

Stochastic Surface Walking Method and Applications to Real Materials

Cheng Shang and Zhi-Pan Liu

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Abstract

The macroscopic properties of a material are generally governed by its potential energy surface (PES) that determines not only thermodynamics but also kinetics. A thoroughly search of the global PES of material, however, has been a great challenge in theory. Three major hurdles, namely, the high energy barrier in material transformation, the large entropy due to huge structural configurations, and the large atomic degrees of freedom, are often encountered simultaneously in computational simulation of material. Owing to these, the limitation in the timescale of current simulations restricts heavily theoreticians to address many important questions in material science. In this chapter, we introduce a

C. Shang · Z.-P. Liu (⊠)

Collaborative Innovation Center of Chemistry for Energy Material, Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Key Laboratory of Computational Physical Science (Ministry of Education), Department of Chemistry, Fudan University, Shanghai, China e-mail: zpliu@fudan.edu.cn

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W. Andreoni, S. Yip (eds.), *Handbook of Materials Modeling*, https://doi.org/10.1007/978-3-319-50257-1_75-1

newly developed theoretical method, stochastic surface walking (SSW) method targeting for both global PES exploration and reaction pathway sampling. The SSW PES sampling is automated, unbiased, and taking into account the second derivative information. The algorithm of SSW is summarized here in detail, focusing on its mechanism to follow low energy pathways while being able to overcome high barriers. SSW simulation has recently been applied to different areas in material and reaction systems. Several typical examples of PES exploration by combining SSW with first principles and neural network potential calculations are presented to illustrate the power of SSW for unbiased PES exploration and pathway searching.

1 Introduction

The structure prediction and the reaction pathway search are two important themes in modern computational simulation. While both of them are closely related to the exploration of the potential energy surface (PES), the former focuses on the thermodynamics properties and the latter aims to provide kinetics quantities on material transformation. Since 1990s, there have been a rapid development on the methodology for structure search and a group of successful methods are now available for identifying the most stable minimum on PES, the global minimum (GM) (Wales and Doye 1997; Martonak et al. 2006; Oganov and Glass 2006; Amsler and Goedecker 2010; Wang et al. 2012) of different systems, including molecules, clusters, and solid crystals. On the other hand, the pathway sampling remains challenging in computational approach even for systems with only a few atoms (Wales 2002; Carr et al. 2005), because of the lack of efficient methods to identify the reaction coordinate (Oganov et al. 2011). To find the minimum energy pathway between minima on PES must rank one of the top challenges in PES exploration.

To search the GM on PES, a typical measure for the efficiency of global optimization method, the current algorithms for structure search generally involve aggressive structure changes, which are required to bypass the transition region of PES and prevent long-time trapping in local minimum. For example, the basin hopping (Wales and Doye 1997) method developed by Wales in 1990s starts from one single entry (one structure) on PES and the structure is perturbed by a random hopping with a magnitude of ~ 0.4 Å for each degree of freedom. The PES seen by basin hopping is therefore a transformed PES without saddle regions. Similar to basin hopping, simulate annealing (Kirkpatrick et al. 1983; Pannetier et al. 1990; Schön and Jansen 1996, 2001) and minimum hopping (Amsler and Goedecker 2010) also start from one single entry but utilize molecular dynamics (via heating to high temperature) to overcome the barrier on PES. On the other hand, the methods starting from multiple entries (a group of different initial structures on PES) developed in 2000s, such as evolutionary algorithm (EA) as represented by USPEX (Oganov and Glass 2006), XtalOpt (Lonie and Zurek 2011) and GSGO (Trimarchi and Zunger 2007), and the particle-swarm-optimization (PSO) algorithm

as represented by CALYPSO (Wang et al. 2012), are more popular in predicting unknown crystal structures of material. The symmetry adaptation in structure generation is one of the key techniques to identify rapidly the stable, ordered structures (Wang et al. 2012). Overall, the structure search methods do not yield a continuous trajectory due to the large change between structures, and thus, it is generally not feasible to obtain the low energy pathways.

The enhanced sampling methods (Siepmann and Frenkel 1992; Voter 1997; Rosso et al. 2002: Woods et al. 2003: Maragliano and Vanden-Eijnden 2006), such as metadynamics using the bias potential constraints (Huber et al. 1994; Laio and Parrinello 2002; Raiteri et al. 2005; Martonak et al. 2006) and adiabatic free energy dynamics (AFED) with temperature acceleration (Yu and Tuckerman 2011), are able to generate continuous trajectory during PES search as intrinsic to MD simulation. Thus, this class of methods has been utilized to identify low energy pathways in crystal phase transition. For example, by imposing the collective variable on the lattice degrees of freedom, metadynamics has been utilized to simulate the phase transition from graphite to diamond (Khaliullin et al. 2011). In general, it is a general concern for MD-based techniques to capture the rare event. Since the occurrence of a reaction event depends exponentially on the reaction barrier, the correct description of the reaction coordinate (e.g., collective variable in metadynamics) and the choice of the simulation temperature are key parameters for producing reactions in simulation. Once the reaction occurs in MD, it is then possible to glean the initial state and the final state from MD trajectory and use the double ended transition state (TS) search method to search for the saddle point. Typical choice for finding the TS in crystal phase transition is the generalized solid-state nudged elastic band method (G-SSNEB) (Sheppard et al. 2012) and variable-cell double-ended surface walking method (VC-DESW) (Zhang and Liu 2015a).

In 2013, Liu's group developed a new PES searching method, namely, the stochastic surface walking (SSW) (Shang and Liu 2013) method. It was initially designed for aperiodic systems, i.e., clusters and molecules, and then extended to periodic solid systems (Shang et al. 2014) in 2015. Unlike the traditional methods for the global PES exploration, the searching in SSW is guided by soft mode directions as computed from the second derivatives and utilizes gentle structure perturbation followed by local optimization to follow low energy pathways. The method can thus be applied to both structure prediction and reaction pathway search (Zhang and Liu 2015b). In this chapter, the algorithm of SSW will be described in detail and some recent applications in material discovery and solid phase transition are then presented.

