Localized saddle-point search and application to temperature-accelerated dynamics

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We present a method for speeding up temperature-accelerated dynamics (TAD) simulations by carrying out a localized saddle-point (LSAD) search. In this method, instead of using the entire system to determine the energy barriers of activated processes, the calculation is localized by only including a small chunk of atoms around the atoms directly involved in the transition. Using this method we have obtained $N$-independent scaling for the computational cost of the saddle-point search as a function of system size $N$. The error arising from localization is analyzed using a variety of model systems, including a variety of activated processes on Ag(100) and Cu(100) surfaces, as well as multiatom moves in Cu radiation damage and metal heteroepitaxial growth. Our results show significantly improved scaling of TAD with the LSAD method, for the case of Ag/Ag(100) annealing and Cu/Cu(100) growth, while maintaining a negligibly small error in energy barriers.

I. INTRODUCTION

Recently there has been a great deal of interest in the development of methods for extending the timescales of non-equilibrium simulations, including accelerated dynamics,\textsuperscript{1–13} adaptive kinetic Monte Carlo\textsuperscript{14,15} and self-learning kinetic Monte Carlo\textsuperscript{16–21} Other methods based on metadynamics\textsuperscript{22–25} have also been proposed to speed up slow dynamics, typically for systems trapped in deep energy minima. In addition, a considerable amount of effort has been devoted to the development of efficient computational methods for calculating the minimum energy path and corresponding energy barriers\textsuperscript{26–31} in condensed matter systems.

One particular accelerated dynamics method is temperature-accelerated dynamics\textsuperscript{8,9} (TAD) in which a high-temperature basin-constrained molecular dynamics (MD) simulation is used to speed-up the search for activated events, in order to determine the first transition which will occur at the desired low temperature $T_{\text{low}}$. As part of this method, an efficient saddle-point search algorithm, such as the climbing image nudged elastic band (cNEB) method\textsuperscript{27} is used to determine the minimum energy paths and corresponding energy barriers for all high-temperature transitions from a given energy basin which occur before a well-defined high-temperature “stop-time” is reached. Accordingly, the efficiency with which activation barriers can be determined plays an important role in determining the speed of TAD simulations.

Here we present a method by which a localized saddle-point (LSAD) search may be used to reduce the cost of calculating energy-barriers in TAD simulations, thus improving the scaling behavior of TAD as a function of system size without significantly reducing the accuracy of the resulting calculation. Our method is based on the assumption that only atoms which are sufficiently close to those involved in the transition have a significant effect on the potential energy surface along the minimum energy path. As a result, by carefully choosing the range of atoms to be included in the saddle-point calculation, the error resulting from localization can be minimized while the computational cost of saddle-point calculations is significantly reduced. Since in many TAD simulations, saddle-point calculations constitute a significant portion of the computational time, the development of such a method may be considered to be the first step in the development of a computationally efficient form of TAD with improved scaling as a function of system size.

To demonstrate the improved performance of saddle-point calculations with our LSAD method, we have first applied it to single and multi-atom moves found in Cu/Cu(100) and Cu bulk simulations. In particular, for a Cu monomer hopping on a Cu(100) substrate, the LSAD method yields $N$-independent scaling, instead of $N^{2.8}$ based on the whole system. In addition, we have carried out TAD simulations of Ag/Ag(100) annealing and Cu/Cu(100) growth with and without the LSAD method. As expected, the performance of TAD with the LSAD method is significantly better than without LSAD while the relative performance increases with system size.

The organization of this paper is as follows. In Sec. II, we describe the LSAD method in more detail and also present results for the dependence of the error in the activation barrier as a function of chunk size along with results for the dependence of the cutoff radius on the number of atoms involved in a transition for both homoepitaxial and heteroepitaxial systems. In Sec. III, we present additional results for the performance of the LSAD method in activation barrier calculations for a variety of multiatom moves on the Cu(100) surface and Cu bulk TAD simulations. We then discuss the performance and scaling of TAD simulations of Ag/Ag(100) annealing and Cu/Cu(100) growth carried out with our LSAD method. Finally, in Sec IV we summarize our results.

