

Exchange processes in the contact formation of Pb electrodes

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Motivated by recent experiments on electrochemically controlled Pb atomic-scale switches we have studied the self-diffusion of Pb on flat and stepped surfaces since diffusion processes play an important role in the growth of metal substrate. Kinetic modelling based on Monte-Carlo simulations using a model potential suggests that exchange processes play an important role in the contact formation at the nanoscale. Periodic density functional theory indeed find that the barriers for exchange diffusion across the steps are significantly lower than for hopping diffusion. The consequences for the contact formation in electrochemically controlled switches are discussed.

Keywords: metal deposition, self-diffusion, DFT, Monte Carlo

I. INTRODUCTION

Recently, an electrochemically controlled atomic-scale quantum conductance switch has been realized, where the position and dynamics of a single (or few) atom(s) decides about the current flow and current switching [1–4]. External control over this degree of freedom is maintained in the experiments by the electrochemical electrode potential. However, the details of the basic atomic switching processes are still not fully understood.

As a possible mechanism, a novel switching mechanism has been suggested that is based on the collective deposition of metal atoms from the electrolyte onto the switch [1, 2, 5]. Still, the exact nature of the collective process was not clarified. Here we report the results of a joint theoretical effort in order to elucidate elementary steps in the collective switching mechanism on an atomic scale and to develop concepts to describe the corresponding processes.

The fundamental elementary process occurring in the switch is the deposition of metal atoms from the electrolyte onto the metallic electrodes and the formation of a contact. The specific metal structure growing on the electrode upon metal deposition is controlled by diffusion processes [6–10]. Hence a crucial part in the modeling of the atomic-scale switch is the determination of metal self-diffusion paths and the corresponding diffusion barriers [11].

As the first step, we performed Monte Carlo simulations [12] of the breaking of contacts in a two-dimensional geometry based on simple model potentials. These simulations provide insights into the statistical nature of the motion of the electrode atoms. In particular, they show how the elementary processes - atoms moving over diffusion barriers - transform into collective many-body processes when the junction is (slowly) closed. These

simulations also suggest that exchange processes play an important role in the contact formation at the nanoscale.

In order to check whether exchange processes indeed occur at realistic electrode surfaces, we have then determined metal diffusion paths using total-energy calculations based on density functional theory (DFT). As the specific metal, we have considered lead which has also been used as an electrode material in the quantum conductance switch [13]. To the best of our knowledge, diffusion processes on stepped Pb surfaces have not been addressed yet by DFT calculations, but by a computational study [14] based on embedded atom potentials.

Note that the controlled formation of nanostructures at metal surfaces is of critical importance not only for the realization of the electrochemical quantum conductance switch, but also for several further applications at surfaces and interfaces, including heterogeneous [15–20] and electro-catalysis [21–23], quantum [24–27] and magnetic data storage [28, 29]. However, in spite of the fact that such important diffusion processes have been studied in detail [30–32], it is fair to say that the atomic level understanding of these processes, in particular at complex, structured surfaces, is still limited. It is also important to note that the formation of the contact in the switch occurs at the electrochemical solid/liquid interface which adds further complexity to the system [33–35].

II. THEORETICAL METHODS

First-principles total energy calculations were performed using a periodic DFT program, the Vienna ab initio simulation package (VASP) [36, 37], employing the generalized gradient approximation (GGA) to describe the exchange-correlation effects, employing Perdew, Burke and Ernzerhof (PBE) exchange-correlation functional [38]. The ionic cores are represented by projector augmented wave (PAW) potentials [39] as constructed by Kresse and Joubert [40]. The electronic one-particle

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wave functions are expanded in a plane-wave basis set up to a cutoff energy of 400 eV.

The specific choice of the functional requires special attention due to the fact that lead is a heavy metal where exchange-correlation and relativistic [41] effects may play an important role. However, while for semiconducting lead compounds the inclusion of exact exchange and spin-orbit coupling is necessary in order to reproduce the correct electronic band structure [42, 43], bulk and surface properties of Pb metal are satisfactorily described using semi-local exchange-correlation functionals [44–46].

