

ATOMISTIC STUDIES OF MANIPULATION, GROWTH AND DIFFUSION ON FCC METAL SURFACES

by

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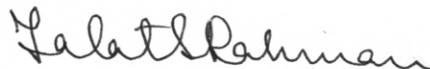
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ABSTRACT

In this dissertation I present an extensive study of several issues related to manipulation, growth and diffusion of atoms and nanoclusters on fcc metal surfaces. One of the important aspects in understanding the effect of adatoms or clusters or even the effect of a tip is to examine the energy landscape of the surface in the presence of these objects. In our study of lateral manipulation using a tip, the use of the Grid method to obtain the energy landscape, has revealed useful information about the shift in the saddle point. Calculations on homogeneous as well as heterogeneous fcc(111) metal systems have been performed. Vertical manipulation on flat, stepped and kinked surfaces have given interesting results about the ease of manipulation on these surfaces. During growth, atoms at the edges of stepped surfaces experience an effect called the Kink Ehrlich Schwoebel Effect (KESE). Fluctuations that occur along the step edges play an important role in island decay for islands in the vicinity of a step edge, as observed in many experiments. Our standard Kinetic Monte Carlo (KMC) study on the vicinals of Cu(001) systems has shown that the KES barrier is in fact responsible for the ledge morphology that we see in our systems. To investigate cluster diffusion on fcc(111) systems which are more complex due to the occurrence of two types of step edge microfacets ((100) and (111)) in them, a KMC technique involving a unique pattern recognition scheme was developed to classify the environment of an atom. The energy barriers for different mechanisms were calculated extensively for Cu/Cu(111) as well as Ag/Ag(111) systems, using the NEB. The intriguing results obtained for these two-dimensional clusters, show

magic cluster sizes having much lower diffusivity at 300 K as compared to the general clusters. The dependence of the diffusion coefficient on temperature as well as size of cluster has also been explored. Diffusion prefactors play an important role in the diffusion mechanisms. Most of the KMC studies assume a fixed prefactor. However, realistically this is not true. To get an understanding of the prefactors and their ratios for the important mechanisms, a study on the Ag/Ag(111) system shows that the ratio of the prefactors for step edge to terrace diffusion > 1 , at low temperatures, which is in agreement with experimental observations. A molecular dynamics (MD) study was also performed to get an understanding of the initial evolution of certain clusters and the important mechanisms involved. All these investigations have given us a deep insight into several intriguing surface phenomena, observed in experiments and theoretical simulations.

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LIST OF PUBLICATIONS

This Dissertation embodies results presented in the following 5 publications:

1. C. Ghosh, A. Kara, and T. S. Rahman, *Theoretical aspects of vertical and lateral manipulation of atoms*, Surf. Sci. 502-503, 519 (2002).
2. M. Rusanen, I. T. Koponen, T. Ala-Nissila, C. Ghosh, and T. S. Rahman, *Morphology of ledge patterns during step flow growth of metal surfaces vicinal to fcc(001)*, Phys. Rev. B 65 (Rapid Comm.), 041404 (2002).
3. Z. Chvoj, C. Ghosh, T. S. Rahman, and M. C. Tringides, *Prefactors for interlayer diffusion on Ag/Ag(111)*, J. Phys.: Condens. Matter 15 (2003) 5223-5230.
4. C. Ghosh, A. Kara, and T. S. Rahman, *Comparative study of adatom manipulation on several fcc metal surfaces*, to be submitted to Phys. Rev. B.
5. C. Ghosh, A. Kara, and T. S. Rahman, *Diffusion of small Cu 2D clusters on Cu(111): A Kinetic Monte Carlo study*, to be submitted.

Work on the following publication has not been presented.

6. A. N. Al-Rawi, A. Kara, P. Staikov, C. Ghosh and T. S. Rahman, *Validity of the Quasi Harmonic Analysis for the Surface Thermal Expansion of Ag(111)*, Phys. Rev. Lett. 86, 2074 (2001).

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Chapter 1

Introduction

Nanotechnology has been one of the most rapidly expanding areas of research in the past few years. With the exceptional quality of research being conducted in physics, chemistry and engineering, the boundaries of research in this area are widening with accelerated pace. Many trace the roots of modern nanotechnology and nanomaterials to a 1959 talk given by Dr. Richard Feynman at a meeting of the American Physical Society, where Feynman proposed the all-too-simple hypothesis that there was “plenty of room at the bottom.” He speculated that future scientists and engineers would build complex structures from atoms and molecules by saying: “Upto now we have been content to dig in the ground to find minerals, ... ultimately in the great future we can arrange the atoms the way we want.” It wasn’t until 1974 that the field was given the name “nanotechnology” however, and that is widely attributed to University of Tokyo researcher Norio Taniguchi. He made the distinction between engineering at the micrometer scale (the basis for modern microelectronics that was just starting to hit its stride in the 70s) and the new field of sub-micrometer engineering that was beginning to emerge. Nascent nanotechnology began to “grow up” and enter the mainstream consciousness in the mid-1980s with work by Richard Smalley at Rice University on what would be called Buckminster Fullerenes (now famously known as “Buckyballs”) and MIT researcher K. Eric Drexler’s publication of “The Engines of Creation.” By the early 1990s, nanotechnology’s capabilities

could not only image and probe atomic structures, but move individual atoms, one at a time, around on a substrate.

One of the first tools used for nanomaterials investigation was the scanning tunneling microscope (STM), developed by Gerd Binnig and Heinrich Röhrer at IBM in 1981 (Nobel Prize in 1986.) The STM formed the basis for what would later become a family of scanning probe tools, or scanning probe microscopy (SPM). The other most widely used member of the SPM family is the atomic force microscope (AFM). Similar to the STM, it uses an atomically sharp tip, but instead of carefully moving it just angstroms from the sample, the AFM actually drags its tip along the sample's surface.

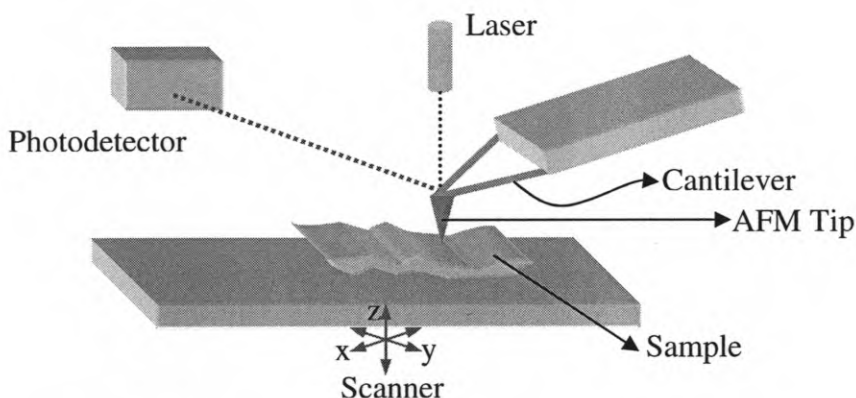


Fig. 1.1 The basic components of an Atomic Force Microscope

During the past few years great effort has been devoted to the fabrication of nanostructures on metal and semiconductor surfaces. The research has been focused on the variety of structures that can be produced, either by serial processes such as atom manipulation with the tip of an STM [1-4] or by parallel techniques such as self-organized growth [5, 6]. At present, modern integrated

circuits contain structures with a lateral extension of 0.2 μm that are only a few atoms thick. However, many of the nanoscale structures formed during nucleation and growth are only metastable and their stability is often a limiting factor for scientists' ability to synthesize new structures. To enlighten the mechanisms involved in stability, by accurate modeling, starting from the basic interactions between the constituent entities is a prerequisite to eventually control the fabrication of nanoscale devices. Thus, studies of surface morphologies and the changes that occur in the surface morphologies that were deliberately created in conditions far from equilibrium or due to thermal fluctuations are also being widely investigated. These include studies of epitaxial growth, island decay, diffusion and evolution of nanoclusters, their equilibrium shapes etc., which in turn give insight into the novel properties of these low-dimensional structures. The growth of surface structures, their patterns and instabilities are challenging topics of research and can provide a great amount of insight for the manufacture of surface structures with controlled properties having specific applications. For example, manufacture of modern computer chips requires the knowledge of surface growth on semiconductor materials. One of the well known experimental techniques for thin film growth is Molecular Beam Epitaxy (MBE). Its main advantage is the ability to control the growth process at the atomic scale (below 10^{-7} meters). However, during the growth process surfaces are often subject to instabilities leading to non-uniform layers. It is thus important to gain a good understanding of the processes leading to these phenomena such as instabilities, ledge morphology, and step fluctuations in order to suppress them during growth.

Stability of surface steps is important in step-flow growth (at high temperatures, the adatoms are more mobile and adhere to substrate steps) since step instabilities eventually lead to the break down of the step flow mode, leading to the formation of three dimensional structures [7]. Theoretical models have been constructed to try and get a detailed understanding of the mechanisms that lead to such mound formation, which eventually restrict the growth of smooth steps [8-14], and the predictions are used to guide experimental work. Most of these models are based on Monte Carlo simulations and more recently the Kinetic Monte Carlo technique. Thus, the key to understanding epitaxial growth, is the identification and elucidation of the different processes that control the evolution and morphology of the surface, the mechanisms that lead to diffusion, phenomena such as mound formation, and the energetics that control these effects. Diffusion processes are of technological importance for growth of patterned substrates and for self-organized growth of low dimensional structures like quantum wires and dots. One of the elementary phenomena in the determination of surface structures and dynamics is the diffusion of adatoms and two dimensional atom clusters. Detailed work by several groups is being conducted in this area to determine the barriers for the various processes leading to diffusion and the more complex mechanisms such as concerted motion (motion of a group of atoms together) of clusters [15-18]. Another aspect in nanostructuring and epitaxy is that of atom manipulation. This technique has created a breakthrough in the field of nanotechnology as mentioned earlier, giving us the ability to manipulate individual atoms to create desired nanostructures. STM experiments are also used

to study diffusion mechanisms that occur on surfaces. Experimental work in this direction [19,20], reveal some interesting details related to growth and diffusion and the kinetics of rapid decay of islands. These indepth studies raise a whole lot of questions, such as how does the presence of a tip alter the potential energy surface of a system, how do the presence of irregularities such as steps and kinks affect the manipulation of atoms, why do instabilities along step edges occur, the energetics and types of mechanisms that are responsible for the diffusion of nanoclusters, what is the role of temperature in diffusion and the diffusion prefactors that are implicit in the mechanisms. Some of the earlier work in this area has tried to answer such questions on the basis of simpler approaches of barrier calculation such as the drag method. The ledge morphologies have been attributed to the Bales-Zangwill instability. Observations of diffusion of nanoclusters have shown dendritic, triangular evolution etc., and to explain the reasons behind these, detailed and elaborate theoretical calculations are needed. Several important issues that play a role in the diffusion process, such as prefactors and ratios between prefactors of several mechanisms need to be explored. Theoretically these studies are being conducted using various techniques like molecular dynamics (MD), kinetic Monte Carlo (KMC) and even a combination of the two for better efficiency of the simulations and a more realistic approach.

This dissertation is an attempt to answer some of these basic yet important questions that could help provide an explanation for these intriguing observations mentioned above and guide future experimental work in these areas. Among the

issues investigated are lateral and vertical manipulation of adatoms which are the two basic modes of manipulation used in experiments. Since during manipulation on surfaces, the tip usually gets coated with the substrate material, we have performed our simulations for several stepped fcc(111) metal surfaces using tips of the same composition and also two heterogeneous cases, that have revealed interesting results. Our study also includes step flow growth of metal surfaces vicinal to fcc (001), where the morphology of ledge patterns is analyzed, which gives us an understanding of the mechanisms responsible for such instabilities during growth. Here, Monte Carlo (MC) simulations of a lattice gas model are performed and the systems used in this study are vicinals of Cu(001). To understand the behavior of nanoclusters in the post-deposition mode, we have examined the diffusion of small Cu clusters on Cu(111) surfaces, where the center-of-mass diffusion is examined for different cluster sizes ranging from 10 to 38 atoms. This range covers the smallest sizes that can be classified into types such as a perfect regular hexagon, $6n+3$ etc. and we can get an understanding of whether certain shapes and sizes affect the diffusivity of the clusters in certain categories. Also, calculations for larger cluster sizes, ranging from 55 to 1000 atoms have been performed to try understanding the scaling of the diffusion coefficient with orders of magnitude in size. A study of the ratio of diffusion prefactors for terrace and step edge diffusion for a Ag/Ag(111) system has also been conducted to try understand how interlayer diffusion controls the transfer of atoms between layers in a film and whether the growth process is layer-by-layer or two-dimensional.

The rest of the dissertation is organized as follows. Chapter 2 contains an outline of crystallographic structures and the basic models used in our simulations. Chapter 3 contains a brief summary of theoretical concepts used in this work and a discussion of the theoretical methods and techniques that have been employed in this study. Chapters 4,5,6, and 7 contain the details of the work done on adatom manipulation, morphology of ledge patterns during step flow growth, analysis of prefactor ratio and diffusion of nanoclusters respectively. Chapter 8 discusses future directions. And finally, the summary and conclusions are presented in Chapter 9.

Chapter 2

Crystal structure and model systems

The physical structure of a solid is essentially described by the arrangement of the atoms, ions or molecules which make up the solid. A crystalline solid consists of atoms arranged in a regular periodic array or “lattice”.

The crystal structure for most elemental metals is a close packed structure which is either body-centered cubic (bcc), face-centered cubic (fcc) or hexagonal closed packed (hcp). In our work, we have considered the fcc crystal structure where the atoms or ions of a solid are placed at each corner, as well as on the center of each face of the unit cubic cell. Thus, I would like to illustrate these structures by appropriate figures as shown below.

2.1 The Basic Crystal Structures

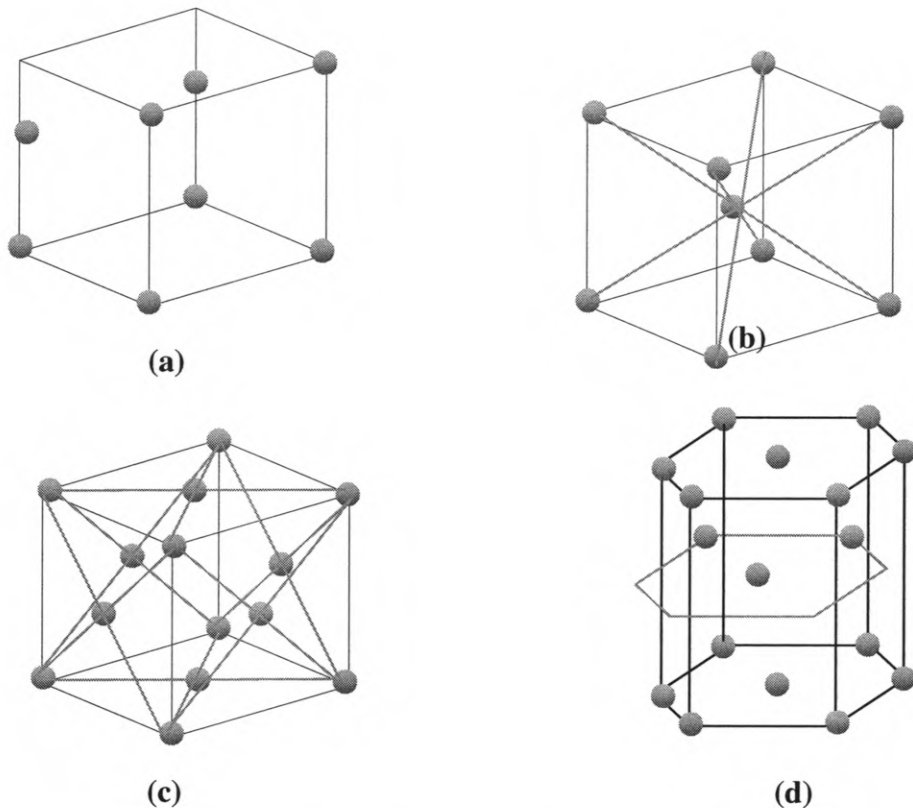


Fig. 2.1 (a) Simple cubic (SC), (b) Body-centered cubic (BC), (c) Face-centered cubic (FCC), (d) Hexagonal closed packed (HCP)

2.2 Miller Indices for crystal directions and planes in a cubic unit cell

Many times we wish to discuss a particular crystal direction or more importantly, a particular plane of atoms within the crystal lattice structure. To do this, a universally accepted system of indices has been developed to describe the crystallographic directions and orientation of crystallographic planes and crystal faces relative to crystallographic axes. This convention is called the system of Miller indices.

For cubic crystals the crystallographic directions are the vectors originating at the origin of the coordinate system of the unit cell and pointing at a defined point in the unit cell. The directions are valid beyond the unit cell and are always reduced to the smallest integers. They are denoted by three numbers (in x, y, z-directions) enclosed by square brackets, e.g. [111], with no commas between numbers. A negative direction index is written with a bar over the index. For example, the indices for the directions with components $(-1, -1, 0)$ and $(-\frac{1}{4}, 1, 0)$ are respectively, $[\bar{1}\bar{1}0]$ and $[\bar{1}40]$. In the second example the components are multiplied by 4 to reduce the coordinates to the smallest integers. Some lattice directions in a cubic crystal are shown in Figure 2.2 If lattice directions are equivalent under the symmetry of the crystal, they form a family of directions. For example, the following cubic edge directions are crystallographically equivalent. Hence they form a family of lattice directions.

$$[100], [010], [001], [\bar{1}00], [0\bar{1}0], [00\bar{1}] \equiv \langle 100 \rangle$$

In a similar way, Miller Indices are a symbolic vector representation for the orientation of an atomic plane in a crystal lattice and are defined as the reciprocals of the fractional intercepts (with the fractions reduced) which the plane makes with the crystallographic axes of the cubic unit cell. Thus a cubic crystal plane with intercepts $(\frac{1}{2}, 1, 1)$, is called a (211) plane after the fractions have been reduced. Some of the cubic crystal planes are represented in Figure 2.3 There is a notation to identify a family of lattice planes which are equivalent crystallographically. For example, the (100), (010), and (001) are equivalent in a

cubic crystal under the symmetry of the crystal, and are collectively specified as the $\{100\}$ planes.

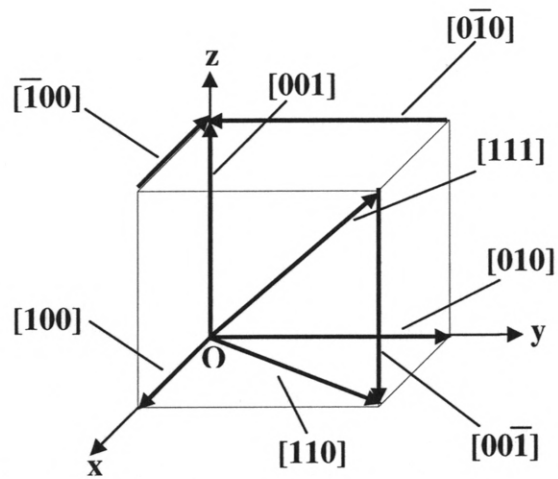


Fig. 2.2 Indices of lattice directions in a cubic crystal.

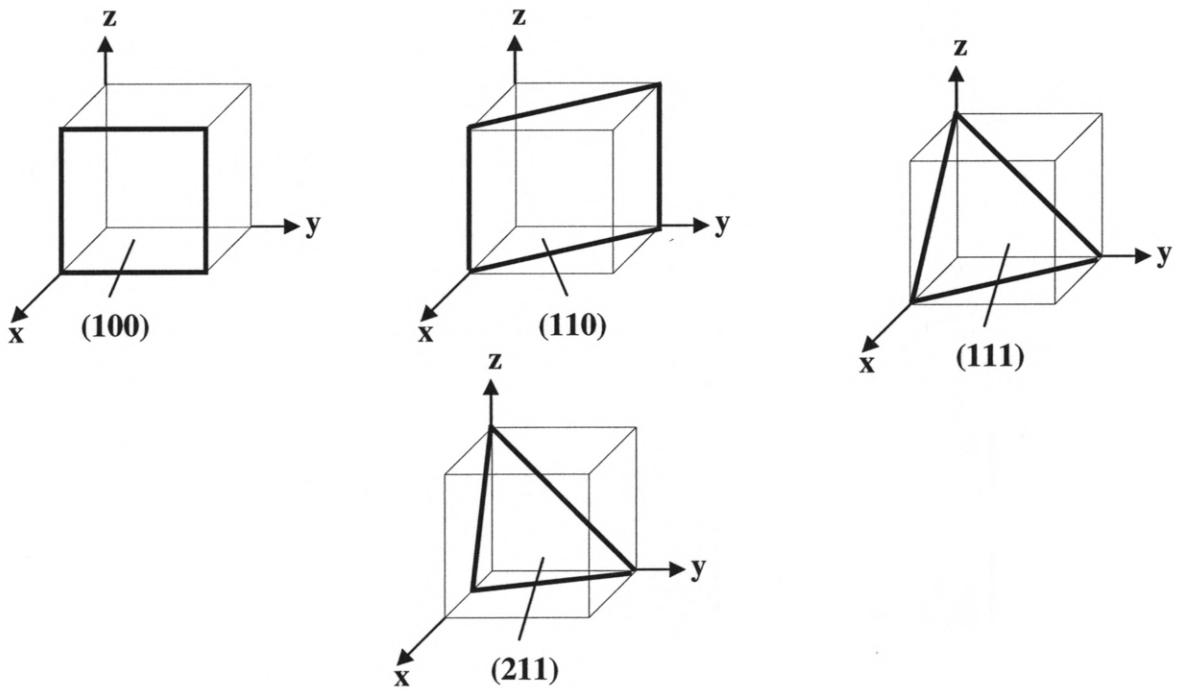


Fig. 2.3 Miller indices of lattice planes in a cubic crystal

2.3 Structures of model systems used

Since the systems studied in this work are mainly the (100) and the (111), and vicinals of the (100) surface, I would like to illustrate the structures for the same.

As can be understood from the above Figure 2.3, the arrangement of atoms on a (100) and (111) surface are as follows:

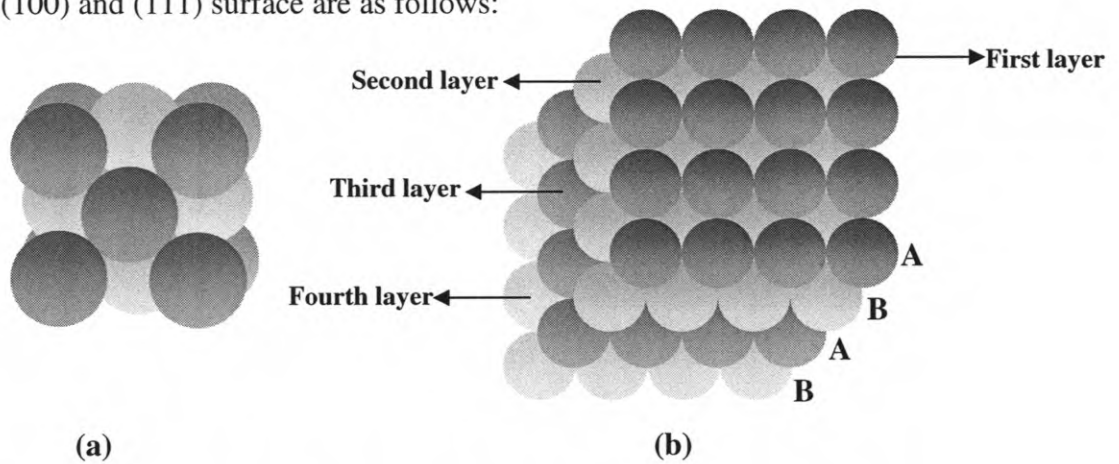


Fig. 2.4 (a) FCC unit cell - (100) face, (b) Stacking of atoms in the (100) surface

In Figure 2.4 (b), with a 45° rotation of (a), one can visualize the 4-fold rotational symmetry of the surface layer atoms. The stacking of the atoms follow the ABABAB... pattern.

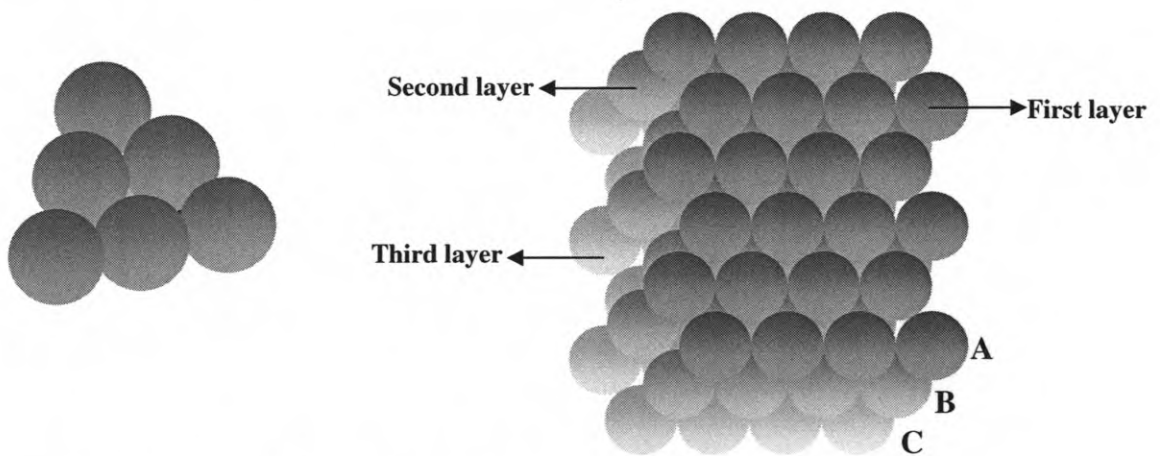


Fig. 2.5 (a) FCC unit cell - (111) face, (b) Stacking of atoms in the (111) surface

Figure 2.5 (a) is the (111) face of the fcc unit cell. There is an atom sitting behind the triangle of atoms which is not visible through the front face of the triangle. Figure 2.5 (b) shows the hexagonal packing of the (111) surface atoms, which follow an ABCABC... stacking pattern. Since this is the most efficient way of packing atoms within a single layer it is known as “close packed”.

For a stepped (111) surface, there are two ways in which steps can occur on the surface. They are shown below. The microfacet can be either a (100) (A-type) step or a (111) (B-type) step. A kinked surface is basically an irregularity along a step edge which causes the step edge to become rough with kinks instead of a smooth straight ledge.

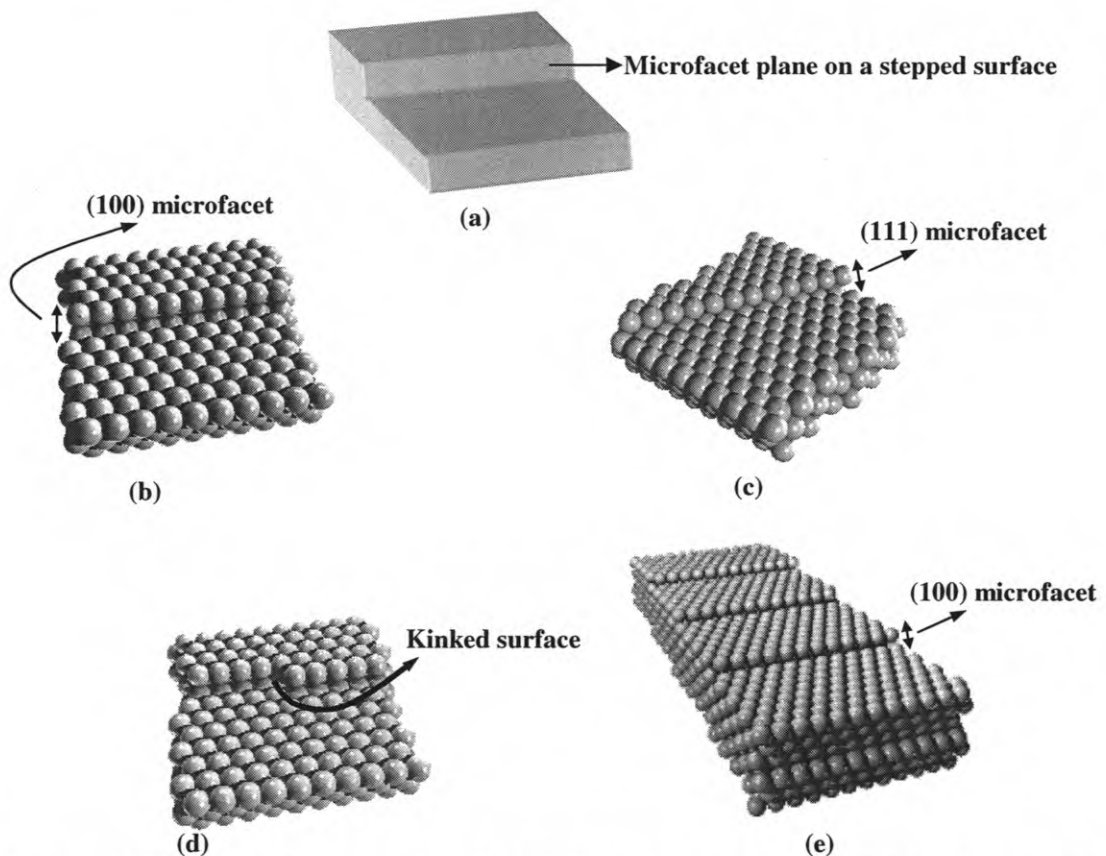


Fig. 2.6 (a) Microfacet on a stepped surface, (b) (100) microfacet on a stepped (111) surface, (c) (111) microfacet on a stepped (111) surface, (d) Kinked (111) surface with a (100) microfacet, (e) (1 1 17) surface, vicinal of (001).