II. LOCALIZED SADDLE-POINT SEARCH

The underlying assumption on which our LSAD method is based is that atoms sufficiently far away from those directly involved in an activated event will have a minimal effect on the minimum energy path and activa-
of $r_{cut,i}$ for different types of atoms, but for simplicity if there is more than one type of atom present, we have used the maximum value of $r_{cut,i}$. Since we are interested in surface problems such as thin-film growth as well as bulk problems, we have considered both a cylindrical cutoff (where the distance $r_m$ is the distance to the cylinder axis which is perpendicular to the surface) as well as a spherical cutoff. We now consider the accuracy and performance of our LSAD calculations.

III. RESULTS

In order to test the accuracy and performance of our localized saddle-point (LSAD) method, we have examined a variety of activated processes observed in homoepitaxial and heteroepitaxial simulations on fcc metal(100) surfaces and have also carried out TAD annealing and thin-film growth simulations with and without LSAD. In addition, we have carried out spatially parallel TAD (parTAD) simulations of radiation damage in Cu, using a three-dimensional extension of our parTAD method\textsuperscript{33,34} based on our synchronous sublattice algorithm.\textsuperscript{35} In all of our simulations, embedded-atom-method (EAM) potentials were used, including potentials developed by Voter-Chen (VC),\textsuperscript{36} Mishin \textit{et al.}\textsuperscript{37} (Mishin EAM), Sheng \textit{et al.}\textsuperscript{38} (Sheng EAM), Adams \textit{et al.}\textsuperscript{39} (AFW EAM), and Bonney.\textsuperscript{40}

In our growth and annealing simulations, we used a substrate composed of five or six layers with the top two or three moving and bottom three fixed and lateral sizes in the range 5$a$ – 12$a$ in units of the lattice constant $a$ (where $a = 4.09$ Å, 3.615 Å and 3.52 Å for Ag, Cu and Ni, respectively) while periodic boundary conditions (PBCs) were applied parallel to the substrate. In contrast, PBCs were applied in all three directions in our 3-dimensional parallel TAD simulations of Cu radiation damage.\textsuperscript{33,35}

In our TAD simulations the minimum prefactor was set to $\nu_{\text{min}} = 5 \times 10^{11}$ s\(^{-1}\) and the uncertainty $\delta = 0.05$ was used. Our high-temperature MD simulations were carried out using a Langevin thermostat\textsuperscript{41} with a friction coefficient of $10^{12}$ s\(^{-1}\) and a time step of 4 fs. Energy barriers for attempted events were calculated using the cNEB method with 11 images while Vineyard prefactors\textsuperscript{42} were also measured for some representative cases. In our TAD simulations of Cu/Cu(100) growth at $T_{\text{low}} = 80$ K, atoms were deposited randomly with deposition rate $F = 1$ ML/s, while an initial kinetic energy of 0.2 eV was used for the depositing atoms. While most of our calculations were carried out using a 2 GHz Intel dual-core Mac mini, our annealing and growth simulations were carried out using the 2.6 GHz IBM 1350 Glenn cluster at the Ohio Supercomputing Center (OSC).
A. Dependence of activation barrier on \( r_m \)

Since our LSAD calculations use only a small portion of the whole system, it is important to determine to what extent this may lead to errors in the calculation of activation barriers. We first consider the two relatively low-barrier Ag/Ag(100) diffusion processes shown in Fig. 2(a) - one involving a single-atom “edge-zipping” move and the other involving a two-atom move - using the Voter-Chen EAM potential. As can be seen, restricting the number of moving atoms via a cutoff radius \( r_m \) typically leads to an activation barrier which is somewhat higher than that obtained using the entire system. This is not surprising since one expects “pinning” effects\(^{43} \) to lead to an increase in the energy away from the local minimum. In addition, for a given value of \( r_m \), the cylindrical cutoff tends to yield a smaller error than the spherical cutoff since the cylindrical cutoff includes more atoms. However, in both cases the error in the activation barrier decreases exponentially with increasing cutoff radius \( r_m \). As a result, for both transitions (and for either a cylindrical or a spherical cutoff) we find that for \( r_m = 9.14 \text{ Å} \) (corresponding to \( d_m = 1.65 \text{ Å} \)), the error in the activation barrier is smaller than \( 4 \times 10^{-3} \text{ eV} \).