2 Stochastic Surface Walking (SSW) Method

The central idea of SSW method comes from the bias-potential-driven dynamics (Iannuzzi et al. 2003) and Metropolis Monte Carlo (MC) (Metropolis et al. 1953). It manipulates smoothly the structural configuration from one minimum to another on PES and relies on Metropolis MC at a given temperature to decide the acceptance

of the move. A series of consecutive minimum structures, both local and global, is generated in SSW simulation forming a continuous trajectory, which can provide the key information on the reaction pathways between minima. By applying SSW to a number of systems, Shang and Liu (2013) have shown that the SSW can explore blindly complex PES with high efficiency as demonstrated in Lennard-Jones (e.g., LJ_{75}) and short-range Morse particles (M₈₀).

Each step in SSW, also termed as a MC step, comprises three independent parts, namely, (i) the climbing, (ii) the relaxation, and (iii) the Metropolis MC. As schematically illustrated in a one-dimensional PES in Fig. 1a, such a MC step utilizes the climbing module to move up hill and the relaxation module to locate minimum. Once a minimum is reached, the Metropolis MC is used to judge whether the structure will be accepted or refused. The climbing procedure lies at the heart of the SSW method and is elaborated below in detail.

The climbing module of the SSW involves repeated bias-potential-driven structure extrapolation and local geometry optimization, which drags gradually \mathbf{R}_i^0 to a high energy configuration \mathbf{R}_i^H , where "*i*" is the index of the current MC step (Fig. 1a). Starting from the current minimum \mathbf{R}_i^0 , SSW first generates a random direction \mathbf{N}_i^0 , a normalized vector pointing to a direction to change the current geometry.

To enable an unbiased exploration of PES, the initial direction \mathbf{N}_i^0 by design combines two randomly generated vectors, the so-called global random mode \mathbf{N}_l^g and the local random mode \mathbf{N}_l^l , as Eq. (1).

$$\mathbf{N}_{i}^{0} = \left(\mathbf{N}_{i}^{g} + \lambda \mathbf{N}_{i}^{l}\right) / \left|\mathbf{N}_{i}^{g} + \lambda \mathbf{N}_{i}^{l}\right|$$
(1)

where the mixing parameter λ controls the relative portion of these two displacement directions. Specifically, \mathbf{N}_l^g in our implementation is set as a randomly generated normalized vector that obeys the Maxwell-Boltzmann velocity distribution at 300 K, as utilized in standard molecular dynamics method for generating initial random velocity. As \mathbf{N}_l^g distributes over a group of atoms, it represents a gentle, global displacement pattern of atoms. By contrast, \mathbf{N}_l^i describes a stiff, local atomic move, and in our implementation it is set as a collision movement between two distant atoms. For example, the \mathbf{N}_i^l associated with an atom A (e.g., the first atom in system) and an atom B (the second atom in system) can be derived as Eq. (2), using their coordinates q_A and q_B . The atom pair A and B can be either chosen randomly or learned from the previous trajectories, as long as the two atoms are not in the close contact (i.e., their distance >3 Å).

$$\mathbf{N}_{i}^{l} = \begin{pmatrix} q_{\mathrm{B}} \\ q_{\mathrm{A}} \\ 0 \\ \vdots \end{pmatrix} - \begin{pmatrix} q_{\mathrm{A}} \\ q_{\mathrm{B}} \\ 0 \\ \vdots \end{pmatrix}$$
(2)



Fig. 1 The illustration of (**a**) the SSW method and (**b**) the SSW-crystal method. The real PES is described by the red curve showing separated minima. (**a**): one SSW step from one minimum to another, where the bias Gaussian potentials are imposed only on the atom degrees of freedom; (**b**): one combined lattice and atom displacement step of the SSW-crystal method. The blue arrows and curves represent the lattice displacement and the local relaxation, respectively, as governed by the CBD-cell module, which gradually lifts up the potential energy of the crystal. The green curve represents the consequent atom displacement (at the fixed lattice) as governed by the SSW-module, being a simplified view of (**a**). (Reproduced from Ref. (Shang et al. 2014) with permission from the PCCP Owner Societies)

$$\mathbf{R}_1 = \mathbf{R}_0 + \mathbf{N}_t \cdot \Delta R \tag{3}$$

$$C = \frac{(\mathbf{F}_0 - \mathbf{F}_1) \cdot \mathbf{N}_{\mathbf{t}}}{\Delta R}$$
(4)

$$V_{R1} = V_{real} + V_N \tag{5}$$

$$V_N = -\frac{a}{2} \cdot \left[(\mathbf{R}_1 - \mathbf{R}_1) \cdot \mathbf{N}_i^0 \right]^2 = -\frac{a}{2} \cdot \left(\Delta R \cdot \mathbf{N}_t \cdot \mathbf{N}_i^0 \right)^2 \tag{6}$$

Because reactions with low barriers generally involve soft normal mode directions, it would be ideal to soften the randomly generated N_i^0 towards one eigenvector of Hessian matrix with small eigenvalues (not necessarily the lowest one). However, the direct computation of Hessian is expensive and not affordable in PES search. To solve this, Shang et al. develop a numerical approach, the bias-potential constrained Broyden dimer (BP-CBD) method (Shang and Liu 2012), to soften N_i^0 using Eqs. (3), (4), (5), and (6). Following the unbiased dimer rotation (Henkelman and Jonsson 1999), Shang et al. define two images separated by a fixed distance of ΔR on PES, namely, \mathbf{R}_0 and \mathbf{R}_1 [Eq. (3)). The rotation of the dimer by their force (\mathbf{F}_0 and \mathbf{F}_1) perpendicular to the dimer vector N using constrained Broyden optimization (CBD) (Shang and Liu 2010) will converge to the softest eigenvector of Hessian, and the local curvature [C in Eq. (4)] can be computed according to the finite difference equation. The softest eigenvector is, however, often not the desired one for reaction since it corresponds to the translational and rotational modes (C = 0)in the basin region. Therefore, a biased rotation scheme as implemented in BP-CBD is developed, in which the potential of \mathbf{R}_1 is modified as Eq. (5), where V_N is the bias potential added to the real PES V_{real} of $\mathbf{R_1}$ that is a quadratic function of coordinates \mathbf{R}_1 along \mathbf{N}_i^0 [Eq. (6)]. As long as the parameter *a* [Eq. (6)] is large enough, the biased rotation can guarantee the rotation of dimer will not deviate far away from N_i^0 . The force due to the bias potential in constraining the dimer rotation can be evaluated straightforwardly.

