

# A space–time-ensemble parallel nudged elastic band algorithm for molecular kinetics simulation

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## Abstract

A scalable parallel algorithm has been designed to study long-time dynamics of many-atom systems based on the nudged elastic band method, which performs mutually constrained molecular dynamics simulations for a sequence of atomic configurations (or states) to obtain a minimum energy path between initial and final local minimum-energy states. A directionally heated nudged elastic band method is introduced to search for thermally activated events without the knowledge of final states, which is then applied to an ensemble of bands in a path ensemble method for long-time simulation in the framework of the transition state theory. The resulting molecular kinetics (MK) simulation method is parallelized with a space–time-ensemble parallel nudged elastic band (STEP-NEB) algorithm, which employs spatial decomposition within each state, while temporal parallelism across the states within each band and band-ensemble parallelism are implemented using a hierarchy of communicator constructs in the Message Passing Interface library. The STEP-NEB algorithm exhibits good scalability with respect to spatial, temporal and ensemble decompositions on massively parallel computers. The MK simulation method is used to study low strain-rate deformation of amorphous silica.

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## 1. Introduction

Atomistic mechanisms of material processes often involve a sequence of thermally activated events that occur in complex microstructures. For example, various atomistic events, such as bond switching and double-defect recombination, have been postulated to account for plastic flow in amorphous silica [1, 2], but they are yet to be characterized quantitatively. Atomistic simulation of slow material processes (e.g., low strain-rate deformation) is challenging because of the existence of unexpected events such as the creation of nanometer-scale voids ahead of the crack tip during fracture of amorphous silica [3, 4]. The major computational challenge here is to couple vast spatiotemporal scales for enumerating a sequence of complex atomistic events and accurately evaluating their activation en-

ergies, thereby reliably calculating the rate of the material processes.

To address this challenge, a number of methods have been proposed for long-time dynamics simulations [5]. Among these methods, those based on path integrals [6–8] are computationally advantageous for the study of complex material processes, since they offer excellent scalability on parallel computers. These simulation methods use a sequence of atomic configurations (or states) that interpolate initial and final local minimum-energy states to find transition states [9] and estimate the activation energies of the associated events. The scalability of the path-based simulation methods arises from the temporal concurrency along a path [10], in addition to the spatial decomposition parallelism within each state that constitutes the path [11]. One of the widely used path-based simulation methods is the nudged elastic band (NEB) method [12,13], which is employed in this paper.

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For complex material processes, however, final states of events are often unknown, and thus exhaustive search for events is needed [14–16]. In this paper, a slight modification of the NEB method—directionally heated nudged elastic band (DHNEB) method—is used to search for events without the knowledge of final states, where mutually constrained molecular dynamics (MD) simulations with separate temperature controls are performed for a sequence of states in a band. Such unsupervised search for events can be incorporated into kinetic Monte Carlo simulation [17–20] to study long-time processes, where a requisite event list is generated on the fly [21]. We use a path ensemble method (PEM) to enumerate events by concurrently applying the DHNEB method to an ensemble of bands. The resulting molecular kinetics (MK) simulation provides an additional parallelization axis [22,23], i.e. ensemble parallelism, to the spatiotemporal parallelism of path-based simulation. In this paper, we design a space–time-ensemble nudged elastic band (STEP-NEB) algorithm to implement MK simulation on massively parallel computers.

This paper is organized as follows. The next section describes the DHNEB and MK simulation methods, and their scalable parallelization based on the STEP-NEB algorithm is explained in Section 3. Numerical results are presented in Section 4, and Section 5 contains summary.

## 2. Simulation method

Consider a set of  $N$  atoms and its state represented by a  $3N$ -dimensional vector  $\mathbf{R} \in \mathbb{R}^{3N}$  ( $\mathbb{R}$  is a set of real numbers), which contains the 3-dimensional positions of the  $N$  atoms. Long-time behavior of the system is often studied in the framework of the transition state theory [9], which describes the time evolution of the state in terms of a sequence of thermally activated events. Each event is defined as a triplet of states ( $\mathbf{R}_{\text{init}}, \mathbf{R}_{\text{tst}}, \mathbf{R}_{\text{fin}}$ ) interconnected by a minimum energy path (MEP)  $\mathbf{R}(\lambda)$  ( $\mathbb{R} \rightarrow \mathbb{R}^{3N}$ ;  $\lambda$  is a real-valued parameter such that  $\mathbf{R}_{\text{init}} = \mathbf{R}(\lambda_{\text{init}})$ ,  $\mathbf{R}_{\text{tst}} = \mathbf{R}(\lambda_{\text{tst}})$ , and  $\mathbf{R}_{\text{fin}} = \mathbf{R}(\lambda_{\text{fin}})$  with  $\lambda_{\text{init}} < \lambda_{\text{tst}} < \lambda_{\text{fin}}$ ). The potential energy function  $V(\mathbf{R})$ , which describes how atoms interact with each other, is required to be stationary,  $\partial V / \partial \mathbf{R} = 0$ , at all three states. In addition, the initial ( $\mathbf{R}_{\text{init}}$ ) and final ( $\mathbf{R}_{\text{fin}}$ ) states are local energy minima such that all eigenvalues of the Hessian matrix,  $\mathbf{H} = \partial^2 V / \partial \mathbf{R}^2 \in \mathbb{R}^{3N \times 3N}$ , are positive, whereas the transition state ( $\mathbf{R}_{\text{tst}}$ ) is a saddle point, at which only the lowest Hessian eigenvalue is negative.

Section 2.1 summarizes the nudged elastic band (NEB) method to approximately obtain a MEP given initial and final states, and Section 2.2 introduces its extension, directionally heated nudged elastic band (DHNEB) method, which searches for an event starting only from an initial state. Section 2.3 describes a path ensemble method (PEM) that applies the DHNEB method to an ensemble of bands to implement molecular kinetics (MK) simulation of long-time processes.

### 2.1. Nudged elastic band method

Let a nudged elastic band (NEB) be a sequence of  $S$  states,  $\beta = (\mathbf{R}_0, \dots, \mathbf{R}_{S-1})$ , where the two ends of the band are the

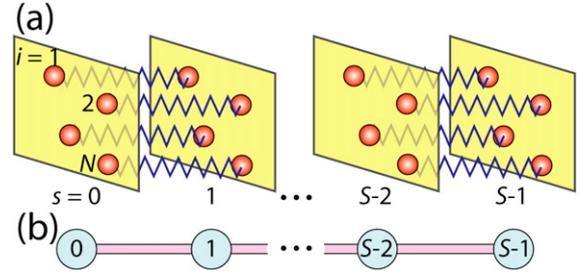


Fig. 1. Schematic of a nudged elastic band. (a) A NEB consists of a sequence of  $S$  states (yellow parallelograms),  $\mathbf{R}_s$  ( $s = 0, \dots, S - 1$ ), where each state consists of  $N$  atoms (red spheres),  $i = 1, \dots, N$ . Corresponding atoms in consecutive states interact via harmonic forces represented by blue wavy lines. (b) Abstraction of a NEB consisting of  $S$  states (cyan circles) connected by harmonic forces (magenta lines). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

initial ( $\mathbf{R}_0 = \mathbf{R}_{\text{init}}$ ) and final ( $\mathbf{R}_{S-1} = \mathbf{R}_{\text{fin}}$ ) states of an event, respectively (see Fig. 1) [12,13]. The band is a discrete approximation to a path  $\mathbf{R}(\lambda)$ .