Within the supercell approach, the Pb electrodes were modeled by slabs of finite thickness separated by a vacuum region of 20 Å, which is sufficient to neglect the interactions between the periodic slabs. Five layers have been used to describe the Pb(100) and Pb(111) surfaces. For the stepped surfaces, 10 layers for Pb(311), 15 layers for Pb(211) / Pb(511) and 20 layers for Pb(711) surfaces have been used. The optimized position were relaxed until the residual forces were smaller than 0.01 eV/Å using a 3×3 supercell for Pb(111)/ Pb(100) and 1×3 supercell for stepped surfaces. A k-point sampling of 5×5×1 k-points was used to perform the integration over the first Brillouin zone. The convergence of the results with respect to these parameters has been carefully checked. To determine the diffusion paths in the exchange mechanism, the nudged elastic band method (NEB) was employed [47], which is an automatic search routine for finding the energy minimum path between specified initial and final state.

In order to understand the qualitative phenomena related to the closure of a junction, it is both sufficient and most efficient to employ Metropolis Monte-Carlo simulations in canonical ensembles [12], using semi-empirical interaction potentials; hence, we simulated the junction dynamics with a tight-binding second-moment approximation model (TBSMA) also known as the Gupta-potentials [48]. Moreover, the collective phenomena are not specific to three spatial dimensions. They appear already in film geometries, as we see, and hence we concentrate on mono-atomic layers in our simulations,

For numerical efficiency we used a potential truncation scheme using a mixed Verlet list automatically updated by a Cell list [12]. A large cutoff ($\sim 7\times$ nearest neighbor distance) was used to avoid any possible truncation errors. The TBSMA used in our simulations is a true many-body potential which for an N-atom system in principle requires N^2 loops for evaluation of energy. Since we define a unit of Monte Carlo time as $10\times N$ computational steps, our simulations roughly have an approximate computational cost of N^3 for a fixed MC time. Our implementation of the truncation scheme along with a look up table for energy calculations brings down the computational time by a factor of 10, effectively, without introducing visible artifacts. A typical simulation usually involves 10^4 to 10^5 MC steps for equilibration followed by 10^6 MC steps for collection of statistics.

III. RESULTS AND DISCUSSION

A. Monte Carlo simulations

The contact formation dynamics is simulated, starting from initial configurations which are then relaxed/equilibrated for 10000 steps per atom, to avoid any artifacts before collection of statistics begins. To observe the time evolution of contact closure an initial situation will be chosen, where the contact layer consists of a single atom, only. One may think about it as an atom that has been quenched when the electrodes have approached each other in the experimental control cycle. The numerical protocol foresees an adiabatically slow process, so that at every distance for most of the observation time the contact is (nearly) equilibrated.

Figure 1 shows three snapshots showing how a contact forms after the electrodes have quenched a single atom, see initial state Fig. 1A. The contact atom is surrounded by vacancies to the left and to the right. In Fig. 1A a single vacancy on each side is shown; for broader junctions it can be many more. These vacancies cannot be filled easily by surface diffusion of the adsorbate atoms (blue), since the associated barrier height for the process is high. It is true, that also a given exchange process is associated by a large barrier height. However, due to the large number of possible exchange paths, these processes can become compatible and in fact dominate in the situation shown in Fig. 1. This is evident, from Figs. 1B and C that indicate the typical exchange processes that have been responsible for filling the junction in our MC-simulations.

Such two-particle exchange can in fact be viewed as the simplest representative of a class of processes involving N particles and M vacancies (or holes); in the example we have $N=2$, $M=1$. The time evolution of these processes is such that all M vacancies are filled with particles thereby creating M new vacancies at other sites. In a loose way of speaking, one could say that M particles (vacancies) have been moved from old positions into new positions. (Processes with $M=0$ are *ring exchange* processes, i.e. cyclic permutations. Due to the fact that atoms are not distinguishable one from another, these processes are not accompanied with density fluctuations. Therefore, they can be ignored for thermodynamic considerations.)

As our previous study shows, on most flat surfaces only processes with $N,M=1$ are important, because motion of N-particles, in general, involves the breaking of $\sim N$ bonds and therefore very high activation barriers. The situation changes, however, in the presence of transport barriers. Note that the step-edge is only the simplest example. In inhomogeneous situations, internal vacancies can exist that are very difficult to reach, or not at all, for an adsorbate particle via a path, that never leaves the vacuum interface. In such a situation (N,M)-processes can become relevant and may provide the only available route for a particle to fill the vacancy (or equivalently, for the vacancy to merge with the vacuum).

