

# A CURVE SWARM ALGORITHM FOR GLOBAL SEARCH OF STATE TRANSITION PATHS

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## Abstract

Atomistic scale simulation can predict state transition processes such as adsorption, diffusion, and reaction. The challenge of the accurate prediction is to obtain a global view of many local minima and saddle points on the potential energy surface (PES) of a material system. The transition conditions are determined by the saddle points on the PES with the minimum energy barrier between local minima. In this paper, a new algorithm is developed to exhaustively search local minima and saddle points within a region of PES in order to provide a global view of the energy landscape. Unlike the existing saddle point search methods, the algorithm represents a transition path by a parametric Bézier curve with control points. It uses multiple groups of such curves, each of which represents a multistage transition path. During the searching process, each group of curves communicates with others to maintain cohesion and avoid collision based on a collective potential model. The algorithm is integrated with density functional theory calculation and demonstrated by diffusion of hydrogen atoms in the FeTiH system.

## Introduction

Creating new materials and new processes by design based on a problem-solving and needs-driven paradigm will be a major mission for product and manufacturing engineers in the future. Computational tools are one of the key components to realize such paradigm. Understanding material properties as well as the detailed physical and chemical processes during synthesis and fabrication at the atomistic scales is essential for rational design of materials and manufacturing. For instance, designing functional materials that are used to store information or energy requires a good understanding the phase transition processes. Enhancing the strength of super alloys needs the knowledge of how defects are initiated and propagated in polycrystalline structures. Improving the scalability of nanomanufacturing requires the fundamental knowledge of physical processes or chemical reactions during the synthesis and fabrication. Atomistic simulation can be very helpful for the predictions of the above phase transition or transformation processes.

The prediction of phase transition processes at atomistic scales requires the information of potential energy surface (PES), which represents the potential of a group of atoms as a function of internal coordinates, is generated. It characterizes the energy levels for various possible configurations of the material system. PES can be regarded as a hyper surface in a high-dimensional configuration space, where the minima correspond to the stable or metastable states. Then a minimum energy path (MEP) [1, 2], which is the lowest energy path for re-organization of the atoms from one stable configuration to another, is located. The maximum potential energy along the MEP is the saddle point which determines the activation energy. The activation energy is the barrier that the material system needs to overcome to complete the transition. The MEP can be interpreted as the steepest descent path on the PES from saddle point(s) connecting the initial and final stable configurations, also respectively known as the reactant and the product, with

local minimum energy level on the PES. Finally the activation energy is obtained by finding the saddle point energy along the MEP and the transition rate is calculated using the transition state theory [3]. The challenge of accurately predicting a phase transition is the knowledge of the true value of transition rate, which is determined by the energy barrier that exists between the initial and final stable configurations. Mathematically it is the saddle point on the PES with the global minimum energy barrier that determines the transition rate.

A number of methods [4-8] that search for saddle points on a PES have been developed over the past few decades. Those methods can generally be categorized into two groups: single-ended methods [9, 10] and double-ended methods[11, 12]. Single-ended methods start with one configuration to search the saddle point on a PES without locating the corresponding MEP. Double-ended methods are to locate the saddle point and corresponding MEP between two starting states. The major group of single-ended methods is eigenvector-following methods [9, 10] that follow the eigenvector of Hessian matrix with local quadratic approximations of the PES. The most popular double-ended ones are chain-of-states methods including nudged elastic methods (NEB) [13, 14] and string methods [15, 16]. Those methods intend to locate a single transition path with one saddle point between reactant and product at a time. Thus they are unable to provide an overview of the PES landscape. Recently, we developed a concurrent search algorithm [17] to locate all local minima and saddle points along a multi-stage transition path simultaneously. The algorithm improves the accuracy of activation energy estimation since it is able to locate all of the local minima and saddle points along the path connecting the reactant and product. However, for complex PES's, the transition from one stable configuration to another could follow more than one possible path. The most interesting path is the one with the lowest energy barrier. Since the existing saddle point search methods are local search methods, the result sensitively depends on the initial guess of the transition path. The path identified by those methods may not be the MEP. Consequently, this will lead to an overestimation of the energy barrier between two states. To solve this problem and provide a global view of the energy landscape, in this paper, a curve swarm algorithm is developed to exhaustively locate the local minima and saddle points within a region on the PES concurrently. The algorithm uses groups of curves to thoroughly search an area on the PES. A collective potential model is developed to avoid collision and maintain cohesion between curve groups.