In our work on atom manipulation, we have used tips of two crystal orientations, the (100) and the (111), and also looked at the relaxations of the tip atoms. To get a better visualization I have illustrated these structures below:

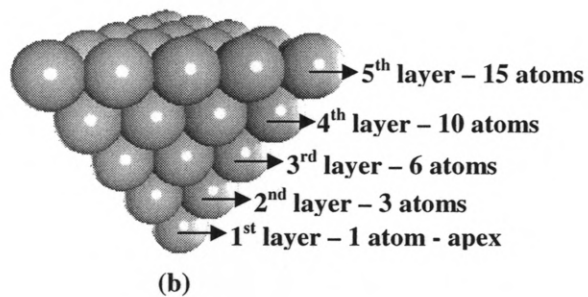
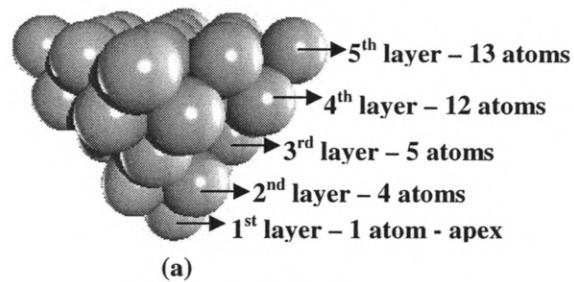


Fig. 2.7 (a) (100) Sharp tip, (b) (111) Sharp tip

Chapter 3

Theoretical techniques

We have used several different theoretical techniques in our calculations of atomic manipulation, evolution of step morphology during epitaxial growth and the diffusion of two dimensional Cu nanoclusters on Cu(111). In the following, I give a brief description of these techniques and of some relevant theoretical concepts.

3.1 Molecular statics calculations

In our work on atom manipulation, to obtain the potential energy surface of the system in the presence of the tip, we have used molecular statics calculations where energy minimization is performed on the system. A description of this technique is provided below.

Molecular statics (MS) calculations is a simple technique that can be used to estimate activation energies for diffusion of various possible processes. In these calculations the total energy of a system of atoms is minimized as a function of all the atom coordinates. It is an iterative process in which, at each iteration, the forces on all atoms are calculated and the atoms are moved in a certain direction of the force over a distance proportional to the force. The process is repeated until the system energy difference between two consecutive moves is smaller than a preset small number [see Ref. 21]. The number of iterations needed for the system to converge depends strongly on the choices of the direction and the proportionality constant in the direction. If these are not correctly chosen,

convergence may be reached either only very slowly (because the atoms hardly move) or the system may start to oscillate because the adjustments overshoot. Thus, speeding up convergence was the focus in the past. Use of the conjugate gradient method [22] has simplified evaluation of the direction and proportionality constants at each iteration. Since thermal vibration of atoms is not taken into account in MS calculations, the activation energies calculated are for the case of $T = 0$ K.

3.1.1 Energy Minimization

Any system always attempts to minimize its total energy and fall to its minimum energy configuration. For example, in the study of adatom manipulation, an adatom, in the presence of a tip is attracted towards the tip and tries to minimize its energy by reaching a corresponding lattice site in the direction of the tip, or attaching itself to the tip apex, thus acquiring the maximum coordination possible and consequently minimizing its total energy. In order to simulate this in our study, we use certain computational routines to minimize the total energy of the system, the details of which are given below.

Energy minimization is one of the basic procedures of molecular modeling. It is a "static" approach, which does not yield information about the motions of atoms. Rather, energy minimization takes a given set of coordinates that describe a conformation of the system and calculates the potential energy and the gradient of the potential energy (which yields the force on each atom). This

information is used to generate a new set of coordinates that are used as input, and the process is repeated until the potential energy is minimized.

An extremum (maximum or minimum point) can be either *global* (truly the highest or lowest function value) or *local* (the highest or lowest in a finite neighborhood and not on the boundary of that neighborhood). (See Fig. 3.1) Finding a global extremum is, in general, a very difficult problem. Two standard heuristics are widely used: (i) find local extrema starting from widely varying starting values of the independent variables and then pick the most extreme of these (if they are not all the same); or (ii) perturb a local extremum by taking a finite amplitude step away from it, and then see if your routine returns you to a better point, or “always” to the same one. Relatively recently, so-called “simulated annealing methods” have demonstrated important successes on a variety of global extremization problems.

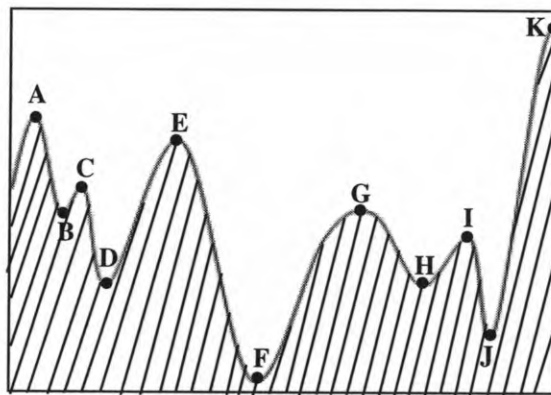


Fig. 3.1. Extrema of a function in an interval. Points A, C, E, G and I are local, but not global maxima. Points B, D, H and J are local, but not global minima. The global maximum occurs at K, which is on the boundary of the interval so that the derivative of the function need not vanish there. The global minimum is at F.

In the absence of any information about the function $F(\mathbf{x})$, the optimum direction to move from a point $\mathbf{x}_I$ towards minimizing the function is just the steepest-descent direction $\mathbf{g}_I$ given by

$$g_1 = -\left. \frac{\partial F}{\partial x} \right|_{x=x_1} \quad (3.1)$$

It is assumed that the direction of steepest descent at the point $\mathbf{x}_1$ can be obtained from the negative of a gradient operator $\mathbf{G}$ acting on the vector $\mathbf{x}_1$, so that

$$\mathbf{g}_1 = -\mathbf{G}\mathbf{x}_1 \quad (3.2)$$

To reduce the value of the function $F(\mathbf{x})$, one should move from the point $\mathbf{x}_1$ in the steepest-descent direction $\mathbf{g}_1$ to the point $\mathbf{x}_1 + b_1\mathbf{g}_1$, where the function is a minimum. This can be done by sampling the function $F(\mathbf{x})$ at a number of points along the line $\mathbf{x}_1 + b\mathbf{g}_1$ in order to determine the value of b at which $F(\mathbf{x}_1 + b\mathbf{g}_1)$ is a minimum. Alternatively, if the gradient operator $\mathbf{G}$ is accessible, the minimum value of the function along the line $\mathbf{x}_1 + b\mathbf{g}_1$ can be found by locating the point where the gradient of the function is orthogonal to the search direction, so that $\mathbf{g}_1 \cdot \mathbf{G}(\mathbf{x}_1 + b_1\mathbf{g}_1) = 0$. It should be noted that this process minimizes only the value of the function along a particular line in the multidimensional space. To find the absolute minimum of the function $F(\mathbf{x})$, one must perform a series of such line minimizations. Thus the vector $\mathbf{x}_1 + b_1\mathbf{g}_1$ is used as the starting vector for the next iteration of the process. This next point is conventionally labeled $\mathbf{x}_2$ so that the subscripts label the iterations of the minimization process. The steps described above can be used to generate a series of vectors $\mathbf{x}_m$ such that the value of the function $F(\mathbf{x})$ decreases at each iteration. Hence, $F(\mathbf{x}_l) < F(\mathbf{x}_k)$ for $l > k$. Each iteration reduces the value of the function $F(\mathbf{x})$ and moves the trial vector $\mathbf{x}_m$ towards the vector that minimizes the function. However, there is no guarantee

that the minimum will be reached in a finite number of iterations. In many cases, a very large number of iterations are required to reach the minimum of the function. The method of steepest-descent performs particularly poorly when the minimum of the function lies in a long narrow valley. The reason for the poor performance in this case is that each steepest-descent vector is orthogonal to the steepest-descent vector of the previous iteration. If the initial steepest-descent vector does not lie at right angles to the axis of the valley, successive vectors will point across rather than along the valley, so that a large number of iterations will be needed to move along the valley towards the minimum of the function. This problem is overcome by using the conjugate gradient method. Also, the rate of convergence of the steepest descent method is limited by the fact that after a minimization is performed along the given gradient direction, a subsequent minimization along the new gradient reintroduces errors proportional to the previous gradient. If the only information one has about the function $F(x)$ is its value and gradient at a set of points, the optimal method would allow one to combine this information, so that each minimization step is independent of the previous ones. To accomplish this, one must first derive the condition that makes one minimization step independent of another.

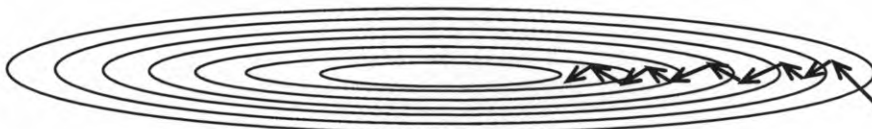


Fig 3.2 Steepest descent method in a long, narrow “valley.” It is an inefficient strategy, taking many steps to reach the valley floor.

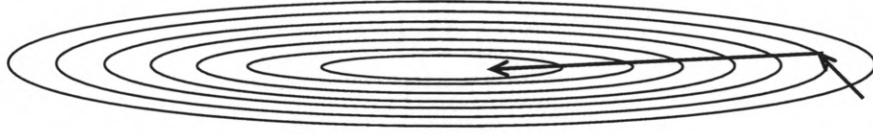


Fig 3.3 The method of Conjugate Gradient – only two steps are required to find the minimum

For simplicity, consider a symmetric and positive-definite function of the form

$$F(x) = \frac{1}{2} x \cdot G \cdot x, \quad (3.3)$$

where, G is the gradient operator. Consider now the minimization of $F(x)$ along some direction d_1 from some point x_1 . The minimum will occur at $x_2 = x_1 + b_1 d_1$, where b_1 satisfies

$$(x_1 + b_1 d_1) \cdot G \cdot d_1 = 0 \quad (3.4a)$$

This is obtained by differentiation of equation (1.3) with respect to b_1 at x_2 . A subsequent minimization along some direction d_2 will then yield $x_3 = x_2 + b_2 d_2$, where, b_2 satisfies

$$(x_1 + b_1 d_1 + b_2 d_2) \cdot G \cdot d_2 = 0 \quad (3.4b)$$

However, the best choice of b_1 and b_2 for the minimization of $F(x)$ along d_1 and d_2 is obtained from the differentiation of equation (1.3) with respect to both b_1 and b_2 at x_3 . This gives

$$(x_1 + b_1 d_1 + b_2 d_2) \cdot G \cdot d_1 = 0 \quad (3.5a)$$

and

$$(x_1 + b_1 d_1 + b_2 d_2) \cdot G \cdot d_2 = 0 \quad (3.5b)$$

It is clear that in order for equations (1.4) and (1.5) to be consistent, and consequently for the minimization along d_1 and d_2 to be independent, one must require that

$$d_1 \cdot G \cdot d_2 = d_2 \cdot G \cdot d_1 = 0 \quad (3.6)$$

This is the condition that the directions d_1 and d_2 be *conjugate* to each other (see [23]) and can be immediately generalized to

$$d_n \cdot G \cdot d_m = 0 \quad \text{for } n \neq m \quad (3.7)$$

The conjugate gradient technique provides a simple and effective procedure for implementation of such a minimization approach. The initial direction is taken to be negative of the gradient at the starting point. A subsequent conjugate direction is then constructed from a linear combination of the new gradient and the previous direction that minimized $F(x)$. In a two-dimensional problem, it is clear that one would need only two conjugate directions, and this would be sufficient to span the space and arrive at the minimum in just two steps, as shown at the bottom of Figure 3.3. It is less clear however, that the current gradient and the previous direction vector would maintain all of the information necessary to include minimization over *all* previous directions in a multidimensional space. The proof that directions generated in this manner are indeed conjugate is the important result of the conjugate gradient derivation. The precise search directions d_i generated by the conjugate gradient method, are obtained from the following algorithm:

$$d_m = g_m + \gamma_m d_{m-1}, \quad (3.8)$$

where,

$$\gamma_m = \frac{g_m \cdot g_m}{g_{m-1} \cdot g_{m-1}}, \quad (3.9)$$

and $\gamma_1 = 0$

Since minimization along the conjugate directions is independent, the dimensionality of the vector space explored in the conjugate gradient technique is reduced by 1 at each iteration. When the dimensionality of the function space has been reduced to zero, there are no directions left in which to minimize the function, so the trial vector must be at the position of the minimum. Therefore, the exact location of the minimum of a quadratic function will be found, conservatively speaking, in a number of iterations that is equal to the dimensionality of the vector space. In practice however, it is usually possible to perform the calculations so that far fewer iterations are required to locate the minimum.

Thus, the basic difference between these techniques is that in the steepest-descent method, each direction is chosen only from information about the function at the present sampling point. In contrast, in the conjugate gradient method, the search direction is generated using information about the function obtained from all the sampling points along the conjugate gradient path. The conjugate gradient is thus an efficient method for locating the minimum of a general function.

3.2 The Kinetic Monte Carlo Method

The Kinetic Monte Carlo (KMC) method is generally used to simulate the evolution of a physical system through numerical sampling of (Markovian) stochastic processes. While the traditional Monte Carlo (MC) method is applied to sample systems in or close to the thermal equilibrium, KMC has a “kinetic” character, in that it also evolves the system in real physical time making it possible to study non-equilibrium processes [24]; see Figure 3.4 below. A connection between Monte Carlo timesteps and the real physical time has been discussed within the theory of Poisson processes [25]. The appeal of the KMC method is that it can treat large length and long time-scale kinetic response while incorporating atomistic information, through appropriately determined transition rates. This is not possible with molecular dynamics calculations, where time scales are limited to the range of nano seconds. For example, the KMC is widely used to simulate surface diffusion and growth processes, in which the energy barriers for the atomic mechanisms are obtained from atomistic calculations (see section 3.3.1) and are provided as input to the KMC technique.

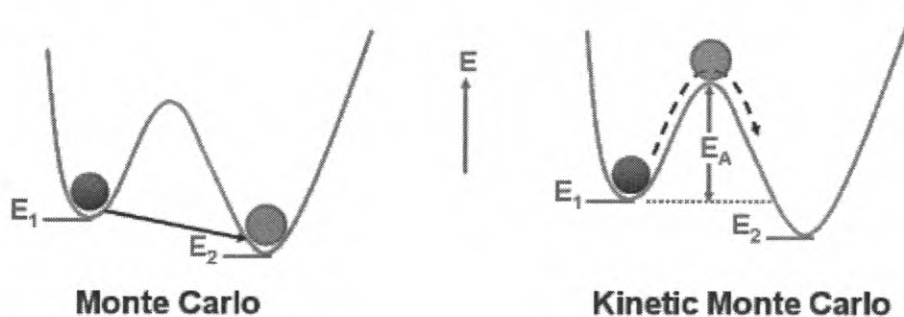


Fig. 3.4 The Monte Carlo and the Kinetic Monte Carlo methods.

The “Monte Carlo method” has its name from the use of “random numbers” to simulate statistical fluctuations in order to numerically generate probability distributions [26]. It is generally believed that the widespread use of Monte Carlo concept began with the Metropolis algorithm in the calculation for a rigid-sphere system [27]. This technique can be readily used to study equilibrium properties of a system of atoms. It does not consider the kinetic path of evolution and thus cannot be used for the study of cluster diffusion. So we use the Kinetic Monte Carlo technique. In the following section we introduce the n – fold algorithm [28], which is believed to be the earliest form of the current KMC concept.

3.2.1 The Bortz-Kalos-Lebowitz (BKL) Monte Carlo algorithm

In the conventional Metropolis algorithm (hit-and-miss method), for a system in its initial configuration c , a final configuration c' is chosen with a uniform probability of $1/N$, where, N is the total number of possible transitions. Next, the transition is accepted with a probability $V_{c \rightarrow c'} / V_{\max}$, where $V_{\max}$ is a maximum transition rate ($V_{\max} \geq V_{c \rightarrow c'}$) and is typically normalized to unity. This means that each possible transition is rejected with a probability $(V_{\max} - V_{c \rightarrow c'}) / V_{\max}$. The transition probability is given by the Boltzmann factor $\exp(-\Delta E / k_B T)$, where, $\Delta E = E_f - E_i$, is the energy difference between the initial and the final states. If the attempt is accepted the system moves into the new configuration, otherwise it is left in the initial state. In this way the system always evolves

toward equilibrium, i.e. (at least locally) to the minimum energy configuration [29]. The advantage of this traditional method is that one requires explicitly the knowledge of only the relative transition probabilities, but the disadvantage is that there can be several unsuccessful events. Due to this, it becomes extremely slow in terms of computation time when simulating systems at low temperature, where many unsuccessful attempts occur to change the configuration of the system. Consequently, the evolution of the system is slow at low temperatures and a large number of Monte Carlo steps are required to collect uncorrelated data for good statistics and analysis.

The BKL algorithm [28] helps improve this problem by increasing the success ratio of the attempts. The aim is to always choose an event with the correct probability; hence the success ratio is always unity. Thus, the time step now becomes stochastic since for each transition there is an associated waiting time where the system stays in its initial configuration. In the traditional MC method, this waiting time is explicitly taken into account through the unsuccessful attempts. Thus, the time must be drawn correctly. Since the events are evenly placed on a time axis the time step Δt is exponentially distributed with the decay constant equal to the total transition rate Γ_c of the configuration c :

$$P(\Delta t) = \Gamma_c \exp(-\Gamma_c \Delta t) \quad (3.10)$$

The reciprocal of the total transition rate is the time the system stays in its initial configuration. Since time is a stochastic variable, time dependent observables have to be measured carefully, by binning the time interval and obtaining the average time for each bin.

Thus, the basic ingredients of the BKL algorithm are as follows:

- (1) Enumerate all possible transitions and label the configurations.
- (2) Determine the next transition $c \rightarrow c'$ with probability $\nu_{c \rightarrow c'} / \Gamma_c$, using a search method such as the binary tree or the n-fold way.
- (3) Conduct transition and update the transition rates and labels.
- (4) Update the search structure for the next transition.
- (5) Update the physical time and all other necessary variables.
- (6) Calculate the required observables and go to the first step.

3.2.2 Algorithm used in our KMC technique

A drawback of the BKL algorithm is that at every iteration Γ_c has to be calculated. This implies that since the local environment of the atom changes after every transition, new transition rates for each site have to be calculated again in order to get the new value of the total rate, Γ_c . Also, it is more complicated than the Metropolis method in that to choose an event with the correct weight, sites with the same transition rate need to be classified into categories and then a site from a chosen class is selected with uniform probability amongst the rest of the members of the same class. Once this is done, and the transition is performed, the sites need to be re-classified into categories. The portion of the simulation code doing this classification is the speed determining section of the code. One way to speed up the code is to construct a binary tree structure for the search routine.

However, in this particular study of diffusion of small-sized clusters, we have considered the diffusion process to proceed by single atom peripheral

motion. A closed database of 49 processes is created for the classification of the sites. A unique pattern recognition scheme has been devised which recognizes the local environment of the peripheral atom and compares it with the uniquely generated patterns for the 49 processes in the database. If a perfect match is obtained, the atom is treated as eligible to perform that process and classified into that category. This is performed for all the peripheral atoms of the cluster. Once this procedure is complete, the microscopic and macroscopic rates of the events are calculated, from which the total rate Γ_{tot} is obtained. The microscopic rate for a process i is given by,

$$\nu_i = \nu_o \exp(-\Delta E_i / k_B T), \quad (3.11)$$

where, ν_o is the attempt frequency which is considered to be 10^{12} /sec (1 THz) for all our calculations. ΔE_i is the activation energy for the process i and k_B is the Boltzmann's constant. The macroscopic rate for a process i is given by,

$$\Gamma_i = N_i \nu_i, \quad (3.12)$$

where, N_i is the number of atoms having rate ν_i . Thus, the total rate Γ_{tot} is given by,

$$\Gamma_{tot} = \sum_i \Gamma_i \quad (3.13)$$

Next, the probabilities of each process are calculated, followed by a random number selection of a process to be performed. The probability of a process i to be selected is given by,

$$P_i = \frac{\Gamma_i}{\Gamma_{tot}} \quad (3.14)$$

Since the processes are weighted, the most probable process is selected for execution, using a linear search. Next, an atom classified into this process is selected randomly with uniform probability and the transition is performed. This is repeated for all iterations.

The flowchart (Figure 3.5) for the KMC method used in our study is shown below:

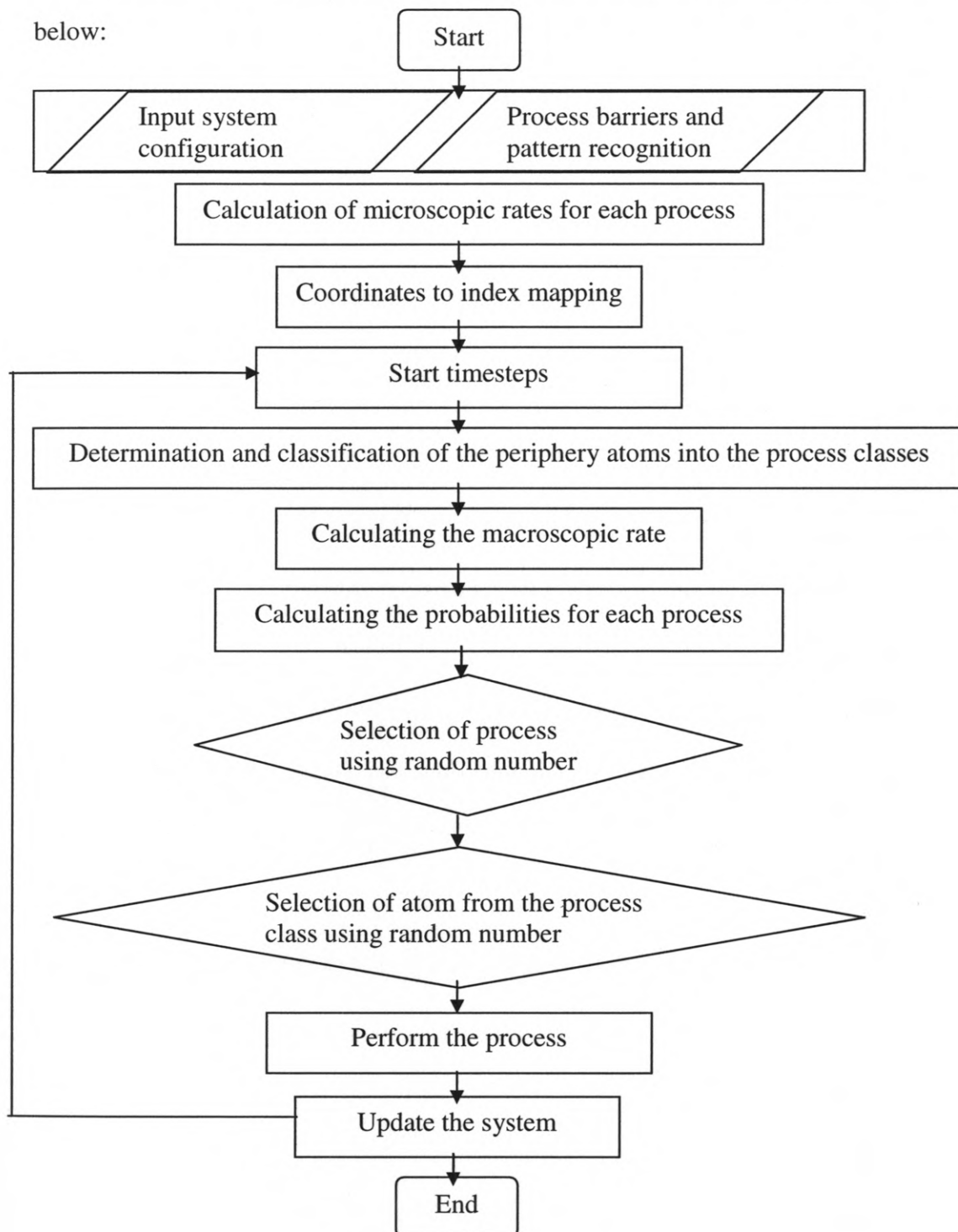


Fig. 3.5 Flowchart for the KMC method.

3.2.3 Linear search

The linear search method is a cumulative and conditional probability process Figure 3.6. Let the normalized probabilities of the different processes be denoted by P_i .

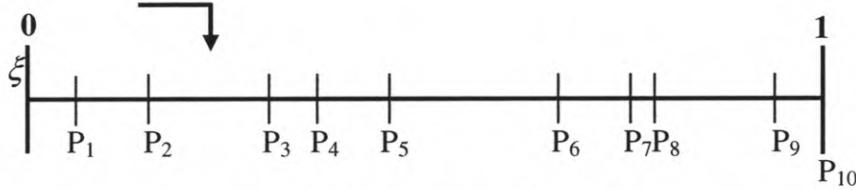


Fig. 3.6 Linear search method

If the random number $\xi [0,1[$ selected, lies between P_2 and P_3 , the process P_3 is selected for execution. Another random number is picked that decides which atom in the class of process P_3 will diffuse. This method works very well for small systems and the speed of execution is comparable to a binary tree search. However, for larger systems, a binary tree implementation is a more efficient option.

3.3 Interaction potentials – Embedded Atom Method

The above sections of this chapter are a description of the techniques used in our simulations. However, to simulate the energetics of a system and to study several problems in solid-state physics we require a detailed understanding of the interaction potentials between the atoms of the system. This in turn requires a model of a solid which is both accurate and computationally simple. In our work on atom manipulation and in calculating the energy barriers for diffusion of

clusters, we have made use of potentials from the Embedded Atom Method. In earlier times, pair-potentials were used for simplicity. However, the major problem with pair potentials for solid metals is that they have no environmental dependence so the bulk atom is too much like a surface atom. For metals, the strength of the individual bonds decrease as the local environment becomes more crowded, corresponding to the behavior expected from Pauli's "exclusion principle." In contrast, with 2-body potentials the "strength" of the individual bonds does not depend on environment. Thus, capturing the environmental dependence of bonding is crucial for metallic systems. The interaction between a pair of atoms is dependent on the other atoms in the system since the charge density of each atom is affected by the presence of the rest of the atoms. This is inefficient in dealing with systems involving surfaces, grain boundaries, vacancies etc, where the local environment is far from bulk behavior. Thus, we require the use of a many-body interaction potential. For the calculations of the energetics of the system used in this dissertation, we have used the EAM interaction potential, which was proposed by Daw, Foiles, and Baskes [30]. This method can be applied to a system with a random arrangement of atoms. It has proved highly efficient and successful in the cases of fcc metals.

In this approach the overall electron density in a metal is assumed to be a linear-superposition of the contribution of each atom. The electron density in the vicinity of each atom can then be expressed as a sum of the density contributed by the atom in question plus the electron density from all the surrounding atoms, or in other words, the background electron density. This background density is

assumed to be a constant since it is a slow varying function of position. In addition there is an electrostatic energy contribution due to the core-core overlap. Thus the two terms that contributing to the total energy of the system can be written as follows:

$$E_{tot} = \sum_i F_i(\rho_i) + \frac{1}{2} \sum_i \sum_{j \neq i} \phi_{ij}(r_{ij}), \quad (3.15)$$

where, ρ_i is the electron density at site i , F_i is the energy required to place atom i into that electron density and ϕ_{ij} is the core-core pair repulsion between atoms i and j . The electron density at each site is computed from a superposition of atomic electron densities:

$$\rho_i = \sum_{j \neq i} f_j(r_{ij}), \quad (3.16)$$

where, $f_j(r_{ij})$ is the contribution to the electron density at atom i due to atom j at the distance r_{ij} from atom i . With this approximation for the electron density the computational work required in this method is comparable to that in the pair-potential models. The embedding functions F and the pair interactions ϕ are determined empirically by adjusting the above equations so that they reproduce the zero-temperature equation of state of the solid, the elastic constants of the solid and the vacancy formation energy.

3.3.1 The Nudged Elastic Band Method

As mentioned in section 3.2, the activation energy barriers for an atom to diffuse are an input to the KMC technique. The determination of the lowest energy path

for a system of atoms that have rearranged from one stable configuration to another is an important problem in condensed matter physics. This lowest energy path is referred to as the ‘minimum energy path’ (MEP). It is used in the definition of the reaction coordinate of a transition during diffusion process in solids. The potential energy maximum along the MEP is the saddle point energy which gives the activation energy barrier, a quantity of central importance in the estimation of the transition rate within harmonic transition state theory [31].

Several methods have been presented for identifying the MEP, one of which is the Elastic Band Method. This method calculates the energy barrier when a system makes a transition from one stable configuration to another, by using a series of intermediate atomic configurations (images), between the initial and final states. These images are generated by interpolation. They are connected via “elastic bands” and are minimized simultaneously to give the barrier between the two states.

