An extended-Lagrangian scheme for charge equilibration in reactive molecular dynamics simulations

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ABSTRACT

Reactive molecular dynamics (RMD) simulations describe chemical reactions at orders-of-magnitude faster computing speed compared with quantum molecular dynamics (QMD) simulations. A major computational bottleneck of RMD is charge-equilibration (QEq) calculation to describe charge transfer between atoms. Here, we eliminate the speed-limiting iterative minimization of the Coulombic energy in QEq calculation by adapting an extended-Lagrangian scheme that was recently proposed in the context of QMD simulations, Souvatzis and Niklasson (2014). The resulting XRMD simulation code drastically improves energy conservation compared with our previous RMD code, Nomura et al. (2008), while substantially reducing the time-to-solution. The XRMD code has been implemented on parallel computers based on spatial decomposition, achieving a weak-scaling parallel efficiency of 0.977 on 786,432 IBM Blue Gene/Q cores for a 67.6 billion-atom system.

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1. Introduction

Molecular dynamics (MD) simulations follow time evolution of the positions, $\mathbf{r}^N = \{\mathbf{r}_i \mid i = 1, \ldots, N\}$, of N atoms by numerically integrating Newton's equations of motion, where the atomic force law is mathematically encoded in the interatomic potential energy $E(\mathbf{r}^N)$ [1]. Reliable interatomic potentials are key to accurately describing thermomechanical properties of materials. To describe material processes involving chemical reactions, in particular, quantum molecular dynamics (QMD) simulations [2–5] determine the force law by minimizing the potential, $E(\mathbf{r}^N, \psi^{N\mathrm{el}})$, as a functional of electronic wave functions $\psi^{N\mathrm{el}}(\mathbf{r}) = \{\psi_n(\mathbf{r}) \mid n = 1, \ldots, N_{\mathrm{el}}\}$ (N_{el} is the number of wave functions) usually in the framework of density functional theory (DFT) [6]. Despite remarkable progresses in $O(N)$ DFT algorithms [7–10], the largest QMD simulations to date have been limited to $N \sim 10^4$ for the duration of 10^{-11} s [11,12]. To extend the limited spatiotemporal scales covered by QMD simulations, reactive molecular dynamics

(RMD) simulation methods [13] have been developed based on a first principles-based reactive force-field (ReaxFF) approach [14, 15]. The ReaxFF approach significantly reduces the computational cost of simulating chemical reactions, while reproducing the energy surfaces and barriers as well as charge distributions of DFT calculations. RMD simulations describe formation and breakage of chemical bonds using reactive bond orders [14,16,17]. The most intensive computation in RMD simulations arises from a charge-equilibration (QEq) scheme [18–20] to describe charge transfer between atoms. QEq treats variable atomic charges as dynamic variables, $q^N = \{q_i \mid i = 1, \ldots, N\}$. The charges and the resulting force law are determined by minimizing the potential, $E(\mathbf{r}^N, q^N)$, with respect to q^N at every MD step. This variable N-charge problem is commonly solved iteratively with the conjugate gradient (CG) method [21,22]. Though recent advancements in parallel ReaxFF algorithms [23–25] have enabled large RMD simulations [26–28] involving multimillion atoms, QEq computation remains to be the major bottleneck toward achieving billion-atom RMD simulations based on ReaxFF. The problem is that an excessively large number of CG iterations are required to reach sufficient convergence of charges q^N to guarantee the conservation of the total energy as a function of time. Insufficiently converged charges act as a heat sink of energy, and the resulting broken time reversibility causes the total energy to drift over time. A similar

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trade-off between the computational speed and energy conservation is encountered in QMD simulations, where insufficient convergence of the iterative refinement of wave functions $\psi^{N_{el}}$ causes serious energy drift. Niklasson proposed an extended Lagrangian scheme [29–31] that achieves excellent long-time energy conservation with drastically reduced number of iterations. In fact, an extended Lagrangian scheme with no iteration (i.e. requiring only one evaluation of energy gradient) has recently been demonstrated [32]. The key idea is to introduce auxiliary wave functions as dynamic variables that are numerically integrated by reversible, symplectic integration schemes to address the broken reversibility problem, while the auxiliary wave functions are constrained to iteratively determined wave functions by a harmonic potential.

In this paper, the extended Lagrangian scheme [29–32] is adapted to RMD simulations, thereby eliminating speed-limiting iterations in QEq calculation. The resulting XRMD simulation code drastically improves the energy conservation compared with our previous RMD code [23], while substantially reducing the time-to-solution. This paper presents key features and implementation details of XRMD. The rest of the paper is organized as follows. The next section describes the computational method. Benchmark results are presented in Section 3, and Section 4 contains conclusions.