In our algorithm, the transition path is represented by a parametric Bézier curve that is defined by some control points. Each control point represents an image along the transition path. For each Bézier curve in one group, two end control points are minimized to locate two local minima, while intermediate control points move along their corresponding search directions to refine the shape of the curve. If the refined curve crosses an extra energy basin with local minimum, it is broken into two curves that represent two stages of transition at one breakpoint. The breakpoint is then minimized to locate the extra local minimum. The shape of each of the newly created curves is refined following the same procedure as the previous one for one curve. The process continues until each curve crosses only two adjacent energy basins and their end control points locate two local minima. Then the algorithm selects the control point with the maximum energy within each of those curves and let it climb up to locate the saddle point. Different from the previous concurrent search algorithm, the intermediate control points in the proposed curve swarm algorithm are subject to both collective forces and true potential forces when moving along the search direction.

In the remainder of the paper, the curve swarm algorithm is first presented. Then the algorithm is demonstrated by examples of the Rastrigin function, Schwefel function, and the diffusion process of the hydrogen atoms in the FeTiH system.

## Curve Swarm Search Algorithm

Previously we developed a concurrent search algorithm [17] for searching multiple local minima and saddle points along one transition path without the prior knowledge of initial and final stable configurations on a PES simultaneously. The algorithm uses a Bézier curve to represent a transition path. Each control point represents one intermediate state (i.e. atomic configuration) along the transition path. The searching algorithm consists of three stages: 1) a single transition pathway search, 2) multiple transition pathway search, and 3) climbing process to locate the saddle position. The curve swarm search algorithm uses groups of curves to search local minima and saddle points, which is an extension of the concurrent search algorithm.

### A Single Transition Pathway Search in Curve Swarm Algorithm

In the curve swarm algorithm, the intermediate control points are subject to both the collective force, which is from their neighbors, and the true potential force, which is the gradient of the PES. In each iteration, a set of conjugate directions are constructed for each intermediate control point using Eqn.(5) in [17]. Then the intermediate control points move along the directions which are the weighted sum of the collective force and the parallel components of true potential force along the corresponding conjugate direction. That is, for the  $k^{\text{th}}$  intermediate control point on a curve  $\phi$  with at least one end control point not located at the local minimum, the  $i^{\text{th}}$  search direction is

$$\mathbf{D}_{k,\phi}^{(i)} = w_g (-\nabla V(\mathbf{x}_{k,\phi}^{(i-1)}) \cdot \mathbf{s}_{k,\phi}^{(i)}) + w_c \nabla V_{k,\phi}^C \quad (1)$$

in which  $\mathbf{x}_{k,\phi}^{(i-1)}$  is the position for the  $k^{\text{th}}$  intermediate control point after the search along  $(i-1)^{\text{th}}$  search direction  $\mathbf{D}_{k,\phi}^{(i-1)}$ ;  $\mathbf{s}_{k,\phi}^{(i)}$  and  $V_{k,\phi}^C$  are the  $i^{\text{th}}$  conjugate direction and the collective potential for the  $k^{\text{th}}$  point on the curve  $\phi$ , respectively;  $w_g$  and  $w_c$  are the weights for the parallel components of the true potential force and the collective force  $\nabla V_{k,\phi}^C$ , respectively. The collective potential for the  $k^{\text{th}}$  intermediate control point on curve  $\phi$  is defined as a weighted sum of the pairwise potential  $\psi$  between the control point and other curves in its neighboring groups. That is,  $V_{k,\phi}^C = \sum_{l=1}^L w_l \psi(r_{kl})$ , in which  $w_l$  is the weight for the  $l^{\text{th}}$  ( $l=1 \cdots L$ ) curve from its neighbor groups;  $L$  is the total number of curves from its neighboring groups;  $r_{kl}$  is the minimum Euclidean distance between the  $k^{\text{th}}$  point to the  $l^{\text{th}}$  curve in its neighborhood. The key issue here is to model the pairwise potential that is able to maintain cohesion and avoid collision between two curves. The following sections gives a detailed description on the pairwise potential model.