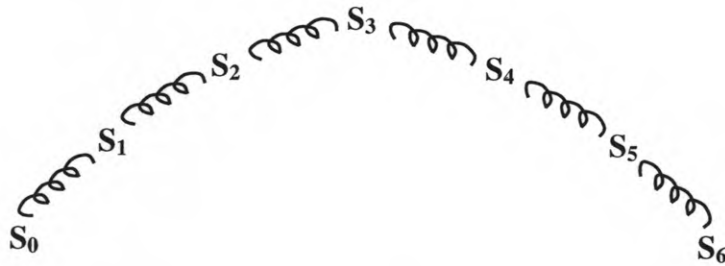


Fig. 3.7 Elastic Band method / Nudged ElasticBand Method - Images connected via elastic bands

The force acting on the image i is given by:

$$\vec{F}_i = -\vec{\nabla} V(\vec{R}_i) + \vec{F}_i^s, \quad (3.17)$$

where,

$$\vec{F}_i^s \equiv k_{i+1}(\vec{R}_{i+1} - \vec{R}_i) - k_i(\vec{R}_i - \vec{R}_{i-1}) \quad (3.18)$$

V is the interaction potential between the atoms in the system, $\mathbf{R}$ is the position coordinate and k is the spring constant. The drawback of this method is that when the spring constant k , is large (eg. $k=1.0$), the elastic band is too stiff and the path cuts the corner and misses the saddle point, whereas if it is too small (eg. $k=0.1$), the elastic band comes closer to the saddle point but the images manage to slide down (slip) and avoid the barrier region which is the most critical region.

In the Nudged Elastic Band NEB method, convergence to the MEP is enabled when sufficiently many images are used in the elastic band. In the Elastic Band method, the corner cutting results from the component of the spring force which is perpendicular to the path and tends to pull images off the MEP. The sliding down results from the component of the true force $-\vec{\nabla}V(\vec{R}_i)$, in the direction of the path. Thus the distance between the images becomes uneven so the net spring force can balance out the component of the true potential force.

To rectify this problem, the minimization of an elastic band is carried out where the perpendicular component of the spring force and the parallel component of the true force are projected out. Thus the force on the image i now is:

$$\vec{F}_i^0 = -\vec{\nabla}V(\vec{R}_i)|_{\perp} + \vec{F}_i^s \cdot \hat{\tau}_{\parallel} \hat{\tau}_{\parallel}, \quad (3.19)$$

where, $\hat{\tau}_{\parallel}$ is the unit tangent to the path, and

$$\vec{\nabla}V(\vec{R}_i)|_{\perp} = \vec{\nabla}V(\vec{R}_i) - \vec{\nabla}V(\vec{R}_i) \cdot \hat{\tau}_{\parallel} \hat{\tau}_{\parallel} \quad (3.20)$$

This projection of the perpendicular component of the true force and the parallel component of the spring force is referred to as “nudging”. The minimization can be carried out using various known techniques, e.g., the steepest descent method. For a more detailed description of the NEB, refer to Ref. [32]. Also, refer to Appendix II for the calculation and plots of the potential energy surface for a selected case.

3.4 Periodic Boundary conditions

An important concept in simulations of large systems is the periodic boundary conditions. Our simulations involve systems of the order of 10^4 atoms. In a real system there are the order 10^{23} particles. Since a typical computer simulation has only about 10^2 to 10^6 particles due to the computational overhead involved when considering large systems, confining the particles within a geometric shape causes problems with surface effects for such small systems. Thus we use periodic boundary conditions (PBC) to reduce this problem and involve effectively replicating the system box in all directions through space. If a particle leaves the system through one side then it will re-enter on the opposite side thus keeping the number of particles constant. It is important to ask whether the properties of a small, infinitely periodic system and the macroscopic system which it represents are the same. This depends both on the range of the intermolecular potential and the phenomenon under investigation. If the range of the potential is large enough in comparison to the box size, then there will be a significant interaction between

a particle and its own periodic image, imposing a degree of symmetry upon a structure which should in reality be isotropic. These issues have to be taken into consideration to perform effective and realistic simulations of the systems desired.

A system that is bounded but free of physical walls can be constructed using periodic boundary conditions, as shown in Figure 3.8. Imposing PBC on a system is equivalent to considering an infinite space filling array of identical copies of the system under study. There are two consequences of this periodicity. The first is that an atom that leaves the simulation region through a particular bounding face immediately reenters the region through the opposite face. The second is that atoms lying within a distance r_c of a boundary interact with atoms in an adjacent copy of the system, or equivalently with atoms near the opposite boundary – a wraparound effect. This wraparound effect must be taken into account in both, the integration of the equations of motion (in the case of molecular dynamics simulations) and in the computations involving the interactions. During energy minimization of a system, the coordinates of the atoms must be examined after each iteration, and if an atom is found to have moved outside the simulation region, its coordinates must be adjusted to bring it back. If, for example, the x coordinate is defined to lie between $-L_x/2$ and $L_x/2$, where L_x is the dimension of the system in the x direction, then if $x_i > L_x/2$, it should be replaced by $x_i - L_x$, and if $x_i < -L_x/2$, it should be replaced by $x_i + L_x$. The effect of the periodicity on the interaction calculations appears while determining the components of the distance $\mathbf{r}$ ($= \mathbf{r}_{ij}$) between pairs of atoms.

This has been used in our work on atom manipulation. However, in our KMC simulations on diffusion, we have used a slightly different concept, where, if the atom diffusing, crosses the boundary of the surface template, it is dragged back to the center of the template along with the rest of the cluster atoms in identical positions with respect to this atom.

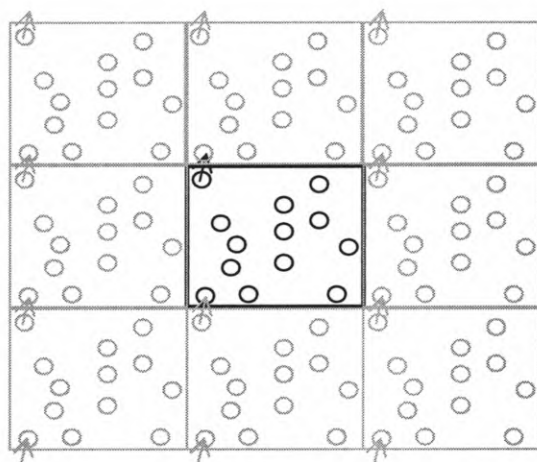


Fig. 3.8 Two dimensional periodic boundary conditions

3.5 Calculation of Diffusion Coefficient

Diffusion is one of the most commonly observed stochastic processes. In solids, mass transport is usually governed by diffusion of adatoms across the surface or along the step edges. Several intriguing surface phenomena such as diffusion of nanoclusters of various shapes and sizes, their dependence on temperature, concerted motion, fast island decay in the vicinity of step edges, ostwald ripening, diffusion of vacancy islands etc. have been observed experimentally [33-50]. Theoretical simulations are being performed extensively by several groups to get

an insight into the energetics and kinetics of these processes [51-72]. In theory, the continuum approach was first developed by Mullins [73]. Further theoretical investigations range from molecular dynamics simulations which are widely used to extract diffusion coefficients [57,58] and prefactors, to *ab initio* calculations [60,74,75] that provide the activation energy barriers. More recently the Kinetic Monte Carlo (KMC) simulations [55,76,77] and combinations of MD and KMC [78] of atomistic models have gained some popularity.

A very early approach in the theory of diffusion was the one proposed by A. Fick (1855), who derived the mathematical equation for heat conduction and thus first put diffusion on a quantitative basis. Another approach was the one by Einstein which is as follows:

$$D = \lim_{t \rightarrow \infty} \frac{\langle [\vec{r}(0) - \vec{r}(t)]^2 \rangle}{2\alpha t}, \quad (3.21)$$

where, $\langle [\vec{r}(0) - \vec{r}(t)]^2 \rangle$, is the ensemble-averaged mean-square displacement of the diffusing particles and α is the dimensionality of the space in which diffusion is occurring. Diffusion can also be considered as a thermally activated process that follows the well known Arrhenius temperature dependence relationship:

$$D = D_0 \exp(-E_A / kT), \quad (3.22)$$

where, E_A is the energy barrier between two equilibrium sites or local minima on the potential energy surface, and D_0 is the prefactor, which depends on the details of the structure, such as the structural energy, the vibrational entropy and the internal energy of the system [79]. The diffusion prefactor can also be obtained from equation 3.22, which can also be written as $\ln D = -E_A/kT + \ln D_0$, where $\ln$

D_0 is the intercept on the y-axis for the plot of $\ln D$ (y-axis) vs. $1/kT$ (x-axis), and $-E_A$ is the slope.

During island diffusion, since the activation energy to move an atom along the cluster perimeter is lower than that required to detach it from the cluster to an isolated site on the surface, periphery diffusion (PD) is considered the more probable mechanism in most cases [64,80,81,82], while evaporation and condensation (EC) of single atoms has also been suggested to explain the experimental observations [83,84]. For detachment and reattachment processes, the cluster is said to diffuse via terrace diffusion (TD) [78]. These are the three basic mechanisms in island diffusion. In our study, we have only considered periphery diffusion mechanisms which have relatively lower activation barriers as compared to the terrace diffusion mechanisms. These various kinds of diffusion processes are responsible for the scaling of the diffusion coefficient with the size of the cluster. Measurements of the scaling exponent can determine which mechanism (e.g., periphery diffusion or evaporation condensation) causes island diffusion [85,86,87].

Chapter 4

Theoretical aspects of vertical and lateral manipulation of atoms on several fcc(111) metal surfaces

Using total energy calculations, based on interaction potentials from the embedded atom method, we show that the presence of the tip not only lowers the barrier for lateral diffusion of the adatom towards it, but also shifts the corresponding saddle point. For a Cu adatom at a (100) microfaceted step on Cu(111) this shift is $0.6\text{\AA}$. The effect of the tip geometry and shape on the energetics of lateral manipulation was found to be subtle. Also, for a set of fcc metals our total energy calculations, based on many body potentials, show that activation barriers for lateral manipulation of an adatom at a step edge, depends on the tip/substrate composition. Of the six homogeneous systems studied, manipulation on stepped Ag(111) showed the lowest energy barrier for adatom hopping towards the tip, although the relative probability for this process may be largest for adatoms along steps on Cu(111). We find that manipulation is not so favourable in heterogeneous systems. Useful insight is obtained for the systems of a Pt adatom along a step on Pt(111) manipulated by a Cu(100) tip and the reverse case of a Cu adatom along a step on Cu(111) with a Pt(100) tip, by looking at the atomic relaxations and the binding energies of the adatom, tip and its neighbors, which explains their behavior. Additionally, atomic relaxations of the tip and its neighboring atoms are found to be prominent in vertical manipulation in which tip induced changes in the bonding of the adatom to its low coordinated surroundings

help explain the relative ease with which an adatom next to a step edge or a kink site may be pulled, as compared to that on a flat surface.

4.1 Introduction

In recent times, a whole new set of experiments has surfaced with the invention of the Scanning Tunneling Microscope (STM) [1-4]. Manipulation of individual atoms, both laterally and vertically have been performed in various research laboratories [1-4,88-92], leading to applications including nanostructuring of surfaces and altering chemical reactions, both of which play crucial roles in the progress of nanotechnology. Because of the vicinity of the tip to the adatom and its neighbours, questions are automatically raised about the changes in the potential energy surface and atomic relaxations brought about by the tip, and their dependencies on the structure and composition of the tip. Questions are also raised about the stability of the tip and whether the ease of manipulation correlates with the cohesive energy of the constituents, in the case of manipulation on homogeneous systems (the adatom, tip and surface of same elements). As we shall see, more detailed examination of the potential energy surface, however, reveals effects of the tip that were not uncovered in these earlier studies. While for several types of vertical manipulation the picking up of an atom at one point and dropping it off at another, on the atomic scale, depends on the bias voltage that is applied, for lateral manipulation the magnitude of the electric field is weak [90]. Studies of lateral manipulation on homogeneous systems [93,94] indicate that most characteristics may be explained through considerations

of system energetics dictated by interatomic forces alone. Furthermore, in a related detailed study of the influence of the tip on the potential energy surface seen by Cu adatom at the step edge, not only the diffusion barriers but also the saddle points were shown to be perturbed [95]. These previous studies had focussed on Cu [94,95] and Au [93] because of their direct relevance to experimental data. As in Ref. [93], our model system has been inspired by the experimental work carried out earlier by Meyer et al. [96,97]. To motivate future experiments and to understand the trends in atomic manipulation for a set of metallic systems, there is a need to undertake such a study.

We have also carried out a comparative study of the lateral manipulation of adatoms on six metal surfaces. Additionally we have considered two heterogeneous Pt/Cu systems to examine possible asymmetries in the ease of manipulation. We have also probed in detail the rationale for the differences in the vertical manipulation of adatoms from stepped, kinked and flat surfaces. Special attention has been given to atomic relaxations brought about in the presence of the tip. As shown in a recent study [98], atomic relaxations of the tip atoms and those in their vicinity may be quite pronounced. Since it is not yet computationally feasible to carry out calculations of the type we have in mind with first principles electronic structure methods [99], we have employed interaction potentials from the embedded atom method (EAM) [30] to examine the energetics of atom manipulation on metal surfaces.

4.2 Model Systems

The model system for the manipulation process consists of two parts: the adatom on a metal substrate, and the tip, which is a nanostructure itself (Fig. 4.1(a)). The substrate consists of 8 atomic layers in fcc stacking with (111) orientation having 10×12 atoms in each layer. Calculations have been performed on larger systems and we have arrived at the conclusion that the above dimensions are sufficient to avoid problems arising from the finite size of the simulation cell. Deleting 7 and 7.5 atomic chains respectively from the surface layer creates the (100) microfaceted step and the kinked surfaces respectively. Lateral manipulations are carried out in this work, on the stepped surface only, while vertical manipulation is performed on flat, stepped and kinked surfaces, for comparison. Simulations with sharp as well as blunt tips having either fcc(100) or fcc(111) geometry have been performed. Sharp tips consist of 35 metal atoms with 1 atom at the tip apex (Fig. 2.7(a),(b)). The blunt tips have 34 atoms, since the apex atom has been removed, leaving the (100) and (111) tips with 4 and 3 atoms at the apex, respectively. The heights (length in the Z direction) of the blunt and sharp tips are thus $8.32\text{\AA}$ and $10.40\text{\AA}$ respectively. Since the interactions potentials for the materials considered are short ranged, the tip sizes chosen here are sufficient to examine their effect on the potential energy surface in the vicinity of the adatom. We have defined the lateral separation between the adatom and the tip as in Fig. 4.1(b). The metals studied for lateral manipulation are Cu, Ag, Au, Pt, Ni and Pd (so chosen because of the availability of reliable interaction potentials).

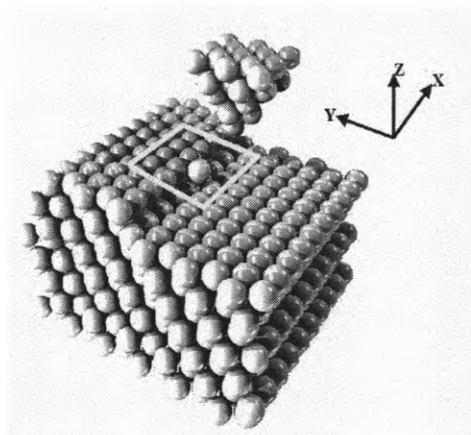


Fig. 4.1(a) Model System for lateral manipulation. Shown here is the grid along which the adatom is placed. Ref. [95].

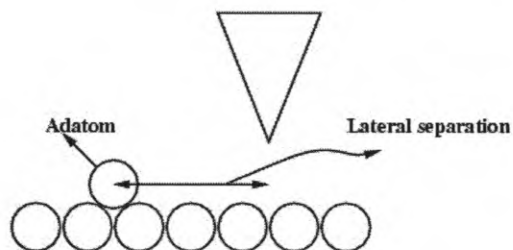


Fig. 4.1(b) Lateral separation between tip and adatom

4.3 Theoretical Method

To obtain the energetics of the systems, we have carried out our calculations employing interaction potentials from the embedded atom method (EAM) [30], with parameterization by Voter and Chen [98], since it is not yet computationally feasible to perform such extensive systematic studies of the potential energy surfaces using first principles electronic structure methods. The total energy of the system consisting of the tip, the adatom and the substrate (Fig. 4.1(a)) is minimized using the conjugate gradient method [22]. The experiments that have motivated our calculations were performed at temperatures below 50K and the

time scales for atomic motion are about 1ps. Thus we do not expect surface vibrations to play a significant role here and have not considered dynamical effects like vibrational entropy and atomic vibrational amplitudes, which might play a role at higher surface temperatures. Also, the zero point motion of atoms like Cu are not significant to change the qualitative behavior of these systems. Furthermore, Van der Waals forces are also not expected to be predominant [92], since the tip radius is taken to be just a few angstroms and the vertical separations between the tip and the adatom range from $3.0\text{\AA}$ to about $7.5\text{\AA}$.

During energy minimization calculations, all atoms of the last two layers of the cell are kept rigid. Also, the four atoms at the corners of the stepped surface, as well as, those at the two corners of the lower terrace are kept rigid. Top two layers of the tip are kept rigid and the rest are allowed to relax to their equilibrium positions for each simulation. The results quoted in this paper are for the fully relaxed tip and surface systems.

For lateral manipulation, the total energy is calculated for each configuration of the system with the adatom placed at every point along a fine $10\text{\AA} \times 10\text{\AA}$ grid consisting of 100×100 points (Fig. 4.1(c)), which covers part of the upper and lower terraces adjoining the step. In regions away from the tip, the usual symmetry of the surface was reflected. The contour plot in Fig. 4.2(a), which is a 2D top view of the same potential energy surface, has been obtained through the application of a graphics package (Xfarbe) [100]. The 3D potential energy surface (Fig. 4.2(b)) of the system was obtained from the total energy of the system for each of the 10^4 configurations. Its plot clearly showed the

perturbation caused by the presence of the tip. From the calculated potential energy surface, the activation energies for the adatom to diffuse in various directions were easily obtained.

In the case of vertical manipulation the adatom is constrained in the Z direction (normal to the surface). This prevents the adatom from falling back to the surface when it is raised in small intervals from surface to tip during the energy minimization process. The plots of the total energy versus the Z coordinate of the adatom were obtained for several tip heights. For the case when the tip is directly above the adatom, the relaxations of the adatom, the tip atoms and the neighboring atoms are calculated using the data in the initial and final (after minimization) configuration files. From these relaxations, we can determine the spacing between the tip and the adatom when the repulsive forces come into play. We can also determine which of the neighboring atoms are strongly affected by the tip and consequently which atom/atoms can be pulled by the tip easily.

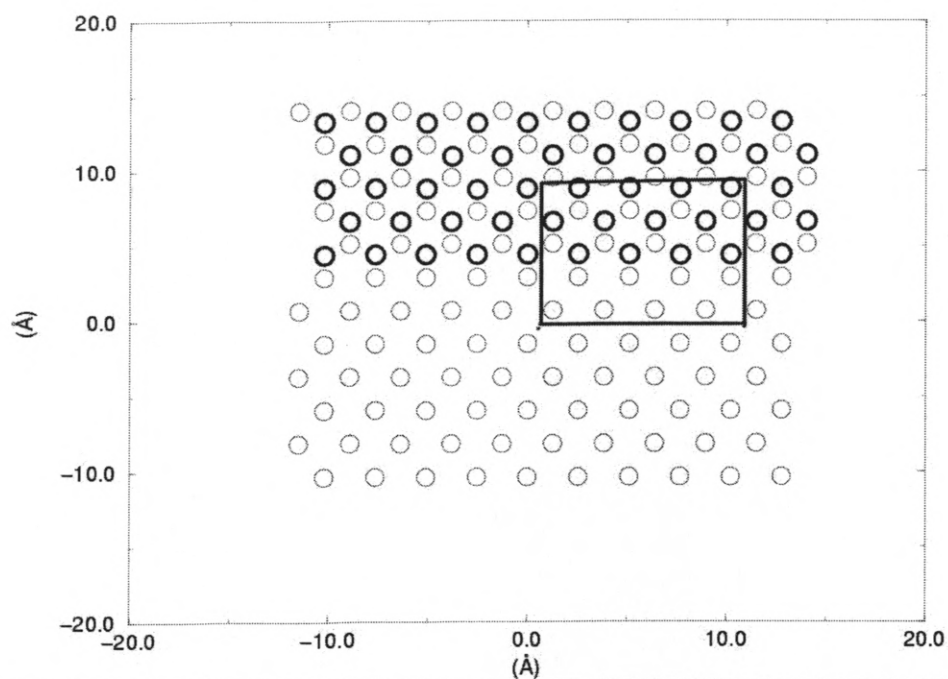


Fig. 4.1(c) Top view of the grid along which the adatom is placed in steps of $0.1\text{\AA}$. Dark circles are atoms of the top terrace of the stepped surface and the lighter circles are the atoms of the layer beneath.

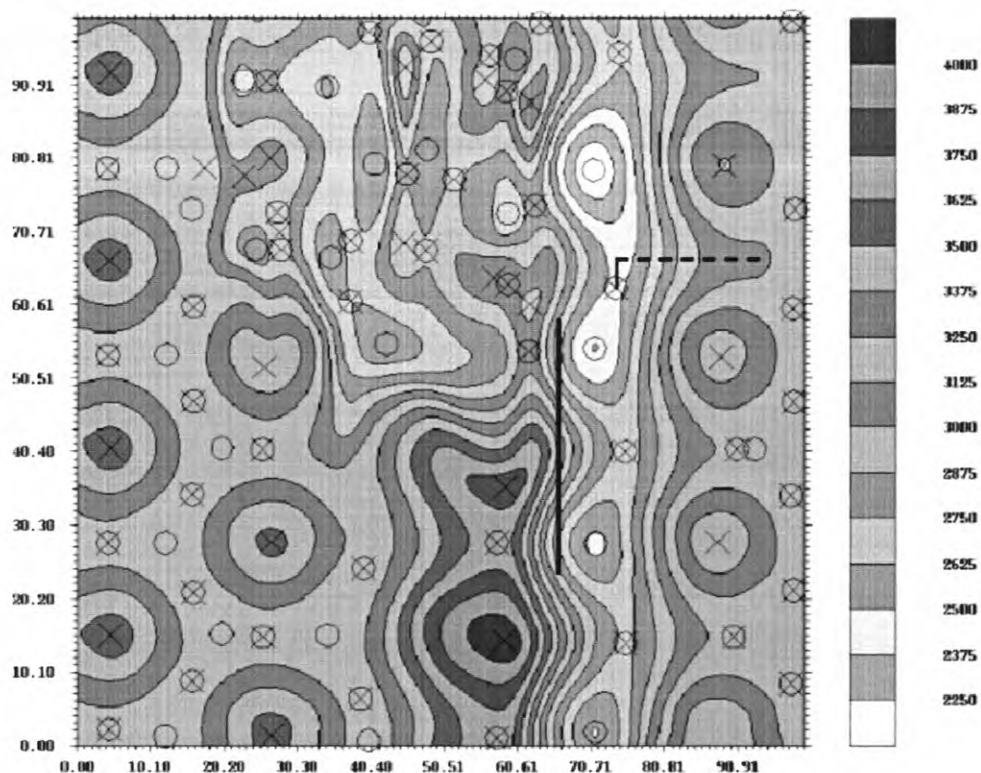


Fig. 4.2(a) Top view of the contour plot of the total energy of the system, showing the perturbation due to the tip (upper middle part). The long dark line indicates the direction along the step edge (reaction coordinate). The small line shows the shift in the position of the saddle point ($\otimes$) with respect to its ideal position (which is where the dashed line meets the small line). The circles indicate the minima (fcc and hcp sites), the crosses, the maxima (as can be seen, these are the atop sites) and the circles with crosses, the saddle points (bridge sites). Ref. [95].

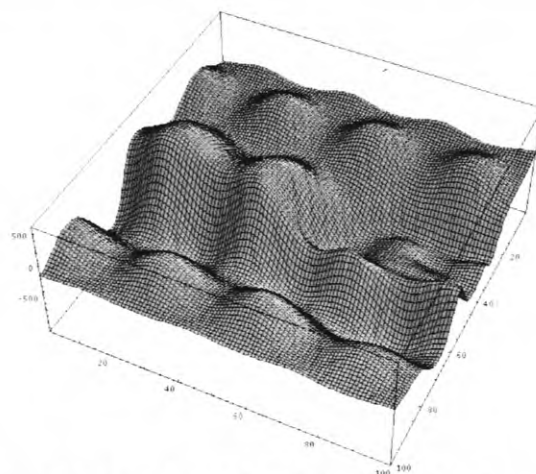


Fig. 4.2(b) 3D plot of the PES when the tip is $2.75\text{\AA}$ above the adatom which is along the step edge. Ref. [95].

4.4 Results

In this section we discuss the results of the different aspects of manipulation, lateral and vertical. We examine the effects of the tip geometry, shape, and height from the substrate on the characteristics of the manipulation process. As expected beyond a certain separation between the tip and the substrate, the tip itself gets distorted. We report here results only for those tip heights for which the tip atoms remain intact.

4.4.1 Lateral Manipulation

To establish the importance of the usage of the grid, we consider the lateral manipulation of a Cu adatom at a (100)-microfaceted Cu(111) step face using a sharp Cu(111) tip, for direct comparison with results from Ref. [93]. The plot in Fig. 4.3(a) shows that the qualitative features of the calculated energy barriers for an adatom to diffuse in the direction of the tip, and away from it (opbarrier), are similar to those in Ref. [93]. However, in the present work the minimum barrier is not zero. Instead it is 146.6 meV and is reached at a tip-adatom lateral separation of about 2.0Å (Table 4.1) and a vertical separation of 2.75Å. We observe that sharp Cu(111) tips approaching the adatom vertically any closer than 2.75Å get distorted due to the attractive forces between the surface and the tip. Such distortion of the tip was also found in Ref. [94]. The 2D and 3D contour plots in Figs. 4.1(a) and 4.2(b) clearly show that when the tip is far away from the substrate the system is not perturbed and the potential energy surface for the adatom has the substrate symmetry. The region in the vicinity of the tip

shows a perturbation and the saddle point shifts with respect to its original unperturbed position. This is why the diffusion barriers calculated with respect to the actual saddle point (see Fig. 4.3) are different from those in Ref. [93] in which the saddle point was assumed to be at the bridge site. The shift in the saddle point is clearly marked in the Fig. 4.2(a).

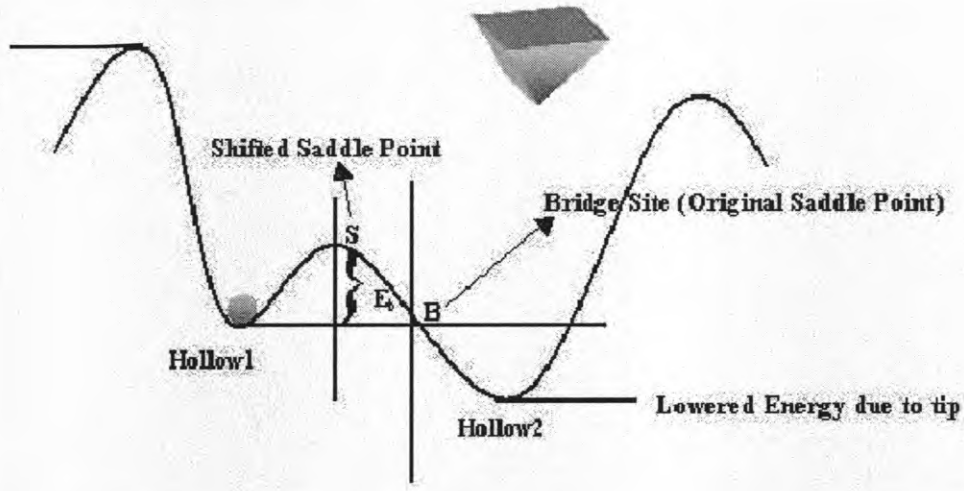


Fig. 4.3 Broken symmetry due to the tip. Subtracting the energies at points **Hollow1** and **B** would yield a zero barrier, but considering the shifted barrier **S** and subtracting the energies at points **Hollow1** and **S** gives a positive barrier E_b . Ref. [95].

To examine the effect of the tip geometry on lateral manipulation, we present in Figs. 4.4(a) (sharp tips) and 4.4(b) (blunt tips) the results for a Cu tip of (100) and (111) geometry. These results show the Cu(100) tip to be more effective in lateral manipulation as compared to the Cu(111) tip, as the barrier here is lowered to 61.7 meV. For the case of a blunt (111) tip, the lowest tip-adatom vertical separation achieved without distorting the tip is 3.0Å. For this case, the lowest barrier for the adatom to diffuse towards the tip is found to be 143 meV at a lateral separation of about 2.0Å. This value should be compared

with the negative barrier obtained in Ref. [93], whose implication would have been a preference of the adatom for the bridge site rather than the next hollow site. This would have meant that a lateral motion would not take place at all. The usage of the denser grid is thus found to provide better sampling of the potential energy surface. Comparison of the barriers in Fig. 4.4(a) and Fig. 4.4(b) shows the blunt Cu(100) tip to be effective in reducing the barrier over a larger lateral separation range than the sharp tip. In Table 4.1 we have summarized our calculated activation barriers for lateral manipulation with sharp and blunt tips with either (111) or (100) geometry.