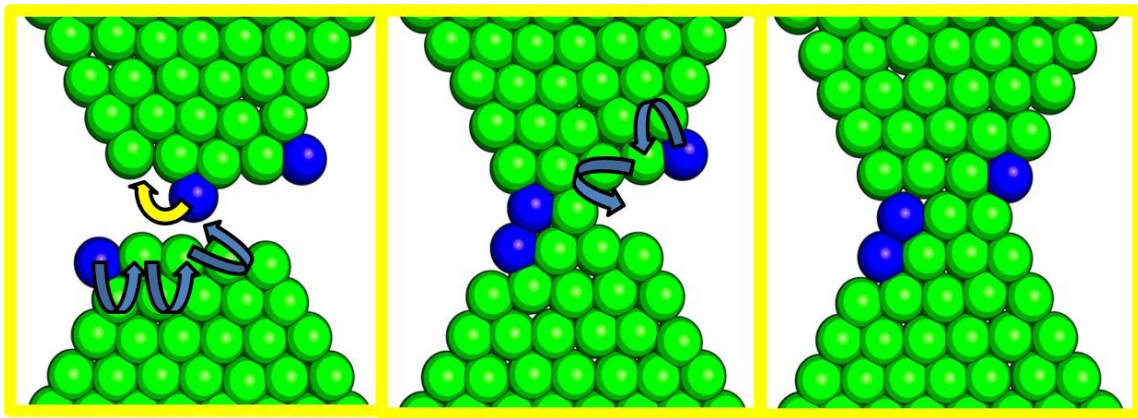


FIG. 1. Three snapshots (A), (B), (C) of a 3-atom junction towards closure: Yellow arrows denote (1, 1) processes while the blue arrow denotes (N, 1), N being number of arrows, whereas the green/blue balls denotes the initial interface-adatoms. The arrows indicate where the atoms would end up in the next frame as a result of these processes. E.g., in going from (A) to (B) we encounter a (1,1) hopping of an adatom and a (3,1) exchange process.

A general quantitative analysis that could illuminate under what precise conditions (N,M) exchange processes with $N > 1$ start to dominate over the simple hopping is challenging. On the one hand, it should comprise an estimate of the height of a multi-particle tunneling barrier that is the characteristic feature of the collective hopping phenomena that we describe here. On the other hand, also required is an enumeration of all those (N,M)-reorderings that share the starting and end-configurations. Summarizing in a symbolic notation, one could say that we have for the thermodynamic weight A_1 of a given (N,1)-exchange process

$$A_1(N) \sim e^{W(N)} e^{-P(N)} \quad (1)$$

with an entropic term $W(N) \simeq w(N)N$ and a hopping barrier for the N-particle process $P(N) \approx \nu(T)N/T$. Microscopic details of the contact enter the prefactors and coefficients of these expressions. They determine the length the typical length of the optimal reorganization paths.

After these general remarks, we study the situation in the following in more detail by analyzing a specific example employing DFT calculations: the diffusion process of Pb-atoms on flat and stepped Pb surfaces.

B. Barriers for Pb self-diffusion

Barriers for self-diffusion of Pb on Pb substrates were calculated based on the importance of diffusion for growth processes. After metal deposition on a surface, the resulting surface structure is determined by the fact whether the deposited atoms propagate further on via diffusion and how facile the diffusion is. Generally speaking, there are two kinds of diffusion mechanisms, the hopping mechanism and the exchange mechanism which are illustrated in Figs. 2 a and b, respectively. The hopping

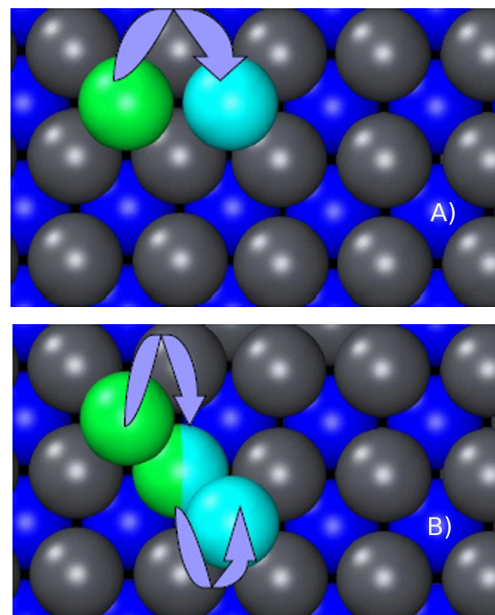


FIG. 2. Illustration of a) hopping diffusion, b) exchange diffusion on a (100) surface.