The NEB method obtains a MEP iteratively by integrating mutually constrained ordinary differential equations to follow the dynamics of the states:

$$\mathbf{M} \frac{d^2}{dt^2} \mathbf{R}_s = \mathbf{F}_s - \mathbf{M} \gamma_s \frac{d}{dt} \mathbf{R}_s \quad (s = 0, \dots, S - 1), \quad (1)$$

where  $\mathbf{M} = \text{diag}(m_1, m_1, m_1, \dots, m_N, m_N, m_N) \in \mathbb{R}^{3N \times 3N}$  is a diagonal mass matrix ( $m_i$  is the mass of the  $i$ th atom) and  $\gamma_s$  ( $\sim 10^{-2} \text{ fs}^{-1}$ ) is the friction coefficient in the  $s$ th state. The force  $\mathbf{F}_s$  acting on the  $s$ th state is derived from the interatomic potential energy  $V(\mathbf{R})$  as

$$\mathbf{F}_s = \begin{cases} -\frac{\partial V}{\partial \mathbf{R}_s} \Big|_{\perp} + \mathbf{F}_s^{\text{spr}} \Big|_{\parallel} \\ = (\mathbf{I} - \hat{\tau}_s \hat{\tau}_s^T) \left( -\frac{\partial V}{\partial \mathbf{R}_s} \right) & (1 \leq s \leq S - 2) \\ + k_{\text{spr}} (\|\tau_s^+\| - \|\tau_s^-\|) \hat{\tau}_s \\ -\frac{\partial V}{\partial \mathbf{R}_s} & (s = 0, S - 1), \end{cases} \quad (2)$$

where  $\mathbf{I} \in \mathbb{R}^{3N \times 3N}$  is the identity matrix,  $\hat{\tau}_s = \tau_s / \|\tau_s\| \in \mathbb{R}^{3N}$  is a normalized tangential vector along the band ( $\|\tau_s\|$  is the norm of vector  $\tau_s$ ), and the superscript T denotes a transpose. The tangential vector  $\tau_s$  is defined as follows. Let

$$\tau_s^+ = \mathbf{R}_{s+1} - \mathbf{R}_s; \quad \tau_s^- = \mathbf{R}_s - \mathbf{R}_{s-1} \quad (3)$$

be vectors that connect consecutive images. Then, the tangential vector  $\tau_s$  is defined as

$$\tau_s = \begin{cases} \text{if } V(\mathbf{R}_{s+1}) > V(\mathbf{R}_s) > V(\mathbf{R}_{s-1}), \\ \tau_s^+, \\ \text{else if } V(\mathbf{R}_{s+1}) < V(\mathbf{R}_s) < V(\mathbf{R}_{s-1}), \\ \tau_s^-, \\ \text{else if } V(\mathbf{R}_{s+1}) > V(\mathbf{R}_s), \\ \tau_s^+ \Delta V_s^{\text{max}} + \tau_s^- \Delta V_s^{\text{min}}, \\ \text{else } \tau_s^+ \Delta V_s^{\text{min}} + \tau_s^- \Delta V_s^{\text{max}}, \end{cases} \quad (4)$$

where

$$\Delta V_s^{fn} = fn(|V(\mathbf{R}_{s+1}) - V(\mathbf{R}_s)|, |V(\mathbf{R}_{s-1}) - V(\mathbf{R}_s)|) \quad (fn = \max, \min) \quad (5)$$

and the max and min functions return the greater and smaller of the arguments, respectively. In Eq. (2),  $k_{\text{spr}}$  is a harmonic spring force constant that mutually constrains the motion of consecutive states. The tangential spring forces  $\mathbf{F}_s^{\text{spr}} \parallel$  thus drive the states  $\mathbf{R}_s$  equidistant from each other along the path  $\mathbf{R}(\lambda)$ , whereas the perpendicular force  $-\partial V/\partial \mathbf{R}_s \perp$  drives each system toward an energy minimum perpendicular to the path. It has been shown that a band with zero forces,  $\mathbf{F}_s = 0$  ( $s = 0, \dots, S-1$ ), is a discretized approximation to a MEP [12,13]. It should be noted that a number of different definitions have been used for the tangential vectors in the NEB method [24]. In this paper, we adopt the definition given in Ref. [13].

To numerically integrate the second-order ordinary differential equations, Eq. (1), each state  $\mathbf{R}_s$  is augmented with corresponding velocities  $\mathbf{U}_s = d\mathbf{R}_s/dt \in \mathbb{R}^{3N}$ , and accordingly a band is extended to  $\beta = ((\mathbf{R}_0, \mathbf{U}_0), \dots, (\mathbf{R}_{S-1}, \mathbf{U}_{S-1}))$ . Integration of Eq. (1) brings the band to a zero-force configuration (hence a MEP) by gradually decelerating the velocities through the frictional forces  $-\mathbf{M}\gamma_s d\mathbf{R}_s/dt$ . For each extended state  $(\mathbf{R}_s, \mathbf{U}_s)$ , Eq. (1) is equivalent to molecular dynamics (MD) simulation [25], except that the interstate forces  $\mathbf{F}_s^{\text{spr}} \parallel$  are added and the physical intrastate forces  $-\partial V/\partial \mathbf{R}_s$  are projected orthogonal to the path in Eq. (2) for the intermediate ( $s = 1, \dots, S-2$ ) states. This makes it rather trivial to convert an existing MD program to a NEB program. It is also noteworthy that the dynamics of the initial ( $s = 0$ ) and final ( $s = S-1$ ) ends of the band are not constrained by those of the intermediate states, and thus Eq. (1) brings the initial and final states to physical local minimum-energy configurations even when starting from approximate minima. This is in contrast to the conventional NEB algorithm that does not relax the initial and final ends of the band, which are assumed to be local minimum-energy states.

## 2.2. Directionally heated nudged elastic band (DHNEB) method

In the standard NEB method described in Section 2.1, the frictional forces  $-\mathbf{M}\gamma_s d\mathbf{R}_s/dt$  in Eq. (1) are used to quench the band to a zero-force configuration, thereby attaining a MEP, given both initial and final states. Our directionally heated nudged elastic band (DHNEB) method instead generates an event  $(\mathbf{R}_{\text{init}}, \mathbf{R}_{\text{tst}}, \mathbf{R}_{\text{fin}})$  starting only from an initial state  $\mathbf{R}_{\text{init}}$  (i.e. without the knowledge of a final state  $\mathbf{R}_{\text{fin}}$ ). To do so, the DHNEB method adds a separate heat bath [26] to the MD simulation of each state in the band, so that it is maintained at a desired temperature. For state  $s$ , Eq. (1) is thus integrated either: (a) with a heat bath at temperature  $T_s$  and zero friction ( $\gamma_s = 0$ ) for thermalization; or (b) without heat bath but with finite friction ( $\gamma_s \neq 0$ ) for quenching.