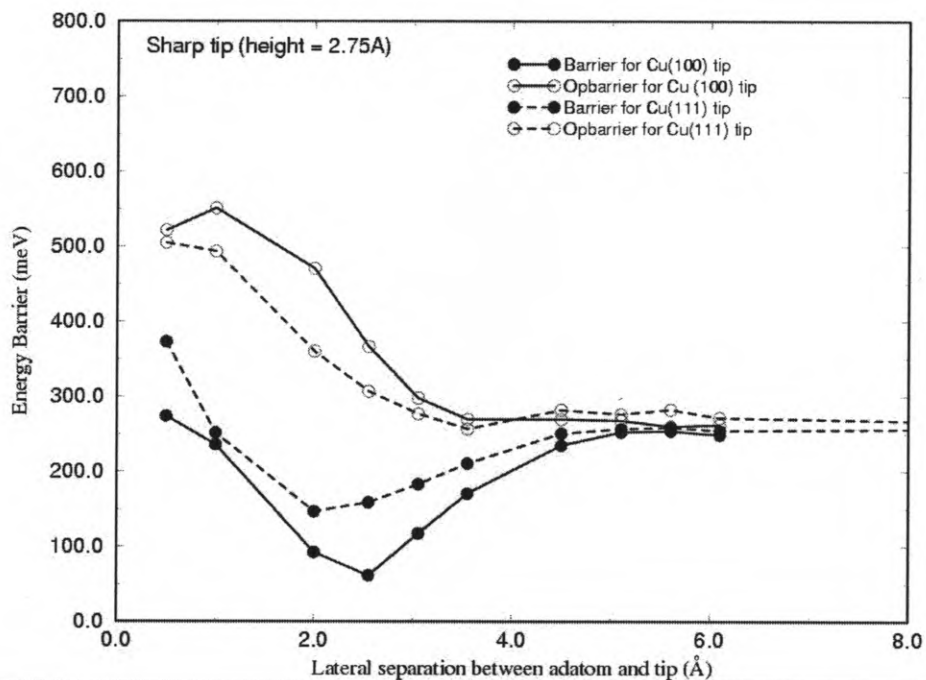


Fig. 4.4(a) Barrier (filled circles) and op-barrier (open circles) for (100) and (111) sharp tips for a tip apex-adatom separation of 2.75 Å. Solid lines are for the (100) tip and the dashed lines are for the (111) tip. Ref. [95].

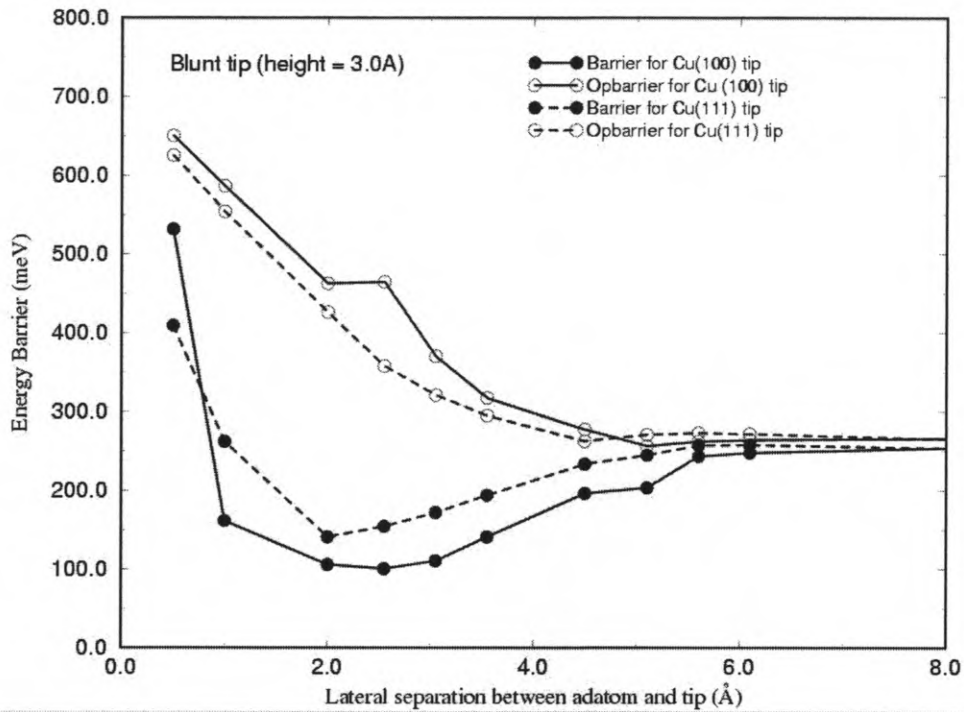


Fig. 4.4(b) Barrier (filled circles) and op-barrier (open circles) for (100) and (111) blunt tips for a tip-adatom separation of $3.0\text{\AA}$. Solid lines are for the (100) tip and the dashed lines are for the (111) tip. Ref. [95].

Table 4.1 Comparison of energy barriers for lateral manipulation on a stepped Cu(111) surface with a (100) step microfacet, for various types of tips. Ref. [95].

Tip geometry	Shape	Tip-adatom separation ($\text{\AA}$)	Activation Barrier (meV)	Lateral separation ($\text{\AA}$)
Cu(100)	Sharp	2.75	61.7	2.55
Cu(111)	Sharp	2.75	146.9	2.00
Cu(100)	Sharp	3.50	203.9	2.00
Cu(111)	Sharp	3.50	223.2	2.55
Cu(100)	Blunt	3.00	100.5	2.55
Cu(111)	Blunt	3.00	141.3	2.00
Cu(100)	Blunt	3.50	199.1	3.05
Cu(111)	Blunt	3.50	202.9	2.00

We also discuss the results of the comparative study of lateral manipulation on six different fcc metal surfaces, the ratios of the energy barriers to the cohesive energy and the relaxations of the tip and the nearest neighbor

atoms. Since beyond a certain separation between the tip and the substrate, the tip itself gets distorted [94], we report here results only for the lowest tip-adatom separation for which the tip remains intact. As seen from our results above, a sharp tip with (100) geometry is more effective as compared to the (111) tip in lowering the activation barrier. Thus, all calculations for the lateral manipulations presented here have been performed using a sharp Cu(100) tip placed between $2.75\text{\AA}$ - $3.5\text{\AA}$ above the step edge.

The lowest barriers are reached at a vertical separation of about $2.75\text{\AA}$ [95]. In the presence of the tip, the saddle point shifts with respect to its original unperturbed position and diffusion barriers need to be calculated with respect to this shifted saddle point [95] to ensure that the influence of the tip is properly incorporated in the energetics of the system.

The results for the lateral manipulation of adatoms on six metals, Ag, Au, Pt, Ni and Pd are summarized in Table 4.2. In each case, the tip, adatom and substrate are composed of the same element. In each of the six cases considered, lowest diffusion barriers are found at tip-adatom lateral separations between $2.0\text{\AA}$ - $3.0\text{\AA}$, which is in the range of the nearest neighbor separation. Ag is found to have the lowest barrier of 50 meV with a saddle point shift of $0.7\text{\AA}$, while the barrier in the direction away from the tip (opbarrier) is 215 meV. But as can be seen from Table 4.2, it is Cu that shows the highest ratio of opbarrier to barrier in the presence of the tip. Hence, the relative probability for adatom manipulation by a tip is higher for Cu than for Ag. We find an anomaly in the case of Pt, where the barrier in the presence of the tip is found to be higher than that in the absence of

the tip. Looking into the relaxation patterns of this case (Fig. 4.7) we find a significantly large relaxation of the tip apex atom towards the adatom and the adatom towards the tip. This is also observed in the table with the binding energies of the individual atoms (Table 4.5) where the adatom and the tip apex atom show much lower binding energies in the vicinity of each other. This indicates a very strong interaction between these atoms, which in turn leads to the large dip in the potential energy curve in Fig. 4.5(b). As the adatom gets laterally closer to the tip, and has to cross over a bridge site, the energy increases as expected. In all the other metals, this hump in the potential energy curve is lower than the hump in the absence of the tip, showing the manipulative effect of the tip. But in the case of Pt, we find that this hump, which is the energy barrier in the presence of the tip, is 870 meV whereas in the absence of the tip it is 620.8 meV. This anomaly indicates that the adatom has a very low probability to hop towards the tip as compared to when in the absence of the tip, and that the presence of the tip hinders the motion of the adatom. This anomaly could be due to the interaction potentials from EAM, which are not as accurate for the Pt metal. But nevertheless, it is an interesting result and needs deeper investigation. If it is infact due to the EAM potentials then one should note that similar calculations on Pt metal provide a good check of the reliability of these potentials for this metal.

To find a trend in the behavior of these metals with respect to adatom manipulation we have compared the energetics responsible for manipulation to the cohesive energy of the system. We have thus summarized in Table 4.3 the ratio of the barrier, opbarriers, and their difference to the cohesive energy. We

have also included in the table, the relative enhancement of the opbarriers to the barrier. If we take these energetics to be measures of ease of manipulation, both Cu and Ag appear to fair better than the other four metals. In fact, Cu has a small edge over Ag. Of course, these conclusions are derived within the context and accuracy of EAM potentials. Nevertheless, the trend in the six metals is interesting.

In the case of the two heterogeneous systems that we have considered, we find that a Pt tip lowers the barrier for a Cu adatom to hop towards it on a Cu substrate to 180 meV which is 3 times larger than the barrier found for the homogeneous Cu system (see Table 4.2). The Pt tip is thus not as effective as a Cu one for manipulation purposes. However, in the reverse case of a Cu tip on a Pt substrate with a Pt adatom, the barrier is found to be slightly lower than that in a full Pt system (Table 4.2).

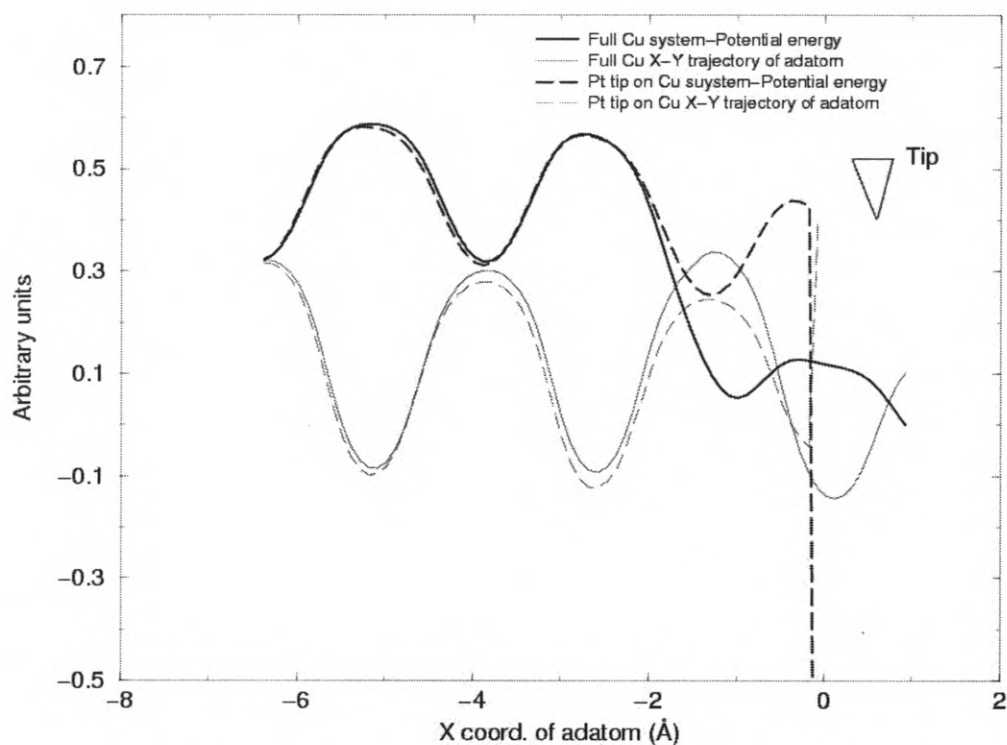


Fig. 4.5(a) Potential energy plot and the adatom X-Y trajectory plot for a Cu/Cu system and a Pt/Cu system.

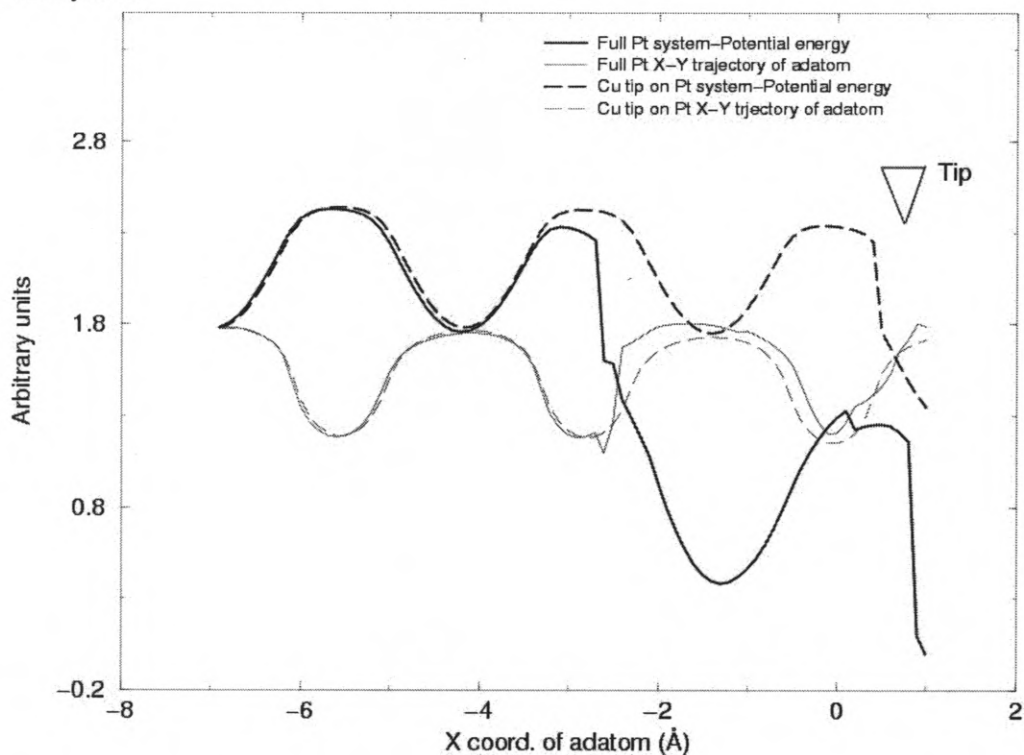


Fig. 4.5(b) Potential energy plot and the adatom X-Y trajectory plot for a Cu/Cu system and a Cu/Pt system.

Table 4.2 Comparison of energy barriers for lateral manipulation on stepped fcc (111) metals for a tip height between 2.75Å – 3.5Å above the step edge.

Metal	Barrier in the absence of tip (meV)	Barrier in the presence of tip (meV)	Opbarrier (meV)	Shift in saddle point (Å)	Lateral separation between tip and adatom (Å) when barrier is lowest
Cu	267	61.7	512	0.6	2.55
Pt tip on Cu surf.	267	180	300	0.3	2.6
Pt	620.8	870	1940	0.5	2.6
Cu tip on Pt surf.	620.8	590	670	0.1	2.1
Ag	215.5	50.1	283.6	0.7	2.6
Ni	308.3	131.3	386.4	0.45	2.4
Pd	355	190.1	426.9	0.4	2.5
Au	416.7	324.3	414.9	0.12	2.6

Table 4.3 Comparison of energy barriers and cohesive energy

Metal	Cohesive Energy (meV)	Ratio of Barrier in presence of tip to Cohesive Energy	Ratio of Opbarrier in presence of tip to Cohesive Energy	Ratio of (Opbarrier- Barrier) to Cohesive Energy	(Opbarrier- Barrier) / Barrier in absence of tip
Ag	2960	0.0169	0.0958	0.0788	1.083
Cu	3500	0.0176	0.1047	0.0870	1.141
Ni	4435	0.0296	0.0871	0.0575	0.827
Pd	3936	0.0483	0.1084	0.0601	0.667
Au	3780	0.0858	0.1097	0.0239	0.217
Pt	5852	0.1487	0.3315	0.1828	1.723

To understand this very interesting result of the asymmetric behavior in the Pt/Cu and Cu/Pt systems, we turn to considerations of the relaxations of the adatom, its nearest neighbor atoms and the tip atoms.

4.4.1.1 Relaxations of adatom, neighboring atoms and tip atoms - Cu/Pt and Pt/Cu systems

The relaxations of the adatom, its neighboring atoms and the tip atoms are discussed below. To make a comparison between the homogeneous and heterogeneous systems, we have included the cases for the pure Cu/Cu and Pt/Pt systems. The Fig. 4.6 shows the labelling of the adatom, its nearest neighbors.

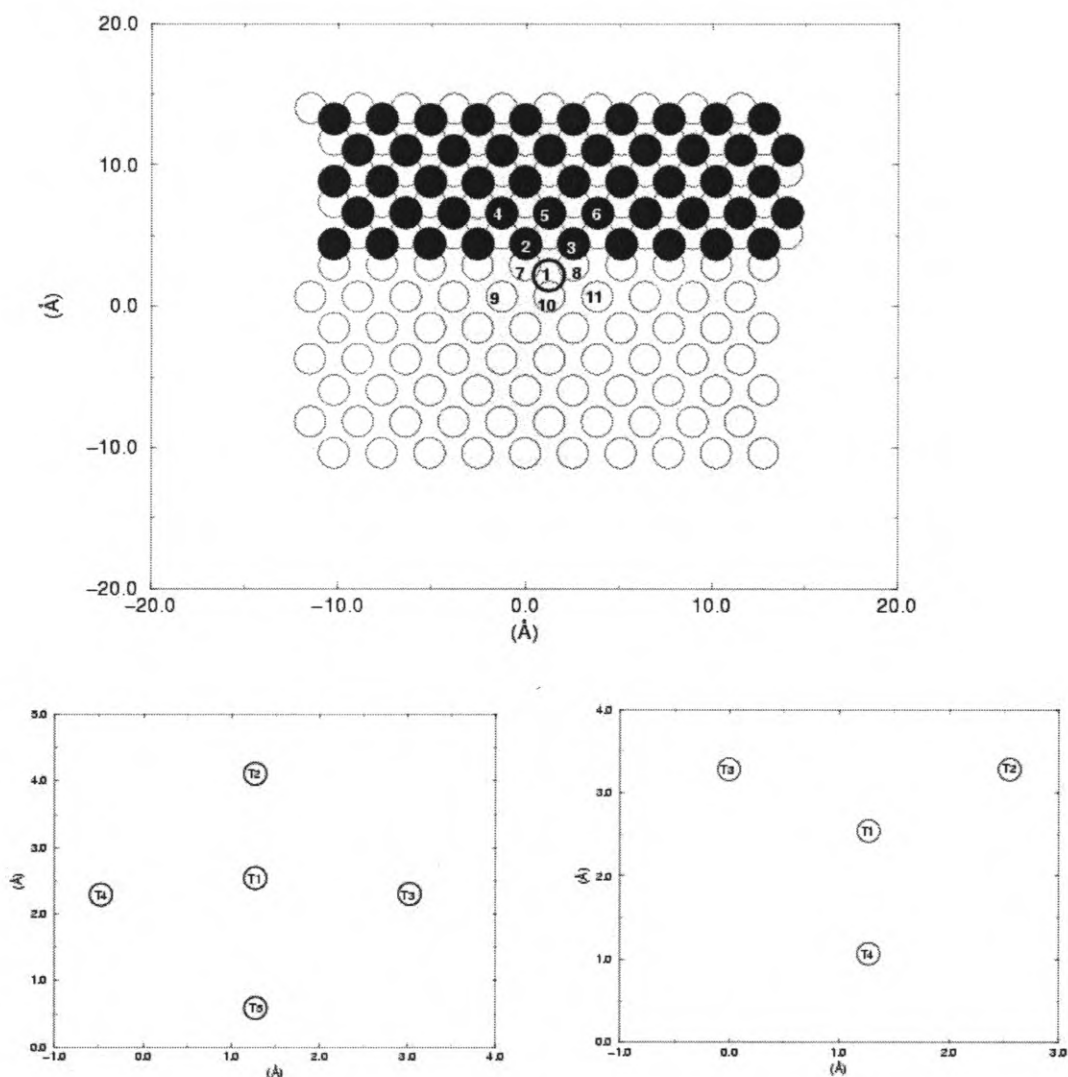


Fig. 4.6 Labels for adatom (1) and its neighboring atoms. Below Left – Labels for the (100) tip atoms. Below Right – Labels for the (111) tip atoms. The apex atom in each case is labelled T1.

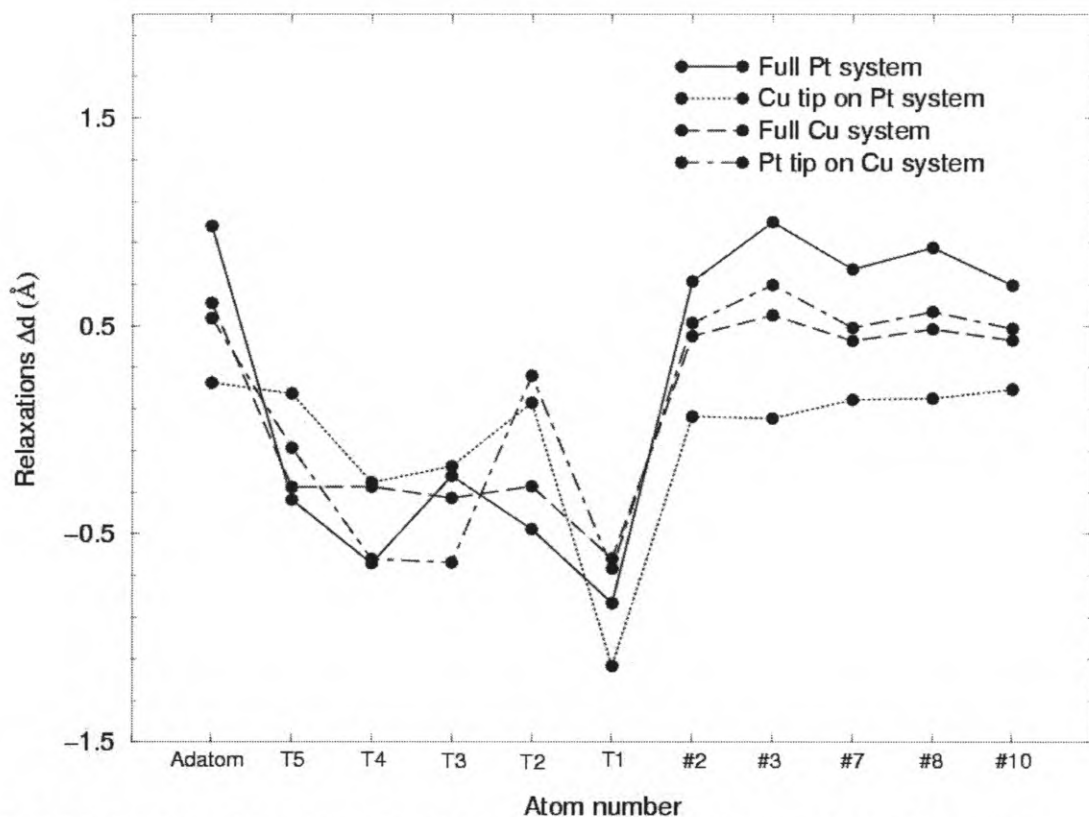


Fig. 4.7 Relaxations of the adatom, its neighboring atoms and the tip atoms for the four systems, Pt tip on Pt surface, Cu tip on Pt surface, Cu tip on Cu surface and Pt tip on Cu surface, at a tip height is between $2.75\text{\AA}$ - $3.5\text{\AA}$, and lateral separation at the value when the barrier is minimum, from Table 4.2.

From the Fig. 4.7 it can be seen that at the tip height of $2.75\text{\AA}$ (for the pure Cu and the pure Pt systems), $3.0\text{\AA}$ for the Cu tip on Pt system, and $3.5\text{\AA}$ for the Pt tip on Cu system, and lateral separation between tip and adatom at the value when the barrier is the minimum, the tip apex atom T1 as well as most of the tip atoms (refer to Fig. 4.6 for the atom labellings) have a downward relaxation towards the adatom (negative value). The adatom relaxes upwards towards the tip. Since the nearest neighbors of the adatom also relax upwards providing coordination effects to the adatom, this could be the reason for the lowering of the energy. Considering this, we have examined the total nearest neighbor distance between the adatom

and its neighbors for the position where the energy is lowered in the vicinity of the tip, as well as for the position where the adatom is far away from the tip (Table 4.4).

Table 4.4 Total nearest neighbor distance between adatom and its nearest neighbors

System	Total NN distance when energy is minimum (close to the tip) (Å)	Total NN distance at position away from the tip (Å)
Pure Cu	10.275	9.876
Pt tip on Cu	9.916	9.885
Pure Pt	10.898	10.451
Cu tip on Pt	10.724	10.442

From the above data we find that the total NN distance is infact smaller (atoms are closer to each other) when away from the tip as compared to when in the vicinity of the tip. We can thus conclude that even though the nearest neighbors of the adatom relax towards the tip, they do not provide as much coordination effect as they did when the adatom was far away from the tip. In the vicinity of the tip, the attraction of the adatom towards the tip is more enhanced than its neighbors, making their corresponding bonds slightly looser. Consequently, this would mean that we have to look deeper to explain the reason for the lowering of the energy, since it is not due to coordination effects. Next we look at the individual binding energies of the adatom, its nearest neighbors and the tip atoms (Table 4.5).

Table 4.5 Binding energies of the adatom, its nearest neighbors (when in the vicinity of the tip) and the tip atoms.

System	Atom number	Binding energy in the vicinity of the tip (eV)	Binding energy at position away from the tip (eV)
Pure Cu system	Adatom	-2.685	-2.525
	#2	-2.980	-2.855
	#3	-3.129	-2.988
	#7	-3.386	-3.299
	#8	-3.402	-3.307
	#10	-3.232	-3.127
	T1 (Tip apex)	-2.756	-2.563
	T2	-2.703	-2.690
	T3	-2.630	-2.646
	T4	-2.691	-2.646
	T5	-2.610	-2.595
Pt tip on Cu system	Adatom	-2.615	-2.524
	#2	-3.023	-2.895
	#3	-4.349	-4.224
	#7	-3.378	-3.299
	#8	-3.401	-3.312
	#10	-3.234	-3.128
	T1 (Tip apex)	-1.845	-1.853
	T2	-4.607	-4.605
	T3	-4.499	-4.498
	T4	-4.491	-4.502
	T5	-4.210	-4.207
Pure Pt system	Adatom	-4.833	-4.291
	#2	-5.067	-4.851
	#3	-5.405	-5.106
	#7	-5.591	-5.468
	#8	-5.646	-5.491
	#10	-5.388	-5.254
	T1 (Tip apex)	-4.961	-4.425
	T2	-4.839	-4.695
	T3	-4.644	-4.612
	T4	-4.778	-4.567
	T5	-4.529	-4.499
Cu tip on Pt system	Adatom	-3.894	-4.292
	#2	-4.209	-4.837
	#3	-4.175	-4.182
	#7	-5.559	-5.470
	#8	-5.560	-5.464
	#10	-5.367	-5.252
	T1 (Tip apex)	-7.274	-6.334
	T2	-2.508	-2.568
	T3	-2.539	-2.554
	T4	-2.601	-2.538
	T5	-2.442	-2.443

From the above table it can be seen that the binding energies of the atoms are lower when in the vicinity of tip, (when the adatom is ready to hop), as compared to the binding energies when away from the tip. This indicates that the adatom, its nearest neighbors and the tip atoms (especially the apex) strongly interact with each other, causing the lowering of the energy at this position. For the pure Cu system, the binding energies of the adatom and the tip apex when close to and away from the tip are not so dramatic. When the Cu tip is replaced with a Pt tip, the tip apex does not interact strongly with the Cu system. Thus there is no significant effect created by its presence. But for the pure Pt system, there is a significant difference in the binding energies of the adatom and the tip apex, showing a very strong interaction to bind with each other and thus the dramatic lowering of the energy as seen in the potential energy curve of Fig. 4.5(b). When the tip is replaced with a Cu tip, only the tip apex is seen interacting with the Pt system, but the Pt adatom and its closest neighbors, atom #2 and #3, do not interact with the tip. This is consistent with the potential energy curve in Fig. 4.5(b) where there is almost no change in its symmetric behavior even in the presence of the tip

4.4.2 Vertical Manipulation

Vertical manipulation is generally more difficult as compared to lateral manipulation because the activation energy barriers needed to lift the adatom from the surface may be substantially higher than those for lateral manipulation. However, a careful study shows that during the process of bringing the tip closer

to the adatom, the barrier to jump to the tip does vanish at a certain height (tip-substrate distance) and the adatom can be pulled to the tip apex [88,89]. We present in Figs. 4.8(a) and 4.8(b) the results obtained for a blunt Cu(100) tip, as we have found it to be more effective than a sharp tip in vertical manipulation. Figure 4.8(a) shows that as the tip is lowered the energy profile of the system changes from a double-well like curve, to one in which the barrier hump disappears and the two wells merge into a single one. In other words, the left minimum of the curves (which is the position of adatom near the surface) merges with the right minimum (adatom at tip apex), showing that the energy barrier for the adatom to be pulled up by the tip goes to zero at a certain tip height.

Interestingly, for the kinked and the stepped surfaces we find a “floating region” (at a tip height between $7.5\text{\AA}$ - $6.5\text{\AA}$), in which the total energy of the system is a minimum at a point between the surface and the tip apex. This is reflected in Fig. 4.8(a) for adatom manipulation on the stepped Cu(111) surface. In this region the adatom is equally attracted to the surface and the tip and may float in between. For the adatom on the flat surface such a region is not conspicuous.