2. Methods

2.1. Charge-equilibration (QEq) method

The interatomic potential energy in ReaxFF is composed of a number of bonded and nonbonded terms [14,15]. The nonbonded terms are Coulombic and van der Waals energies. The Coulombic energy is expressed as

$$E_{Coulomb}(\mathbf{r}^N, q^N) = \sum_i \chi_i q_i + \frac{1}{2} \sum_i \sum_j q_i H(r_{ij}) q_j, \qquad (1)$$

where $\mathbf{r}_i$, χ_i, and q_i are the position, electronegativity, and charge of the ith atom, respectively, and r_{ij} is the distance between a pair of atoms i and j. In Eq. (1), the Coulombic interaction is defined as

$$H(r_{ij}) = J_i \delta_{ij} + \frac{T(r_{ij})}{\left[r_{ij}^3 + \gamma_{ij}^{-3}\right]^{1/3}} (1 - \delta_{ij}), \qquad (2)$$

where J_i is the self-Coulomb repulsion coefficient, γ_{ij} is a parameter for the smeared Coulombic function, and the Kronecker delta is $\delta_{ij} = 1 \ (i = j)$ or $0 \ (i \neq j)$. The Coulombic interaction is screened using a taper function, $T(r)$, which has a finite range with a cutoff length of r_c.

In ReaxFF, atomic charges q_i are variables that change dynamically in time. When atomic positions are updated during RMD simulation, the QEq subroutine updates charge distribution q^N by minimizing $E_{Coulomb}$ subject to charge-neutrality constraint, $\Sigma_i q_i = 0$. With the Lagrange-multiplier method, the constrained energy minimization is equivalent to solving the electronegativity equalization problem [18,22,33,19],

$$g_i \equiv -\frac{\partial E_{Coulomb}}{\partial q_i} = -\mu, \qquad (3)$$

where μ is the electrochemical potential. We solve this problem iteratively using the CG method [21,23,34].

2.2. Extended Lagrangian QEq scheme

Our extended Lagrangian QEq scheme introduces auxiliary variables, $\theta^N = \{\theta_i \mid i = 1, \ldots, N\}$. System dynamics for extended Lagrangian reactive molecular dynamics (XRMD) simulations is derived from the extended Lagrangian,

$$L_{XRMD} = L_{RMD} + \frac{\mu}{2} \sum_i \dot{\theta}_i^2 - \frac{\mu\omega^2}{2} \sum_i (\theta_i - q_i)^2, \qquad (4)$$

Table 1
Energy deviation during MD simulation for 1 ps.

Method	Energy deviation (10^{-3} kcal/mol/atom)
XRMD	6.8
RMD (CG tolerance: 10^{-8})	4.1
RMD (one CG iteration per MD step)	499

where L_{RMD} is the RMD Lagrangian,

$$L_{MD} = \sum_i \frac{m_i}{2} \dot{r}_i^2 - E(\mathbf{r}^N), \qquad (5)$$

with m_i being the mass of the ith atom and the dot denoting time derivative. In Eq. (4), μ and ω are fictitious mass and frequency parameters for the auxiliary charge degrees of freedom.

The time evolution of the dynamical system described by L_{XRMD} is determined by Euler–Lagrange equations of motion. In the limit of $\mu \to 0$, the equations become

$$m_i \ddot{\mathbf{r}}_i = -\frac{\partial}{\partial \mathbf{r}_i} E(\mathbf{r}^N), \qquad (6)$$

$$\ddot{\theta}_i = \omega^2 (q_i - \theta_i). \qquad (7)$$

We numerically integrate Eqs. (6) and (7) using the velocity Verlet algorithm with a unit time step of δt. At each time step, we perform just one step of CG iteration toward minimizing the Coulombic energy, Eq. (1), as a function of q^N using the gradient in Eq. (3). We use the auxiliary variable θ^N as an initial guess for the CG optimization of q^N. For extended Lagrangian-based QMD simulations, the recommended value for the dimensionless parameter, $K = \omega^2 \delta t^2$, is 2 [31]. We have found that the same value works for XRMD as well, and $K = 2$ will be used in the numerical tests discussed below.

We have implemented the extended Lagrangian QEq scheme in our scalable parallel RMD simulation code [23]. All XRMD computations are parallelized using spatial decomposition, where the simulated system is decomposed into spatially localized subsystems and each processor is assigned computations associated with one subsystem. Message passing is used to exchange necessary data for the computations utilizing the message passing interface (MPI) library. The XRMD program is written in Fortran 90.

3. Results

We test our extended Lagrangian QEq scheme and the parallel XRMD code using oxidation of a silicon carbide nanoparticle (n-SiC) as an example. We adopt ReaxFF parameterization by Newsome et al. [35,36]. A n-SiC composed of 25 silicon (Si) and 25 carbon (C) atoms is placed in oxygen environment. We place 50 oxygen (O_2) molecules randomly around the n-SiC using a Monte Carlo procedure. The total number of atoms is 150 in a cubic box of side 16.289 Å. Fig. 1(a) shows the initial configuration of the n-SiC + O_2 system. The equations of motion are integrated using a unit time step of 0.25 fs. We first thermalize the system at temperature 300 K by velocity scaling. Subsequently, we switch to the microcanonical ensemble to test the energy conservation. Single MPI process is used for this test.

Fig. 1(b) shows the total energy as a function of time during MD simulation. We compare three cases: (1) XRMD code; (2) RMD code, where CG iterations at each MD step are continued until the change in the Coulombic energy $E_{Coulomb}$ per iteration falls below 10^{-8} of $|E_{Coulomb}|$; and (3) RMD code performing only one CG iteration per MD step. Total energy conservation of XRMD is comparable to converged RMD, while RMD with single CG step exhibits significant energy drift. Table 1 summarizes total energy drift during 1 ps MD simulation with the three methods.