$$V_{m-to-H} = V_{real} + \sum_{n=1}^{H} v_n = V_{real} + \sum_{n=1}^{H} w_n \times \exp\left[-\frac{\left(\mathbf{R}^t - \mathbf{R}_t^{n-1}\right)^2 \cdot \mathbf{N}_i^{n^2}}{2 \times ds^2}\right]$$
(7)

$$\mathbf{F}_{tot} = \mathbf{F}_{real} + \sum_{n} w_{n} \cdot \exp\left[-\frac{\left(\mathbf{R}^{t} - \mathbf{R}_{t}^{n-1}\right)^{2} \cdot \mathbf{N}_{i}^{n2}}{2 \times ds^{2}}\right] \cdot \frac{\left(\mathbf{R}^{t} - \mathbf{R}_{t}^{n-1}\right) \cdot \mathbf{N}_{i}^{n}}{2 \times ds^{2}} \cdot \mathbf{N}_{i}^{n}$$
(8)

On moving from \mathbf{R}_{i}^{m} to a high energy configuration \mathbf{R}_{i}^{H} , a modified PES $V_{m-to-H} (= V_{real} + \sum_{k=1}^{n} v_{k})$ is utilized, as shown in Eq. (7), in which a series of bias Gaussian potential v_{n} (*n* is the index of the bias potential, $n = 1, 2 \cdots H$) is added one by one consecutively along the direction \mathbf{N}_{i}^{n} and thus creates a series of local minima \mathbf{R}_{i}^{n} along the moving trajectory on the modified PES. Similar techniques have been used in Metadynamics (Iannuzzi et al. 2003). The local minima \mathbf{R}_{i}^{n} is identified using local geometry optimization, where the force can be evaluated according to Eq. (8). The *w* and *ds* in Eq. (7) control the height and the width of Gaussian function v_{n} , respectively. While *w* can be computed on-the-fly to guarantee the success of the uphill, *ds* is left as an adjustable parameter in SSW simulation.

It should be mentioned that \mathbf{N}_i^n will always be updated from the initial random direction \mathbf{N}_i^0 at each \mathbf{R}_t^n and is then refined using BP-CBD rotation.

To sum, the uphill movement from \mathbf{R}_i^m to \mathbf{R}_i^H is a repeated procedure containing (i) updating the direction \mathbf{N}_i^n at \mathbf{R}_t^n ; (ii) adding a new Gaussian function v_n and displacing \mathbf{R}_t^n along the direction \mathbf{N}_i^n by a magnitude of ds ($\mathbf{R}_t^n + \mathbf{N}_i^n \cdot ds$); and (iii) relaxing to \mathbf{R}_t^{n+1} on the modified PES.

The overall efficiency of SSW method depends on the choice of the step length of surface walking ds and the max number of Gaussian potentials H. A typical value of ds ranges from 0.2 to 0.6 Å, being 10% to 40% bond length of chemical bonding. The max number of Gaussian potentials (H) is also system-dependent and in general a number in the range of $6\sim15$ is a sensible choice. With large ds and large H, a large scope of PES can be explored rapidly, but it is at the expense of the resolution on the reaction pathway between minima. Typically, for complex Lennard-Jones clusters (e.g., LJ₇₅ with multiple funnels and high barrier), the SSW simulation requires 300~400 energy/force evaluation per MC step with ds = 0.6 and H = 14. It takes typically 70~80% computational efforts (energy and gradient evaluation) on the climbing and the left 20~30% on the relaxation to a minimum.

3 SSW-Crystal Method

The SSW method can be extended to explore the PES of periodic crystal systems, named as the SSW-crystal method. Due to the additional degrees of freedom from the lattice, the key issue in the SSW-crystal method is to couple effectively the lattice and the atom movement in the solid structure displacement. In fact, there are a number of possible ways to couple the lattice and atom displacement. One simplest way is as introduced in Shang et al.'s work in 2014 (Shang et al. 2014), in which the cell movement and atom movement are operated alternatively in one MC step. A more sophisticated way is to combine the lattice parameters and atom coordinates into a generalized coordinate, based on which PES is explored. The generalized coordinate approach is similar to that implemented for TS search between two crystal phases in variable-cell double-ended surface walking method (Zhang and Liu 2015a). Below we mainly introduce the simplest way to couple the lattice and atom displacement in the original SSW-crystal method.

The SSW-crystal method is constituted by three parts, the atom displacement module using the SSW method (SSW module), the lattice displacement module using the CBD method to treat cell vector displacement (CBD-cell module), and the Metropolis MC module. The SSW module and the CBD-cell module are responsible for the displacement of atom and lattice coordinates, respectively. By coupling these two modules, the SSW-crystal can mimic the collective movement in crystal phase transition that involves generally both the atom and the lattice degrees of freedom. Shown schematically in Fig. 1b is such a combined CBD-cell (blue curve) and SSW (green curve) displacement to manipulate one crystal structure from one minimum

to another. Compared to the SSW method, only the CBD-cell module is new, and it is elaborated in the following.

The CBD-cell module to displace lattice mimics the way to displace atom in SSW method. In short, a few cycles are performed to displace smoothly the lattice along one soft lattice mode direction. It has been found that the displacement along the soft lattice modes, instead of a random direction or hard lattice modes, is critical for achieving the high efficiency of crystal PES exploration. Each CBD-cell cycle (blue arrows/curves in Fig. 1b) contains three steps, namely, the soft lattice mode identification, the lattice displacement, and the local relaxation of atoms in the fixed lattice. Specifically, the lattice displacement is achieved by displacing the current lattice \mathbf{L}_0^n (*n* is the index of the current CBD-cell cycle) along a soft lattice mode direction \mathbf{N}_{cell} to yield a new lattice \mathbf{L}_0^{n+1} , as described in Eq. (9). The lattice L is a nine dimensional (3 × 3) vector. After the lattice displacement, the local energy minimization is then performed on the fixed lattice.

$$\mathbf{L}_0^{n+1} = \mathbf{L}_0^n + \Delta L \cdot \mathbf{N_{cell}}$$
(9)

In the equation, ΔL represents a small displacement for the lattice, which is under the constraints for the maximum change in the lattice length (e.g., *a*, *b*, and *c* **axis**) and the volume. Typically, $\Delta L = 0.15 \times \sqrt{\sum l_{ij}^2}, l_{ij} \in L_0^n$, i.e., ΔL being about 15% change in the cell vector. It is obvious that the quality of **N**_{cell} determines largely how efficient the PES exploration of solid will be.