A plot of the energy barriers versus the inverse of the tip height, in Fig. 4.8(b), shows that at large tip heights, the barrier to pull an adatom from a flat surface is lower than that from a stepped or a kinked surface as is expected from considerations of the local coordination of the adatom on these surfaces: the adatom needs to break 3 bonds in the case of the flat, 5 for the stepped, and 6 for the kinked surface, to detach from them. However, as the tip is lowered its impact

on the potential energy surface is more pronounced on the stepped and kinked surfaces than the flat one and it becomes easier to extract an atom from a stepped or a kinked surface. This crossover point at which the decrease in barriers becomes more rapid for the stepped and the kinked surfaces as compared to the flat surface, is clearly seen in the Fig. 4.8(b). This unexpected result implies that the presence of the tip not only weakens the bonding of the adatom, but it also highly affects the local environment of the adatom, especially in the case of the low-coordinated surroundings of the stepped and the kinked surfaces.

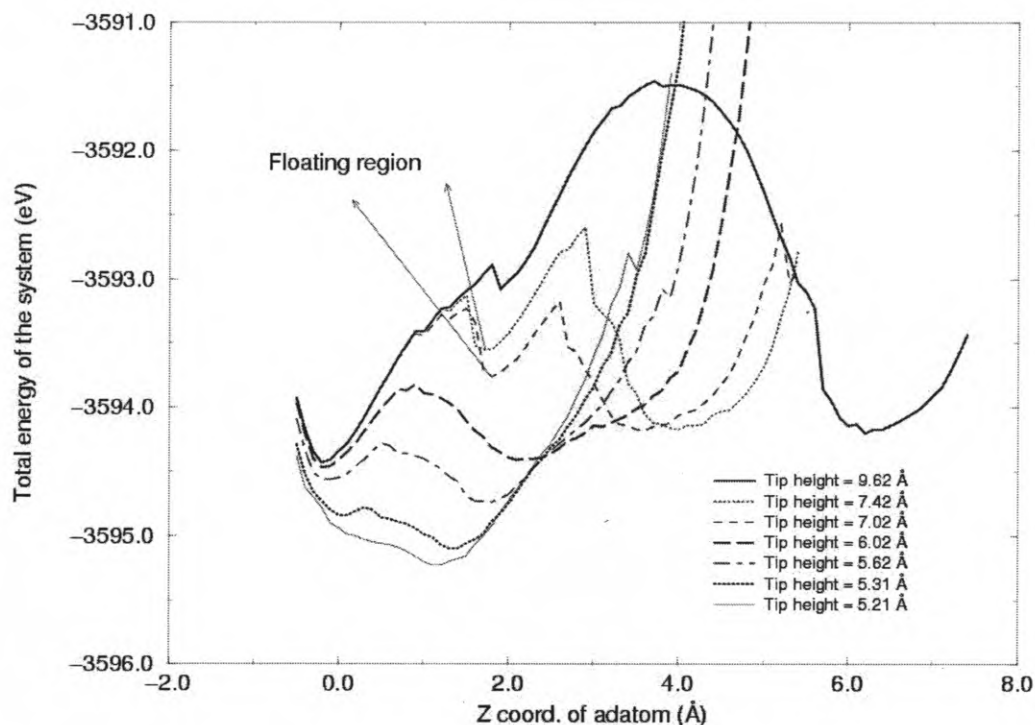


Fig. 4.8(a) Vertical Manipulation – disappearance of the barrier for a stepped Cu(111) surface as the tip is lowered towards the adatom. The floating region is also seen. Ref. [95].

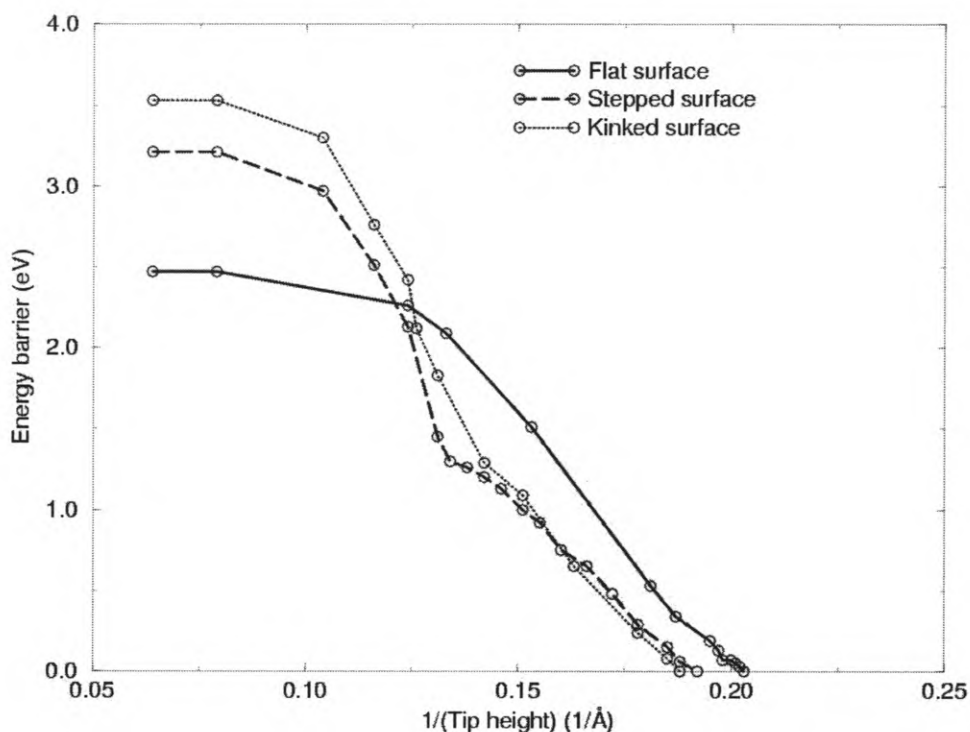


Fig. 4.8(b) Comparison of the barriers for the flat, stepped and kinked Cu(111) surfaces with respect to the inverse of the tip height. Ref. [95].

4.4.2.1 Relaxations – in the presence of different tip geometries and shapes on flat, stepped and kinked surfaces

To understand and study the process of vertical manipulation in more detail, we also look into the relaxations of the adatom as well as its neighboring atoms in the presence of a (100) as well as a (111) sharp tip. As will be seen, the combined relaxations of the neighboring atoms provide a rationale for understanding the results for vertical manipulation on flat, stepped and kinked surfaces. Since a sharp tip is found to lower the energy barriers slightly more than a blunt tip, we present results for atomic relaxations for the cases of the (100) and the (111) sharp tip for the homogeneous Cu system. For the labelling of the atoms on the surface and on the tips, the reader is referred to Fig. 4.6.

In Figs. 4.9(a), (b), (c) and (d) we have plotted the relaxations (difference in the z coordinate of the atom for the relaxed and unrelaxed system) of the adatom and its five nearest neighbors, as a function of the height of the tip apex atom, which lies just above the adatom, for the (100) and (111) sharp tips and the (100) and (111) blunt tips respectively. We find that for a (100) sharp tip, at a tip-adatom separation is $2.5\text{\AA}$, the adatom and atoms 2 and 3 relax towards the tip by more than $0.1\text{\AA}$. Atoms 7, 8 and 10, on the other hand, relax much less because they are further away from the tip (Fig. 4.9(a)). Notice the similar trends in the relaxation patterns of atoms 2 and 3 and of atoms 7, 8 and 10, which is related to their symmetric positions with respect to the tip apex. Figs. 4.10(a), (b), (c) and (d) show the relaxations of the tip atoms of the (100) and (111) sharp tips and the (100) and (111) blunt tips respectively. For the (100) sharp tip, the tip apex atom and its other atoms relax upward into itself, seeking higher coordination from its own atoms (Fig. 4.10(a)). At higher tip-adatom separations, the relaxations of the adatom and its neighbors are negligible and those of the tip atoms are in an upward direction towards the tip structure itself, forming a more compact tip, or a tightening effect. If we look at the corresponding relaxations that occur in the presence of a (100) blunt tip, we find that again the adatom and its neighbors, atoms #2, 3 have a stronger attraction (about $0.65\text{\AA}$) towards the tip at a tip height of $3.0\text{\AA}$ (Fig. 4.9(c)), which is much higher than that seen for a sharp (100) tip. Atom #7, 8, and 10 have slightly lower relaxations as compared to the adatom and atoms #2, 3. Most of the tip atoms relax downward towards the adatom and its

neighbors at low heights of the tip, $3.0\text{\AA}$ and $3.5\text{\AA}$ (Fig. 4.10(c)). Thus it is clear that the blunt tip is more efficient for vertical manipulation.

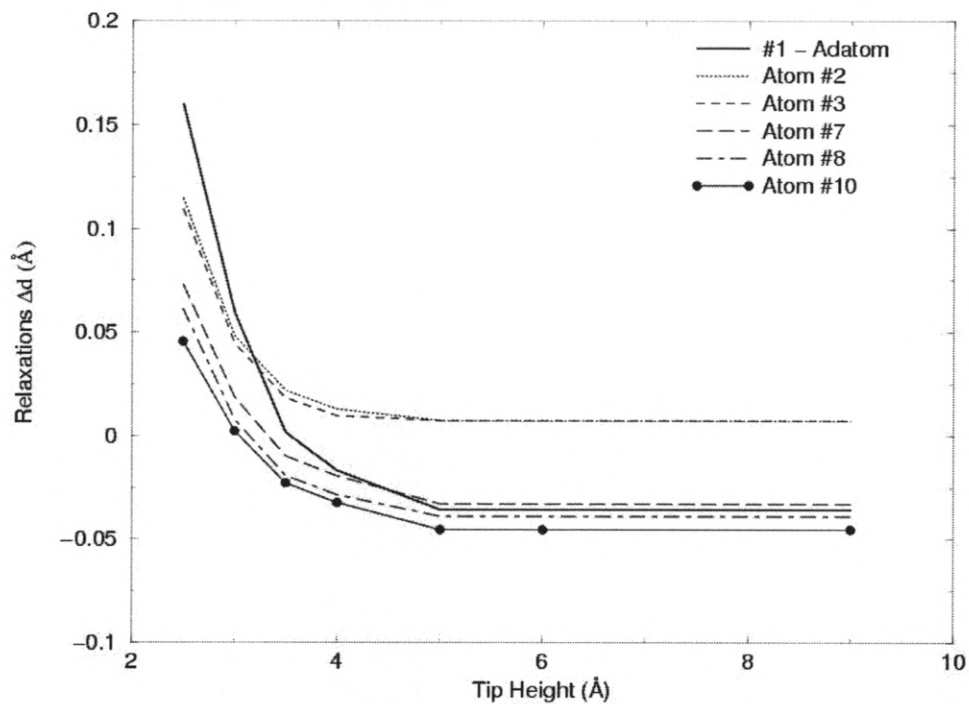


Fig. 4.9(a) Relaxations of the adatom and its neighboring atoms in the presence of the (100) sharp tip directly above the adatom. Positive values indicate relaxation towards the tip.

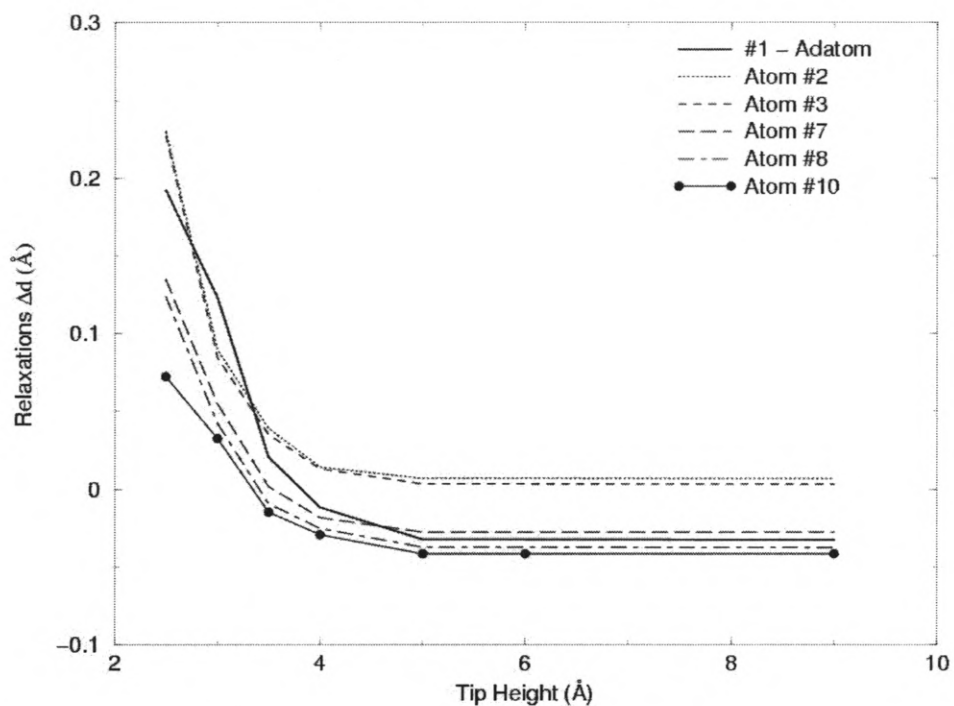


Fig. 4.9(b) Relaxations of the adatom and its neighboring atoms in the presence of the (111) sharp tip directly above the adatom. Positive values indicate relaxation towards the tip.

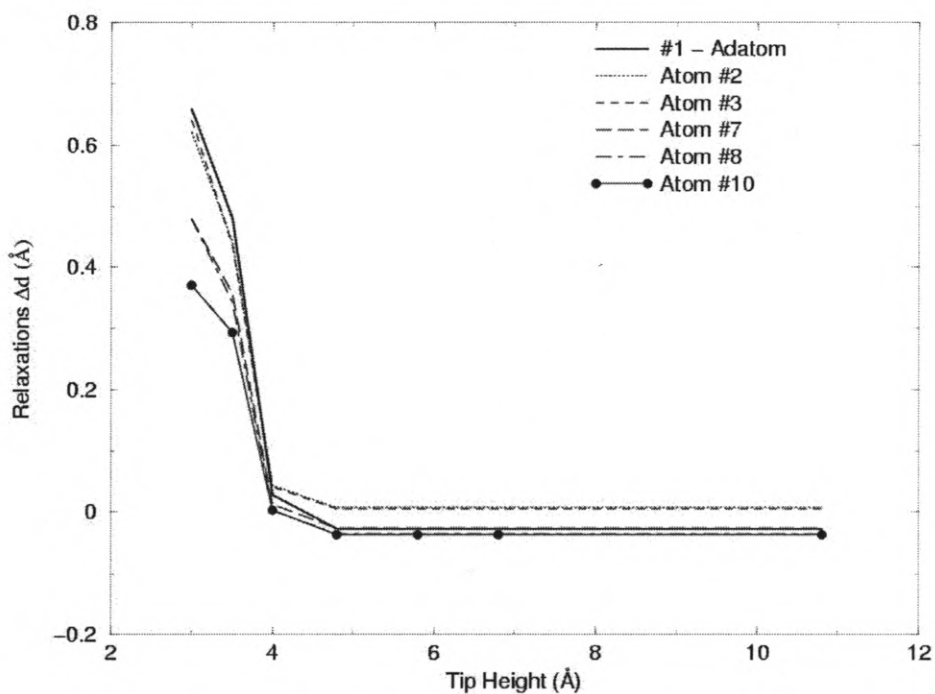


Fig. 4.9(c) Relaxations of the adatom and its neighboring atoms in the presence of the (100) blunt tip directly above the adatom. Positive values indicate relaxation towards the tip.

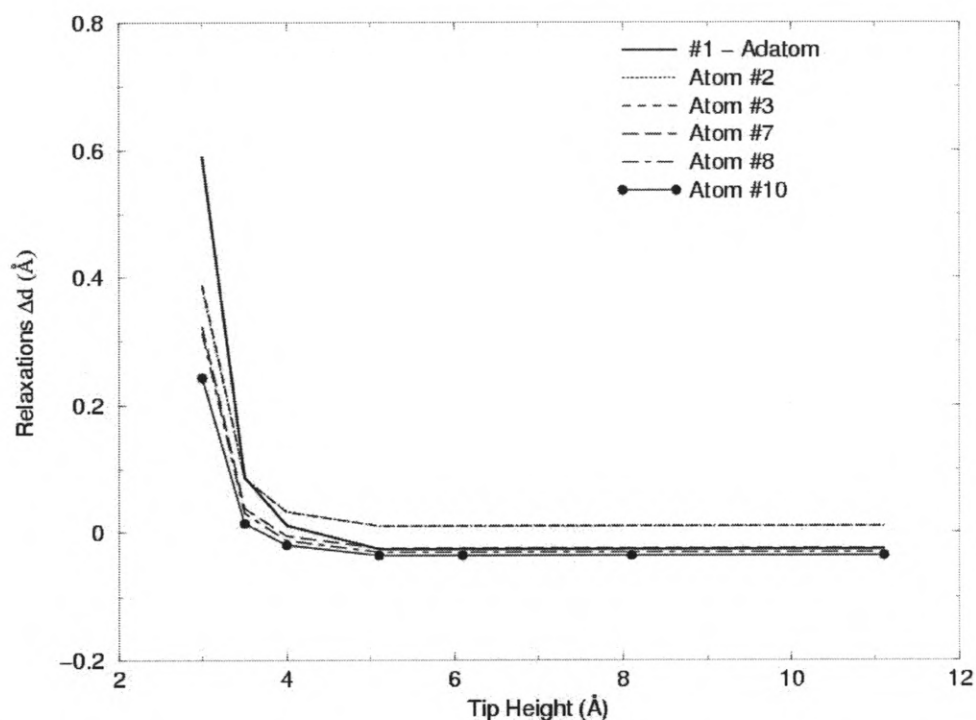


Fig. 4.9(d) Relaxations of the adatom and its neighboring atoms in the presence of the (111) blunt tip directly above the adatom. Positive values indicate relaxation towards the tip.

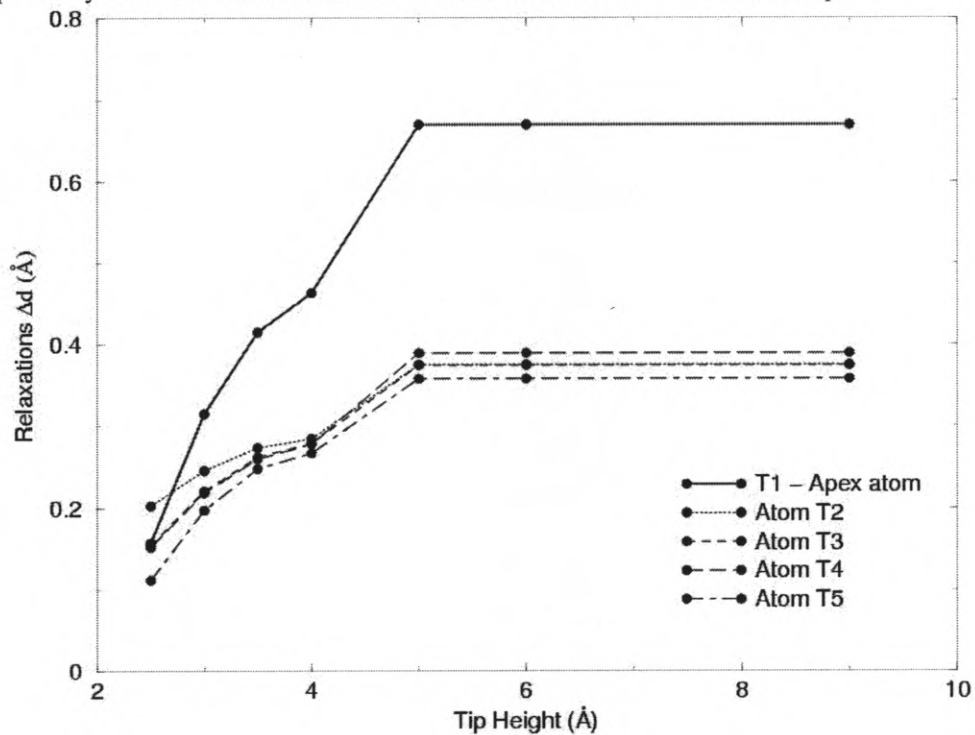


Fig. 4.10(a) Relaxations of atoms of the (100) sharp tip. Positive values of relaxations are for atom recoiling into the tip and negative for relaxing towards the adatom.

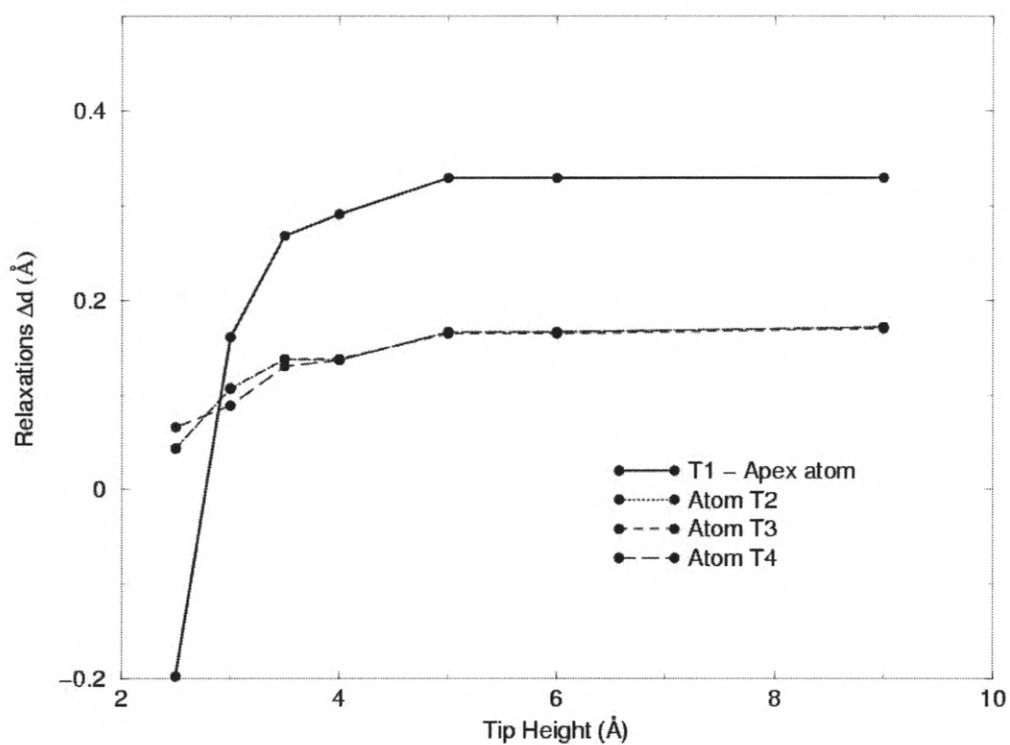


Fig. 4.10(b) Relaxations of atoms of the (111) sharp tip atoms. Positive values of relaxations are for atom recoiling into the tip and negative for relaxing towards the adatom.

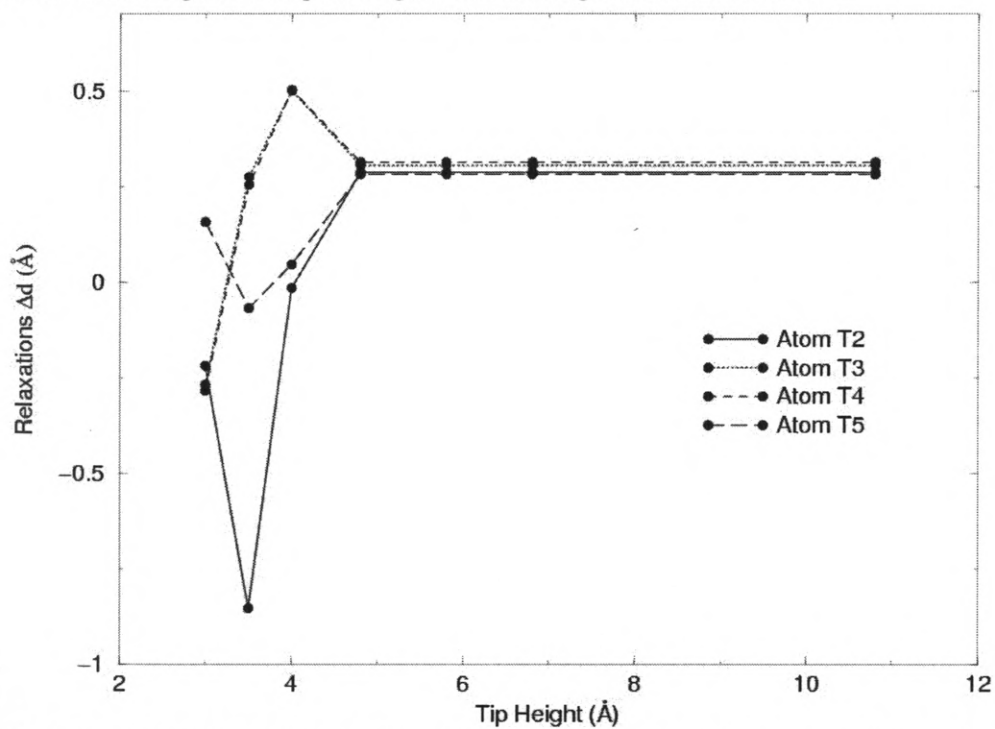


Fig. 4.10(c) Relaxations of atoms of the (100) blunt tip. Positive values of relaxations are for atom recoiling into the tip and negative for relaxing towards the adatom.

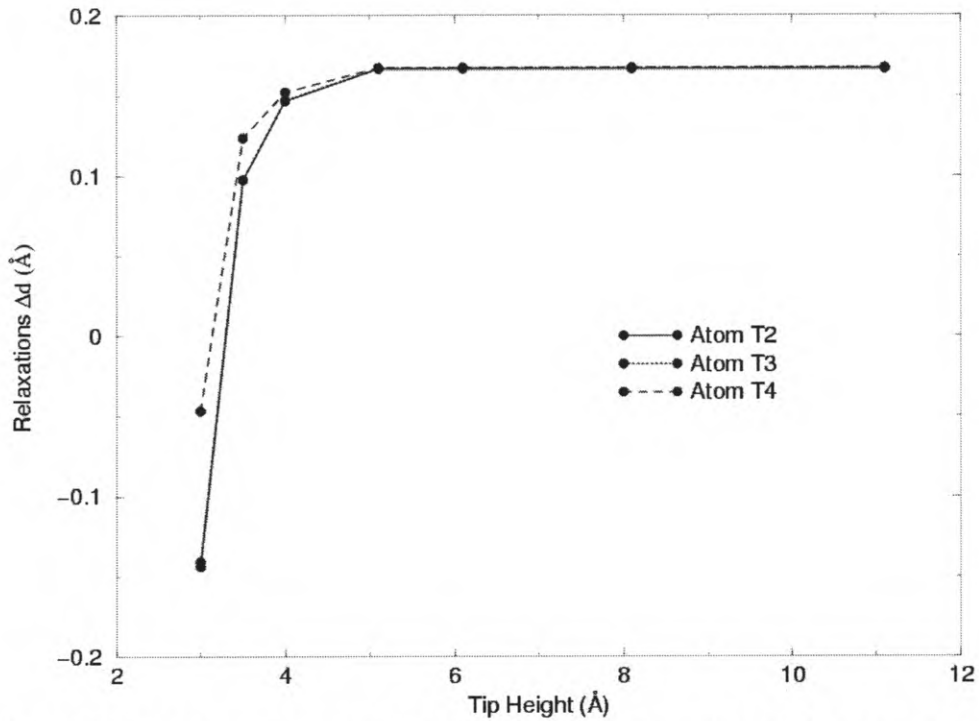


Fig. 4.10(d) Relaxations of atoms of the (111) blunt tip. Positive values of relaxations are for atom recoiling into the tip and negative for relaxing towards the adatom.

Moving on to the case of the sharp and blunt (111) tips, we find that in the presence of a (111) sharp tip, at a tip-adatom separation of $2.5\text{\AA}$ are somewhat different from those for the (100) tip, as relaxations are larger (up to $0.2\text{\AA}$). Here too the adatom as well as all neighboring atoms relax towards the tip (Fig. 4.9(b)). Again, atoms 2 and 3 show similar trends, and atoms 7, 8 and 10 are affected similarly. The tip apex atom relaxes downward towards the adatom (Fig. 4.10(b)), as if the tip has a loosening effect. This was not the case for the (100) sharp tip and this could be the reason for the larger upward relaxation of the adatom and its neighbors at this height. At larger tip-adatom separations, the relaxations of the adatom and its neighbors are negligible and those of the tip atoms are upward, towards the tip structure. Looking at the corresponding plots for the blunt (111) tip, we find that for a low tip height of $3.0\text{\AA}$, the adatom and its neighbors show

much larger relaxations towards the tip as compared to a sharp (111) tip (Fig. 4.9(d)). At this height, the 3 apex atoms of the blunt (111) tip relax downward (Fig. 4.10(d)), towards the adatom, which eventually leads to the pick up of the adatom. These relaxations of the tip apex atoms, the adatom and its neighboring atoms give us a clearer picture of which atoms are affected by the tip presence and thus assist in the manipulation process by providing coordination effects.