mechanism is typically considered as the usual mode of the diffusion by which atoms move between the adjacent equilibrium sites. It is mainly operative on closed packed metal surfaces. In the exchange mechanism, the adatom displaces a surface atom which then becomes the adatom. It has typically been observed on (100) surfaces such as Pt(100) [49] or Ir(100) [50]. Whereas in the hopping mechanism the transition state corresponds to the hopping atom in a two-fold coordination, in the exchange mechanism there are two atoms in a three-fold coordination at the transition state on a flat surface. Which mechanism is operative is hence determined by the fact whether one atom in a two-fold mechanism is more fa-

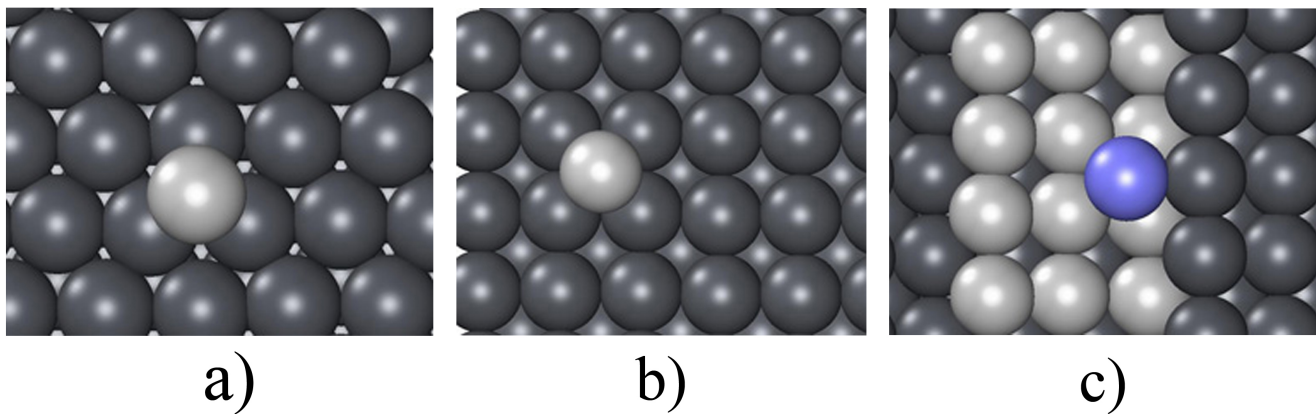


FIG. 3. Optimized adsorption position of a Pb adatom on a) Pb(111) , b) Pb(100), c) Pb(511) according to the DFT calculations.

avorable than two atoms in a three-fold mechanism. Thus the exchange mechanism is operative at flat metal surfaces that favor a three-fold coordination with the three-valent aluminum being the prototypical example. On stepped surfaces, however, the diffusion across a barrier is hindered by the relatively large Schwoebel-Ehrlich barrier while the exchange mechanism might involve rather high-coordinated configurations.

As the first step to address the diffusion paths, we determined the optimum adsorption position of a Pb adatom on flat and stepped Pb surfaces (see Fig. 3). For Pb(111) and Pb(100) we find, as expected, that the equilibrium geometry are the threefold hollow site (Fig. 3) and the fourfold hollow site (Fig. 3b), respectively. On Pb(111), the adatom adsorption height is 2.23 Å, the distance to the nearest neighbors is 3.13 Å which is 12% shorter than the interatomic distance in the bulk. As for Pb(100), the adatom adsorption height is 1.96 Å, and the distance to the nearest neighbors is 3.21 Å which is 9% shorter than the interatomic distance in the bulk. These trends are typical for adsorbed metal atoms and can be explained in terms of the correlation between bond strength and coordination [51].