$$\mathbf{L}_1 = \mathbf{L}_0 + dL \cdot \mathbf{N}_{cell}^t \tag{10}$$

$$F_{rot}^{L} = 2\left(\dot{\mathbf{L}}_{0} - \dot{\mathbf{L}}_{1}\right) - 2\left[\left(\dot{\mathbf{L}}_{0} - \dot{\mathbf{L}}_{1}\right) \cdot \mathbf{N}_{cell}^{t}\right] \cdot \mathbf{N}_{cell}^{t}$$
(11)

$$\dot{L}_{ij} = \partial H / \partial L_{ij} = -\Omega \sum_{k} (\sigma_{ik} - p_{\text{ext}}) \left[\left(\mathbf{L}^{t} \right)^{-1} \right]_{kj}$$
(12)

To generate a physically meaningful N_{cell} , Shang et al. also use CBD rotation method (Shang and Liu 2010) to identify one soft mode of the lattice Hessian, starting from a random vector N (a nine-component vector, three rotational modes are projected out in CBD rotation). The CBD rotation algorithm for lattice is summarized in Eqs. (10) and (11), where \dot{L} denotes the first derivative of the enthalpy (H) with respect to the lattice; σ is the stress tensor, Ω is the volume, and p_{ext} is the external pressure; L_1 and L_0 are two lattice configurations, namely, a dimer, separated by a fixed Euclidean distance of dL along N_{cell}^t . In CBD rotation, the dimer will rotate to minimize the rotation force (F_{rot}^L) until a preset criterion is reached. N_{cell} will in principle converge to the softest eigenstate of the lattice Hessian matrix. The curvature (eigenvalue) of the N_{cell} can then be derived using the numerical finite difference as:

$$C_{cell} = \left(\dot{\mathbf{L}}_0 - \dot{\mathbf{L}}_1\right) \cdot \mathbf{N}_{cell}^t / dL \tag{13}$$

The CBD rotation method is able to fast identify one soft lattice mode starting from a random vector, typically within a few steps of energy/force evaluations. Taking α -quartz (SiO₂)₁₂ crystal as an example where the SiO₂ PES is described by the BKS (Beest, Kramer and Santen) potential (van Beest et al. 1990), Shang et al. have performed the numerical experiment to examine the efficiency of CBD for the softest lattice mode finding. The six lattice modes of quartz can be numerically calculated and the curvature C_{cell} of them are 4.98, 5.81, 8.47, 20.1, 21.7, 35.0 (×10⁻² a.u.). As the representatives, the calculated softest (N_{cell}^1) and hardest (N_{cell}^6) lattice modes are shown in Eqs. (14) and (15). Obviously, the softest lattice mode represents the expansion along *c* axis and the compression along *a* and *b* axes, while the hardest lattice mode represents the compression along all three directions. Averaged over 5000 independent runs initialized from random vectors, the CBD rotation prefers clearly the soft lattice modes: the probability for converging to three soft modes and to three hard modes are 57.8% and 4.7%, respectively. The rest 37.5% converges to the hybrid modes.

$$N_{cell}^{1} = \begin{pmatrix} -0.16 & 0.08 & -0.03\\ 0.52 & -0.74 & -0.02\\ -0.04 & -0.03 & 0.38 \end{pmatrix}$$
(14)

$$N_{cell}^{6} = \begin{pmatrix} 0.33 \ 0.24 \ 0.02 \\ 0.08 \ 0.35 \ 0.00 \\ 0.03 \ 0.00 \ 0.83 \end{pmatrix}$$
(15)

4 SSW Reaction Sampling (SSW-RS)

4.1 Reaction Sampling

Because the SSW simulation produces a continuous trajectory between minimum and each displacement follows the soft mode direction, the SSW simulation can also be utilized to identify low energy reaction pathways. The SSW reaction sampling (SSW-RS) developed in 2015 (Zhang and Liu 2015b), as illustrated in Fig. 2, aims to generate an ensemble of reactant-product (R/P) pairs between two connected minima on PES. The two structures of the R/P pair can be utilized later for TS location using the double-ended TS searching method.

As shown in Fig. 2, the SSW reaction sampling starts from one random configuration of reactant, which is the input structure and may well not be the most stable configuration of the reactant. During the simulation, the structures nearby this reactant will be visited, including the conformation isomers of the same reactant (the same phase region) and the likely products with different bonding patterns (the other phase regions). Different from the Metropolis MC scheme in the global structure search, a special structure selection module (to decide whether a new minimum is accepted or refused) is designed to judge whether a (desirable) reaction occurs



or not. If a new minimum in the other phase regions is identified, it is recorded as the product of the current SSW step. Then the program will reject the new minimum and continue the PES exploration from the reactant; on the other hand, if the new minimum identified is still at the same reactant phase, the simulation will accept the new isomeric structure and continue the structure exploration. The whole procedure will be repeated until a large number of R/P pairs are collected. Typically, a few hundreds of R/P pairs are required to reveal the lowest energy pathway of an elementary reaction step (see Fig. 2).

The probability for accepting a new minimum in the structure selection module is thus described by P_r in Eq. (16)

$$P_r = \begin{cases} 0, \text{ reaction occurs} \\ 1, \text{ otherwise} \end{cases}$$
(16)

where the occurrence of reaction is characterized by a group of preset conditions, e.g., a dramatic change of system energy, the making/breaking of chemical bonds and the change of the local chirality of atom for molecular reactions, the change of crystal symmetry, and the change of structure order parameter for crystal phase transition. These conditions need to constitute a sensitive measure for detecting the occurrence of a desirable reaction from SSW trajectory. The probability *P* for recording an R/P pair is given in Eqs. (17) and (18).

$$P = (1 - P_r) \cdot P_{mc} \tag{17}$$

$$P_{mc} = \begin{cases} \exp\left[\frac{E(\mathbf{R}^{m}) - E(\mathbf{R}^{mt})}{kT}\right], when \ E(\mathbf{R}^{m}) < E(\mathbf{R}^{mt}) \\ 1, otherwise \end{cases}$$
(18)

where P_{mc} is the Metropolis MC probability for accepting the new minimum \mathbf{R}^{mt} or reverting to the starting minimum \mathbf{R}^{m} . The Metropolis NC scheme in reaction

sampling helps to screen the highly endothermic reactions, which will not be considered for subsequent pathway building.

