we ran both algorithms using three different step-sizes (Δt = 1 fs, 2 fs, 2.5 fs) and two different MD simulation lengths (150 and 1000 time steps, respectively). The fourth-order modified Hamiltonian was used in the TSHMC approach. The parameter σ in (12) was set to 0.1, which led to a rejection rate of about 40% in the momentum update within the TSHMC simulation. Total and potential energies for the three simulation approaches are compared in Fig. 1. The average energies are in good agreement within the simulation

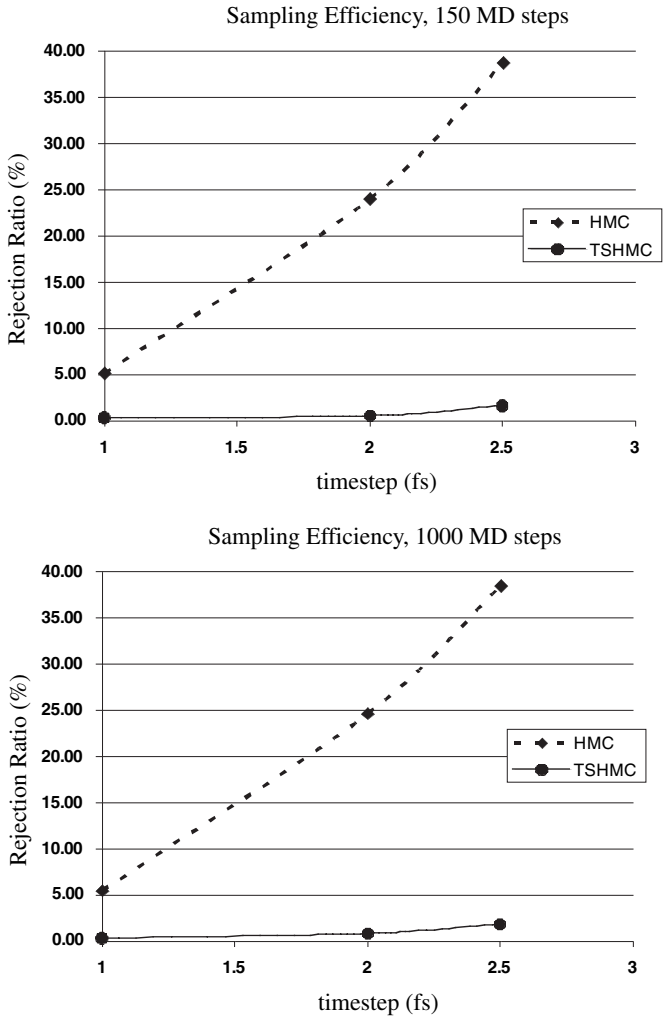

Figure 2. Sampling efficiency of HMC and TSHMC as a function of step-size and number of MD steps (per HMC step)

accuracy. As expected, TSHMC demonstrates much smoother energy profiles than the other two simulation methods due to higher-order energy conservation in the modified Hamiltonian. The magnitudes of energy fluctuations in both HMC approaches are significantly smaller than those observed for the standard constant temperature MD simulations. The sampling efficiency of HMC and TSHMC as a function of step-size and number of MD steps (per HMC step) is presented in Fig. 2. Observed rejection rates are almost identical for both choices of the MD simulation length, which suggests that the MD simulation length per HMC step does not affect much the acceptance/rejection rate at least for this particular model problem. On the

contrary, the step size Δt has a pronounced impact on the number of accepted configurations in HMC and TSHMC. The number of rejected configurations increases with increasing time steps in both HMC methods. However, the increase is visibly faster in standard HMC. In TSHMC the rejection rate is still rather low, around 2% for the largest tested step-size Δt. This is 20 times less than the rejection rate observed in the corresponding standard HMC simulation.

6 Conclusion

We have suggested and implemented a modified HMC algorithm, which, in its most general form, can be viewed as a thermodynamically consistent implementation of dissipative particle dynamics (DPD). (See, for example, [3] for inconsistency problems with known time-stepping method for DPD.) In addtion, we have also investigated the effect of modified energies to increase the acceptance rate of standard HMC. The results for our particular formulation of the modified energies are in line with the observations of IZAGUIRRE & HAMPTON [14] for the SHMC method. We re-emphasize that the TSHMC method is different from SHMC in two regards:

(i) a simplified evaluation of modified energies for the Störmer-Verlet method,
(ii) a thermodynamically consistent DPD-type (partial) momentum update.

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