### Pairwise Potential Model

Since the collective force between two curves could be either attractive or repulsive depending on the distance between two curves, the collective potential model used here is the Lennard-Jones potential. The potential is defined as  $\psi = 4\varepsilon[(\sigma/r)^{12} - \sigma/r]^6$ , where  $\varepsilon$  is the depth of the potential well;  $\sigma$  is the characteristic distance at which the pairwise potential is zero;  $r$  is the distance between two atoms or molecules. The central issue here is to define the three parameters, which are  $\varepsilon$ ,  $\sigma$ , and distance  $r$ , to make the model well serve the purpose of maintaining cohesion and avoiding collision among curves.

The Depth of the Potential Well  $\varepsilon$ : Since the curves in this algorithm evolve under the forces from both true potential (i.e. energy potential) and imaginary potential (i.e. collective potential among curves), the criteria of determining  $\varepsilon$  is that the value of imaginary collective potentials has the same magnitude as the energy potential of the system. To capture more information of

the potential energy surface, the depth of the potential well is adaptive. Based on this criterion,  $\varepsilon$  is defined as the average of the potential energies,  $E_{end1}$  and  $E_{end2}$ , at the two local minima identified by the end control points of the breakable curve, which is  $\varepsilon = (E_{end1} + E_{end2}) / 2$ .

**The Characteristic Distance  $\sigma$ :** The characteristic distance  $\sigma$  is the distance at which the pairwise potential is zero. Since the movements of the curves are directly controlled by the collective forces, it is difficult to directly define the distance at which the potential between two curves is zero. Since the algorithm breaks one curve at a breakpoint, the zero-force distance  $r_0$  associated with two curve sections which share the same breakpoint is defined as the minimum distance between the breakpoint  $\mathbf{x}_{break}$  and the corresponding two end control points  $\mathbf{x}_{end1}$  and  $\mathbf{x}_{end2}$ , i.e.  $r_0 = \min(\|\mathbf{x}_{break} - \mathbf{x}_{end1}\|, \|\mathbf{x}_{break} - \mathbf{x}_{end2}\|)$ . The characteristic distance is determined by solving equation  $\partial\psi / \partial r = 0$  which produces  $r = 2^{1/6} \sigma$ . By replacing  $r$  by  $r_0$  in  $r = 2^{1/6} \sigma$ , the characteristic distance is calculated as  $\sigma = 0.8909r_0$ .

In the algorithm, both the depth of the potential well  $\varepsilon$  and the characteristic distance  $\sigma$  are adaptive to precisely capture the information of energy landscape on the fly during the searching process. In calculating the pairwise interacting forces between two newly created curves and other groups, the depth of the potential well  $\varepsilon$  and the characteristic distance  $\sigma$  are updated using the position of the breakpoint of the two curves and the end control points.

**Pairwise Force:** The pairwise force between one curve and its neighboring curve is the gradient of the pairwise potential as

$$f(\mathbf{x}) = \frac{\partial\psi}{\partial r} \nabla r(\mathbf{x}) \quad (2)$$

in which  $r$  is the distance between two curves. For the Lennard-Jones potential, the pairwise force calculated from Eqn.(2) will be infinite when  $r(\mathbf{x})$  approaches zero. As a result, the collective force which is the weighted sum of the pairwise forces will dominate the searching process and push two curves too far away from each other, which violates the cohesion criterion. On the other hand, when two curves are far away from each other, they should not interact with each other since there may be a third curve between them as the curves are usually evenly distributed. However, the force calculated from the pairwise force model is not zero, which violates the requirement. To resolve these two issues, we introduce two cut-off distances. The first one is introduced to keep the collective force at the same magnitude with the true potential force, which is defined as  $r_L = c_{cut} \sigma$ , where  $c_{cut}$  is a constant. That is, if  $r(\mathbf{x}) < r_L$ , the pairwise force is defined as the force calculated at  $r(\mathbf{x}) = r_L$ . The second cut-off distance is introduced to deactivate the interaction among curves when they are far away from each other, which is defined as  $r_U = 2.5\sigma$ . If  $r(\mathbf{x}) > r_U$ , the pairwise force is set to be zero. Hence, the pairwise force in this algorithm is defined as

$$f(\mathbf{x}) = \begin{cases} 0 & \text{if } r(\mathbf{x}) > r_U \\ \frac{\partial\psi}{\partial r} \nabla r(\mathbf{x}) & \text{if } r_L < r(\mathbf{x}) < r_U \\ \frac{\partial\psi}{\partial r} (c_{cut} \sigma) \frac{\mathbf{x} - \mathbf{x}_{l\_curve}}{c_{cut} \sigma} & \text{if } r(\mathbf{x}) < r_L \end{cases} \quad (3)$$