In support of our earlier statement that relaxations of neighboring atoms play a major role in the above results for the three surfaces, we make a comparison of the sum of the displacements and that of the individual energies of the nearest neighbor atoms as the adatom is raised from the surface to the tip apex. Fig. 4.11(a), which shows the comparison of the sum of displacements of the nearest neighbor atoms for the three surfaces, is for the case of a tip height of $5.3\text{\AA}$, at which a zero barrier is experienced by the kinked surface. This figure clearly indicates that for the kinked surface the perturbations caused by the tip to the neighboring atoms is higher than that for the stepped and the flat surface, making it easier for an adatom pick up. Similarly, we find the stepped surface to be more perturbed by the tip as compared to the flat surface. Table 4.6 gives a direct comparison of the barriers for the three types of surfaces, the flat, stepped and kinked surfaces at different heights. It is seen that the barrier for the kinked surface reaches zero at a tip height of $5.3\text{\AA}$, whereas the tip has to be brought a little closer to pick the adatom from a stepped surface ($5.2\text{\AA}$) and still closer for a flat surface ($4.92\text{\AA}$). Fig. 4.11(b) shows the sum of energies of the nearest neighbor atoms, as the adatom is raised from the surface to the tip apex. Thus, the

energy of each nearest neighbor atom (as calculated in the figure itself) for the case of the kinked surface is greater than the other two, the flat surface being the lowest. The figures thus illustrate that the perturbation in the local environment of the low coordinated kinked and stepped surfaces is more pronounced. A recent theoretical work [101] also concluded that at very small tip-adatom separations, during contact formation, the relaxations of the tip atoms and the surface atoms finally lead to the pick up of the adatom.

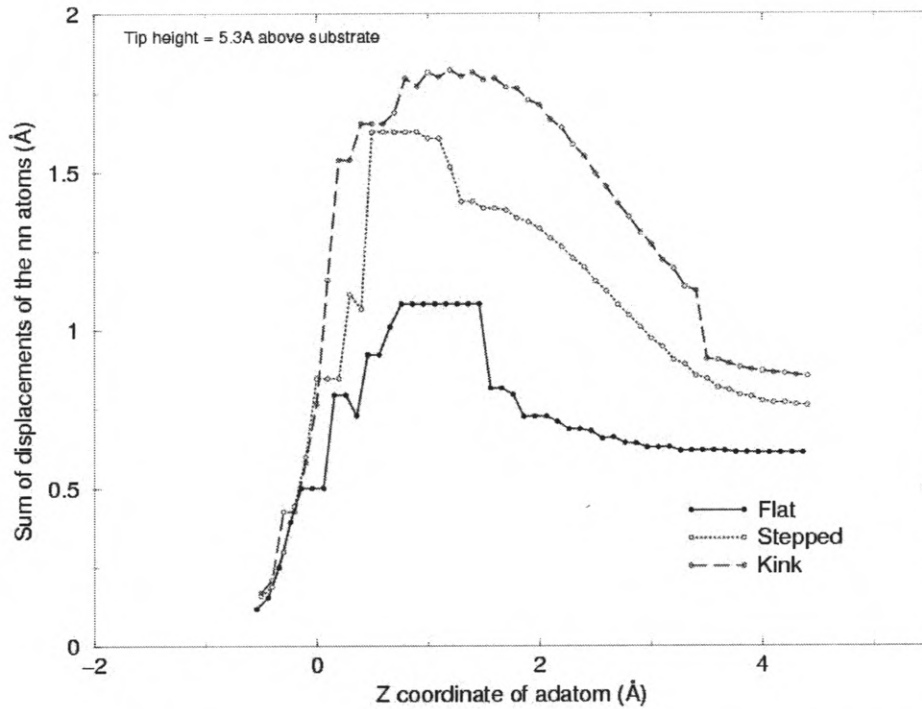


Fig. 4.11(a) Comparison of the sum of the displacements of the nearest neighbor atoms as the adatom is raised from surface to the tip apex.

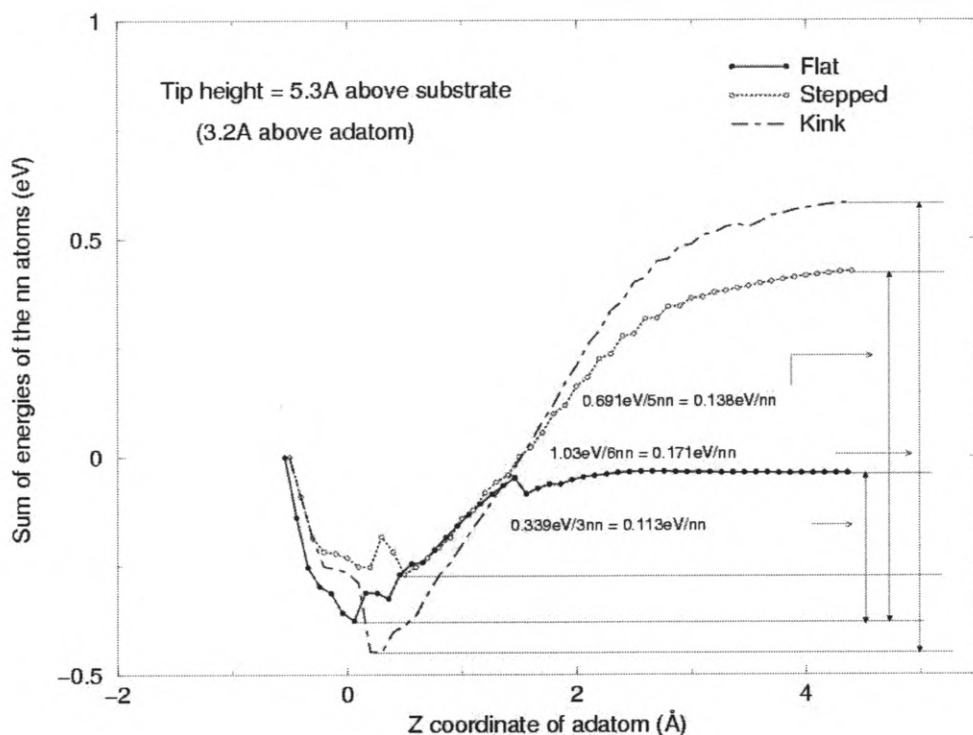


Fig. 4.11(b) Comparison of the sum of the individual energies of the nearest neighbor atoms as the adatom is raised from the surface to the tip apex.

Table 4.6 Comparison of energy barriers for vertical manipulation on flat, stepped and kinked Cu(111) surfaces for different tip heights.

Surface Tip Height (Å)	Flat Barrier (eV)	Stepped Barrier (eV)	Kinked Barrier (eV)
12.5	2.47	3.21	3.53
8.0	2.26	2.13	2.42
7.5	2.09	1.45	1.83
6.5	1.51	1.00	1.09
5.5	0.53	0.29	0.24
5.3	0.34	0.06	0.00
5.2	—	0.00	—
5.1	0.19	—	—
4.92	0.00	—	—

4.5 Conclusions

In summary, we have shown that in the presence of a tip, the saddle point for an adatom to diffuse laterally from one hollow site to the next, along a (100)-microfaceted step edge on Cu(111), shifts away from the bridge site. The activation barrier for the adatom to hop towards the tip is considerably lowered but does not vanish. The lowest barrier is reached at a lateral separation between $2.0\text{\AA}$ - $3.0\text{\AA}$. Our results show that the qualitative changes in the potential energy surface are independent of the shape and geometry of the tip but we see a quantitative difference when considering the tip details. Although a sharp tip lowers the barrier slightly more than a blunt tip, the effect of the blunt tip extends over a larger range of lateral separations, which may be traced to the higher coordination it offers to the adatom. From the results for vertical manipulation we find that a blunt tip is most effective in lowering the barrier to zero as it gradually comes closer to the adatom.

We have also examined the trends in the lowering of the activation barrier for the adatom to hop towards the tip during lateral manipulation for six metals and two heterogeneous cases of a Cu(100) tip on a Pt(111) stepped surface with an adatom, and a Pt(100) tip above a Cu(111) stepped surface with a Cu adatom. The lowest barrier is reached at a lateral separation between $2.0\text{\AA}$ - $3.0\text{\AA}$. The role of cohesive energy, which is specific of each metal and defined as the energy to extract an atom out of its crystal lattice, is necessary to be considered, along with the energy barriers of the atom to hop from one site to the other, to make a direct comparison between the different metals studied. Thus, the ratios of the barriers

and opbarriers to the cohesive energy help in explaining this interesting result of the changes in the potential energy surface due to the interatomic potentials. Among all the transition metals studied with the same tip-substrate elemental composition, Ag is found to have the lowest barrier of 50 meV with a saddle point shift of $0.7\text{\AA}$. However, even though Cu had the next lowest barrier of 61.7 meV with a saddle point shift of $0.6\text{\AA}$, it is Cu that is the easiest to manipulate. This is concluded from the ratios of the opbarrier to the barrier in the presence of the tip and also the ratios of difference in the opbarrier and barrier to the cohesive energy and to the barrier in the absence of the tip. These ratios indicate that the probability of the adatom to be pulled towards the tip is the highest in the case of Cu as compared to the other metals. We find an anomaly in the case of the Pt metal where the presence of the tip is found to hinder the motion of the adatom along the step edge as compared to when in the absence of the tip. This could be due to the EAM potentials that are not as accurate for the Pt metal. However, we cannot rule out the fact that it is an interesting result and needs deeper investigation. For the heterogeneous cases, of a Pt tip on a Cu surface with a Cu adatom and a Cu tip on a Pt surface with a Pt adatom, the lowering of the barrier is found to be due to the interaction between the tip and the adatom. This is indicated by the binding energies of the adatom, its nearest neighbors and the tip atoms. The Cu tip is more effective in lowering the barrier on a Pt surface with a Pt adatom as compared to a Pt tip. However, for the reverse case, a Pt tip is not as effective in lowering the barrier for a Cu surface with a Cu adatom as compared to a Cu tip. The shift in the saddle point is insignificant and is found to be $0.3\text{\AA}$.

for the Pt tip on Cu surface with a Cu adatom and 0.1Å for a Cu tip on a Pt surface with a Pt adatom.

During vertical manipulation, in the absence of tip the energy required to pull an adatom from a flat surface (2.47eV) is lower than that from a stepped (3.21eV) and a kinked surface (3.53eV). As the tip is lowered to facilitate manipulation, the changes in the surface energetics are such that it is easier to extract an adatom from a stepped or a kinked surface than from a flat one, implying that the tip affects the low coordinated local environment of the adatom, which assists in its extraction. In addition, for specific tip heights, there is a floating region on the kinked and stepped surfaces in which the adatom is found to be equally attracted to the substrate and to the tip apex atoms.

The relaxations of the tip apex atoms, the adatom and the neighboring atoms show that a blunt tip is more effective in vertical manipulation. The comparisons of the sum of displacements of the nearest neighbor atoms as the adatom is raised from the surface to the tip apex as well as the comparison of the sum of the individual energies of the nearest neighbor atoms as the adatom is raised from the surface to the tip apex indicate the contribution of the local environment to the lowering of the barrier for vertical manipulation by providing coordination effects. From this detailed study, we obtain useful and interesting information about adatom manipulations for homogeneous and heterogeneous systems, the modifications to the potential energy surface in the presence of the tip and relaxations of the atoms assisting in the process, thus providing us with important factors that can help in the manipulation process.

Chapter 5

Morphology of ledge patterns during step flow growth of metal surfaces vicinal to fcc(001)

The morphological development of step edge patterns in the presence of meandering instability during step flow growth is studied by simulations and numerical integration of a continuum model. It is demonstrated that the kink Ehrlich-Schwoebel barrier responsible for the instability leads to an invariant shape of the step profiles. The step morphologies change with increasing coverage from a somewhat triangular shape to a more flat, invariant steady state form. The average pattern shape extracted from the simulations is shown to be in good agreement with that obtained from numerical integration of the continuum theory. This work is published and can be referred to in Ref. [102].

5.1 Introduction

Epitaxial growth on vicinal surfaces is known to give rise to interesting growth instabilities under suitable conditions, e.g. to step bunching, mound formation and meandering of the step edges [103]. The meandering instability emerges when the interlayer mass transport from the upper side of the step is reduced due to the Ehrlich-Schwoebel barrier [104,105] enhancing growth of protrusions at the step edges. This is now known as the Bales-Zangwill instability (BZI) [106] which tends to destabilize the ledge morphology due to terrace diffusion and asymmetric interlayer crossing. There is no diffusion along the ledges in BZI. However, recently it was found that in the case of 1+1 dimensional growth there is an

analogous phenomenon due to the *kink Ehrlich-Schwoebel barrier* for going around a kink site at the step edge. The corresponding kink Ehrlich-Schwoebel effect (KESE) leads to growth of unstable structures at the step edges with a dynamically selected wavelength [107]. The ledge instabilities were originally found and reported experimentally on the Cu(1,1,17) vicinal surface [108] but attributed to the BZI scenario. More recent STM experiments on the Cu(1,1,17) surface proposed that the formation of the regular patterns is due to the KESE [109]. Since then theoretical studies of the meandering instability have shown that the KESE indeed supercedes the BZI in the formation of the periodic patterns [107,110,111] and eventually leads to an in-phase motion of the step edge structures [110,111].

Instability and wavelength selection of the step edge patterns due to the KESE have been studied within the framework of a continuum step model [107], the solid-on-solid (SOS) lattice model [11,111], and semi-realistic Monte Carlo (MC) simulations [110]. In particular, in the recent MC work [110] it was shown that on vicinal Cu(1,1,m) surfaces the observed instability is due to the KESE and the competing BZI is of no importance in the length and time scales considered. The role of dimer nucleation in determining the selected wavelength was confirmed, in good agreement with the theoretical scaling relation [112] and more recent SOS simulations [111]. In the MC simulations, there was evidence of phase locking of the ledge structures at the largest coverages studied, but this was not quantitatively confirmed.

Regarding the step morphologies, a triangular shape has been predicted to occur for a strong KESE and a rounded, more flat shape for a weak KESE [107]. However, the MC simulations of Ref. [110] indicate that in the case of a strong KESE there is in fact an interesting shape transition from narrow, somewhat triangular shapes in the initial stage of growth to more rounded patterns in the large coverage regime. Moreover, the MC simulations of Ref. [110] and SOS model results of Ref. [111] are in disagreement with asymptotic evolution of the step profiles as predicted by the continuum theories [113,114]. In this work we study the ledge morphologies of growing steps on the vicinal Cu(1,1,m) surfaces in detail. In particular, we study the onset of the in-phase growth and the phase-locking of the step profiles in the presence of a strong KESE. Our results show that the ledge morphologies assume an invariant shape due to an interplay between various mass transport currents and phase-locking of the steps. We show how the ledge profiles from the MC simulations can be reproduced by explicitly including the relevant mass transport currents on the surface. On continuum level this indicates a delicate balance between the various currents that determines and stabilizes the invariant ledge shapes.

5.2 Theoretical Details

5.2.1 Step Instabilities

During surface growth, islands grow on the terraces between steps. Moreover, islands are also stepped structures. Island boundaries as well as steps on vicinal surfaces are one-dimensional objects, and consequently even in equilibrium they

are rough at any finite temperature. During surface growth step edge structures are susceptible to instabilities for several reasons, e.g., asymmetric mass currents along the different surface directions. It is well known that the instability of straight step edges is caused by the Ehrlich-Schwoebel barrier. Surface morphologies during growth are strongly dependent on the energy barriers related to microscopic processes. For example, on many surfaces an adatom close to the downhill step edge is more likely to be reflected back than to cross the edge due to the Ehrlich-Schwoebel (ES) barrier [104,105]. The extra barrier can be understood on the basis of low coordination of an adatom at the intermediate position between the initial and final states during step crossing. The large ES barrier induces different effects on growth morphology: It is responsible for the instabilities associated with mound formation on flat surfaces [115] and meandering of surface steps on vicinal surfaces [106,116], but also stabilization of vicinal surfaces against step bunching [117]. If the average terrace width is considered as L , a terrace larger than L receives more mass from the deposition flux as compared to the other terraces and thus the step edge in the uphill direction advances faster than the other steps. On the other hand, if a terrace width is smaller than L , the step edge in the uphill direction has a smaller velocity than the other steps until the average terrace width is reached by all the terraces. The same ES barrier is also responsible for the instabilities of steps. If there is a fluctuation in the step edges, the adatoms that are deposited tend to attach to the protrusions at the step edges rather than the other areas. For a non-zero ES barrier this effect is asymmetric with respect to the lower and the upper terraces. Thus

protrusions in the lower terrace gather more mass than the upper terrace. This leads to meandering of steps and is the origin of the Bales-Zangwill (BZ) instability [106]. Moreover, simulations using a solid-on-solid (SOS) model have shown that after the BZ instability has developed a secondary instability sets in leading to mounds also on a vicinal surface [7,118].

5.2.2 Kink Ehrlich-Schwoebel Effect

The first experimental results and also the meandering instability observed in SOS simulations [118] were interpreted through the BZ explanation [108]. But recent STM experiments on vicinal Cu surfaces demonstrated that the selected wavelength does not quantitatively agree with the BZ prediction [109].

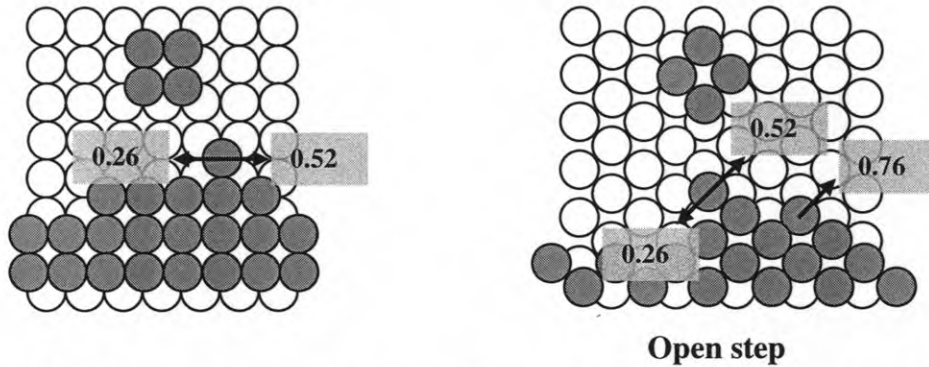


Fig. 5.1 A top view of an fcc surface with (a) close-packed and (b) open step edges. Solid circles correspond to the upper and open circles the lower terrace. Energy barriers on a Cu surface [119] for a few processes denoted by the arrows are given in the units of eV.

The first simplified SOS model simulations suggested that the kink Ehrlich-Schwoebel effect (KESE) may lead to formation of step instabilities [11,120,110]. In addition, SOS simulations have shown that both the BZ and KESE instabilities are possible, depending on the relative importance of edge diffusion [117]. However, quantitative data of the selected wavelength and the structure of the

patterns were still unresolved. Also, most results were for the weak KESE while one assumes that on Cu surfaces the opposite is true. From calculations of energy barriers, it is found that an extra barrier of about 0.25 eV for kink rounding at close-packed step edges is present [119]. However, experimental evidences of the KES barrier are still few [121,122]. But in case, the KES barrier does exist, it could have rather large consequences on the interpretation of experiments, especially determining the value of the ES barrier via the time-dependent step correlation function [123]. During the growth of a vicinal surface incoming adatoms landing on terraces will eventually attach to step edges if terrace nucleation is suppressed. On many surfaces an adatom at the edge preferentially diffuses along the step rather than detaching back to the terrace (for simple metal surfaces, see Ref. [119]). Consequently, the formation of one-dimensional (1D) islands at the edge takes place. As the first row of 1D islands at the edge grow large enough subsequent adatoms coming to the step attach on top of them. Now, KESE for a non-zero kink ES barrier ensures that almost all adatoms stay on top of the first-row islands and cross the kink sites only rarely. Thus, KESE induces destabilizing mass currents along the up-kink direction and unstable structures onto the step edges, in analog of the mounding instability on flat surfaces [107,124]. This destabilizing character of KESE applies well to close-packed steps where the KES barrier is believed to exist. For example, on fcc surfaces one can have both close-packed and open steps (see Figure 5.1) with different energy barriers at the edge. Based on symmetry arguments one can argue that KESE is actually stabilizing open steps [107,125]. This is further elucidated in Figure 5.1.

At open steps adatoms diffuse along steps via a two-step process. Thus protrusions have triangular shapes with close-packed sides. An adatom attaching to the side of the triangle preferentially seeks the two-fold coordinated site close to the edge since at the tip of the triangle it experiences the KES barrier. Of course, it might be the case that for open steps strain effects could play an important part and influence diffusion processes at the edge.

5.2.3 Wavelength of patterns

Define a scale L_n as a characteristic length of an edge above which islands form, i.e. at the edges with $L > L_n$ nucleation occurs. In the case of dimer nucleation in 1D the length is given by [126,127]

$$L_n \propto \left(\frac{D_s}{\Phi_s} \right)^{1/4}, \quad (3.12)$$

where, $D_s \propto \exp(-E/kBT)$, E_s is the diffusion barrier along the straight edge, and $\Phi_s = \Phi L$ is the flux onto the edge. For weak KESE the wavelength λ of unstable step patterns can be determined from the linear stability analysis and turns out to be [127,128]

$$\lambda \propto \sqrt{\frac{L_n^3}{L_s}}, \quad (3.13)$$

where, $L_s = \exp[(E_k - E_s)/kBT] - 1$ is the kink ES length [107] and E_k is the KES barrier. For strong KESE Eq. (1.13) is no longer valid. In this case one can assume that λ is set by dimer nucleation at the onset of growth so that $\lambda \approx L_n$.

5.3 Model System

The model system used here is as in Ref. [110], based on MC simulations of a lattice gas model with energetics from the effective medium theory (for more details, see Refs. [110,129]). Our MC method is efficient enough to simulate growth of Cu up to ten monolayers (ML) under realistic temperature and flux conditions. The temperature range explored here was $T = 240 - 310$ K and the flux $F = 3 \times 10^{-3} - 1.0$ ML/s. Thus the ratio between the terrace diffusion and the flux $D/F \approx 6 \times 10^5 - 9 \times 10^7$ in units of the lattice constant $a = 0.361$ nm, corresponding to a typical molecular beam epitaxy regime [130]. The energetics of the model also specifies the important length scales controlling step flow growth. These are l_c , the length scale for dimer nucleation at the step edge [112], and the kink Schwoebel length [107] $l_s = \exp[(E_s - E_d)/k_B T] - 1$ which is related to the energy barriers $E_s = 0.52$ eV and $E_d = 0.26$ eV for jumps around a kink site and along a straight edge, respectively. For the close packed [110] ledges, $l_s \approx 10^4$ and $l_c \approx 10^2$ around room temperature corresponding to strong KESE [107,111,113]. In Ref. [110] it was shown that the wavelength of the step edge patterns is given by $l_c = (12D_s/FL)^\alpha$, D_s being the adatom diffusion constant along the straight edge, with a scaling exponent $\alpha \approx 0.23$, and an effective barrier of $E_{\text{eff}} = 75 \pm 10$ meV. Both are in good agreement with the exact values which give $\alpha = 1/4$ (Ref. [112]) and $E_{\text{eff}} = E_d/4 = 65$ meV, respectively. A previous study [110] was done on a Cu(1,1,17) surface but we have checked the results also with smaller terrace widths.

5.4 Results

Simulation results for the step edge profiles on Cu(1,1,17) are shown in Figs. 5.2(a)-(c) after deposition of $\theta = 0.4, 2.0$, and 10.0 ML, respectively, at $T = 300$ K with $F = 6 \times 10^{-2}$ ML/s. In the beginning of growth (Fig. 5.2(a)) the shape of the patterns is somewhat triangular as predicted for a relatively strong KESE [113]. The meandering structures are not yet completely in the same phase indicating that the diffusion field has not yet coupled the subsequent step edge trains, a typical feature for KESE dominated meandering [111]. However, a selection of the relatively well-defined wavelength for all ledges is apparent already at this stage of growth [110]. At larger coverages the meandering of steps begins gradually to phase-lock, seen in Fig. 5.2(b), and in-phase growth and phase-locking seem complete at largest studied coverage of 10 ML shown in Fig 5.2(c). However, now the average shape of the patterns is clearly different from that at low coverages. The shape of the average patterns is more rounded, as predicted for a weak KESE. In Fig. 5.2(d) we show this change by comparing average ledge profiles after 0.4 and 2.0 ML, respectively [131].

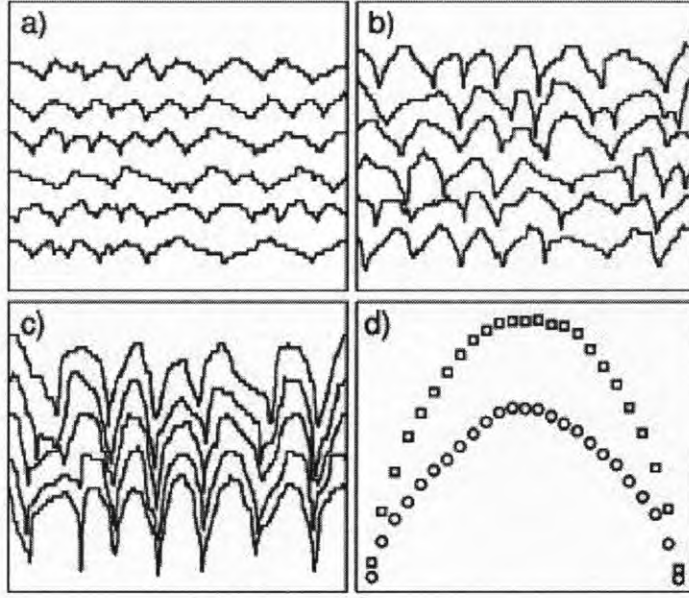


Fig. 5.2 Snapshots of typical ledge profiles with step orientations in the close packed [110] direction at $T = 300$ K with $F = 8 \times 10^{-2}$ ML/s for coverages $\theta = 0.4, 2.0$, and 10.0 , in Figs. (a) – (c) (lateral and vertical scales are $1000 a$ and $70 a$, respectively). In (d) the shape transition is shown. The profiles have been obtained by averaging over the meander periods at $\theta = 0.4$ ML (circles) and at $\theta = 2.0$ ML (squares). The horizontal direction is scaled with the wavelength $\lambda = 120a$ and in the vertical direction with the roughness $w = 1.4a$ and $w = 5.6a$ for coverages 0.4 ML and 2.0 ML, respectively

From Fig. 5.2 it is clear that there is no coarsening of the structures when the coverage is large enough. The steady state pattern shape seems to be governed by geometric constraints, which is a sign of asymmetry of the growth rates between bottom and top parts of the steps. This asymmetry is a general feature in many models of step growth with or without coarsening [127,128,132]. Moreover, a quantitative inspection of the patterns at larger coverages, suggest that the profiles have an invariant shape. This can be seen by examining the n th lateral moments $M_n(\theta) = \langle \zeta_i(x, \theta) x^n \rangle_{i,x}$ of the meander periods $\zeta_i(x, \theta)$, shown in Fig. 5.3(a). The scaled even moments approach their steady state values already at $\theta \approx 2$ ML. The patterns are still changing, however, which can be seen from the

roughness of the step $w(\theta) = \sqrt{\langle \zeta(x, \theta)^2 \rangle_x}$, where $\zeta(x, \theta)$ is the step profile. It does not show any sign of saturation up to the largest coverage in the simulations. Instead the roughness follows $w(\theta) \sim \theta^\beta$ with $\beta \approx 0.3$ as shown in Fig. 5.3(b). It is interesting to note that although the roughness does not saturate the shape of the periodic structures attains an invariant form.

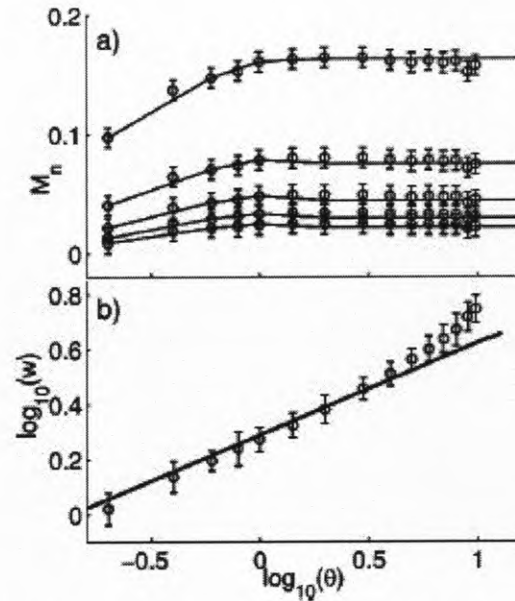


Fig. 5.3 (a) Lateral moments M_n of the step meander periods ($n=2,4,6,8,10$ from top to bottom) as a function of coverage in a semi-logarithmic scale. The moments approach constant values already before 2.0 ML. (b) Width w of the profiles as a function of the coverage. No saturation is observed up to 10 ML. The slope of the solid line corresponds to $\beta = 1/3$.