4.2 Pathway Building

Once enough R/P pairs are collected, the low energy pathways connecting these R/P pairs can then be determined by building the pathway between them. The pathway building tool utilized in our work is the double-ended surface walking (DESW) method (Zhang et al. 2013), which can treat both aperiodic and periodic systems (Zhang and Liu 2015a). The DESW method follows the same uphill mechanism in SSW method, i.e., repeated bias potential addition and local relaxation. It can fast connect a pseudopathway between an R/P pair, which has been shown to mimic the true MEP at the TS region. The DESW pseudopathway building helps to screen unlikely pathways in an efficient way: only those with relatively low energy pseudopathway will be considered further to locate the TS explicitly. In DESW, because the reactant and the product obtained from the SSW reaction sampling may be separated by more than one minimum, the highest energy TS along the pathway will be first identified. The barrier calculated with respect to the GM energy of reactant will be utilized a quantitative measure to compare different pathways and to select finally the low energy pathways. The exact knowledge on the minimum energy pathway (MEP) at this stage is in fact not essential (MEP may be calculated only for a few lowest energy pathways that are important for kinetics).

The pathway sampling in the multiple-step reaction systems is even more challenging for the presence of multiple intermediates. Liu group (Wei et al. 2017; Zhang et al. 2017a, b) have shown recently that by carrying out the SSW-RS sampling from every likely intermediates, the whole reaction network can be established eventually. The methods, such as Dijkstra's algorithm (Dijkstra 1959), can be utilized to analyze the network and identify the reaction mechanism. If the overall rate of the reaction system is the concern, one can construct the transition rate matrix and utilize the kinetics methods (such as kinetic MC) to simulate the reaction kinetics.

While the key elements of the SSW-RS for reactivity prediction share common features with the approaches proposed in recent years (Maeda et al. 2009; Maeda et al. 2014; Schaefer et al. 2014), the SSW-RS has its own advantages in both the reaction sampling and the pathway building. Thanks to the generality of the SSW method, the SSW-RS is also a general purpose tool for sampling different type of reactions, ranging from the association and dissociation molecular reactions (Zhang and Liu 2015b), to the surface catalytic reaction (Zhang et al. 2017a) and to the solid phase transition reactions (Zhu et al. 2015). This leads to the easy implementation and high transferability of the SSW-RS method for different applications. Taking molecular reactions as example, the SSW-RS can sample simultaneously both the reactant conformations, a very flat PES with many likely conformations, and the bond making/breaking reactions that have high reaction barriers. These features of the SSW-RS method will be demonstrated in the following section.

5 Application Examples

For the distinct features of SSW method (and the derived methods), such as the evaluation of second derivatives of the PES and the gentle structure perturbation, the SSW provides a unique tool to explore unbiasedly the global PES of a material and in the meantime to identify the reaction pathways between phases of concern. Besides, the gentle movement helps greatly the electronic structure calculation, allowing one to use the one-electron wavefunctions and the charge density of the earlier configuration, enabling a long-time stable PES sampling.

In this section, we describe a few typical applications of the SSW methods, including the global PES and phase transition searching of TiO₂, ZrO₂, and carbon. All these simulations are based on density-functional theory (DFT), where the exchange-correlation functional used is the generalized gradient approximation as parameterized by Perdew, Burke, and Ernzerhof (GGA-PBE) (Perdew et al. 1996). Corrections for van-der Waals dispersion are added in the case of carbon crystal systems using the Grimme-D3 approximation (Grimme et al. 2010). The interaction between atomic cores and valence electrons is described using the projector augmented wave method (Kresse and Joubert 1999). All calculations use plane-waves basis sets. For more details, the reader is referred to the original articles cited below.

5.1 Global PES and New Crystal Phases of TiO₂

The SSW method can be utilized to establish the global PES of material and thus identify new crystal phases. This is exemplified in TiO₂ system, an important functional material widely utilized as coating materials and catalysts in many fields. In particular, the photoactivity of TiO₂ was hotly investigated for water splitting (Li et al. 2010; Li and Liu 2011; Zhao and Liu 2014; Zhao et al. 2015). The PES of TiO₂ is highly complex as evident by the fact that many possible polymorphs are present in nature (the most common phases of TiO₂ at the ambient conditions are rutile, anatase, brookite, and TiO₂-B (Penn and Banfield 1999; Bakardjieva et al. 2006; Cheng et al. 2015)). New stable TiO₂ phases have long been searched for in material science.

In 2017, Huang et al. (2017) constructed TiO_2 neural network (NN) potential using SSW global PES data generated from first principles density functional theory (DFT) calculations in small unit cells (below 12-atom). Six independent SSW global search using NN potential (SSW-NN) were then carried out in a larger supercell (48-atom), 10,000 minima visited in each run. In total, 6151 distinct minima were obtained after removing duplicated structures. Figure 3a shows the global PES contour plot projected onto the structural order parameter (OP₂) and the total energy (E). The corresponding density of states (DOS) is plotted in Fig. 3b.

The global PES shows that the crystalline region of TiO₂ is below ~ 0.2 eV per formula unit (eV/f.u.) with respect to the GM (TiO₂-B phase), and contains 224 distinct crystal phases (180 of them are newly found from SSW-NN simulation).



Fig. 3 (a) PES contour plot for TiO_2 distinct minima sampled from SSW-NN global search. (b) Density of states (DOS) plot for TiO_2 phases in (a), showing that amorphous structures appear in the 0.2~0.7 eV/f.u. window. (c) The percentage of differently coordinated Ti for TiO₂ structures. [TiO₅] and [TiO₆] are main structural features for amorphous structures. (Reproduced from Ref. (Zhang et al. 2017b) with permission from the PCCP Owner Societies)

It is noted that the number of distinct crystalline structure is substantially large considering that there are only $\sim 10 \text{ TiO}_2$ phases reported from experiment (Cheng et al. 2015). From 0.2 to 0.7 eV/f.u., one can see a salient deep-blue zone due to the energy degeneracy of structures, featuring a high, continuous, and broad peak in the DOS plot (Fig. 3b). This zone is dominated by amorphous structures.