To determine how the cutoff \( r_m \) corresponding to a given error in the activation barrier depends on the number of atoms \( n \) involved in the transition, we have also examined a variety of additional activated processes observed in simulations of metal homoepitaxial and heteroepitaxial growth. In particular, Fig. 3 shows the value of the chunk radius \( r_m \) as a function of \( n \) (with \( n \) ranging from 1 to 8) needed to ensure an error of \( 10^{-3} \text{ eV} \) or less in the activation barrier \( E_a \) obtained for a variety of Ag/Ag(100) and Cu/Cu(100) surface diffusion processes, including monomer diffusion, edge diffusion, two types of edge-zipping for Ag/Ag(100) (see Fig. 1.1 and Fig. 4.1 in Ref. 44), atom attraction \( E_a = 0.229 \text{ eV} \) for Ag/Ag(100)), and several multitatom moves such as the formation of a misfit dislocation on a Cu substrate by a Cu monomer. As can be seen in Fig. 3, the radius \( r_m \) appears to increase with \( n \). In particular, for Cu/Cu(100) the dependence may be described by \( r_m \sim n^{0.2} \) (i.e. \( d_m = c \times n^{0.2} \) for \( n \leq 6 \) with a constant \( c \simeq 1.65 \) for an error of \( 10^{-3} \text{ eV} \). For the Mishin et al. Cu EAM potential, which has a larger cutoff than the Voter-Chen potential, the radius \( r_m \) shows a similar increase with \( n \) but with slightly different energy barriers in each case. For Ag/Ag(100), the value of \( c \) is slightly smaller with \( c \simeq 1.55 \) due to a larger \( r_{\text{cut}} \).

The increase of \( r_m \) with \( n \) may be generally explained by an increase in the local distortions of atoms surrounding the transition with increasing \( n \). However, in some cases the local distortion can be quite large even if a relatively small number of atoms (based on the initial and final configurations) are involved in the transition, and in these cases a somewhat larger chunk radius \( r_m \) may be needed even though \( n \) is small. One example is Ni...
monomer exchange with a Ni(100) substrate atom (corresponding to \( n = 2 \)) for which the VC and Sheng Ni EAM potentials result in energy barriers of 1.17 eV and 0.85 eV with chunk sizes of \( r_m = 12.5 \) Å and 12.1 Å, respectively, for an error of \( 10^{-3} \) eV, while for the AFW EAM potential, \( r_m = 13.8 \) Å with an energy barrier of 1.37 eV. Similarly, for Cu/Cu(100), the same process yields \( r_m = 13.9 \) Å and a barrier of 0.80 eV with VC EAM potential. However, in all of these cases the distortion at the saddle-point is relatively large, and as a result, additional atoms (corresponding to those which have been displaced a distance larger than \( d_c \) at the saddle-point) also participate in the transition.

This suggests that in general it may be desirable to include the saddle-point configuration as well as the initial and final configurations in defining the number of atoms \( n \) involved in a transition. For example, an initial LSAD calculation may be carried out using a value of \( r_m \) based on the displacements of the initial and final configurations, followed by a more accurate LSAD calculation which takes into account any additional atoms which are displaced at the saddle-point. However, we note that in the applications of the LSAD method to low-temperature TAD simulations considered here, the dominant attempted events observed are single atom moves while high-barrier processes such as the monomer exchange discussed above are unlikely to be accepted. Thus, we expect that at such low temperatures one may still use the power-law form for the chunk size to further improve the performance of TAD by carrying out LSAD calculations.