Our simulation results show that the profile shape is rather insensitive to deposition and temperature conditions. This suggests that the invariant shape is not dependent on the relative magnitudes of the various diffusion processes but rather is a result of geometric constraints due to crowding and in-phase evolution of the step edges. In order to justify this assumption we compare the MC profiles

with continuum profiles which are obtained as stationary solutions to the dynamic equation $\partial_t \zeta = -\partial_x J_{tot}$ where, J_{tot} is the total mass current at the step edge. The most important partial currents which we take into account in the total current here, when expressed in terms of the variable $m(x) = (\partial_x \zeta) / \sqrt{1 + (\partial_x \zeta)^2}$ and appropriately scaled are the mass current due to the destabilizing strong KESE (Ref. [107])

$$J_k = \frac{m(\sqrt{1-m^2} - |m|)\sqrt{1-m^2}}{(|m| + L_c^{-1}\sqrt{1-m^2})^2}, \quad (5.1)$$

the stabilizing current due to the Gibbs-Thomson effect and edge diffusion [11,12,18]

$$J_e = \frac{2D_s \tilde{\Gamma}}{F} (\sqrt{1-m^2} + \frac{D_L}{D_s L}) (\partial_{xx} m) \sqrt{1-m^2}, \quad (5.2)$$

the current into the step edge from the deposition flux [113,114,133]

$$J_d = Lm\sqrt{1-m^2}, \quad (5.3)$$

and the front-back symmetry breaking current [114,127,128]

$$J_{SB} = -\frac{D_s \tilde{\Gamma} L}{F} (\partial_x m)(\partial_{xx} m) \sqrt{1-m^2} + \frac{L^2}{3} m(\partial_x m)(3-m^2). \quad (5.4)$$

In these expressions L is the terrace width, D_s is the macroscopic diffusion constant on the terrace, D_L is the macroscopic diffusion constant along the step edge, and $\tilde{\Gamma}$ is the step stiffness (see Refs. 12 and 19 for the definitions and experimental values of the parameters, respectively). All length scales are given in the units of the lattice constant. By requiring the condition of stationarity

$$J_{tot} \equiv J_k + J_e + J_d + J_{SB} = 0, \quad (5.5)$$

we obtain a second order differential equation for $m(x)$. The stationary profiles are obtained by solving Eq. (5) numerically for given initial conditions $m(\pm L) = \pm m_0$ [134]. The stationary solution is found using the value $\pm m_0 \approx 0.97$ as the boundary condition in order to match the end points with the slopes of the patterns obtained from the MC simulations [135]. The other parameter values of the integration are based on known energetics of Cu, yielding $I_c = 700 - 1600$, $I_s = 2 \times 10^4 - 2 \times 10^5$, $D_L/D_S L = 250 - 700$, and $D_S \tilde{\Gamma}/F = 0.5 - 4000$ in the range $T = 240 - 300$ K and $F = 3 \times 10^{-3} - 10^{-1}$ ML/s. For the step stiffness we used the expression $\tilde{\Gamma} = \exp[E_k/k_B T]/2$, where $E_k = 0.13$ eV is the kink energy [136]. In all cases we set $L = 10$ for the terrace width. The resulting profiles are shown in Fig. 5.4 with various values of the parameters. The shape is rather independent of the details of the currents in agreement with simulations. In Fig. 5.4 the average shapes obtained from the simulations are plotted with a few different flux rates. In the inset we show how the resulting profile deviates from the complete one when each of the mass currents is forced to be small.

In Fig. 5.5 we show the mass currents using the integrated profile as an input. It is now seen that for the invariant profile there is a delicate compensation of the currents, the Gibbs-Thomson current compensated by the sum of the KESE, the deposition, and the symmetry breaking currents. This compensation happens for the specific shape of the profile, and cannot take place e.g. in the case of a triangular shaped profile as obtained in the initial stages of growth. In determination of the stationary profile shape the front-back symmetry breaking

and the geometric constraints contained implicitly in the initial conditions are crucial.

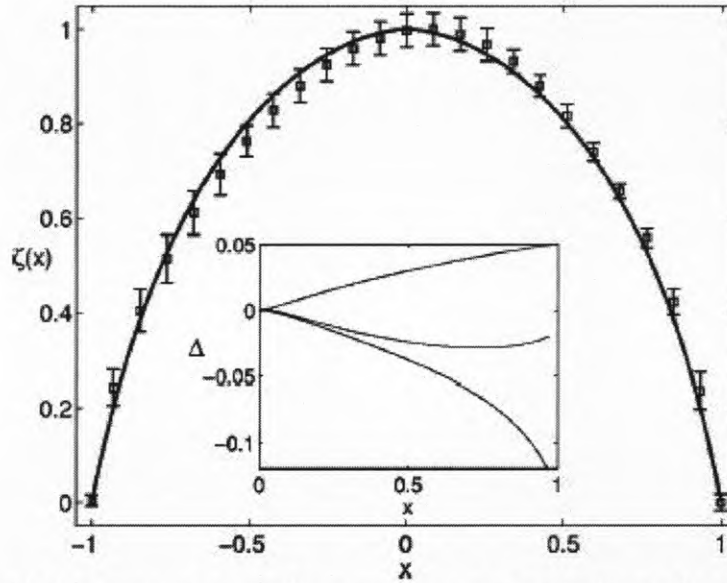


Fig. 5.4 The average shape of the step patterns at $T = 300$ K and $\theta = 8.0$ ML with $F = 6 \times 10^{-2}$ ML/s (squares). Changing the temperature or the flux as described in the text does not have any effects within the error bars. The solid line is the stationary profile obtained by integration of Eq. (5.5). Good agreement between the average and the integrated profiles is evident. The inset displays the relative differences of the profiles, $\Delta = (\zeta_{all} - \zeta_i)/\zeta_{all}$, where ζ_{all} is the profile with all currents included, and $i = k, e, SB$ denotes the solution with only a small contribution for the KESE current from the Gibbs-Thomson and symmetry breaking currents, respectively (from top to bottom in the inset).

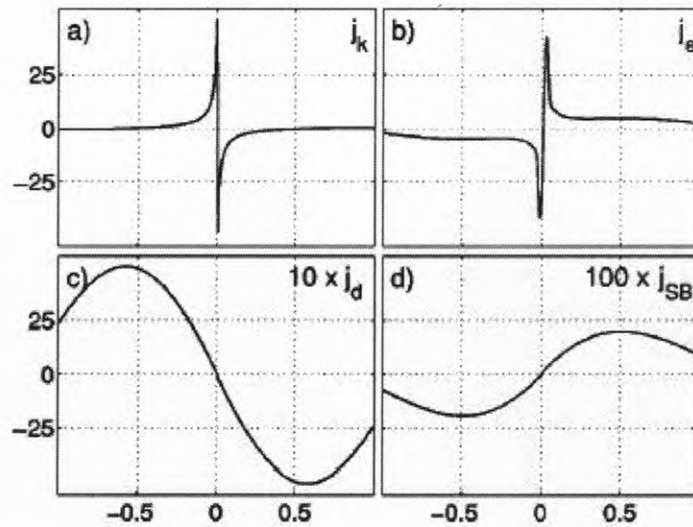


Fig. 5.5 The mass currents Eqs. (5.1)-(5.4) are shown using the integrated profile as an input. Note the difference between the vertical scales for (c) and (d).

5.5 Conclusions

In summary, the MC [Ref. 110] and the SOS [Ref. 111] simulations have proven that the KESE is the dominant mechanism behind the meandering instability and that it leads to the selection of the dominant wavelength determined by dimer nucleation at step edges. In this work we have shown that the KESE also induces an invariant shape of the step profiles during in-phase growth. This occurs even though the overall roughness of the step structures $w(\theta)$ shows no signs of saturation. The value of the corresponding scaling exponent $\beta \approx 0.3$ is consistent with the case of an isolated step [120]. The SOS model gives for the strong KESE an exponent $\beta \approx 0.57$ [107], while for a collection of steps in the phase-locking regime $\beta = 1/2$ [113,114,133]. This puzzling behavior of dynamical scaling is apparently related to the strict in-phase growth and consequent formation of the invariant shape of the profile. The fact that the shape remains invariant although the roughness does not show any sign of saturation, indicates a subtle coupling of the step edge currents with the stationary morphology. By numerically integrating the continuum equation we have shown how the interplay between various surface currents determines the invariant step shapes.

Chapter 6

Prefactors for interlayer diffusion on Ag/Ag(111)

Interlayer diffusion controls the transfer of atoms between layers in a film and is the key factor determining whether growth is layer-by-layer or 2-dimensional. Analysis of recent experimental data on Ag/Ag(111) taken at two sets of temperatures provide similar values for the step edge barrier ΔE_s but not for the ratio of the prefactors v_s/v_t where v_t is the prefactor for diffusion on a terrace and v_s the prefactor at a step edge site. A prefactor ratio larger than 1, $v_s/v_t > 1$, is extracted from the measurements at low temperature ($T < 150\text{K}$), while $v_s/v_t \sim 1$ is found in the experiments done at a higher temperature ($T \sim 300\text{K}$). Since the conclusion $v_s/v_t \sim 1$ is based on a steady state analysis of island decay, we examine whether this condition is fulfilled for Ag/Ag(111). We show that the low value of the terrace diffusion barrier on Ag(111) ($E_t \approx 0.1\text{eV}$) offers an alternative interpretation to the steady state analysis, i.e. an independent detachment model. Alternatively, we propose an independent detachment model. Re-analysis of the data in terms of this model results also in $v_s/v_t > 1$, in good agreement with the low temperature experiments. This work is published and can be referred to in Ref. [137].

6.1 Introduction

The interlayer probability for an atom encountering a step, to hop from a higher to a lower level, plays decisive role in determining the type of growth mode observed in the system [138]. A strong step edge barrier (and therefore a low interlayer probability) is commonly assumed to be the reason for 3-dimensional growth mode. This is the case of Ag/Ag(111) [139-141], which is the subject of this paper.

In simulations of growth and cluster diffusion, usually a fixed diffusion prefactor is assumed for simplicity. But to make the simulations more realistic we need to understand the effect of prefactors on growth and diffusion and implement it into the simulations.

From Arrhenius fits, two parameters are normally extracted, the activation energy E which is a measure of the effective barrier the diffusing atom overcomes, and the prefactor D_0 which is commonly related to the vibrational frequency at the energy minimum of the initial site. It has been observed that when both E and D_0 change systematically with the control variable (i.e., coverage, strain, step density) there is a strong correlation in the way they change: As E increases it is found that there is correspondingly an increase in the value of D_0 , the so-called “compensation” effect. In most cases there is a linear relation between E and $\ln D_0$. Recent experiments during epitaxial growth have shown that the barrier experienced by the adatom depends on the initial site from which it is hopping (whether it is a terrace site or a site at the step). Atoms hopping from sites at the step experience an additional barrier ΔE_s (which is usually positive). This barrier controls the amount of mass transported from higher to lower levels.

Usually the probability p of interlayer diffusion is described by an Arrhenius form

$$p = (v_s/v_t)\exp(-\Delta E_s/kT), \quad (6.1)$$

where v_s is prefactor at the step edge, v_t the prefactor on the terrace, ΔE_s is the step edge barrier, k is Boltzmann constant and T is temperature. Several methods have been applied with different experimental techniques (e.g. STM and diffraction) and over different temperature ranges to measure the interlayer probability and to separate out the two contributions to p , i.e. the prefactor ratio v_s/v_t and the step edge barrier ΔE_s [142-146]. Results obtained from these experiments are not in full agreement [147-149]. Experiments carried out at low temperatures ($T < 150$ K) under growth conditions indicate $v_s/v_t > 1$ while quasi-equilibrium experiments carried out close to 300K $v_s/v_t \sim 1$. In this paper we discuss possible reasons for the discrepancy.

A distinguishing feature of the analysis of experiments carried out at the higher temperature is that it is based on a comparison of the decay rates of small adatom and vacancy islands of radius r located at the center of larger vacancy island of radius R . It is easy to see that the small vacancy island decays over longer time than the small adatom island. One possible reason is because the diffusing atoms experience a step edge barrier at the small vacancy island but not at the edge of the small adatom island. This slows down the filling of the vacancy island and therefore its decay. For the experiments of [142] the decay rate for a $r = 7$ nm adatom island located at the center of a $R = 70$ nm vacancy island is found at 300 K to be 25 times faster than the decay rate of a similar vacancy located

within a similar vacancy island. Such experiments were analyzed under the assumption of quasi-equilibrium (i.e. steady state conditions hold) and that the detachment rate is determined thermodynamically. The step edge barrier parameters $\Delta E_s = 0.13$ eV, $v_s/v_t \sim 1$ and line tension $\gamma = 0.75$ eV/nm for Ag(111) steps were extracted. The steady state condition implies that the density of adatoms $\rho(r')$ within the annular disc $R \geq r' \geq r$ depends only on radius r' and is a solution to the 2D diffusion equation.

On the other hand, the terrace diffusion coefficient D_t for Ag(111) can be estimated from a different experiment as $D_t = 2 \times 10^{11} \text{ s}^{-1} \exp(-0.1 \text{ eV}/kT)$ [143]. If one combines the average atom detachment rate $E(r)$ and the terrace diffusion, under the assumption of steady state [142], then the equilibrium concentration in front of a straight step, is $\rho_\infty = nE(r)/D_t = 0.25 \times 10^{-9} \text{ atoms/nm}^2$, using the atomic density of Ag(111) $n = 13.8 \text{ atoms/nm}^2$. The equilibrium concentration ρ_{eq} in front of an island of radius r is thus given by

$$\rho_{eq} = \rho_\infty \exp(\gamma/kTnr). \quad (6.2)$$

For the measured step energy $\gamma = 0.75$ eV/nm, the equilibrium concentrations outside the island with $r = 7$ nm is $\rho_{eq}(r) = 0.33 \times 10^{-9} \text{ atoms/nm}^2$ and outside the vacancy island with $R = 70$ nm it is $\rho_{eq}(R) = 0.24 \times 10^{-9} \text{ atoms/nm}^2$. The difference in equilibrium concentration $\rho_{eq}(r) - \rho_{eq}(R)$ is less than $10^{-9} \text{ atoms/nm}^2$ at 300 K. If steady state conditions hold, the actual concentrations at the two boundaries at r and R deviate from the equilibrium

values by less than 10^{-10} , the concentration outside the small island slightly lower and the one outside the large island slightly higher than their corresponding equilibrium values. This small difference between the actual and equilibrium concentrations provides the concentration gradient for atoms to diffuse irreversibly from the small adatom island to the larger vacancy island and for the adatom island to decay (the flow of atoms is in the opposite direction for the decay of the small vacancy island).

It is unclear whether the steady state model of analysis is applicable in case of such small concentration differences. Further work is necessary to clarify this question. Furthermore the ratio of the detachment rates for the adatom to the vacancy island is simply determined by their curvature since this ratio is

$$E(r)/E(-R) = \rho_{eq}(r)/\rho_{eq}(-R) = \exp(\gamma/kTnr)/\exp(-\gamma/kTnR) \quad (6.3)$$

which is only 1.09 for the parameters of Ag(111) at 300K. On the other hand as will be discussed below, the energetic barriers at the island perimeter are sufficiently high. Differences in shape between the adatom (convex) and vacancy (concave) islands lead to different rate limiting processes for each case and to a much higher difference in their average detachment rates.

6.2 Theoretical Method

If steady state does not hold we propose an alternative way of analyzing the island decay in terms of independent atom detachment. The basic parameters are the energy barriers for the elementary processes of atom detachment from the different local environments at the island perimeter and diffusion i.e. whether the

atom detaches from a site on a straight step, a kink site, whether the step is A- or B- type, etc. Activation energy barriers for the various processes are calculated using the Nudged Elastic Band technique [32], which uses a series of intermediate atomic configurations (images) between well defined initial and final states before and after the barrier is crossed. These images are connected via a series of "elastic bands" and the total energy of the system is minimized simultaneously to give the barrier between the two states. For an atomistic description of the system and the calculations of the total energy we have resorted to a reliable, many-body interaction potential which is based on the embedded atom method [30]. Although not as accurate as *ab initio* electronic structure calculations, these semiempirical potentials have provided a good description of the structure, energetics, and dynamics of a set of fcc metal surfaces, including Ag. In the energy minimization technique all atoms in the system are allowed to relax, except where constraint is necessary for technical reasons. The model calculation system consists of 16×8 atoms in a layer with 8 layers. The A ((100)-microfacet) or B ((111)-microfacet) type step is created by deleting about half the atoms from the top layer in the required direction. Configurations having kinks, adatoms and more than one step are created accordingly by either deleting or adding atoms.

Earlier [150] a simple bond counting had been used to determine the different barriers (i.e. the coordination number of an atom in a given configuration times its nearest neighbor interaction energy). Now we estimate the corresponding energy barriers more accurately with nudged elastic band techniques. The parameters for each microscopic process are summarized in Table 6.1. In the case

of diffusion along steps, the energy barriers, were published in [18,151]. Our values are a little higher. The probabilities are compared with the faster process – diffusion on terrace - whose probability is assumed to be 1. (We have used the calculated than the measured terrace barrier but none of the conclusions below is affected).

Although in earlier work [150] the probability for an atom emitted at the boundary of one of the small islands to reach either the boundary of the other island or to re-adsorb at the boundary, from which it had detached was determined. However, the actual time taken by these events was not reported. The probabilities of reaching the two boundaries (at r or R and be caught irreversibly) do not depend on the terrace diffusion coefficient, but the times to reach the boundaries do. In addition these times are needed to decide whether the assumption of steady state is justified or not. To answer this question, we have simulated the random walk of the adatoms released at r or R using a Monte Carlo method. We obtain the time for the random walk to be completed for the four possible outcomes (if an atom is released at r or R and if it is eventually caught at r or R) measured in terms of the elementary hopping time on the terrace. These times are listed in Table 6.2.

6.3 Results and Analysis

Inspection of Table 6.1 and Table 6.2 shows that the steady state condition cannot be satisfied for Ag/Ag(111) since the faster detachment time for an atom at the island boundary (P_{3B} process) is 10^4 larger than the longer hopping time in the annular region between the islands.

An alternative way to analyze the island decay experiments is in terms of the independent detachment model to deduce the prefactor ratio v_s/v_t . For the island boundary we use the island shapes extracted experimentally in [152] and shown schematically in Fig. 6.1. (The descriptions of the various mechanisms in Fig. 7.3 are more well defined than the ones in Figs. 6.1 and 6.2).

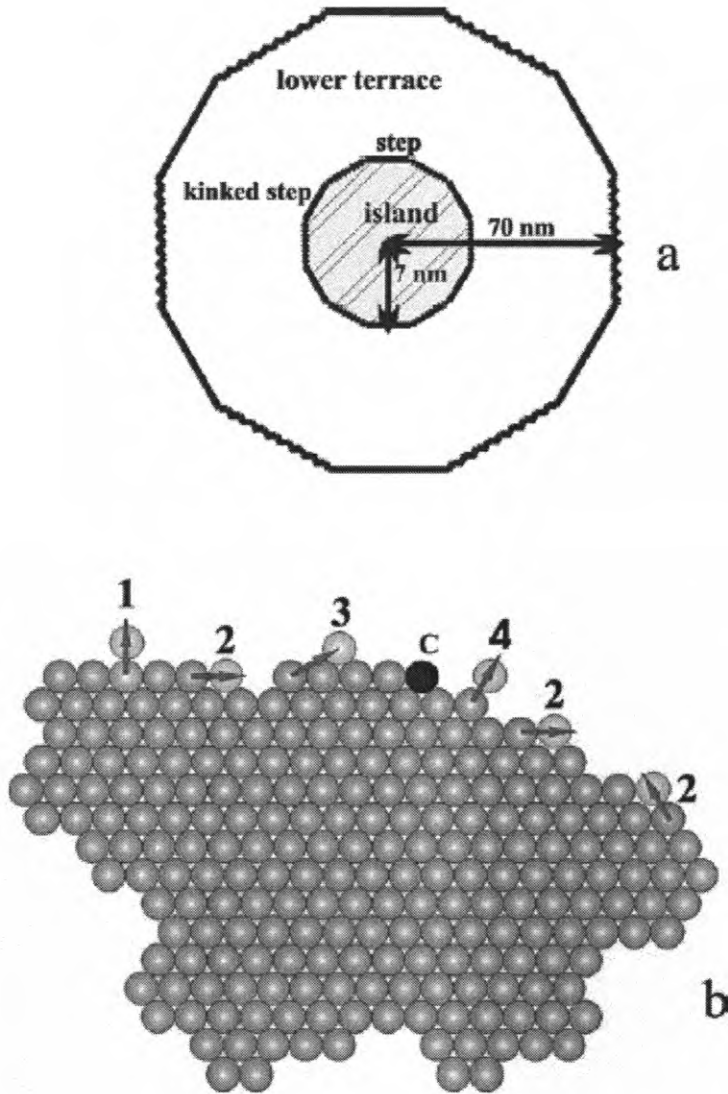


Fig. 6.1 Illustration of an adatom island decay geometry. (a) The island shape has kinked and straight segments as found in [147]. In the middle of a large vacancy island of radius R initially an adatom island of radius r is present. The height of the small island is the same as the surrounding region of the vacancy island. (b) The processes on the island edge: 1 – detachment from straight segment (P_{1A} , P_{1B}), 2 – diffusion along step (P_{2A} , P_{2B}), 3 – kink rounding (P_{4A} , P_{4B}) and 4 – kink detachment (P_{3A} , P_{3B}). Atom c is a corner atom with 3 bonds.

The island boundary consists of kinked and straight segments of approximately equal length. For the adatom island we assume that all the atoms at the kinked segments evaporate first within τ_k (the time for a kink atom i.e. an atom with

three nearest neighbors), since the atoms at the kinked segment detach independently. Once these atoms detach, then atoms from the straight segments follow sequentially, since the corner atoms at the straight segments (which also have 3 nearest neighbors) need to detach before the neighboring straight step atom becomes a kink atom with 3 neighbors. The straight segment proceeds to “unzip” in time $(n_s/2) \tau_k$ with n_s the number of atoms at the straight segment, since there are two corner atoms to initiate the “unzipping”. The asymmetry between concave and convex island shapes can be best illustrated if we express the barriers in terms of an effective nearest neighbor interaction energy e . For the initial adatom island $r = 7$ nm we have $n_s = 12$ so the average detachment time from the adatom island is

$$\tau_a = (1+n_s/2) \tau_k = 7\tau_k, \quad (6.4)$$

where

$$\tau_k = v^{-1} \exp(3e/kT) \quad (6.5)$$

is the time to detach from a kink site.

Similarly we find the average time τ_v for an atom to detach from the larger vacancy island $R = 70$ nm. In the independent detachment model, this time determines the decay of the smaller vacancy island, since the released atoms, diffuse “instantaneously” to refill the smaller vacancy island at r . This process is schematically shown in Fig. 6.2. As argued before, first the atoms at the kinked segments detach within τ_k . Although there are equilibrium fluctuations at the straight segments at finite temperatures which can generate kinks, these kinks cannot account for the decay of the island under the non-equilibrium conditions

assumed in the independent detachment model, which is based on the irreversible decay of the island. For an atom to detach it is necessary for two sequential processes to occur: first the generation of the kink atoms (as in equilibrium) with barrier 2ε (where ε is the nearest neighbor interaction energy), and in addition, the same atom detaches to the terrace by breaking two bonds so the combined process will have a total barrier $\varepsilon_t = 2\varepsilon + 2\varepsilon = 4\varepsilon$. The time needed for this process is approximated

$$\tau = v^{-1} \exp(4\varepsilon/kT) = \exp(\varepsilon/kT) \tau_k \quad (6.6)$$

This proves the essential asymmetry between the decay of the vacancy and adatom islands. The corner atoms at a vacancy island have five nearest neighbors so they cannot initiate the "unzipping" as in the adatom island. An atom at straight step needs to detach with a higher barrier (as shown in eq.(6.6)) to generate a kink. Since it is known experimentally that the shape of the islands remains unchanged (presumably because of the very fast edge diffusion around the perimeter), it is not possible to have all the successive kinked rows detaching before atoms at the straight edge detach. Besides, the number of atoms available within the six triangular kinked regions is only around 100 atoms while the refilling of the small vacancy island requires more than 1200 atoms. So there is a need for atoms at the straight segment to detach and generate the kinked atoms.

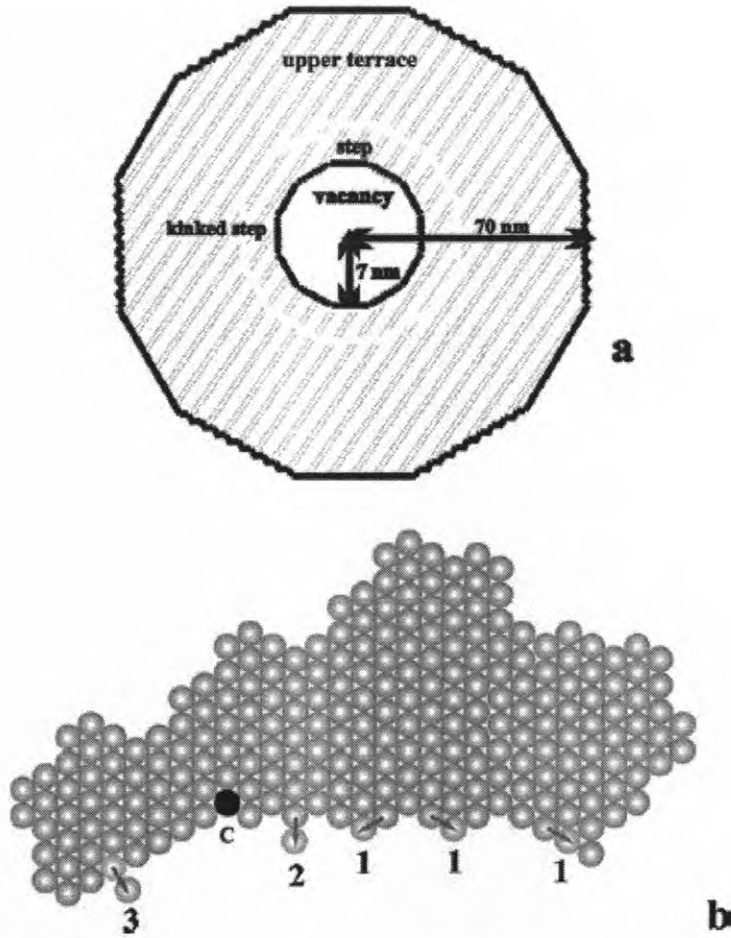


Fig. 6.2 Illustration of an adatom island decay geometry. (a) The island shape has kinked and straight segments as found in [147]. In the middle of a large vacancy island of radius R a small vacancy island of radius r is initially created. The height of the small vacancy island is two layers lower than the surrounding region of the large vacancy island. (b) The processes on the large island edge: 1 – diffusion along step (P_{2A} , P_{2B}), 2 – kink detachment (P_{3A} , P_{3B}) and 3 – detachment from straight segment (P_{1A} , P_{1B}). Atom c is a corner atom with 5 bonds.

Assuming the vacancy island shape to be the one of Fig. 6.2(a), since as seen in experiments it remains unchanged, the kink atom can be generated anywhere on the straight edge, so the “unzipping” involves n atoms (with $n_s/2 < n < n_s$). The average time it will take the straight segment to “unzip” will be $(3/4n'_s)\tau_k$. Since these processes happen successively, the total time will be

$$\tau_v = (1 + \exp(\epsilon/kT) + (3/4n'_s))\tau_k. \quad (6.7)$$

For $R = 70$ nm, $n'_s = 120$, $\varepsilon = 0.2$ eV [142], comparable to the calculated barriers of Table 6.1 in the range $0.15 - 0.19$ eV, we have $\tau_v = 2400\tau_k$. These times need to be averaged over the total number of atoms emitted since the perimeter of the larger vacancy island involves more atoms than the perimeter of the small adatom island. The detachment rates of the islands, $E(r)$ and $E(-R)$, are the mean average number of atoms detached per unit of time.

$$E(r) = \frac{2\pi r}{a} \frac{1}{\tau_a}, \quad E(-R) = \frac{2\pi R}{a} \frac{1}{\tau_v}, \quad (6.8)$$

where a is the lattice constant. The ratio of detachment rates:

$$E(r)/E(-R) = (r/R)\tau_v/\tau_a \approx 35, \quad (6.9)$$

much larger than the ratio 1.09, from (6.3), for steady state model (where $\gamma = 0.75$ eV/nm [142]).

We can now write expressions for the adatom and vacancy island decay rates within the independent detachment model. For the adatom island:

$$n \frac{dA_a}{dt} = \frac{2\pi r}{a} E(r)P_r - \frac{2\pi R}{a} E(-R)P_R \approx \frac{2\pi r}{a} E(r)P_r \quad (6.10)$$

where A_a is area of adatom island, $n = 13.8$ atoms/nm² is 2-dimensional density of Ag(111) and

$$P_r = c/(r \ln r/a), \quad (6.11)$$

is the probability of an atom detached from the island at r to reach the boundary at R .

$$P_R = c/(R \ln (R/a)) \quad (6.12)$$

is the similar value for the atoms detached at R to reach the island boundary at r (c is constant which normalizes probability). According to relations (6.9), (6.11) and (6.12), $rE(r)P_r \gg RE(-R)P_R$, so we can neglect the second term in the right-hand side of equation (6.10).