On Pb(511), the adatom prefers to adsorb at the lower side of the step edge in direct contact with one step atom in an bridge-like site with respect to the atoms of the lower terrace. (Fig. 3 c). Because of this bridge-like configuration, the adsorption height is 3.27 Å with respect to the lower terrace, and the distance between the adatom and the step edge is 3.39 Å. As all other considered (n11) stepped surfaces with odd n have rather similar properties, we focus in the discussion on the (511) surfaces and just report the results for the other stepped surfaces.

Table I shows the diffusion barriers on the flat Pb(100) and Pb(111) surfaces. On the Pb(111) surface, we obtained an energy barrier of only 0.01 eV for the hopping mechanism and 0.11 eV for the exchange mechanism which is about 10 times larger than for the hopping process. But interestingly enough, on Pb(100) the diffusion barrier of the exchange mechanism is 0.47 eV which is 0.17 eV lower than for hopping indicating that the ex-

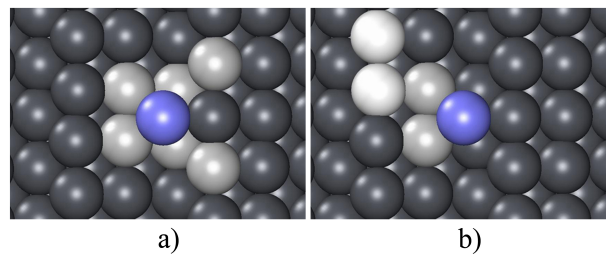


FIG. 4. Surface atoms (in light grey) which might exchange with the adatom (in blue). a) diffusion along the step edge. b) diffusion perpendicular to the step edge. The atoms colored in light grey may be involved in the diffusion across the terrace while the atoms colored in white may be part of the exchange mechanism across the step.

change diffusion is the favorable mechanism on Pb(100).

The diffusion constant is given by the Arrhenius formula: $D = D_0 \exp(-E_d/k_B T)$, where E_d is the diffusion barrier. Many studies show that the prefactor D_0 for exchange diffusion is usually 10-15 times larger than the one for hopping diffusion [52, 53], hence the exchange is obviously favored for Pb(100), which is similar for Au(100). Note that the two atoms exchanging each other are rather close to each other at the transition state, only about 3.15 Å. Furthermore, the dimer is only 1.44 Å above the surface, so that the two atoms can be described as practically being fivefold coordinated. Hence it is obviously this high coordination that makes the exchange diffusion on Pb(100) more favorable than the hopping diffusion.

At stepped surface, the diffusion paths are much more

TABLE I. Diffusion barriers for Pb adatoms on flat Pb surfaces.

Surface	Hopping (eV)	Exchange (eV)
Pb(111)	0.01	0.11
Pb(100)	0.64	0.47

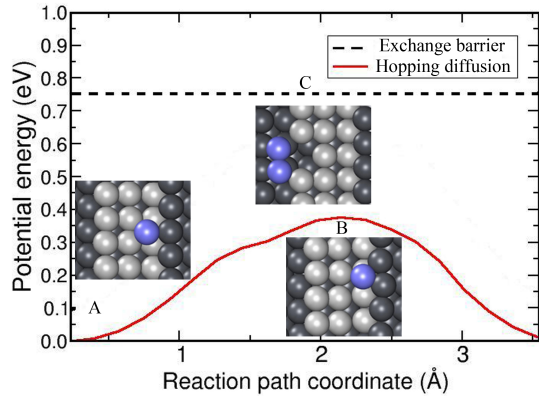


FIG. 5. Minimum energy path of the hopping mechanism for the diffusion along the step at Pb(511). Insets A and B illustrate the initial and transition state of the hopping mechanism. The barrier for the exchange mechanism is indicated by the dashed line, its configuration is shown in inset C.

complex. First of all, one has to distinguish diffusion along the step edge from diffusion perpendicular to the step edge, i.e. across the step edge. For the exchange mechanism along and across the step edge, there are several possibilities. All the atoms in light grey and white in Fig. 4 may be partners in the exchange diffusion of the adatom along and perpendicular to the step.

The minimum energy diffusion paths on Pb(511) are illustrated in Figs. 5 and 6. As shown in Fig. 5, for the diffusion along the step edge, the barrier of hopping diffusion is 0.39 eV lower than for the exchange mechanism. The hopping process occurs close to the step edge (inset B of Fig. 5) and involves some relaxation of the step edge atoms. This relatively low barrier can be explained by the fact that the coordination of the hopping atom does not change significantly along the diffusion path. In the exchange mechanism, on the other hand, the step edge atom has to detach almost entirely from the lower terrace making this mechanism rather unfavorable. The mechanism is quite similar to the diffusion process on Al(110) in the so-called in-channel diffusion [52].

