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Searching for transition paths in multidimensional space with a fixed repulsive bias potential

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An efficient method for searching for transition paths in a multidimensional configuration space is proposed. It is based on using a fixed, locally repulsive bias potential, which forces the system to move from a given initial state to a different final state. This simple method is very effective in determining nearby configurations and possible transition paths for many-particle systems. Once the approximate transition paths are known, the corresponding activation energies can be computed using, e.g., the nudged elastic band method. The usefulness of the present method is demonstrated for both classical and quantum-mechanical systems.

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Numerous problems in condensed-matter physics and related fields involve searching for possible transition paths in a multidimensional configuration space. Examples of such problems are structural transformations, e.g., phase transitions and different kinds of kinetic processes in chemical reactions, polymer dynamics and folding, surface diffusion, and growth. If the interatomic potential of the system is known, then for finding possible transition paths between different configurations one needs to make systematic search for the topology of the corresponding potential-energy surface (PES) in a multidimensional space. In many cases this is a very complicated task due to the large number of degrees of freedom in the system. For example, in the problem of two-dimensional (2D) cluster diffusion it is relatively easy to consider possible diffusion moves of small clusters, but when the number N of atoms in a cluster increases the problem will be nontrivial even with clusters as small as $N=10$ (Ref. 1).

A standard way of generating transition paths and the evaluation of the actual transition rates along these paths for classical systems is to use the molecular-dynamics (MD) simulation technique.[2] However, MD simulations become impractical for rare (activated) events which occur with a very small probability at temperatures much lower than the barrier height. Possible solutions to this problem include various activation and acceleration techniques, most notably the hyperdynamics method.[3,4] In this class of methods there is a bias potential that is applied in the system to speed up the dynamics. There are also methods based on transition path sampling, either using Monte Carlo techniques[5] or path-integral approach to the Langevin equation.[6] However, all these methods are very time consuming for systematic searching of transition paths and the evaluation of the transition rates, in particular for many-particle processes.

A simpler task is to determine the minimum-energy path without evaluating the transition rate. The knowledge of the minimum-energy path is itself of interest, since it yields the activation barrier for the transition. Moreover, the transition rate can be approximately evaluated via the transition state theory with the knowledge of the transition state (saddle-point configuration). There are several existent methods available for this task.[7] In the simulated annealing method[8] the system is first heated up and then cooled down to find its equilibrium configuration. This method has widely been used in solving complex optimization type of problems (such as, spin-glass systems[9]) where the main interest is the minimum-energy ground state.[10] More systematic methods include the activation-relaxation technique,[11] the eigenvector-following (EF),[12] and the dimer method.[13] These methods allow one to locate all the nearest saddle points in principle. The EF method has successfully been used in many cases, e.g., in studies of 2D cluster diffusion,[1] the conformations of biological molecules,[14] and the structures of binary clusters.[15]

The fundamental problem in searching for saddle points in many-particle systems is that there is simply no single method that can guarantee that all saddle points have been found. In complicated systems it is thus a useful and practical strategy to try several different methods to make sure that at least the most important transition paths have been identified. In this Brief Report we propose a particularly simple but nevertheless efficient method which we call the repulsive bias potential (RBP) method. It can be used to search for the final states for a system and approximate transition paths starting from any given initial configuration. Once these are known, both the exact paths and the corresponding energy barriers can be determined by using the nudged elastic band (NEB) method[16] with the result from the RBP method as the input for the initial trial transition path. Note that using a simple linear interpolation between the initial and final states in the NEB often leads to instabilities or high activation energy transition paths. That is why the RBP and NEB methods have to be used in tandem. We demonstrate below the efficiency of this approach using examples from both classical and quantum-mechanical systems.

The basic idea of the RBP method is to locally modify the PES of the system with a fixed, repulsive bias potential to make the initial configuration unstable, but to keep the other nearby minima unaffected. The resultant potential can be written as

$$U_{tot}(\vec{R})=U(\vec{R})+A\prod_{i=1}^{n}\exp\{-(|\vec{r}_i-\vec{r}_{0i}|/\alpha)^2\}. \qquad (1)$$

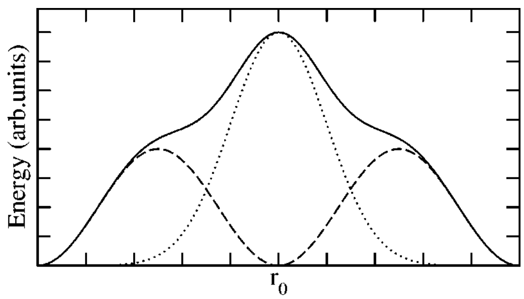

FIG. 1. A schematic picture of a 1D PES: the true (dashed), repulsive bias (dotted), and total modified potential (solid curve).