The Ti coordination number x ($[TiO_x]$) for all structures is analyzed to understand the difference between amorphous and crystalline phases. The evolution of the Ti coordination in solids with the increase of energy is plotted in Fig. 3c. This is done by counting and averaging the Ti coordination for structures in the same energy interval, E to E + dE (5 meV/f.u.). Figure 3c shows that $[TiO_4]$, $[TiO_5]$, $[TiO_6]$, and $[TiO_7]$ constitute the major coordination environment for Ti. For the low energy crystal phases (e.g., rutile, anatase, TiO_2 -B), they generally contain only TiO_6 octahedra (100% $[TiO_6]$, energy lower than 25 meV/f.u.). The $[TiO_5]$ starts to appear above 30 meV/f.u. This and $[TiO_6]$ correspond to the dominant coordination for amorphous structures. By contrast, $[TiO_4]$ and $[TiO_7]$ are rare coordination in TiO_2 solids: they appear at high energies and are found either in high pressure phases ($[TiO_7]$) or in open structures ($[TiO_4]$, e.g., cage, 2-D layer).

Interestingly, the SSW-NN PES exploration discovers stable porous structures, which could be potentially useful as molecular sieves and catalysts. Two such phases with open cages labeled as phase-87 (I4/m, #87) and phase-139 (I4/mmm, #139) rank 10 and 23 in the minimum energy spectrum respectively, having the similar stability as the common rutile phase that ranks 30 in the spectrum. The [TiO₅] coordination is the key structure feature in these porous TiO₂ structures, and they are found to be good candidates for anode material in Li ion battery (Ma et al. 2017). Importantly, the calculated barrier for the phase-87 to anatase transition is 0.22 eV/f.u., which is quite high considering that the barrier from TiO₂-B to anatase is only 0.12 eV/f.u. (Zhu et al. 2014) and the experimental temperature for TiO₂-B to anatase conversion is $\sim 673 \text{ K}$ (Zhang and Banfield 1999). Our results indicate that

the porous phase-87 is kinetically stable. One can argue then that, once synthesized, the new phase could be stabilized at ambient conditions.

5.2 Zirconia Phase Transitions

The crystal-to-crystal phase transition has long been a great challenge for computer simulations. Recently, the SSW-RS method has been utilized to provide important insights into the phase transition mechanism and kinetics. As a prototype system for crystal phase transition, the tetragonal-to-monoclinic (t-m) phase transformation in ZrO₂ (Kelly and Rose 2002) is widely exploited in mechanical ceramic toughening (Jin 2005) and in heterogeneous catalysis for tuning surface activity (Wang, et al. 2007). This phase transition is rapid and reversible above ~ 1000 °C and incurs an appreciable volume increase (by 4.2%) that is in accompany with the decrease in the coordination number of Zr from 8 to 7. Although it was long regarded as a diffusionless Martensitic phase transition (Wolten 1963; Bhattacharya et al. 2004), the transformation kinetics at the atomic level has been debated for over 60 years.

Using SSW-RS method, Guan et al. (2015) in 2015 have determined the lowest energy transition pathways and resolve the physical origin of two types of orientation relationship (OR) in ZrO₂ t-m phase transition. From 269 pathways of t-m phase transition obtained from SSW-RS, they identified three distinct lowest energy pathways. The overall potential energy profiles of these pathways are shown in Fig. 4a. Path I and Path II are pathways for t-m phase transition with the same apparent OR, i.e., $(100)_m//(110)_t$; $[001]_m//[001]_t$, being the Type-C OR in literatures. Unlike Path I, Path II is an indirect channel involving an intermediate orthorhombic phase, o-phase (Pbc2/1, #29), with OR as $(100)_m//(001)_o$; $[001]_m//[100]_o$ and $(001)_o//(110)_t$; $[100]_o//[001]_t$. The 3-D contour plot of Path II is illustrated in Fig. 4b. Path III is a branch channel involving the ferroelastic transformation of the t-phase itself by switching the *c* and *b* axis of crystal. The OR is $(110)_t//((110)_t)^{\cdot}$; $[001]_t//[110]_t^{\cdot}$. When Path III (t-t') is followed by Path I or II (t-m), the apparent OR of t-m phase transition is switched to $(100)_m//(110)_t$; $[010]_m//[001]_t$, which turns out to be Type-B OR in literature.

The calculated barriers of Path I and II leaving t-phase are extremely low, 2.6 and 3.5 meV/f.u. relative to t-phase, respectively, while that for Path III is 29.2 meV/f.u., being much higher than the previous two pathways. Compared to the t-phase to o-phase (t-o), the o-phase to m-phase (o-m) in Path II needs to overcome much higher barrier (32.1 meV/f.u.), which indicates the o-phase is a trapping state at low temperatures. Because o-phase is only 0.60% larger than t-phase in volume, the transformation toughening is largely prevented as the o-phase forms at low temperatures. Although the volume of o-phase is close to t-phase, the Zr in o-phase is 7 coordinated; half of the O atoms are 4 coordinated and the others are 3 coordinated, which are the same as those in m-phase. In short, in Path II, the t-o phase transition breaks four Zr-O bonds per cell (12-atom) but has little change in lattice; the o-m phase transition involves a large lattice distortion while keeping the overall coordination.



Fig. 4 (a) Potential energy profile for the lowest energy pathways from tetragonal phase (T or T') to monoclinic (M) phase. (b) The 3-D PES of Path II obtained by the linear interpolation of lattice parameters (x axis) and atomic fractional coordinates (y axis) from structure snapshots in Path II. (c) The local structure change during phase transition following Path I and III viewed down from the determined atomic habit plane, (110)t or (100)m surface. The Zr-Zr distances labeled are in Å. Zr: cyan; O: red. (Reprinted with permission from (Guan et al. 2015). Copyright 2015 American Chemical Society)

The reaction pathway obtained from SSW-RS also reveals in detail how atoms displace during the phase transition. The atomic movement on $(110)_t$ and $(100)_m$ in Path I and Path III is illustrated in Fig. 4c, where both two types of OR can be generated. The $(110)_t$ and $(100)_m$ surfaces are determined to be the atomic habit planes (interface) in the phase transition, which fulfill the following criteria: (i) having minimum strain as evidenced by the close lattice parameters, e.g., $(110)_t$: 5.15×5.31 Å; $(100)_m$: 5.28×5.40 Å (Fig. 4c); (ii) having minimum atomic movement in phase transition; (iii) acting as a coherent interface with close atomic match between two phases, forming a heterophase junction.

Unlike the two lowest energy pathways, Path III is not directly leading to m-phase but a ferroelastic transformation of t-phase. Such a reorientation of the individual tetragonal domain is enabled by a permutation of the **b** and **c** axis in $(110)_t$ habit plane. The t-t' phase transition goes through TS₄ that has a cubic-phase-like lattice (P4/nbm, #125). The diagonal Zr-Zr distances in the habit plane are all 5.20 Å (Fig. 4c), giving rise to a volume drop of 1.3% from t-phase to TS₄.