Given a local minimum-energy state  $\mathbf{R}_{\text{init}}$ , the DHNEB method starts with an initial band, in which all states  $\mathbf{R}_s$  ( $s = 0, \dots, S-1$ ) are located near  $\mathbf{R}_{\text{init}}$ . This is achieved by a thermalization phase that duplicates  $\mathbf{R}_{\text{init}}$  in all  $S$  states  $\mathbf{R}_s$ , initializes atom velocities  $\mathbf{U}_s$  randomly according to the Maxwell-Boltzmann distribution at a common temperature  $T_s = T$ , and then integrates Eq. (1) for time  $t_{\text{therm}} \sim 0.1$  ps, with the force

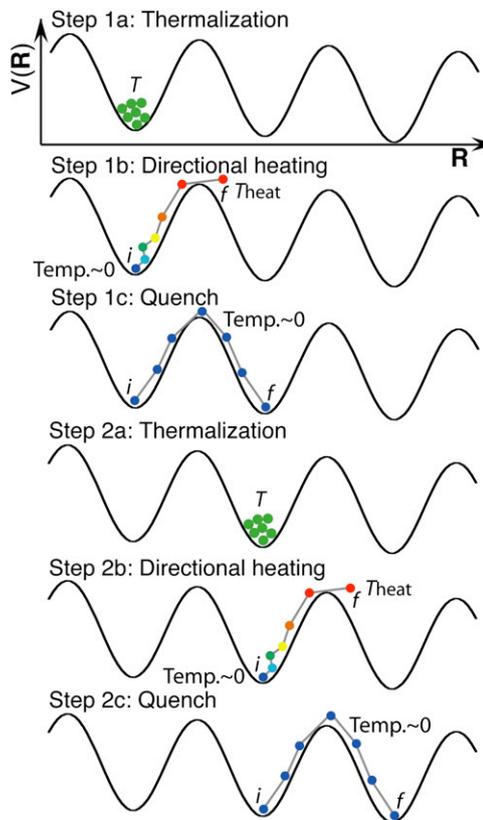


Fig. 2. Algorithmic steps of the directionally heated nudged elastic band method, which consist of thermalization, directional heating, and quench of a band. Black solid curves represent the potential energy surface  $V(\mathbf{R})$ , whereas circles (with color-coded temperature) are the states interconnected by harmonic forces (gray lines) to form the band. The letters  $i$  and  $f$  mark the initial and final ends of the band. The figure illustrates two consecutive calls to the DHNEB algorithm, where the final state of the first call is used as the initial state in the second call. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

replaced by the physical force  $\mathbf{F}_s = -\partial V/\partial \mathbf{R}_s$ . Here, no frictional force is applied (i.e.  $\gamma_s = 0$ ), and the temperature of each state is kept at  $T$  using a heat bath (see Fig. 2). Note that this is equivalent to performing MD simulations independently for the  $S$  states.

In the next directional heating phase of the DHNEB method, the final end ( $s = S-1$ ) of the band is heated to  $T_{S-1} = T_{\text{heat}}$  ( $T_{\text{heat}} \gg T$ ) using a heat bath, while the initial and intermediate ( $s = 0, \dots, S-2$ ) states are quenched through the frictional forces using a common friction coefficient  $\gamma_s = \gamma$  in Eq. (1) without temperature control. The directional heating allows the final state to escape the concave region (where  $\partial^2 V/\partial \mathbf{R}^2 > 0$ ) of the initial local energy minimum to explore another minimum assisted by high temperature, while the initial state is anchored to  $\mathbf{R}_{\text{init}}$  due to the quench. The time duration of the directional heating phase is  $t_{\text{heat}} \sim 1$  ps.

After the directional heating locates a new local energy minimum, the quench phase of the algorithm integrates Eq. (1) for  $t_{\text{quench}} \sim 2$  ps by turning off the heat bath attached to the final state and applying frictional force  $\gamma_{S-1} = \gamma$ , so that  $\mathbf{R}_{S-1}$  reaches a new local minimum-energy state  $\mathbf{R}_{\text{fin}}$ . (The initial and intermediate ( $s = 0, \dots, S-2$ ) states are quenched as well us-

Table 1  
Directionally heated nudged elastic band algorithm

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**Algorithm DHNEB**

**Input:**

$\mathbf{R}_{\text{init}} \in \mathbb{R}^{3N}$ : an initial local minimum-energy state  
 $T$ : temperature at which the system is thermalized  
 $T_{\text{heat}}$ : temperature to which the final end,  $\mathbf{R}_{S-1}$ , of the band is heated in the directional heating phase  
 $\gamma$ : friction coefficient  
 $t_{\text{therm}}$ : time duration to thermalize the system  
 $t_{\text{heat}}$ : time duration to directionally heat the band  
 $t_{\text{quench}}$ : time duration to quench the band

**Output:**

event  $e = (\mathbf{R}_{\text{init}}, \mathbf{R}_{\text{tst}}, \mathbf{R}_{\text{fin}})$ : a triplet of initial, transition and final states

**Variable:**

$\beta = ((\mathbf{R}_0, \mathbf{U}_0), \dots, (\mathbf{R}_{S-1}, \mathbf{U}_{S-1}))$ : a nudged elastic band, where  $\mathbf{R}_s$  and  $\mathbf{U}_s$  are the atomic positions and velocities in the  $s$ th state

**Steps:**

1. initialize band  $\beta$  at atomic positions  $\mathbf{R}_s \leftarrow \mathbf{R}_{\text{init}}$  with random velocities  $\mathbf{U}_s$  according to the Maxwell–Boltzmann distribution at temperature  $T$  for all states,  $s = 0, \dots, S-1$
  2. *thermalization*: call NEBDyn( $\beta, t_{\text{therm}}, -\partial V/\partial \mathbf{R}_s, T_s = T$  for  $s \in [0, S-1]$ )
  3. *directional heating*: call NEBDyn( $\beta, t_{\text{heat}}, \mathbf{F}_s, \gamma_s = \gamma$  for  $s \in [0, S-2]$  and  $T_{S-1} = T_{\text{heat}}$ )
  4. *quench*: call NEBDyn( $\beta, t_{\text{quench}}, \mathbf{F}_s, \gamma_s = \gamma$  for  $s \in [0, S-1]$ )
  5.  $\mathbf{R}_{\text{fin}} \leftarrow \mathbf{R}_{S-1}$ ;  $\mathbf{R}_{\text{tst}} \leftarrow \arg \min(V(\mathbf{R}_s))$  ( $s = 0, \dots, S-1$ )
- 

ing the same friction coefficient  $\gamma_s = \gamma$ .) The quench phase of the DHNEB algorithm embodies the standard NEB method, and thus the band converges to a MEP connecting the original and new local minima. The transition state  $\mathbf{R}_{\text{tst}}$  of the corresponding event is determined as the state with the highest potential energy, i.e.  $\mathbf{R}_{\text{tst}} \leftarrow \arg \min(V(\mathbf{R}_s))$  ( $s = 0, \dots, S-1$ ). It should be noted that this is an approximate transition state due to the discrete approximation to the MEP. The approximation can be systematically improved by increasing the number of states  $S$  in the band or by using the climbing image NEB method [27].