Here $U(\vec{R})$ is the original PES of the system, with $\vec{R}$ a $3N$-dimensional position vector for all the atoms in the system. It has been modified by a bias potential that acts only on a set of n active atoms with coordinates $\{\vec{r}_i\}$ and equilibrium positions $\{\vec{r}_{0i}\}$. The optimal choice of the set of active atoms depends on the particular problem on hand as discussed below. The technical implementation of the repulsion is trivial for both classical and quantum-mechanical systems. Other form of bias potential can also be used, e.g.,

$$U_{tot}(\vec{R}) = U(\vec{R}) + A\sum_{i=1}^{n} \exp\{-(|\vec{r}_i - \vec{r}_{0i}|/\alpha)^2\}. \qquad (2)$$

When the strength A and range α of the RBP have been chosen appropriately (as will be discussed below), forces computed from Eq. (1) or (2) can be used to displace the system from its initial state to escape to a nearby minimum. Total-energy minimization is performed on the modified PES to activate transitions in the system. After the transition state, in which the total energy of the system starts to decrease, one can also turn off the repulsive bias and continue normally with energy minimization.

Using local bias potentials has been previously suggested in conjunction with accelerated MD,[4,17] but the RBP method has some fundamental differences. First, the bias potential here is fixed and chosen to be above the saddle point controlling the transition to be made, and thus RBP cannot be used for true dynamical studies. Second, the bias potential does not yield the exact transition path in the original PES. It has to be used as an input trial path in, for example, the NEB method[16] to yield the transition path.

A schematic picture of the minimization with RBP in a 1D case is given in Fig. 1. If the system is initially on top of the new unstable maximum and it is given a random displacement, it will evolve along the modified PES and the final state corresponds to a nearby minimum configuration. To achieve this, it is important that the parameters A and α be chosen such that there are no new local minima in U_{tot}. Increasing A allows the system to overcome large energy barriers, and it should be at least about twice the typical energy scale E of the system, i.e., $A \approx 2E$, but even larger repulsion can be used to go to the final state faster. Increasing α increases the range of repulsion, thus moving the system further away from the initial state. The parameter α should correspond to the distance ℓ from the initial state to the saddle point of the barrier to be crossed over, i.e., $\alpha \approx (\ell/2)$. We note that the bias potential need not be spherically symmetric, either, if some directions are preferred in the search.

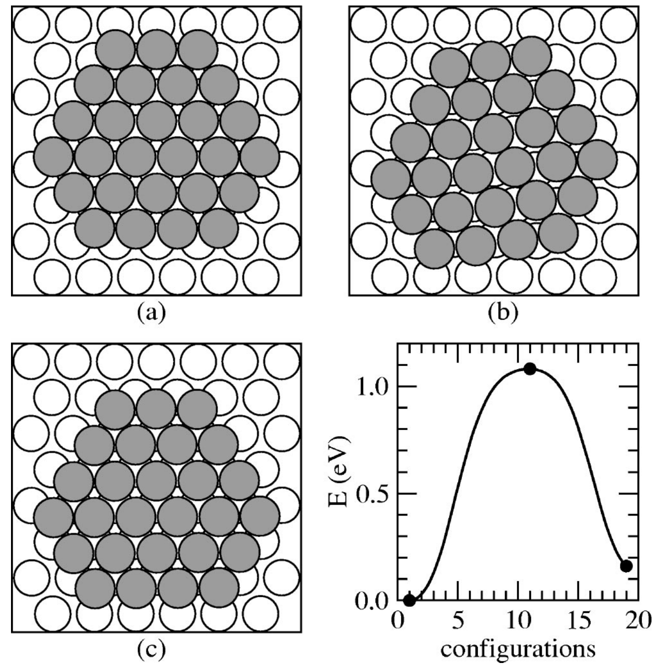

FIG. 2. Concerted motion of a 27-atom Cu adatom island on a Cu(111) surface (cluster atoms are filled and substrate atoms open circles). Only some of the substrate atoms are shown here. The last panel shows the energy profile, the dots represent the energies of the (a) initial, (b) transition, and (c) final states. See text for details.