The collective force is the weighted sum of the pairwise forces as

$$F(\mathbf{x}) = \sum_{l=1}^L w_l f_l(\mathbf{x}) \quad (4)$$

**Minimum Euclidean Distance  $r$ :** The minimum Euclidean distance is used to calculate the force to push two curves away at their closest position. Since it is computationally expensive to locate exactly the closest position between two curves using traditional distance based optimization methods, the minimum Euclidean distance is approximated by locating several pairs of control points. Each intermediate control point on curve  $\phi$  has its own corresponding collective forces which are the weighted sums of the pairwise forces from  $\phi$ 's neighboring curves. To obtain the pairwise forces for each intermediate control point on curve  $\phi$ , the algorithm first locates the minimum distance between a control point of the curve and its neighboring curves. To locate the pair of control points with the minimum distance between a newly created curve and one of its neighboring curves, we first represent the locations of their intermediate control points in two separate matrices with identical row dimensions. Starting with the first column of the matrix for the newly created curve, the Euclidean distance between this location and each location in the matrix of its neighboring curve is calculated. The process is then repeated for all the columns in the matrix of the newly created curve. The pairwise forces for the  $i^{\text{th}}$  intermediate control point on curve  $\phi$  with respect to the neighboring curve are calculated using Eqn.(3). The same procedure is then applied to calculate the pairwise force for each of the intermediate control point. After all the pairwise forces are obtained, the collective force for each of the intermediate control point is calculated using Eqn.(4).

After the collective forces for each intermediate control point are obtained, the shape of the curve can be refined by moving the intermediate control points along their corresponding search directions which are determined using Eqn.(1). The detailed description of moving two end control points, redistribution of the intermediate control points, curve subdivision scheme to divide the breakable curves, and climbing process can be found in Ref. [17].

### Demonstration

Here the Rastrigin function and Schwefel function, which are among the most used benchmark functions for global optimization, are first used to demonstrate the new algorithm and visualize the searching process and results. The algorithm's capability to exhaustively search local minima and saddle points within an area by comparing the results from the curve swarm algorithm and the ones from the concurrent search algorithm without applying collective force. The results are shown in Figure 1 for Rastrigin function and Figure 2 for Schwefel function. Figure 1 (a) shows that two curves may duplicate the search efforts and find the same result when there is no communication among curves. Figure 1 (b) shows that the collective force introduced in the curve swarm algorithm pushed those two curves away and pulled the third curve which is far away closer. Similarly, there are overlaps among curves in Figure 2 (a). After introducing the collective force, there is no overlap among curves in Figure 2 (b), which indicates that the curve swarm algorithm works well to avoid collision. Since computational cost is always the concern for searching algorithms, the scalability of our algorithm is tested by gradually increasing the number of the initial curves on the PES. Figure 1 (c) shows a near quadratic relationship between the total CPU time and the total number of initial curves which is acceptable in terms of computational efficiency. The convergence is also tested by gradually increasing the number of initial curves within one fixed area. Figure 2(c) shows the result of convergence test. For saddle point, more initial curves are needed to converge.

We also apply the algorithm to the FeTiH system to study the diffusion process of the hydrogen atoms. Three initial curves are first given to start the search. A total of 14 paths with 17 local

minima are located. Figure 3 shows the atomic structures of three examples of those transition paths. The total energy of each image is also shown on the top of the corresponding structure. For example, Figure 3 (a) shows the transition from the initial state with the total energy of  $-37.1027\text{eV}$  to the final state with the total energy of  $-40.5671\text{eV}$ . In the figure, red atoms are Fe's, gray ones are Ti's, and blue small ones are H's. To reach the final state, the atomic structure of FeTiH gradually changes from the first image to the last one following the sequence of the pictures shown in Figure 3 (a). Along this transition path, the fifth image with the highest energy level ( $-35.0117\text{eV}$ ) is the estimation of the saddle point along the path. The energy difference between the fifth image and the initial one is the activation energy, which is  $2.091\text{eV}$ . Similarly, the fourth image along the path in Figure 3 (b) is the saddle point for the transition from the initial state with the total energy  $-38.1313\text{eV}$  to final state with the energy of  $-39.7098\text{eV}$ . The activation energy for this transition process is  $9.9719\text{eV}$ . The second image in Figure 3 (c) is the saddle point for the transition from the initial state with the total energy  $-40.5484\text{eV}$  to final state with the energy of  $-40.1526\text{ eV}$ . The activation energy for this transition process is  $8.8485\text{ eV}$ .