Table 1 shows the DHNEB algorithm that finds an event  $e = (\mathbf{R}_{\text{init}}, \mathbf{R}_{\text{tst}}, \mathbf{R}_{\text{fin}})$ , given an initial local minimum-energy state  $\mathbf{R}_{\text{init}}$ . The thermalization, directional heating, and quench phases of the DHNEB algorithm are implemented by calling the NEB dynamics algorithm, NEBDyn, in Table 2, which integrates Eq. (1) numerically with time discretization unit  $\Delta t$  ( $\sim 1$  fs) using a symplectic, reversible time integrator [28]. The inputs to the NEBDyn algorithm are: (a) initial band augmented with velocities,  $\beta = ((\mathbf{R}_0, \mathbf{U}_0), \dots, (\mathbf{R}_{S-1}, \mathbf{U}_{S-1}))$ ; (b) simulated time duration  $t$ , for which Eq. (1) is integrated; (c) forces—either the mutually constrained forces  $\mathbf{F}_s$  in Eq. (2) or the physical forces  $-\partial V/\partial \mathbf{R}_s$  ( $s = 0, \dots, S-1$ ); and (d) either a friction coefficient  $\gamma_s$  or a desired temperature  $T_s$  for each state  $s \in [0, S-1]$ . The output from the NEBDyn algorithm is the updated band  $\beta$  after the time integration for  $t$ . The DHNEB algorithm can be applied repeatedly to search for the next event by starting a new thermalization–directional heating–quench cycle, using the previous  $\mathbf{R}_{\text{fin}}$  as a new  $\mathbf{R}_{\text{init}}$ . Fig. 2 illustrates two thermalization–directional heating–quench cycles of the DHNEB algorithm.

As a method to explore the energy landscape, the DHNEB algorithm is equivalent to other simulation methods such as simulated annealing [29] and temperature-accelerated dynamics [30]. An advantage of the DHNEB algorithm is the integration of activation-barrier estimation into event search, which

Table 2  
Nudged elastic band dynamics algorithm

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**Algorithm NEBDyn**

**Input:**

initial band  $\beta = ((\mathbf{R}_0, \mathbf{U}_0), \dots, (\mathbf{R}_{S-1}, \mathbf{U}_{S-1}))$   
 $t$ : simulated time duration  
 $\tilde{\mathbf{F}}_s = \mathbf{F}_s$  or  $-\partial V/\partial \mathbf{R}_s$  ( $s = 0, \dots, S-1$ ): constrained forces in Eq. (2) or physical forces  
 $T_s$  or  $\gamma_s$  ( $s = 0, \dots, S-1$ ): desired temperatures or friction coefficients

**Output:**

updated band  $\beta = ((\mathbf{R}_0, \mathbf{U}_0), \dots, (\mathbf{R}_{S-1}, \mathbf{U}_{S-1}))$

**Steps:**

**for**  $\forall s \in [0, S-1]$  with a desired temperature  $T_s$   
  augment the state  $(\mathbf{R}_s, \mathbf{U}_s)$  with a heat-bath degree of freedom with temperature  $T_s$   
  compute initial forces  $\tilde{\mathbf{F}}_s$  ( $\{\mathbf{R}_s | s = 0, \dots, S-1\}$ ) for all states,  $s = 0, \dots, S-1$   
  **do**  $step = 1$  **to**  $\lfloor t/\Delta t \rfloor$  //  $\Delta t$  is the time discretization unit  
     $\mathbf{U}_s \leftarrow \mathbf{U}_s + (\Delta t/2)\mathbf{M}^{-1}\tilde{\mathbf{F}}_s$  ( $s = 0, \dots, S-1$ ) // update velocities  
     $\mathbf{R}_s \leftarrow \mathbf{R}_s + \Delta t\mathbf{U}_s$  ( $s = 0, \dots, S-1$ ) // update atomic positions  
    update forces  $\tilde{\mathbf{F}}_s$  ( $\{\mathbf{R}_s | s = 0, \dots, S-1\}$ ) for all states,  $s = 0, \dots, S-1$   
     $\mathbf{U}_s \leftarrow \mathbf{U}_s + (\Delta t/2)\mathbf{M}^{-1}\tilde{\mathbf{F}}_s$  ( $s = 0, \dots, S-1$ ) // update velocities  
  **for**  $\forall s \in [0, S-1]$  with a friction coefficient  $\gamma_s$   
     $\mathbf{U}_s \leftarrow \exp(-\gamma_s \Delta t)\mathbf{U}_s$  // damp velocities

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makes the programming straightforward when a massive number of events and their activation barriers need to be enumerated. The quality of the obtained energy landscape by all these methods can be improved by increasing the size of the statistical ensemble, which will be addressed in the next subsection.

### 2.3. Path ensemble method (PEM) for molecular kinetics (MK) simulation

The DHNEB method is a stochastic simulation method that finds an event assisted by temperature, starting from a given initial state. For many-atom systems, however, a large number of events may exist for each initial state [31,32]. To con-

Table 3  
Molecular kinetics simulation algorithm

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**Algorithm MK**

**Input:**

$\mathbf{R}_{\text{init}} \in \mathbb{R}^{3N}$ : an initial local minimum-energy state  
 $N_{\text{step}}$ : total number of simulation steps  
 $T$ : temperature  
 $T_{\text{heat}}$ : temperature for directional heating in the DHNEB algorithm in Table 1  
 $t_{\text{therm}}$ : time duration to thermalize the system  
 $t_{\text{heat}}$ : time duration to directionally heat the band

**Output:**

$(e_*^{(1)}, e_*^{(2)}, \dots, e_*^{(N_{\text{step}})})$ : a sequence of events that are selected according to Eq. (7), one at a simulation step  
 $(t_*^{(1)}, t_*^{(2)}, \dots, t_*^{(N_{\text{step}})})$ : a sequence of times when the events occur

**Variable:**

$E = \{\beta_b \mid b = 0, \dots, B-1\}$ : ensemble of  $B$  nudged elastic bands  
 $t$ : simulated time

**Steps:**

```

t ← 0
do l = 1 to Nstep
  for ∀βb ∈ E
    eb = (Rinit(b), Rtst(b), Rfin(b)) ← DHNEB(Rinit) // generate an event by calling the DHNEB algorithm
    Δb ← V(Rtst(b)) − V(Rinit(b)) // calculate the activation energy
    rb = {ttherm + theat exp[ $\frac{\Delta_b}{k_B} (\frac{1}{T} - \frac{1}{T_{\text{heat}}})$ ]}-1 // estimate the reaction rate of event b
  r ← ∑b=0B-1 rb
  for ∀βb ∈ E
    Pb ← rb/r // calculate the probability that event b occurs
  select an event b* ∈ [0, B-1] according to probability distribution Pb
  e*(l) ← eb*
  t ← t − ln(ξ)/r, where ξ is a uniform random number in the range [0, 1]
  t*(l) ← t
  Rinit ← Rfin(b*)

```

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struct a list of multiple events, we introduce a path ensemble method (PEM), which applies the DHNEB method to an ensemble of  $B$  bands,  $E = \{\beta_b \mid b = 0, \dots, B-1\}$ , starting from a common initial state  $\mathbf{R}_{\text{init}}$  but with different random velocities. This generates a list of possible events  $\{e_b = (\mathbf{R}_{\text{init}}^{(b)}, \mathbf{R}_{\text{tst}}^{(b)}, \mathbf{R}_{\text{fin}}^{(b)}) \mid b = 0, \dots, B-1\}$  with the associated barrier energies  $\{\Delta_b = V(\mathbf{R}_{\text{tst}}^{(b)}) - V(\mathbf{R}_{\text{init}}^{(b)}) \mid b = 0, \dots, B-1\}$ . In the framework of the transition state theory [9], we calculate the rate of the  $b$ th event as [30]

$$r_b = \left\{ t_{\text{therm}} + t_{\text{heat}} \exp \left[ \frac{\Delta_b}{k_B} \left( \frac{1}{T} - \frac{1}{T_{\text{heat}}} \right) \right] \right\}^{-1}, \quad (6)$$

where  $t_{\text{therm}}$  and  $t_{\text{heat}}$  are the time durations of the thermalization and directional heating phases of the DHNEB method, respectively,  $k_B$  is the Boltzmann constant, and  $T$  and  $T_{\text{heat}}$  are the temperatures used for the thermalization and directional heating phases of the DHNEB method, respectively (see Section 2.2).