The results suggest that the OR of t-m phase transition should be dominated by Type-C OR (Bansal and Heuer 1974). However, Type-B OR, although less often observed, was reported experimentally in the phase transition of high temperature zirconia single crystals (Wolten 1964) and in 3YSZ ceramics (Wu and Chiang 2011). To resolve this puzzle, the phase transition pathways under three different external pressures (hydrostatic) at 5, 7, and 10 GPa are computed to mimic the large stress-field that is developed at grain boundaries owing to the volume expansion during t-m phase transition. Among three pathways, only Path III is facilitated at high

pressures, which turns out to be the lowest energy channel (Δ Ha III = 17.5 meV) at 5 GPa compared to other two pathways (18.6 and 60.2 meV). This is in fact not surprising because the cubic-phase-like TS₄ has the smallest volume in all the located TSs and phases, and thus a compressive field helps to reduce the barrier greatly (the volumes of TS_1 and TS_2 are larger than t-phase, and that of TS_3 is also larger than o-phase). The result indicates that under high pressure condition the Type-B OR would be the more favorable OR for the t-m phase transition. Actually there are some experimental evidences that are consistent with this finding. For example, Chien et al. (1998) utilize Vickers microindentation experiment to induce the phase transition of Y-stabilized ZrO_2 from t-phase to m-phase. They observe the ferroelastic domain switching of t-phase together with the t-m Martensitic transition and importantly, only Type-B OR is found in the experiment. We emphasize that the presence of the o-phase does not add new OR. An important implication from current theoretical sampling on PES of ZrO₂ is that multiple energy-nearlydegenerate reaction channels can coexist in solid-to-solid phase transition and share the same OR. The knowledge of OR that is possible to obtain from experiment is in fact not enough to unravel the mechanism and kinetics of the solid-to-solid phase transition.

5.3 Graphite to Diamond Phase Transition

The graphite (G) to diamond transformation investigated by Xie et al. (2017) in 2017 is a good example to illustrate how to combine SSW and SSW-RS to resolve the mechanism of complex material structural transformation. It has long been a dream in human history (DeCarli and Jamieson 1961; Bundy and Kasper 1967; Hanneman et al. 1967; Naka et al. 1976) to convert graphite to diamond at mild reaction conditions. Modern research shows that the growth of large diamond crystals is kinetically hindered. The cubic diamond (CD), despite thermodynamically most stable among carbon allotropes above ~5 GPa, is not the main product under mild static compression of graphite, ~ 15 GPa and ~1000 °C (Bundy and Kasper 1967; Yagi et al. 1992; Britun et al. 2004; Németh et al. 2014). In fact, the product is the dominated by hexagonal diamond (HD) and heterophase junctions. While great efforts have been devoted in past decades to understand the diamond phase growth from graphite matrix, the kinetics data computed from theory are still at odds with general experimental findings (Fahy et al. 1987; Scandolo et al. 1995; Tateyama et al. 1996; Mujica et al. 2003; Khaliullin et al. 2011; Xiao and Henkelman 2012).

Xie et al. (2017) first used the SSW method to scan the phase space of carbon allotropes. To identify the likely intermediates during diamond growth, they focused on those less stable, less ordered heterophase junctions that are transient in kinetics. SSW simulations with the environment dependent interatomic potential (EDIP) (Marks 2000) for carbon were carried out using different supercells up to 32-atom per cell at 15 GPa. The simulations were terminated until no more new types of junctions were revealed from PES exploration (>10⁶ minima collected).



Fig. 5 Finding metastable heterophase junctions from SSW global PES exploration under 15 GPa. The right-bottom figure plots energy against average coordination number of 4000 structures. Different structures could have the same interface. (gh1)-to-(ghc2) show the structure of seven most stable interfaces from DFT. The dashed lines mark the close-packed planes, i.e., (111) for CD and (001) for HD. For gh2 interface, the interface is normal with (001)_{HD}. The interface atoms are orange colored for clarity. (Reprinted with permission from (Xie et al. 2017). Copyright 2017 American Chemical Society)

In total, more than 4000 minima were identified that are distinct from graphite and have relative low energetics (0.3 eV per atom above graphite). The energetics of the phases against the average carbon coordination number (N_c) is plotted in Fig. 5 (N_c is calculated by counting the first neighbors, where the C-C distance below 1.70 Å is regarded as bonding; N_c for diamond and graphite is 4 and 3, respectively). It shows that a large number of mixed phase intermediates (N_c in between 3 and 4) are obtained from SSW global structure search. By inspecting the geometry of all these structures closely, the metastable heterophase junctions that contain graphite component were screened out and distinguished according to the interface type and crystallographic orientation relationships (OR). There are seven types low energy heterophase junctions as indexed from gc1 to ghc2 in Fig. 5 and their associated interfaces are listed in Table 1.

For these heterophase junctions, gc1 is the only G/CD biphase junction; gh1 to gh4 are G/HD biphase junctions differing by the interfaces; and ghc1 and ghc2 are G/HD/CD three-phase junctions. HD/CD structure can be considered as a diamond structure with stacking faults on the close-packed plane. They belong to four distinct ORs as follows:

OR1: (001)G//(111)CD, [100]G//[110]CD; OR2: (001)G//(211)CD; [100]G//[110]CD;

	-					
Name	Interface	ORa	γ	ΔS	Ea	
gc1	(001) _G //(111) _{CD}	1	0.41	-3.7%	0.79	
gh1	$(001)_{\rm G}//(100)_{\rm HD}$	3	0.23	0.7%	0.47	
gh2	(110) _G //(110) _{HD}	3	0.24	22.6%	0.55	
gh3	(100) _G //(001) _{HD}	3	0.35	25.2%	0.87	
gh4	(001) _G //(001) _{HD}	4	0.42	-2.6%	0.85	
ghc1	(100) _G //(111) _{CD} (100) _G //(001) _{HD}	2,3	-	23.8%	0.84	
ghc2	(001) _G //(111) _{CD} (001) _G //(001) _{HD}	1,4	-	-3.2%	0.80	

Table 1 Structure and energetics of metastable heterophase junctions in graphite-to-diamond solid phase transition. (Reprinted with permission from (Xie et al. 2017). Copyright 2017 American Chemical Society)

^aListed data include the interface planes, the crystallographic OR, the interfacial energy (γ , eV/Å²), the reaction barrier (E_a, eV per interface atom) for the heterogeneous pathway mediated by the corresponding junction, the area misfit between connecting phases at the interface (Δ S, with respect to graphite)

OR3: (001)G//(100)HD, [110]G//[001]HD; OR4: (001)G//(001)HD, [010]G//[010]HD.