We now consider the dependence of \( r_m \) on \( n \) in heteroepitaxial systems. In particular, Fig. 4 shows the dependence of \( r_m \) corresponding to an error in the calculated activation barrier of \( 10^{-3} \) eV or less on the number of atoms \( n \) participating in the transition, for a variety of activated processes observed in Ni/Cu(100) and Cu/Ni(100) growth using the MVB EAM potential. Some of the representative diffusion moves are also shown along with their barriers. As can be seen, in this case the value of \( r_m \) needed to ensure an error of less than \( 10^{-3} \) eV in the calculated activation barrier shows no clear dependence on the number \( n \) of participating atoms. The lack of any trend with \( n \) in these heteroepitaxial systems may be due to the fact that the displacement near the saddle point produces a relatively small distortion compared to the longer-range strain-field due to misfit strain.

**B. Dependence of prefactor on \( r_m \)**

While the prefactor for activated events is not typically calculated in TAD simulations (since the low-temperature time is determined by the high-temperature time combined with the activation energy) in some cases it may be of interest to efficiently calculate prefactors in the course of a TAD simulation. Accordingly, we have also examined the effects of the cutoff \( r_m \) on the prefactor for five different activated processes: (i) Ag/Ag(100) monomer, edge-zipping and dimer edge diffusion where the latter two cases correspond to the Ag adatom moves shown in Fig. 2(a), (ii) a three Cu-atom interlayer diffusion move with activation energy 0.523 eV shown in Fig. 3, and (iii) a two-atom exchange move in Ni/Cu(100) with activation barrier 0.468 eV shown in Fig. 4. The prefactor \( \nu \) was calculated using the Vineyard formula,

\[
\nu = \prod_{i=1}^{N_p} \nu_i^{\nu_i} / \prod_{i=1}^{N_s} \nu_i^{\nu_i},
\]

where \( N_p \) is the number of atoms used in the prefactor calculation and \( \nu_i^{\nu_i} \) and \( \nu_i^{\nu_s} \) denote the vibration frequencies at the initial and transition states, respectively.

Fig. 5 shows the ratio of \( \nu_{\text{LSAD}} / \nu \) as a function of the cutoff radius \( r_m \), where \( \nu \) and \( \nu_{\text{LSAD}} \) are the prefactors measured using the whole system and ‘reduced’ system for both a cylindrical and a spherical cutoff. We note that measuring a vibration frequency is a time-consuming calculation whose computational cost increases as \( N_p^3 \). Thus, given the time-consuming nature of Vineyard calculations, the LSAD method should provide an efficient means for estimating the prefactor, especially for large systems. As can be seen in Fig. 5, the ratio \( \nu_{\text{LSAD}} / \nu \) converges somewhat more slowly with increasing \( r_m \) than the activation barrier while the rate of convergence depends on the activated process. In particular, for a cutoff \( r_m = 11 \) Å (corresponding to an error of \( 2 \times 10^{-3} \) eV in the energy barrier) the corresponding prefactor ratio \( \nu_{\text{LSAD}} / \nu \simeq 0.9(0.8) \) with the cylindrical (spherical)
chunk method. In addition, just as was found for the tors in units of THz for whole (localized) system respectively.

C. Performance

We first consider the performance of the LSAD method in speeding up saddle-point calculations, where the performance can be defined as

\[ \text{Performance} = \frac{t}{t_{\text{LSAD}}} \]  \hspace{1cm} (2)

and \( t\) and \( t_{\text{LSAD}} \) are the execution times obtained without and with the LSAD method, respectively. In particular, we have considered three representative cases, Cu surface diffusion on a \( 9a \times 9a \) substrate, a Ni adatom exchange move with a Cu substrate atom on a \( 12a \times 12a \) substrate, and a complex Cu atom move triggered by Cu interstitials found in our simulations of Cu radiation damage with a system size of \( 16a \times 16a \times 16a \). We note that for this bulk Cu system, the spherical cutoff is more appropriate.