In kinetic Monte Carlo simulation [17–20], these rates are used to numerically integrate the master equation that governs transitions among local minimum-energy states to describe the long-time dynamics of the system. Specifically, we select one event  $b^*$  from the list of possible events according to probability

$$P_b = \frac{r_b}{r} = \frac{r_b}{\sum_{b=0}^{B-1} r_b}, \quad (7)$$

and the state is changed to the corresponding final state  $\mathbf{R}_{\text{fin}}^{(b^*)}$ . According to the probability density,  $p(t_{\text{evt}}) = r \exp(-rt_{\text{evt}})$ , of the time span between two successive events in a Poisson process, the simulated time is advanced by

$$t_{\text{evt}} = -\ln(\xi)/r, \quad (8)$$

where  $\xi$  is a uniform random number in the range  $[0, 1]$ . This procedure is repeated by using  $\mathbf{R}_{\text{fin}}^{(b^*)}$  as the initial state  $\mathbf{R}_{\text{init}}$  in the next simulation step.

Table 3 shows the resulting molecular kinetics (MK) simulation algorithm to study long-time processes. It starts with a given local minimum-energy state  $\mathbf{R}_{\text{init}}$ , and returns a sequence of events  $(e_*^{(1)}, e_*^{(2)}, \dots, e_*^{(N_{\text{step}})})$ , where  $N_{\text{step}}$  is the total number of MK simulation steps. At the  $l$ th simulation step, an event  $e_*^{(l)}$  is selected according to the probability, Eq. (7). In addition, the algorithm returns the sequence of times  $(t_*^{(1)}, t_*^{(2)}, \dots, t_*^{(N_{\text{step}})})$ , at which these events occur.

### 3. Space–time-ensemble parallel nudged elastic band (STEP-NEB) algorithm

The MK simulation method is implemented on parallel computers based on a space–time-ensemble parallel nudged elastic band (STEP-NEB) algorithm. It first assigns the  $B$  bands in the ensemble to separate groups of processors (ensemble decomposition), each of which is in turn decomposed into  $S$  processor

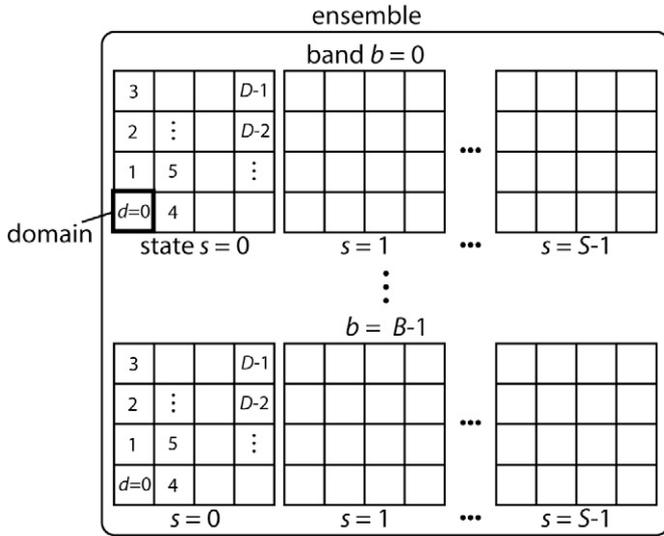


Fig. 3. Processor indexing in the space–time–ensemble parallel nudged elastic band algorithm. Ensemble decomposition first divides the processors into  $B$  groups  $comm_b$  ( $b = 0, \dots, B - 1$ ), each assigned a band in the ensemble. Temporal decomposition in turn divides each  $comm_b$  into  $S$  subgroups  $comm_{b,s}$  ( $s = 0, \dots, S - 1$ ), each for a state in band  $b$ . Spatial decomposition then divides each state into  $D$  spatial domains.

subgroups (temporal decomposition) representing the  $S$  states that constitute each band (see Fig. 3). We then use spatial decomposition within each state for further parallelization.

The parallel program is written in Fortran 90 and Message Passing Interface (MPI) [33] languages, in which all processors constitute an overall MPI communicator, MPI\_COMM\_WORLD. (The MPI communicator construct combines a processor group and a context, in such a way that messages with different contexts are not intermixed.) The processors are first grouped into  $B$  processor groups, each consisting of  $SD$  processors, by defining  $B$  MPI communicators  $comm_b$  ( $b = 0, \dots, B - 1$ ) as subsets of MPI\_COMM\_WORLD. The communicator  $comm_b$ , which performs the computation associated with the  $b$ th band, is in turn grouped into  $S$  sub-communicators  $comm_{b,s}$  ( $s = 0, \dots, S - 1$ ), each consisting of  $D$  processors. The communicator  $comm_{b,s}$  performs parallel MD simulation for the  $s$ th state in the  $b$ th band using  $D$  processors. Due to this hierarchical decomposition (see Fig. 3), the total number of processors in the STEP-NEB algorithm is given by

$$P = BSD. \quad (9)$$

One advantage of the hybrid task (ensemble and time) + spatial decomposition approach [34] implemented with MPI communicators is that the program can be easily converted to a hybrid Grid remote procedure call (GridRPC) + MPI program to be run on a Grid of distributed parallel computers, in which the number of processors changes dynamically on demand, resources are allocated adaptively, and tasks are migrated automatically in response to unexpected faults [35].

We employ spatial decomposition to parallelize the computation within each  $comm_{b,s}$  [36]. Here, the total volume of the simulated system is divided into  $D$  domains of equal volume, and each domain is assigned to a processor in an array

of  $D$  processors. Specifically, we use regular 3-dimensional mesh topology that maps atom  $i$  at position  $\mathbf{r}_i = (r_{ix}, r_{iy}, r_{iz})$  to processor  $d(\mathbf{r}_i)$  in an array of  $D = D_x D_y D_z$  processors:

$$\begin{cases} d(\mathbf{r}_i) = d_x(r_{ix})D_y D_z + d_y(r_{iy})D_z + d_z(r_{iz}), \\ d_\alpha(r_{i\alpha}) = \lfloor r_{i\alpha} D_\alpha / L_\alpha \rfloor \quad (\alpha = x, y, z), \end{cases} \quad (10)$$

where  $L_\alpha$  is the simulation box size in the  $\alpha$  direction ( $\alpha = x, y, z$ ). The  $P$  processors are globally indexed in such a way that the  $d$ th domain of the  $s$ th state in the  $b$ th band is assigned to processor

$$p = bSD + sD + d. \quad (11)$$

Fig. 4 shows the resulting tree structure of the processor organization in the space–time–ensemble parallelism.

To calculate the intrastate force  $-\partial V / \partial \mathbf{R}_s$  acting on an atom in a spatial domain, the coordinates of the atoms in the boundaries of neighbor domains are “cached” from the corresponding processors within the same communicator  $comm_{b,s}$  [36]. After updating the atomic positions due to time stepping, some atoms may have moved out of its domain. These atoms are “migrated” to the proper neighbor processors within the same  $comm_{b,s}$  [36]. With the spatial decomposition, the computational cost scales as  $N/D$ , while communication scales in proportion to  $(N/D)^{2/3}$ . For long-range interatomic potentials used in MD simulations, tree-based algorithms such as the fast multipole method (FMM) [37] incur an  $O(\log D)$  overhead, which is negligible for coarse-grained ( $N/D \gg D$ ) applications [38].