For the diffusion across the terrace perpendicular to the step edge, the exchange mechanism is most favor-

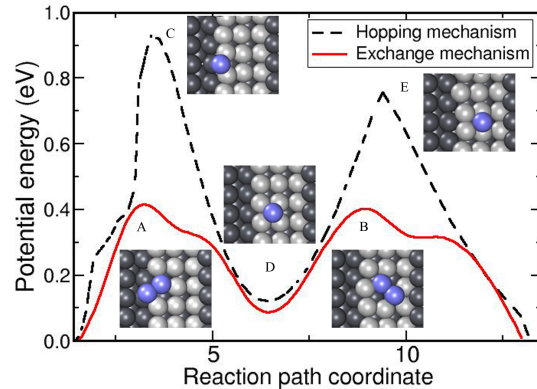


FIG. 6. Minimum energy path of the hopping and exchange mechanisms on Pb(511) across the step edge. Insets A and B show intermediate states of the exchange diffusion whereas insets C and E illustrate intermediate states in the hopping diffusion. Inset D shows the metastable intermediate on the terrace.

able, as Fig. 6 shows. The diffusion in the middle of the terrace is almost the same as the diffusion process on the flat Pb(100) surface with a very similar energy barrier. Across the step edge, the energy barrier for the exchange process is much lower than for the hopping mechanism. The high barrier in the hopping mechanism of 0.93 eV is caused by the low coordination at the transition state, whereas in the exchange process (inset A of Fig. 6), the coordination number of the adatom is only reduced from five at the initial state at the lower edge of the step to four at the transition state leading to a relatively low diffusion barrier.

All calculated diffusion barriers at the considered stepped Pb surfaces, Pb(311), Pb(511) and Pb(711), are listed in Table II. As already mentioned above, all of the stepped surfaces have rather similar properties, as far as diffusion is concerned. Whereas along the steps the hopping mechanism is favored, across the steps the diffusion occurs in a exchange mechanism. These results are in qualitative agreement with previous calculations using the embedded atom method [14]. As a consequence, the diffusion barriers along and across the steps do not differ substantially facilitating the particle transport on the surface.

Upon changing the electrode potential and thus the charge state of the surface, a new equilibrium structure of a nanostructured electrode might result [54, 55]. To assume the new equilibrium configuration, deposition and transport processes have to occur. It is true that also the diffusion barriers can vary as a function of the electrode potential [56, 57], and we are currently addressing this issue in an ongoing project. Also the structure of the aqueous electrolyte at stepped surfaces is modified compared to flat electrodes [58, 59]. However, it has been estimated from the dipole moments of the diffusing metal

TABLE II. Diffusion barriers at stepped Pb surfaces for diffusion along the steps (para) and across the steps (perp).

Surface	Hopping (eV)	Exchange (eV)
Pb(311)para	0.33	0.36
Pb(311)perp	0.95	0.57
Pb(511)para	0.36	0.75
Pb(511)perp	0.93	0.41
Pb(711)para	0.37	0.73
Pb(711)perp	0.97	0.56

particles in the initial and the transition state that diffusion barrier do not change substantially as a function of the electrode potential [57]. Thus the already rather low diffusion barriers for Pb self-diffusion on flat and stepped surfaces enable fast structural changes upon changing the equilibrium conditions. Hence our results are consistent with the proposed atomic mechanism occurring in the electrochemically controlled atomic-scale quantum conductance switch [1, 5, 13].

IV. CONCLUSIONS

In a combination of Monte Carlo simulations and first-principles electronic structure calculations we have addressed elementary processes that may be relevant in the collective switching mechanism occurring in the atomic-scale quantum conductance switch. The Monte Carlo simulations using a model potential exchange processes and in fact more generalized versions of them can play an important role in the closing dynamics of junctions with large conductances. The DFT calculations indeed

revealed that diffusion processes across the step edges of nanostructured surfaces are facilitated through the exchange mechanism making diffusion across the steps almost as facile as along the steps.

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