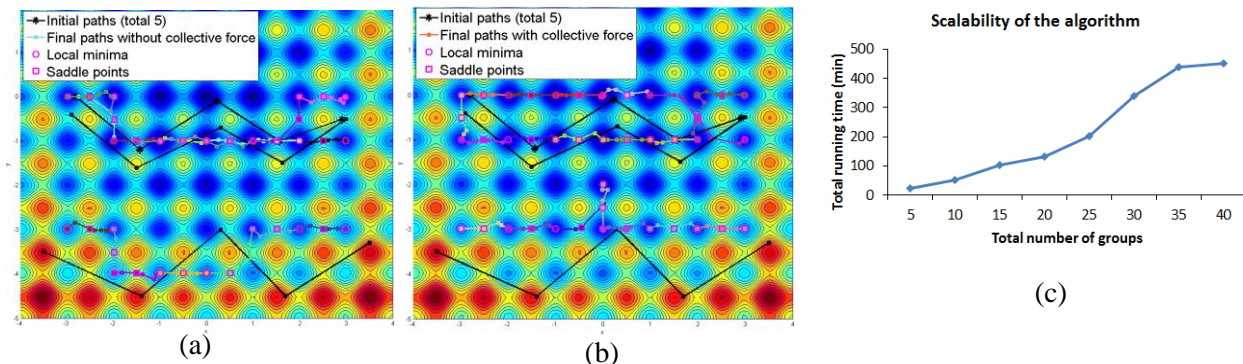


Figure 1: Test result for curve swarm algorithm by example of Rastrigin function (a) concurrent search algorithm without collective force (b) curve swarm algorithm (c) scalability test

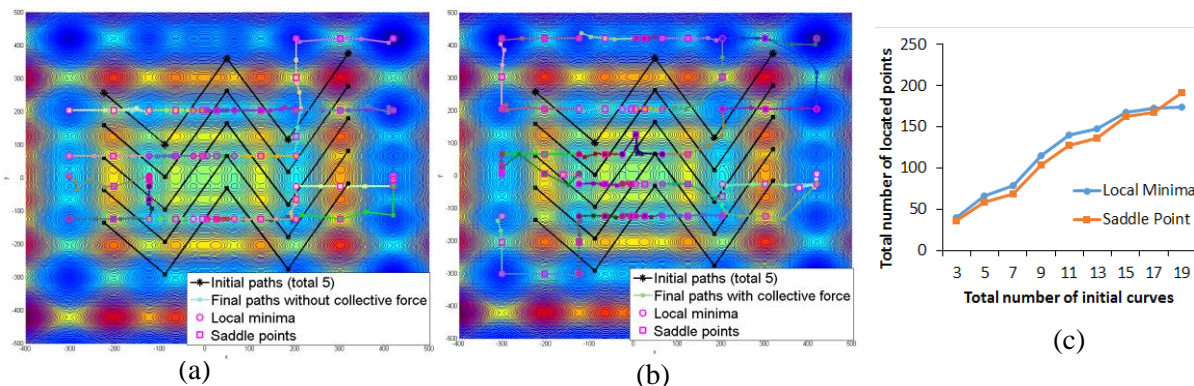


Figure 2: Test result for curve swarm algorithm by example of Schwefel function (a) concurrent search algorithm without collective force (b) curve swarm algorithm (c) convergence test