The RBP method has already been used successfully by us to find transition paths for nucleation of dislocations in 2D strained overlayers.[18] Here we present a more systematic study of the method using three different cases as examples: first a system with an embedded atom model (EAM) potential, second a Lennard-Jones (LJ) system, and finally a system where the PES has been obtained from first-principles (FP) calculations.

The first example concerns activated diffusion of 2D adatom clusters on metal surfaces, which is of great importance in multiscale modeling of thin-film growth. Recent experiments show that even large clusters can show considerable mobility.[19] In a recent paper,[1] cluster diffusion mechanisms were studied using a combination of the EF and NEB methods. As a result many new many-particle mechanisms were discovered, including row shearing and dimer rotation. However, when the number of the atoms in the cluster increases, the EF method becomes unpractical. To this end, we consider a 27-atom Cu adatom island on a Cu(111) surface (see Fig. 2). This is a good test system since it is known that in this geometry there are concerted many-particle mechanisms. The lattice parameter used for Cu is 3.615 Å, and the size of the substrate is four layers and 330 atoms per layer. We use the EAM potential,[20] and the bias potential of Eq. (1) has $A = 100$ eV and $\alpha = 3.2$ Å for all the cluster atoms and the atoms of two topmost surface layers. The random displacements of the active atoms are taken from a MD simulation.

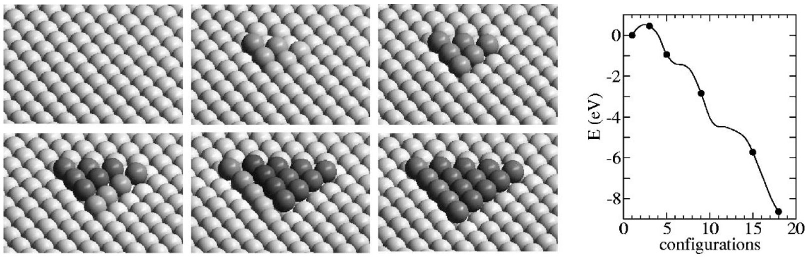

FIG. 3. Emergence of a stacking-fault tetrahedron in the system of five-layer-thick LJ-Pd slab on an LJ-Cu(111) substrate. The LJ-Pd atoms rise on the surface from the slab and are darker here. The energies corresponding to the snapshots are marked by dots in the energy profile (right).

In Fig. 2 we show one of the concerted movements activated by RBP, together with the minimum-energy path as obtained using NEB. The barrier here is in excess of 1 eV, which implies that standard MD simulations at room temperature is not feasible. Notice that the energy of the final state is a little higher than that of the initial state since in the final state the atoms are at the hcp sites while in the initial state they are located at the fcc sites, which is the global minimum state for the fcc(111) geometry.

The second example concerns the nucleation of a misfit dislocation in a strained epitaxial adsorbate layer on a substrate. This problem plays an important role in the formation and stability of thin heterostructures. The system contains five layers of LJ atoms in the fcc(111) geometry with a lattice parameter of 3.615 Å (corresponding to Cu) and a five-layer film with a lattice misfit of $+8\%$ [corresponding to Pd on Cu(111)], each layer containing 160 atoms. The bias parameters in Eq. (1) are $A=100$ eV and $\alpha=4.5$ Å for all the atoms in the film and in the three topmost substrate layers. The activation is done just by moving one LJ-Pd atom at the film-substrate interface. In Fig. 3 we show a series of configurations where a wedge of atoms emerges on the surface when a stacking-fault tetrahedron forms. Structures of the same kind have also been seen in experiments.[21] The minimum-energy path as obtained from NEB is rather complicated, with weak metastable minima along the path. The activation energy here is 0.46 eV.

The third test case concerns CO oxidation on a Pd(111) surface using a FP potential and the FINGER code.[22] In a previous work[23] different transition paths have been calculated for the catalytic oxidation of CO on Pd(111) using plausible final states and NEB. Starting from the most stable initial state in which the O atom is located at a fcc site and the CO molecule at the next-nearest hcp site, process *A* [Fig. 4(a)] led to a barrier of 2.47 eV for CO oxidation.[23] Unfortunately, this energy is larger than the energy of about 2 eV for CO desorption from O precovered Pd(111). The reaction path for this process went over the top site even though the initial guess for the NEB path went around it. This is because the choosing of the final state fixes the possible NEB paths. However, due to the weak interaction between the CO_2 molecule and the Pd(111) surface, the desorption energy being less than 0.1 eV,[23] there is a very large number of possible final configurations for the CO_2 molecule on the surface. Thus, we can generate them using RBP. There is also process *B* in which first CO is moved "by hand" from the hcp to fcc site and then let to react with O at the fcc site [Fig. 4(b)]. Process *B* led to an activation energy of 1.42 eV which is below the CO desorption energy and is a possible transition path for the oxidation reaction.[23]