To calculate the interstate force  $\mathbf{F}_s^{\text{SPF}}$  acting on the  $i$ th atom in the  $d$ th domain of the  $s$ th state, we need to know the position of the same atom in states  $s - 1$  and  $s + 1$  within the same band  $b$ . However, these corresponding atoms may not reside in the same spatial domain  $d$ , since the atoms migrate among processors in the spatial decomposition scheme. Under an assumption that the distance between any corresponding atoms between consecutive states is bounded by a cutoff distance  $r_c$ , we search for the corresponding atoms in the consecutive states with the aid of global indexing of the  $N$  atoms as follows. In the first step, we augment the set of atomic positions,  $A_{b,s,d} = \{\mathbf{r}_i \mid d(\mathbf{r}_i) = d\}$ , that reside in each spatial subsystem  $d$  of state  $s$  in band  $b$ , by caching atoms that are in the nearest-neighbor domains in the same state  $s$  but are within distance  $r_c$  from domain  $d$ :  $A'_{b,s,d} = A_{b,s,d} \cup \{\mathbf{r}_i \mid (d(\mathbf{r}_i) \neq d) \wedge (\|\mathbf{r}_i - \partial d\| < r_c)\}$ , where  $\partial d$  is the 2D boundary that encloses the 3D spatial domain  $d$ . Each processor  $p = bSD + sD + d$  then copies the augmented atomic positions,  $A'_{b,s-1,d}$  and  $A'_{b,s+1,d}$ , of the same spatial domain  $d$  in the lower ( $s - 1$ ) and upper ( $s + 1$ ) states from processors  $p_- = bSD + (s - 1)D + d$  and  $p_+ = bSD + (s + 1)D + d$ , respectively. (Note that the copying is not required for the initial ( $s = 0$ ) and final ( $s = S - 1$ ) states, since there is no interstate force on them.) For each atom  $i$  in  $A_{b,s,d}$ , we search for the corresponding atoms in  $A'_{b,s-1,d}$  and  $A'_{b,s+1,d}$  by way of its global index. Using the linked-list cell method, the computational time for the search is  $O(N/D)$  [36]. The communication cost of the temporal decomposition is  $O(N/D)$  for copying  $A'_{b,s-1,d}$  and  $A'_{b,s+1,d}$ .

Ensemble decomposition duplicates the above band calculation, each involving  $SD$  processors,  $B$  times on  $P = BSD$

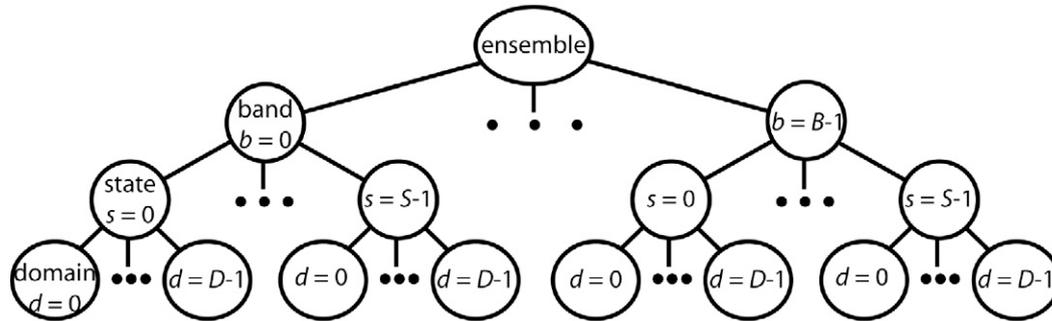


Fig. 4. Tree-structured processor organization in the hierarchical space–time–ensemble parallelization. An ensemble consists of  $B$  bands, each consisting of  $S$  states. Each state in turn contains  $D$  spatial domains.

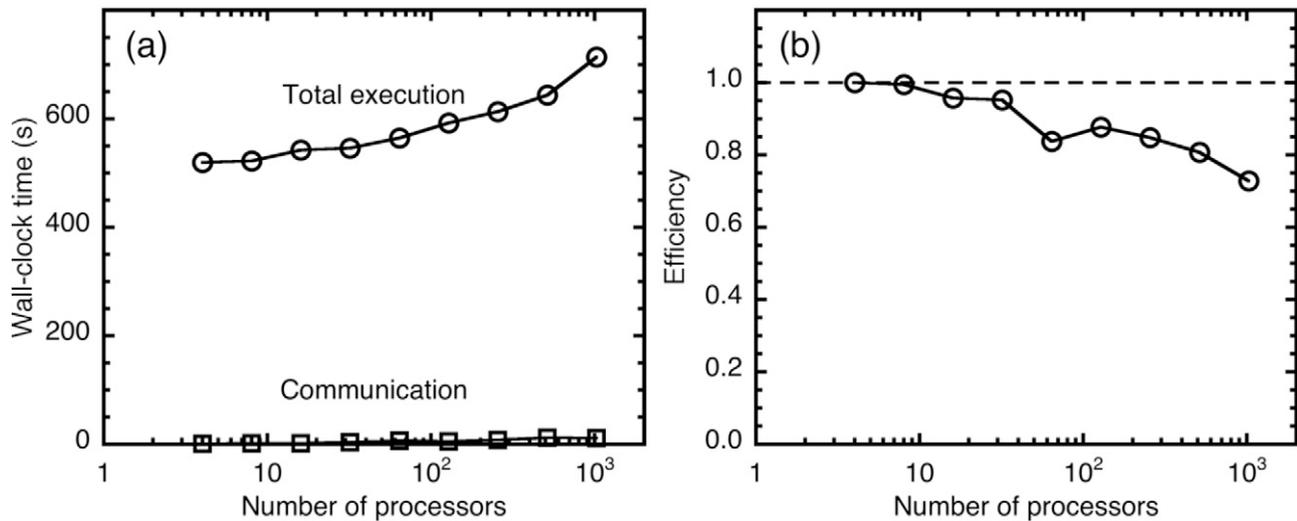


Fig. 5. Weak-scaling (isogranular) test of spatial decomposition in the STEP-NEB algorithm on dual-core, dual-processor AMD Opteron nodes. The total execution (circles) and communication (squares) times (a), as well as the parallel efficiency (b), are plotted as a function of the number of processors  $P = BSD$  for 648,000 $D$ -atom  $\text{SiO}_2$  systems, where  $B = 1$ ,  $S = 4$ , and  $D = 1$ –256.

processors. It involves  $O((N/D) \log(BS))$  overhead to multicast the new initial state  $\mathbf{R}_{\text{init}}$  among processors assigned the same spatial domain, i.e. those with the same  $p \bmod D$ . The multicast cost at the beginning of each MK simulation step is greatly amortized over  $10^3$ – $10^4$  MD steps in the DHNEB method per MK iteration.

## 4. Numerical results

### 4.1. Scalability on parallel computers

Scalability of the STEP-NEB algorithm is tested on a cluster of dual-core, dual-processor AMD Opteron (at clock speed 2 GHz) nodes with Myrinet interconnect, with 4 GB of memory per 4-core node. We define the speed of a program as a product of the total number of atoms and MK simulation steps executed per second. The speedup is the ratio between the speed of  $P$  processors and that of one processor. The parallel efficiency is the speedup divided by  $P$ .