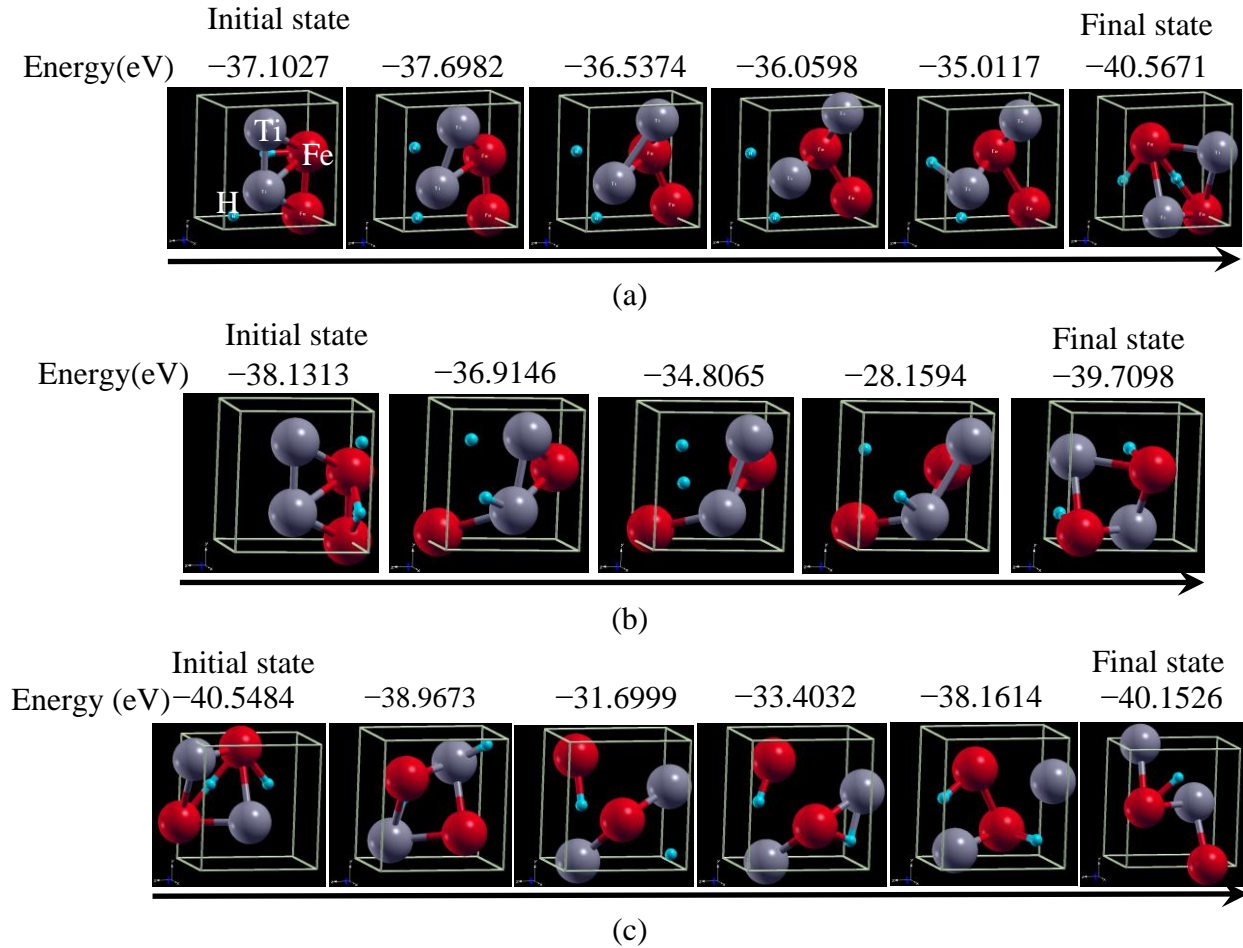


Figure 3: Results of the example transition paths for the diffusion process of the hydrogen atoms in the FeTiH system (a) transition path No. 9; (b) transition path No. 10 (c) transition path No. 13

### Conclusion and Future Work

In this paper, we presented a curve swarm algorithm to survey the energy landscape of a PES, which intends to exhaustively search local minima and saddle point within an area on the PES. Different from the existing transition path and saddle point search methods, the algorithm uses groups of curves instead of one curve during searching. It is able to locate multiple transition paths between two stable configurations. It provides a global view of PES. The algorithm uses the concept of flocking that describes the collective behavior among curve groups during the search process. A collective potential model is devised to serve this purpose.

In the current scheme, the collective potential is defined as a weighted sum of pair potentials between two groups of curves. The weights are assigned to be equal, which does not consider the physical implication of PES's. If the distance between two groups is very large or there exists a third group between them, a slight difference about the collective behaviors could be observed. The equal weights however do not model such differences. In the future, the model could be improved by optimizing the weight function. For example, the weights could be a function of the distance between two groups. The longer the distance is, the lower the weight should be. In the future work, we will test the algorithm with more material systems with higher dimensions.

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