In this work, we try to locate possible final states and reaction paths for CO oxidation with the most stable initial state using the RBP approach. The bias potential of Eq. (2) with $A=15$ eV and $\alpha=1.7$ Å is chosen for the active atoms of CO and O. The energy profiles of the FP transition paths calculated previously are shown in Fig. 4 together with the repulsive bias added. The important point here is that by choosing the parameters properly one can suppress one channel (process *A*) while allowing other channels (such as process *B*) to be generated in the RBP approach. In Fig. 4(c) we show snapshots of a new CO oxidation process (process *C*) together with the corresponding NEB energy profile generated by the present RBP approach. Unfortunately, even though the activation energy 2.1 eV for the new process *C* is smaller than the value 2.47 eV for the process *A*, it is still above the CO desorption energy[24] and not a likely candidate

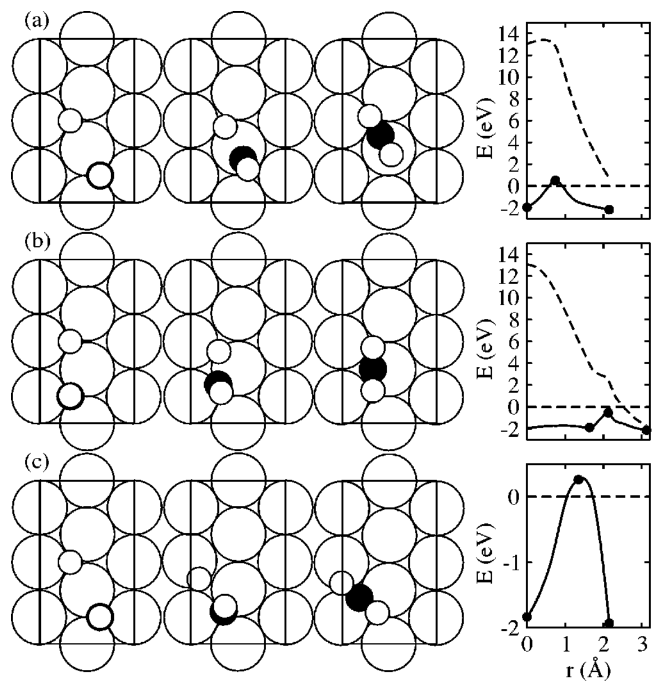

FIG. 4. Snapshots of CO oxidation processes on Pd(111) (from left to right: initial, transition, and final state) together with energy profiles. (a) process *A*, (b) a part of process *B*, and (c) process *C* (see text for details). In snapshots, Pd atoms are represented with large open circles, O atoms with small open circles, and the *C* atom with a small filled circle. In energy profiles, the NEB energy of the process is presented with the solid curve and the dots correspond to the energies of the configurations shown in the snapshots. The dashed energy curves of processes *A* and *B* contain the same repulsive bias. The horizontal dashed lines at zero energy correspond to the energy of CO desorption from O precovered Pd(111).

for a real transition path. Nevertheless, the method provides a valuable tool for calculating transition paths also with FP potentials. With variation of the parameters as well as the form of bias potentials, transition paths such as process *B* or others with even lower barriers can be systematically explored.

Finally, we wish to mention some further technical points regarding the RBP method. First, by making the repulsive bias sufficiently localized around the initial potential minimum, one can activate transitions with the lowest-energy barriers. By changing the parameters one can select different processes to occur, a feature that many other methods do not have. One can easily bias only the atoms that take part in the transition. Doing this in a controlled way requires some prior knowledge or guesswork on the expected transitions, however. The method can be combined with MD simulations (although dynamics will not be correct) and even with FP calculations. The implementation of the bias potential is very easy, and the computational overhead is minimal. The RBP works well together with NEB to determine the exact transition path. The only practical limitations of the method is that the barriers should not be too large or too small for the numerical control of the activation. Overall, even though the present applications only included crystalline systems, we think that the RBP method offers an additional simple, yet powerful tool to activate transitions in any complicated many-particle system.

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