First, we perform a scalability test associated with spatial decomposition. Here, we fix the number of bands in the ensemble  $B = 1$  and that of states per band  $S = 4$ , and vary the number

of spatial domains per state  $D$  from 1 to 256 (i.e. the total number of processors  $P = BSD = 4$ –1024). In our weak-scaling (or isogranularity) test, the number of atoms is scaled linearly with the number of spatial domains:  $N = 648,000D$ . We set  $N_{\text{step}} = 1$  and  $t_{\text{therm}} = t_{\text{heat}} = t_{\text{quench}} = 10\Delta t$ . All the numerical tests in this paper are performed for silica ( $\text{SiO}_2$ ) material, using a many-body interatomic potential [39]. The isogranular scaling test corresponds to a situation, in which the MK program is used to evaluate the barrier energies of a few well-defined events for a large system. This is the case in million-to-billion atom simulations of fracture [40], impact [41], and indentation [42] of materials on a large number of processors  $D$ . Fig. 5(a) shows the total execution and communication times per MK simulation step of the STEP-NEB program on the Opteron cluster for the number of processors  $P = 4, \dots, 1024$ . (The largest number of atoms per state is 165,888,000 for  $D = 256$ .) All four cores per dual-processor, dual-core Opteron node are used for the test. The execution time increases only slightly for large  $P$ , showing excellent scalability. Fig. 5(b) shows the parallel efficiency as a function of the number of processors for the same test; it is 0.728 on 1024 processors.

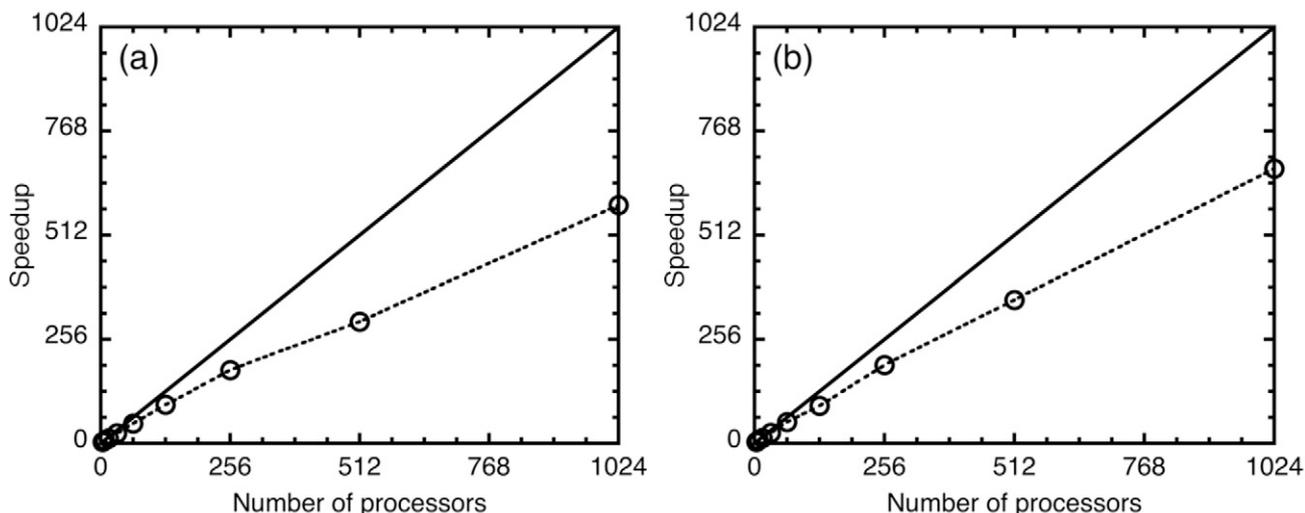


Fig. 6. (a) Speedup of temporal decomposition in the STEP-NEB algorithm (normalized so that the speedup is 4 for  $P = 4$ ) as a function of the number of processors  $P$  ( $P = 4\text{--}1024$ ) for a 192-atom amorphous  $\text{SiO}_2$  system on dual-core, dual-processor AMD Opteron nodes, where we fix  $B = D = 1$ . The circles are measured speedups, whereas the solid line denotes the perfect speedup. (b) Speedup of ensemble decomposition in the STEP-NEB algorithm as a function of the number of processors  $P$  ( $P = 4, \dots, 1024$ ) for silica material ( $N = 192$  atoms). Here, we fix the number of states per band  $S = 4$  and the number of spatial domains per state  $D = 1$ , while the number of bands is varied from  $B = 1$  to 256.

The isogranular parallel efficiency is typically used for very large simulations, and their large granularity,  $N/D$ , makes the parallel efficiency nearly perfect ( $\sim 1$ ). For example, we have recently performed benchmark tests including 134 billion-atom space–time multiresolution MD [36], 1.06 billion-atom chemically reactive force-field MD [43], and 11.8 million-atom (1.04 trillion electronic degrees-of-freedom) quantum-mechanical MD in the framework of the divide-and-conquer density functional theory on adaptive multigrids [44], with the parallel efficiency as high as 0.998 on 131,072 BlueGene/L processors [45]. We expect the isogranular parallel efficiency of the STEP-NEB algorithm to become similarly high for such large-scale applications.

Next, we test the scalability of temporal decomposition, where we fix the number of bands  $B = 1$  and the number of domains per state  $D = 1$ . We vary the number of states per band  $S = 4$  to 1024. Here, the simulated system is amorphous  $\text{SiO}_2$  consisting of  $N = 192$  atoms, and we set  $N_{\text{step}} = 1$  and  $t_{\text{therm}} = t_{\text{heat}} = t_{\text{quench}} = 20\Delta t$ . The test uses all four cores per node. Fig. 6(a) shows the speedup of the STEP-NEB program (we normalize the speedup on 4 processors as 4). The measured speedup on 1024 processors is 586.3, and thus the parallel efficiency is 0.573.

The relatively low efficiency shown in Fig. 6(a) is partly due to the small granularity,  $N/D = 192$ , as well as the non-dedicated operation of the Linux cluster, on which we have observed the reduction of parallel efficiency by  $\sim 0.2$  on 1024 processors for MD simulation [45]. In addition, the efficiency is expected to be higher in production runs, where the number of MD steps per MK simulation step,  $N_{\text{MD}}/N_{\text{step}} = (t_{\text{therm}} + t_{\text{heat}} + t_{\text{quench}})/(\Delta t N_{\text{step}})$ , is well over  $10^3$  (see Section 4.2), compared with 60 in this test. In fact, the parallel efficiency on 1024 processors decreases from 0.573 to 0.450, when  $N_{\text{MD}}/N_{\text{step}}$  is further reduced from 60 to 30. With con-

stant  $B$  and  $N/D$ , the algorithm has a small  $O(\log S)$  overhead for multicasting the new initial state at every MK step, and this multicast cost is amortized over  $N_{\text{MD}}/N_{\text{step}}$  steps. Hence, a larger number of MD steps per MK step leads to higher efficiency.