Fig. 6 shows the error in the energy barrier for these cases along with the corresponding performance as a function of the chunk radius \( r_m \). As can be seen, while the performance decreases with increasing \( r_m \), a performance factor ranging from 3 (for the first two cases) to 9 (for the case of Cu radiation damage) can be obtained with an error in the activation barrier of less than \( 3 \times 10^{-3} \) eV. The superior performance for the case of radiation damage is due to the large system size used in the simulation. We also note that in our parTAD radiation damage simulation using eight processors, there are many low-barrier processes similar to the one shown in Fig. 6(b), which arise due to the presence of a large number of defects such as interstitials and vacancies, and which tend to introduce intermediate states for any moves with moderate or higher barriers. As a result, about 40% of the total TAD simulation time was spent resolving intermediate states and finding saddle points and calculating their barriers. Thus, in this case the LSAD method can significantly improve the performance of TAD, while maintaining a negligibly small error in the energy barrier, as shown in Fig. 6.

We have also investigated the scaling of NEB and Vineyard timings with system size (both with and without LSAD) for the case of Cu monomer diffusion on a Cu(100) substrate. In this case the Sheng EAM potential\(^{38} \) was used while a cylindrical cutoff with \( r_m = 10.725 \text{ Å} \) \((d_m = 1.65)\) yields an error of \( 3 \times 10^{-4} \) eV in the monomer diffusion barrier (0.5353 eV). For a fair comparison, the NEB timing without the LSAD method comes only from NEB calculations including barrier calculations. On the other hand, the NEB timing with the LSAD method also includes the computational cost of constructing chunks for the initial and final states along with their minimization. As can be seen in Fig. 7(a), while the NEB timing without LSAD increases as \( t \sim N^{1.8} \) (where \( N \) is the total number of moving atoms in the system), the timing with LSAD exhibits no \( N \) dependence. Similarly, the Vineyard timing without LSAD shows the expected \( N^3 \) behavior, while the Vineyard
FIG. 7: Comparison of NEB and Vineyard timings measured in sec as a function of the number of moving atoms with and without the LSAD method, for the case of Cu monomer diffusion on a Cu(100) substrate with a cylindrical cutoff $r_m = 10.725 \text{ Å}$.

FIG. 8: Performance of adaptive TAD simulations of Ag/Ag(100) annealing at $T_{\text{low}} = 80$ K with and without LSAD method, compared to regular TAD simulations with fixed high-temperature $T_{\text{high}}$. Here the inset shows the initial configuration, where green color represents Ag adatoms on a Ag(100) substrate of size $5a \times 5a$.

FIG. 9: Timing comparison as function of coverage and substrate size in TAD simulations of Cu/Cu(100) growth at $T_{\text{low}} = 80$ K with and without LSAD, where $\theta = 1.84$ with $r_{\text{cut}} = 4.961 \text{ Å}$ was used for both cylindrical and spherical chunks. (a) Timing as a function of coverage $\theta$ on a substrate size of $12a \times 12a$ and (b) timing per monolayer (ML) as function of substrate size in units of $N_s = 1 \equiv 6a \times 6a$. ($N_s = 2.25$ and 4 correspond to $9a \times 9a$ and $12a \times 12a$, respectively).

timing with LSAD method has no $N$ dependence (see Fig. 7(b)).

We now discuss the performance of TAD simulations carried out with LSAD calculations. As a first example, we consider adaptive TAD simulations of Ag/Ag(100) annealing at $T_{\text{low}} = 80$ K using the VC EAM potential. We note that in this adaptive TAD simulation$^{44}$ the high temperature is not fixed, instead it varies, depending on either the number of attempted events observed or their barriers in order to improve the performance of TAD. In particular, here we have used method III described in Ref. [44], in which the high temperature for the current state was set to the optimal temperature for the lowest-barrier attempted event observed so far. In addition, we started with the same initial configuration used for the previous Ag annealing simulations given in Ref. [44], as also shown in Fig. 8, and measured the execution time to accept ten diffusion events with energy barriers ranging from 0.086 eV to 0.335 eV (for the detailed sequence of diffusion events, see Fig. 4 in Ref. [44]). In our LSAD calculations, we used a cylindrical cutoff with $r_m = 1.65 \times n^{0.2} r_{\text{cut}}$ which yields an error in the activation barrier of less than $2 \times 10^{-3}$ eV. As can be seen in Fig. 8, the LSAD method improves the performance of adaptive TAD by an additional 12%. This somewhat modest improvement is due to the small substrate size ($5a \times 5a$) used in the simulation.