Among them, OR2 is 30 degrees off OR1, and OR4 is 90 degrees off OR3; OR2 does not occur independently but combines with OR3 to yield a C1-type three-phase junction (Scandolo et al. 1995). Only OR1 and OR3 were reported in experiment (Bundy and Kasper 1967; Yagi et al. 1992; Britun et al. 2004). For example, Britun et al. observed CD formation at 7 GPa and 1500 °C with OR1 (Britun et al. 2004).

The presence of multiple metastable heterophase junctions indicates that the kinetics of the pressure-induced graphite transformation is complex, governed by multiple anisotropic reaction channels. Xie et al. then utilized the SSW-RS simulation to determine the phase transition pathways that are mediated by these heterophase junctions.

The SSW-RS simulation starts from one heterophase junction (as listed in Table 1) and the pathways leading to G, HD, and CD phases are collected. After collecting a significant number of R/P pairs, i.e., >200 pairs for each heterophase junction, the TS was explicitly located using DFT and double-ended searching method, based on which the low energy pathways are determined by sorting the computed barriers. All the lowest energy pathways mediated by the seven different junctions were finally determined and the overall barriers of them (the highest energy TS along the pathway with respect to the graphite) are also listed in Table 1. The gh1-pathway (via gh1 junction) and gh2-pathway (via gh2 junctions) are the lowest barrier pathways, being 0.47 and 0.55 eV per interface atom (eV/ia), which is in line with the higher stability of their interfaces. The other pathways with less stable interfaces have much higher barriers, 0.75~0.90 eV/ia.



Figure 6 shows the reaction energy profiles of the lowest energy pathways mediated by gc1, gh1, and gh2 type interfaces. For the gh1 pathway from G to HD, it involves two intermediate states MS1 and MS2, both containing gh1 type interface. The lower overall barrier in gh1 compared to gc1 and gh2 can be attributed to the high stability of the reaction intermediates. The gh1 pathway in Fig. 6 is a representative to illustrate how atoms move during the phase transition.

The reaction initiates via the relative slipping of graphite basal plane along $[1\overline{10}]_G$ by 1/2 C-C length (0.7 Å) followed by the compression at $[001]_G$. From G-to-MS1, the first step, the compression leads to the buckling of three neighboring graphite layers. The neighboring carbon rows along $[1\overline{10}]_G$ in a graphite layer then displace collectively out of the basal plane at opposite directions and approach to the neighboring graphite layers. New C-C bonds are evolved at the TS (TS1_{gh1}) is 1.95 Å, after which a three-atomic-layer HD nucleus is created at MS1, showing the characteristic sp³ bonding of diamond. The remaining steps, MS1-to-MS2 and MS2-to-HD, propagate the interface at $[001]_G$ with the same atom displacement pattern, leading to the growth of HD phase. The graphite basal plane evolves into (100)_{HD}, accompanied by 25.6% compression at $[001]_G$. In the pathway, the stability of the nascent HD nucleus (MS1) in graphite matrix dictates largely the

barrier height (TS1) of transformation, demonstrating the critical role of nucleation in kinetics.

The rate for graphite phase transition following heterogeneous pathways can be estimated: the formation of CD phase is at least 40 times slower compared to that to form HD phase at 1000 °C from microkinetics (by assuming the same prefactor). On the other hand, the reactions to CD phase and other mixed phase microstructures occur simultaneously: the rate difference is less than 1.12 times at 1000 °C. These quantities confirm HD phase is kinetically much favored, which correct the wrong prediction from collective pathways and MD results (Fahy et al. 1987; Scandolo et al. 1995; Tateyama et al. 1996; Khaliullin et al. 2011). Indeed, the G/HD composite with OR3 was commonly observed at 1000 °C (Bundy and Kasper 1967; Yagi et al. 1992; Britun et al. 2004; Németh et al. 2014), where CD phase is not formed yet; Németh et al. observed the mixed phase (CD/HD) at 2200 °C and 19 GPa (Németh et al. 2014) using transmission electron microscopy, indicating that the high temperature is a must to overcome the barrier of CD nucleation. The high HD selectivity is attributed to the presence of three low energy G/HD junctions, i.e., gh1, gh2, and gh3, orthogonal with each other, and two low energy anisotropic pathways via gh1 and gh2 junctions. These maximally stabilize HD nuclei inside graphite and allow for HD propagation in three dimensions (3D). By contrast, there is only one and high barrier gc1-pathway to form CD. Its barrier is similar to the pathways leading to the mixed phases. This indicates that the nascent CD nuclei in 3D inevitably introduce incoherent interfaces inside graphite and thus the CD growth is not favored both thermodynamically and kinetically.

6 Concluding Remarks

This chapter serves as a short overview of the SSW global optimization method and its recent application in material simulation. The SSW method is designed to combine some key features of existing theoretical methods for global structure search and reaction pathway sampling. A major feature in SSW method is the smooth structure perturbation, which mimics that in conventional MD simulations. While MD simulations meet great difficulties in overcoming high barriers, the SSW can go uphill on PES facilely by adding consecutive bias potentials along a soft curvature direction that is generated randomly and softened subsequently. The explicit consideration of the second derivation information and the repeated local relaxation are key techniques to keep the SSW trajectory close to low energy pathways.

Three examples on TiO_2 , ZrO_2 , and carbon are presented to demonstrate the current ability of SSW for global optimization and reaction pathway sampling. The SSW method in combination with first principles calculations can be utilized to generate a rich data on the PES of a material. It can reveal unknown new phases for constructing the phase diagram and help to map out the lowest energy pathways for understanding reaction kinetics. Perhaps more interestingly, this big data may also be utilized for machine learning, for example, to train high dimensional NN

potential of material. Considering that the NN potential is computationally much less demanding than the electronic structure calculation methods, the combination of SSW with machine learning techniques may bring a new era for material simulation in the decade to come.

Acknowledgments This authors acknowledge National Science Foundation of China (21603035, 21533001), Science and Technology Commission of Shanghai Municipality (08DZ2270500), Shanghai Pujiang Program (16PJ1401200) for financial supports.

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