Finally, we test the scalability of ensemble decomposition, where we fix the number of states per band  $S = 4$  and the number of spatial domains per state  $D = 1$ . The number of bands per ensemble is varied from  $B = 1$  to 256. The simulated system is amorphous  $\text{SiO}_2$  consisting of  $N = 192$  atoms, and we set  $N_{\text{step}} = 1$  and  $t_{\text{therm}} = t_{\text{heat}} = t_{\text{quench}} = 20\Delta t$ . Although multiple events are generated independently by different processor groups, the parallel algorithm involves sequential bottlenecks such as the selection of an event that occurs, and accordingly the parallel efficiency degrades for a larger number of processors. Fig. 6(b) shows the speedup of the STEP-NEB program on the Opteron cluster as a function of the number of processors (normalized to be 4 on 4 processors). On 1024 processors, the measured speedup is 675.6, and thus the parallel efficiency of ensemble decomposition is 0.660, which is slightly higher than that of temporal decomposition on the same number of processors.

#### 4.2. Molecular kinetics simulation of low strain-rate deformation of amorphous silica

We use the MK simulation method to study low strain-rate deformation of amorphous silica (a- $\text{SiO}_2$ ) at temperature  $T$  and shear strain rate  $\dot{\epsilon}$ . To do this, we slightly extend the MK simulation algorithm in Table 3: at the end of each MK step, we increment the shear strain imposed on the system by  $\dot{\epsilon} t_{\text{evt}}$ , where  $t_{\text{evt}}$  is defined in Eq. (8). Here, the shear is applied by deforming the MD simulation box tensor [46].

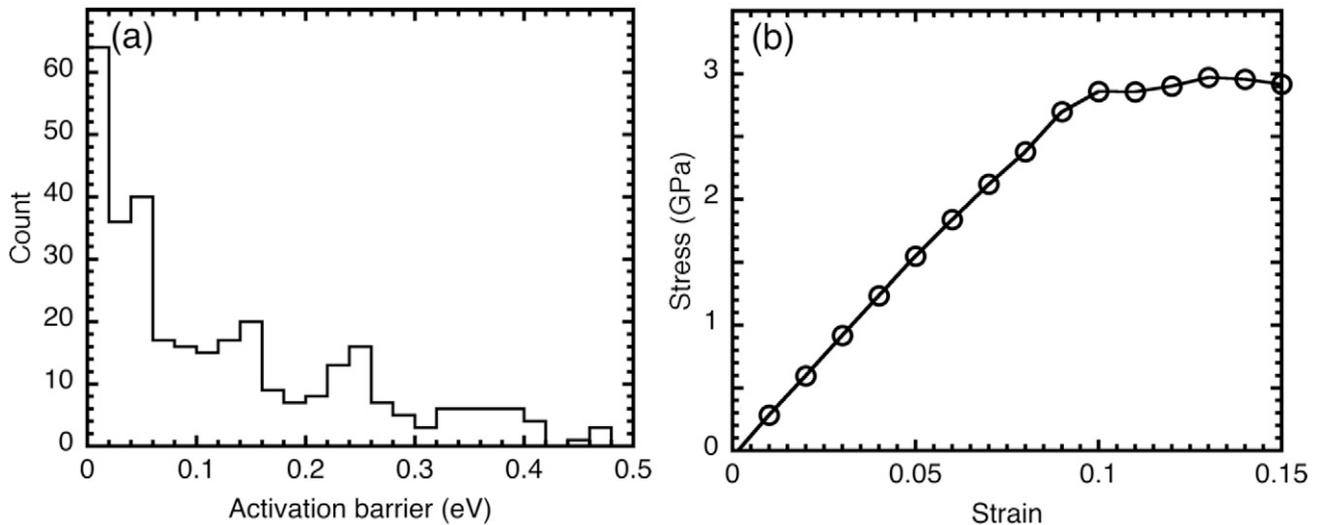


Fig. 7. Molecular kinetics simulation of amorphous silica at strain rate  $10^6 \text{ s}^{-1}$  and temperature 300 K. (a) Histogram of activation barriers for the events at strain between 0.1 and 0.15. (b) Stress-strain relation of the same simulation.

We first prepare an initial a-SiO<sub>2</sub> state containing 192 atoms by a melt-quench procedure, with the periodic boundary condition applied to all directions [47,48]. We then perform MK simulations at strain rate  $\dot{\epsilon} = 10^6 \text{ s}^{-1}$ , using the number of bands per ensemble  $B = 8$ , the number of states per band  $S = 16$ , and the number of spatial domains per state  $D = 1$ . We set the temperatures  $T = 300 \text{ K}$  and  $T_{\text{heat}} = 900 \text{ K}$ , and the MD simulation times  $t_{\text{therm}} = 0.1 \text{ ps}$ ,  $t_{\text{heat}} = 1 \text{ ps}$ , and  $t_{\text{quench}} = 2 \text{ ps}$ . Though we have not introduced explicit convergence criteria to stop the NEB minimization procedure, the quenching phase of the DHNEB algorithm is equivalent to 2000 steepest-descent quench steps of the standard NEB method (with a unit time step of 1 fs), with which forces are typically converged within  $10^{-2} \text{ eV/\text{Å}}$ . For taking statistical averages, multiple MK simulations are performed with the same parameters but different random number sequences. Fig. 7(a) shows a histogram of the activation barriers of the events that are selected according to the probability distribution, Eq. (7), during the simulation (only events for strain range [0.1, 0.15] are included). The histogram demonstrates the existence of many low activation-barrier events in a-SiO<sub>2</sub>, which makes the application of accelerated MD simulation techniques [5] to this system difficult.

Fig. 7(b) shows the calculated stress-strain relation. It is an average over eight MK simulation runs with different random number sequences. Such calculation will be useful for the study of yield stress as a function of the strain rate  $\dot{\epsilon}$ , when the rate is less than  $10^6 \text{ s}^{-1}$ . In contrast, MD simulations are usually applicable only to higher strain rates above  $\dot{\epsilon} = 10^9 \text{ s}^{-1}$ .

To estimate the error of the activation barriers in Fig. 7, we have used a quasi Newton method [49] to obtain the fully converged transition state starting from each approximate transition state (i.e. the state with the highest energy in the band). The estimated error is typically  $10^{-3} \text{ eV/atom}$ , which will not change the results in Fig. 7. However, other quantities such as the lowest Hessian eigenvalue at the approximate transition state have larger uncertainties. The lowest Hessian eigenvalue has an er-

ror on the order of 10%, which necessitates the refinement step for the computation of this quantity.

## 5. Summary

We have designed a scalable parallel algorithm to study long-time dynamics of many-atom systems. A directionally heated nudged elastic band method searches for thermally activated events without the knowledge of final states, which is then applied to an ensemble of bands in a path ensemble method in the framework of the transition state theory. We have parallelized the resulting molecular kinetics simulation method using a space–time-ensemble parallel nudged elastic band algorithm, which employs spatial decomposition within each state, while temporal parallelism across the states within each band and band-ensemble parallelism are implemented using a hierarchy of communicator constructs in the Message Passing Interface library. The STEP-NEB algorithm has exhibited good scalability with respect to spatial, temporal and ensemble decompositions on a massively parallel computer. Finally, we have demonstrated the use of MK simulation for low strain-rate deformation of amorphous silica.

MK simulation of a physical phenomenon produces a massive catalogue of complex atomistic events, and understanding of the phenomenon requires the elucidation of the catalogued events. This necessitates automated (or computerized) identification of primary events as well as their annotation and classification. Such “computational thinking” will be greatly facilitated by discrete abstraction [11,50], such as graph-theory based data mining [51,52], combined with creative massive-date visualization [53] techniques.

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the 5472-processor Linux cluster at the Research Computing Facility and the 2048-processor Linux cluster at the Collaboratory for Advanced Computing and Simulations.

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