Fig. 9(a) shows additional results for the performance of TAD simulations carried out using LSAD calculations, for the case of Cu/Cu(100) growth at $T_{\text{low}} = 80$K with deposition rate $F = 1$ ML/s on a $12a \times 12a$ substrate. In our simulations, we used both cylindrical and spher-
tical cutoffs with \( r_m = 1.65 \times n^{0.2} r_{cut} \) and \( T_{\text{high}} = 550 \) K which is the optimal fixed temperature in this case.\(^{44}\) As can be seen in Fig. 9(a), the TAD simulations with LSAD are approximately 1.4 (2.2) times faster for cylindrical (spherical) cutoffs than those without LSAD. The dependence of the TAD simulation time on substrate size (in units of \( N_s = 6a \times 6a \)) is also shown in Fig. 9(b). As can be seen, the use of LSAD also significantly improves the scaling behavior with system size.

IV. SUMMARY

We have presented an efficient method to speed up the calculation of activation barriers and Vineyard prefactors in large systems, by localizing the saddle-point calculation so that only atoms which are within a specified distance \( r_m \) from those atoms participating in the transition are included. In addition, by carefully examining the dependence of the error on cutoff \( r_m \), we have shown that the errors introduced by such a cutoff can be minimized while still obtaining significant speed-up.

In particular, to understand the effects of the chunk radius \( r_m \) on the error in the activation energy, we have examined a variety of activated events found in Cu/Cu(100) and Ag/Ag(100) homoepitaxial and Ni/Cu(100) and Cu/Ni(100) heteroepitaxial simulations. For the homoepitaxial case, we have found that at least at low temperatures (for which any events deviating from such a power-law are unlikely to be accepted due to their high energy barriers) the cutoff radius satisfies the power-law form \( r_m \sim n^{0.2} r_{cut} \). In contrast, we found that for Ni/Cu(100) and Cu/Ni(100), it is better to use a fixed chunk size in order to take into account the effects of long-range strain field created by lattice mismatch. In addition, we have also examined the effects of chunk size on the Vineyard prefactor. While the convergence is relatively slow and exhibits a strong dependence on the type of activated process, the LSAD method can still be used to efficiently estimate the prefactor.

We note that for computational efficiency we have restricted our definition of atoms ‘participating’ in the transition to include only those atoms whose displacements in the final configuration are larger than a critical value \( d_c \) of the order of a few tenths \( \AA \). However, in general it may be desirable to include the saddle-point configuration as well as the initial and final configurations in defining the number of atoms \( n \) involved in a transition. For example, an initial LSAD calculation may be carried out using a value of \( r_m \) based on the displacements of the initial and final configurations, followed by a more accurate LSAD calculation if additional atoms are displaced at the saddle-point.

Finally, we have demonstrated that the performance of TAD simulations can be significantly improved by the use of LSAD calculations by considering two examples, Ag/Ag(100) annealing and Cu/Cu(100) growth. In both cases, we have found that the speed-up increases with increasing system size. As a result, one can achieve a significant speedup in TAD simulations with larger system sizes, and also significantly improve the scaling of TAD with system size, while maintaining a negligibly small error in the energy barrier.

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40 For the Ni (Cu) EAM potential see Ref. 36 (Ref. 37). For the Cu-Ni cross potential, see G. Bonny et al., Philos. Mag. 89, 3531 (2009).