Similar for the vacancy island

$$n \frac{dA_v}{dt} = \frac{2\pi R}{a} E(-R)P_{Rs} \quad (6.13)$$

where A_v is area of vacancy island and the probability for an atom detached at R to be adsorbed at r after overcoming the reflecting boundary [153] is given by:

$$P_{Rs} = (c/(R \ln R/a))(p/(1 - (1 - p)(1 - P_r))). \quad (6.14)$$

Within our model we can express the ratio of the decay rates of the adatom and vacancy islands in terms of the averaged detachment times. Using (6.8) we obtain

$$(dA_a/dt)/(dA_v/dt) = (P_r/P_{Rs})(r/R)^2 \tau_v/\tau_a. \quad (6.15)$$

Using the data for adatom versus vacancy island decay of Ag/Ag(111) at $T = 300$ K, $r = 7$ nm, $R = 70$ nm, $\Delta E_s = 0.13$ eV, $\tau_v/\tau_a = 35$, $(dA_a/dt)/(dA_v/dt) = 25$, we obtain $p \gg P_{Rs}$ which implies $v_s/v_t > 30$. This brings the value of the prefactor ratio in close agreement with the low temperature growth experiments.

Table 6.1. Energy barriers and relative probabilities of microscopic processes on steps.

Process	Energy barrier ΔE [eV]	Relative probability at T=150 K	Relative probability at T=300 K
P_0 – diffusion on the terrace	0.061	1	1
P_{1A} – detachment from straight step A	0.758	5.3×10^{-24}	2.3×10^{-12}
P_{1B} – detachment from straight step B	0.691	9.2×10^{-22}	3.0×10^{-11}
P_{2A} – diffusion along step A	0.294	1.7×10^{-8}	1.3×10^{-4}
P_{2B} – diffusion along step B	0.338	5.6×10^{-10}	2.3×10^{-5}
P_{3A} – detachment of kink site on A step	0.571	9.3×10^{-18}	3.1×10^{-9}
P_{3B} – detachment of kink site on B step	0.527	2.7×10^{-16}	1.6×10^{-8}
P_{4A} – rounding kink position on A step	0.570	1.0×10^{-18}	3.1×10^{-9}
P_{4B} – rounding kink position on B step	0.582	4.0×10^{-18}	2.1×10^{-9}
P_{5A} – detachment of kink position to the straight segment of the A step	0.471	2.0×10^{-14}	1.4×10^{-7}
P_{5B} – detachment of kink position to the straight segment of the B step	0.540	1.0×10^{-16}	1.0×10^{-8}

Table 6.2. The mean number of jumps to reach appropriate boundary.

Diffusion boundary from to	mean number of jumps
$r \rightarrow R$	3×10^4
$r \rightarrow r$	5×10^2
$R \rightarrow r$	$\sim 10^6$
$R \rightarrow R$	2×10^2

6.4 Conclusions

Because of the large difference between the atom detachment and atom terrace diffusion rates for Ag/Ag(111), we have presented an alternative interpretation of the island versus vacancy decay experiments. Within this interpretation the decay process consists of independent atom detachments, instead of continuous atom emission under steady conditions. With the new analysis one obtains $p \gg P_{Rs}$, which implies $v_s/v_t > 30$ and a better agreement between the high and low

temperature experiments. However further work is needed to specify detailed experimental criteria for deciding the range of validity of the independent versus steady state model in island decay experiments.

Chapter 7

Diffusion of 2D Cu clusters on Cu(111): a Kinetic Monte Carlo Study

We present results of an extensive and detailed study of the diffusion of small 2-D Cu clusters containing 10 to 38 atoms as well as larger clusters of 55-1003 atoms using Kinetic Monte Carlo simulations involving 100 to 500 million steps. Only single atom peripheral hopping mechanisms are allowed, with barriers calculated using the Nudged elastic band technique and potentials from the embedded atom method. These simulations were performed using forty nine basic processes. We find that at room temperature, clusters with magic numbers corresponding to sizes $6n+3$, compact hexagon $([(n*(n+1)/2)*6]+1)$ and compact hexagon+1 have very low diffusivity compared to the "general" ones. All these clusters experience a stick-slip type of motion of the center of mass. At high temperatures the magic cluster sizes show diffusion coefficients comparable to the general clusters. Diffusion coefficients for the general clusters show a strong dependence on the cluster size and temperature.

7.1 Introduction

An important constituent of nanostructuring of material is the process of epitaxial growth which is intimately related to the diffusion, evaporation, condensation and related phenomena of atoms and atomic clusters on surfaces. Experimental studies of the diffusion of adatoms and small atomic clusters on metal surfaces using Field Ion Microscopy (FIM) have already provided us a number of unexpected events such as concerted motion of atoms [154], collective sliding motion of Ir clusters on Ir(111) [70] and others. These studies, together with the availability of reliable many-body interaction potentials, motivated a number of computational and theoretical scientists to simulate and calculate the energetics and dynamics of adatoms and atomic clusters on metal surfaces. The fast developments in the technique of Scanning Tunneling Microscopy (STM) have further exposed interesting characteristics of the dynamics of large adatom and vacancy islands. In fact, it was only after STM measurements of Ag/Ag(100) [80] and Ag/Ag(111) [155] that large two-dimensional islands were believed to be significantly mobile. Furthermore, large vacancy islands were found to be just as mobile as the adatoms [156]. These and related observations led to a series of papers [81,83,84,157] with speculations about the microscopic mechanisms that caused these entities to move. Of particular interest here are processes which can be characterized as periphery diffusion, evaporation/condensation or terrace diffusion. Statistical mechanical calculations based on solid-on-solid (SOS) models predict specific scaling of the diffusion coefficient with the island diameter, depending on the preponderance of one of these three mechanisms. Since these dependencies are

not unequivocally extracted from experimental data, because of the large error bars, the issue is not yet completely settled, although the bias is towards periphery diffusion. Molecular dynamics simulations of Ag/Ag(111), on the other hand, have shown a preference for periphery diffusion, at least for vacancy islands. Even with periphery diffusion as the dominant mechanism of adatom and vacancy island diffusion, several questions about these elastic-continuum based models have remained. Some of these issues were the subject of a paper by Bogicevic *et al* [85] who showed that the exponents in the power law dependence of the diffusion coefficient on island size were themselves temperature dependent and material specific, unlike predictions of the simpler earlier model calculations. While the work of Bogicevic *et al* points to the simplicity of the previous calculations, it also raises questions whether the atomistic model used by them truly brings out the inherent complexity of the system. Our work here is aimed to address this very issue. While we find the application of kinetic Monte Carlo technique to provide a linkage between information at the atomic scale and behavior in the mesoscopic one, we also do not want to prejudice our system by using only a small set of atomic processes arising from a narrow local perspective.

The main point of departure in our work is the usage of a pattern recognition scheme and the provision of a large (49) set of possible single atom processes that the system might undertake. The activation energy barriers for these processes are calculated using reliable interaction potentials and calculational scheme. While these potentials are presently based on the embedded

atom method (EAM) [30], they can just as well be obtained from *ab initio* methods.

7.2 Theoretical details

We use standard kinetic Monte Carlo (KMC) technique along with a unique pattern recognition to simulate the post-deposition 2-D island diffusion on FCC(111). In this simulation, forty-nine basic processes (and their equivalents obtained by applying the symmetry operations for a hexagonal lattice) are determined for single atom peripheral diffusion. At every MC step the active atoms are classified according to the processes they may perform. Here, an atom is called active when the number of its 1st nearest neighbors in the same (111) plane is less than six (i.e. there is at least one neighboring vacancy to move to). The macroscopic rate for every process is hence computed and the corresponding probability determined. The interval between zero and one is then divided in intervals with widths corresponding to the probabilities of all the active processes. A first random number selects the process to be performed and a second one selects the atom to be moved from the list belonging to the selected process (Refer to Fig. 3.6). The classification of the atoms is done using a three shell scheme as illustrated in Fig. 7.1. Here, we use three shells to determine the environment of an active atom. These three shells contain 6, 12 and 18 atoms respectively, labeled from 0 to 35 as shown in Fig. 7.1. However, not all the surrounding 36 atoms are used in the classification of an active atom. We use a “minimum configuration” scheme in which we record, from the 36 atoms, only those sites (vacant or occupied) that will *uniquely* determine the process that is associated with a given

atom. In Fig. 7.1, as an example, we show the minimum configuration associated with diffusion along step A. For this process, the conditions to be met are: i) sites 4, 5, 17 *must* be filled (Black) and ii) sites 0, 1, 2, 3, 6, 7 *must* be vacant (White). The rest of the sites could be either filled or vacant (grey), it does not matter.

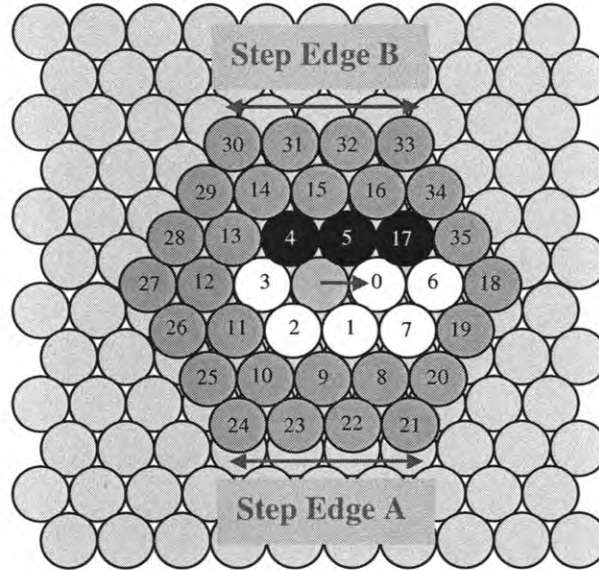


Fig. 7.1 Three shells of nearest neighbor atoms around the central atom (atom selected to move) and the pattern recognition scheme.

For the interactions between the atoms in the systems studied here, we use the embedded atom method (EAM). This is a semi-empirical, many-body interaction potential [30]. The EAM was very successful in reproducing many of the characteristics of the bulk and the surfaces of Cu, Ag, Pd, Pt, Au and Ni [30]. We have also found the EAM potentials to be reliable for examining the temperature dependent structure and dynamics of the low Miller index surfaces of Ag and Cu [158], and for describing the energetics and dynamics of Cu, Ag and Pd vicinals [159,160], and self diffusion on the Ag, Cu, and Ni flat surfaces [79].

The activation energies associated with the different processes are calculated using the Nudged elastic band method [32]. This method has been shown to be efficient for finding the (minimum energy path) MEP between given initial and final states of a process. The MEP is found by constructing a set of images of the system, thirty in our case, between the initial and final states. A spring interaction potential between adjacent images is added to ensure continuity of the path. A minimization procedure for the forces acting on the images brings the images to the MEP. This method determines the activation energy with a typical error of about 10 meV for the processes involved in the studies presented here.

The diffusivity of the islands was studied by following the trace of the center of mass (CM) with time and quantitatively by calculating the mean square displacement (MSD) of the CM as function of time. While calculating the mean square displacement, we first divided our data into equidistant steps with respect to time having the corresponding CM coordinates at that time instant. From this set of data the mean square displacement and hence the diffusion coefficients were obtained by correlating these equidistant data points.

7.3 Model systems

We have studied the dynamics of 15 Cu islands containing between 8 and 38 atoms on Cu(111) surface. We have classified these islands in four categories depending on the number of atoms they contain. If n is this number, the categories are i) compact hexagon; ii) compact hexagon + 1; iii) $3n+1$; and iv) general. The

latter category contains all those islands not fitting in categories (i), (ii) and (iii). All our KMC simulations started with an arbitrary (fractal like) shaped cluster (Fig. 7.2) where all the atoms are connected Table 7.1 contains the classification of these islands.

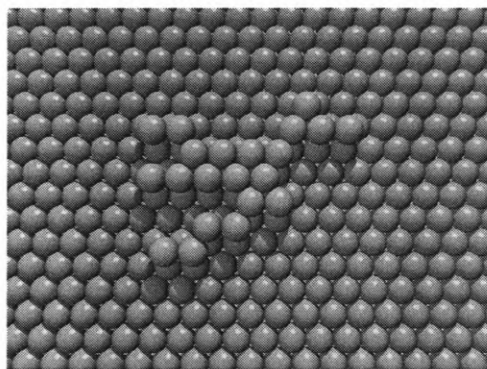


Fig. 7.2 Fractal-like starting configuration for the cluster

Table 7.1 Geometrical details of islands studied

Cluster size	Type of cluster
8	Compact hexagon+1
9	$6n + 3$
10	General
12	General
14	General
15	$6n + 3$
18	General
19	Compact hexagon
20	Compact hexagon+1
21	$6n + 3$
26	General
27	$6n + 3$
33	$6n + 3$
37	Compact hexagon
38	Compact hexagon+1
55	General

7.4 Results

7.4.1 Processes and activation energies

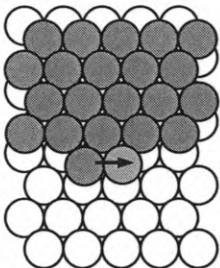
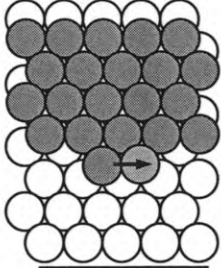
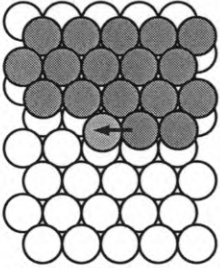
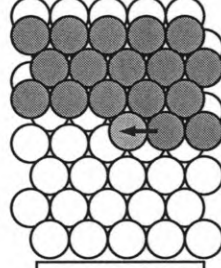
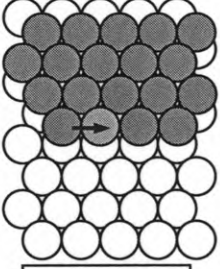
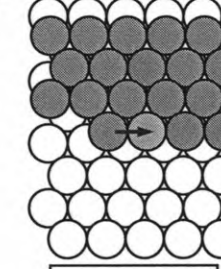
In this section we present the forty nine processes involved in this study of 2D island diffusion on FCC(111). These processes represent all the situations that have been encountered during the preliminary runs involving atoms moving from an fcc site to another fcc site. Only single atom peripheral motion was allowed with no detachment. The next set of 49 figures (Fig. 7.3) illustrates these processes with the arrow showing the initial to the final states. We also provide in the figures the activation energy as determined by the NEB method. The EAM potential used here present a systematic difference in the energetics of processes along step A and step B. For example, the diffusion along step A has an activation energy 43 meV lower than that along the step B. The similar observation is made for the process involving kink detachment along a step. These asymmetries in the energetics will ultimately dictate the probabilities associated with the available processes during the simulation as we will show later in this section. We would also like to point out that some processes necessitates more than one step as our pattern recognition dictates motion from an fcc site to another fcc site. Hence, the rounding of an AA or a BB junction is done in three stages while that of an AB or a BA junction is performed in two.

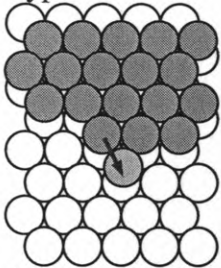
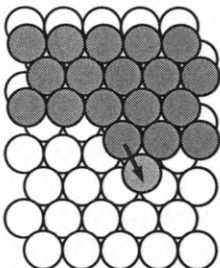
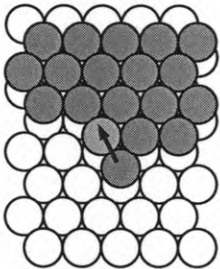
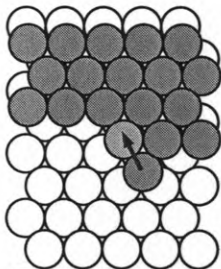
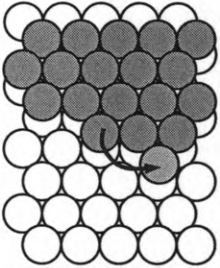
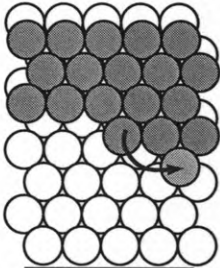


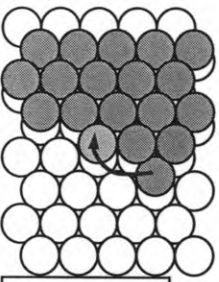
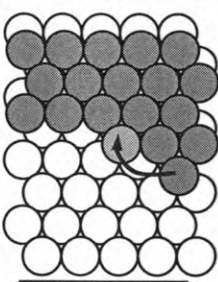
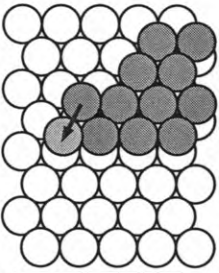
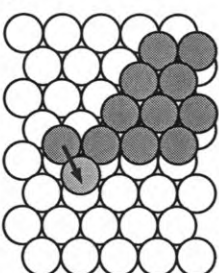
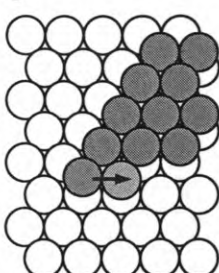
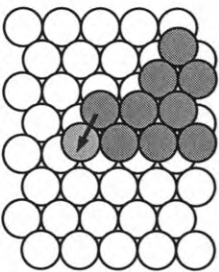
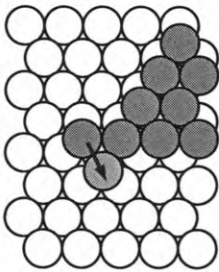
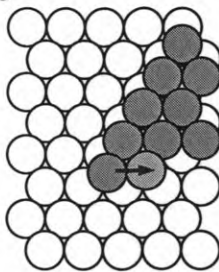
Initial position

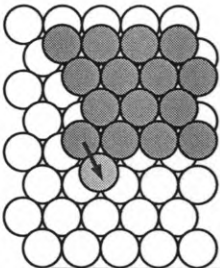
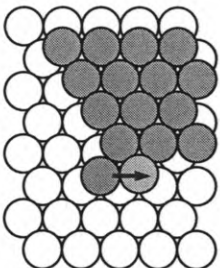
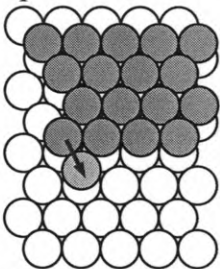
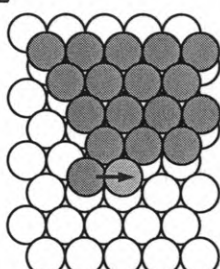
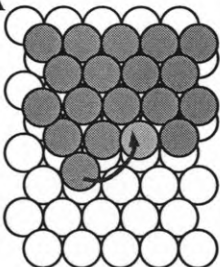
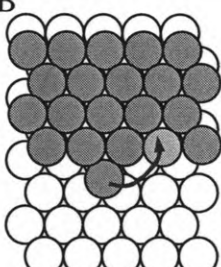


Final position

Step Edge Diffusion	
Type A  0.252 eV	Type B  0.295 eV
Kink detachment along step edge	
Type A  0.519 eV	Type B  0.556 eV
Kink Incorporation	
Type A  0.220 eV	Type B  0.265 eV

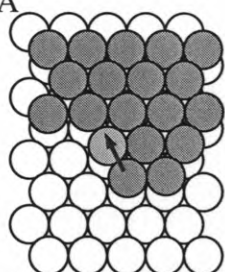
Kink detachment out of step	
Type A  0.658 eV	Type B  0.590 eV
Falling into kink	
Type A  0.074 eV	Type B  0.0069 eV
Kink Rounding	
Type A  0.656 eV	Type B  0.678 eV

KESE		
Type A  0.374 eV	Type B  0.402 eV	
Corner rounding at AA junction – 3 stages		
1  0.313 eV	2  0.143 eV	3  0.0096 eV
Corner rounding at BB junction – 3 stages		
1  0.374 eV	2  0.038 eV	3  0.052 eV

Corner rounding at AB junction – 2 stages	
1  0.317 eV	2  0.0839 eV
Corner rounding at BA junction – 2 stages	
1  0.396 eV	2  0.0148 eV
Step attachment	
Type A  0.336 eV	Type B  0.404 eV

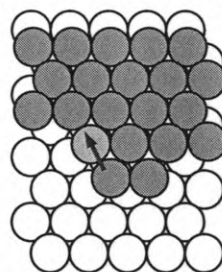
Detach from step and fall into kink

Type A



0.272 eV

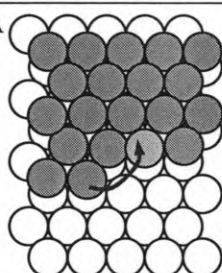
Type B



0.231 eV

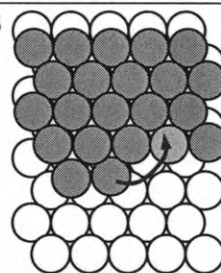
Detach from atom and attach to step

Type A



0.660 eV

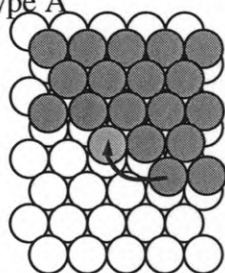
Type B



0.692 eV

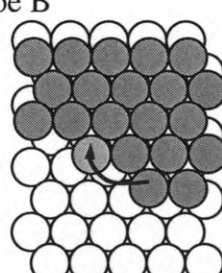
Detach from atom and fall into kink

Type A



0.698 eV

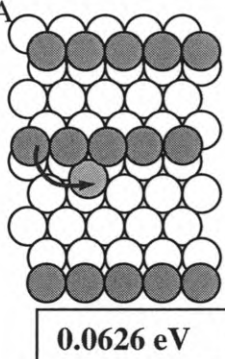
Type B



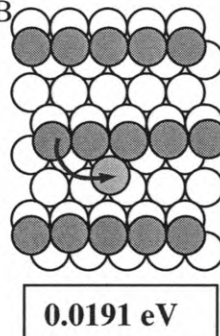
0.690 eV

Rounding a chain

Type A

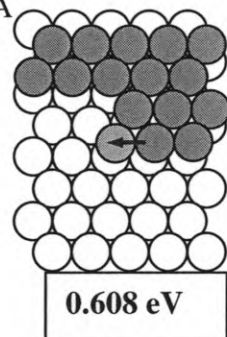


Type B

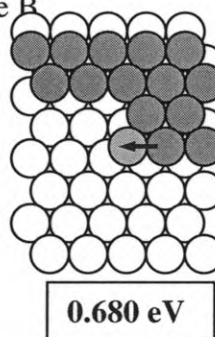


Kink detach along step (small)

Type A

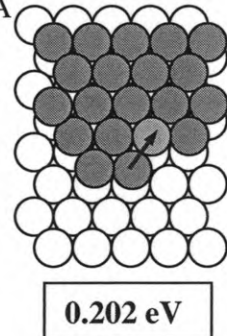


Type B

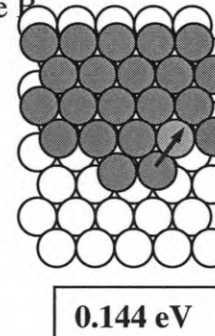


Detach from atom and attach to step (small)

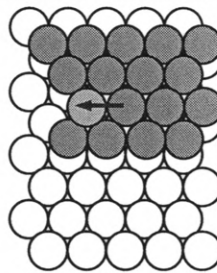
Type A



Type B

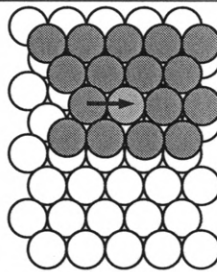


Detach from 5nn to vacancy at 6th nn



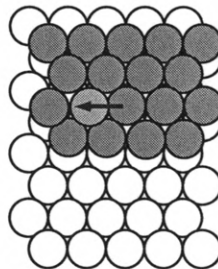
1.209 eV

Reverse of above process—Detach from 6th nn to vacancy of 5nn



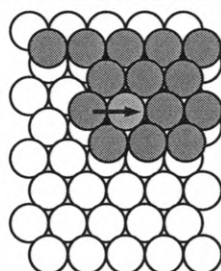
0.167 eV

Move to a vacancy within a closed shell



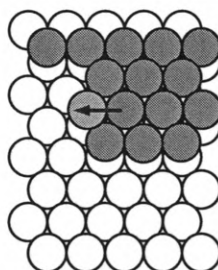
0.452 eV

Detach from an AB corner into 5nn vacancy



0.0142 eV

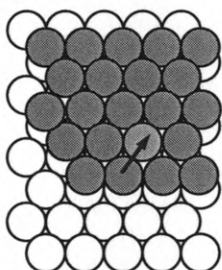
Reverse of above process – Detach from 5nn to a vacancy at 6th nn AB corner



0.829 eV

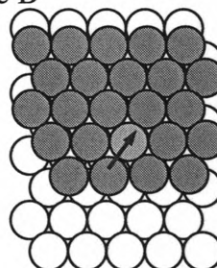
Detach from a step to a vacancy above

Type A



0.191 eV

Type B



0.189 eV

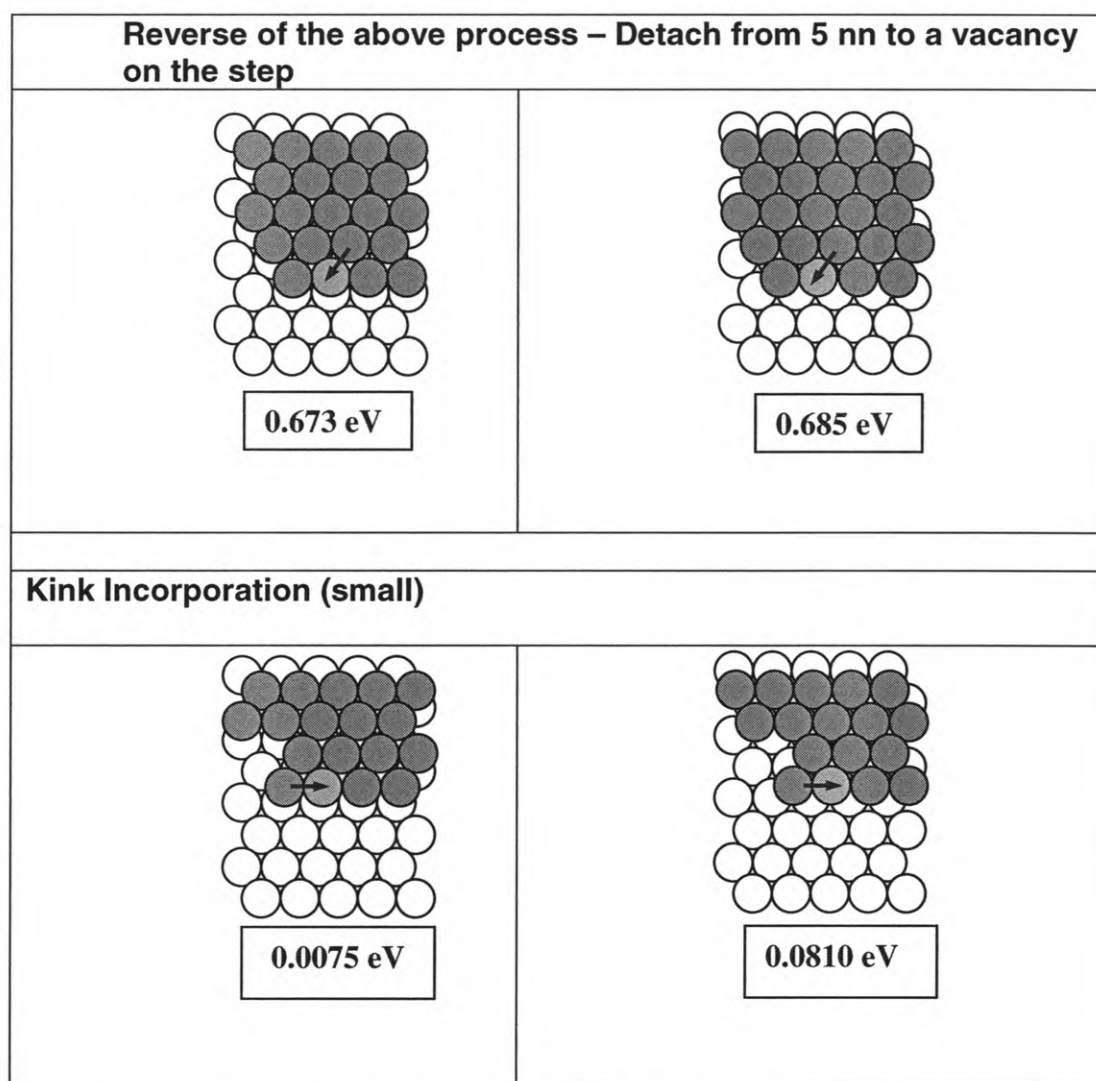


Fig. 7.3 Energy barriers for key diffusion processes for Cu/Cu(111) – NEB

7.4.2 Diffusion of 2D Cu islands

7.4.2.1 Trace of the center of mass

The diffusion of the above mentioned islands was monitored by recording the center of mass motion. We have used a substrate containing 480 atoms (20 by 24) with the island initially placed at the center of the template. In order to use our pattern recognition scheme without any complications, we shift the island back to

the center of the substrate whenever an atom of the island reaches the border of the template. The shift is then recorded to recover the real diffusion path of the center of mass. In the following figures, we show the trace of the CM for 5 islands, containing 10 atoms (general), 18 atoms (general), 19 atoms (compact hexagon), 21 atoms ($6n+3$) and 26 atoms (general). We choose these islands because the physical time elapsed during 100 million MC steps are comparable: 2686 secs, 3634 secs, 2291 secs, 3753 secs and 3854 secs respectively.

We focus here on a qualitative description of the diffusion of these five islands. For the 10 atom island (Fig. 7.4(a)), the trace of the CM covers an area of about 60 by 80 nm and appears to be random and resembling a single atom diffusion.

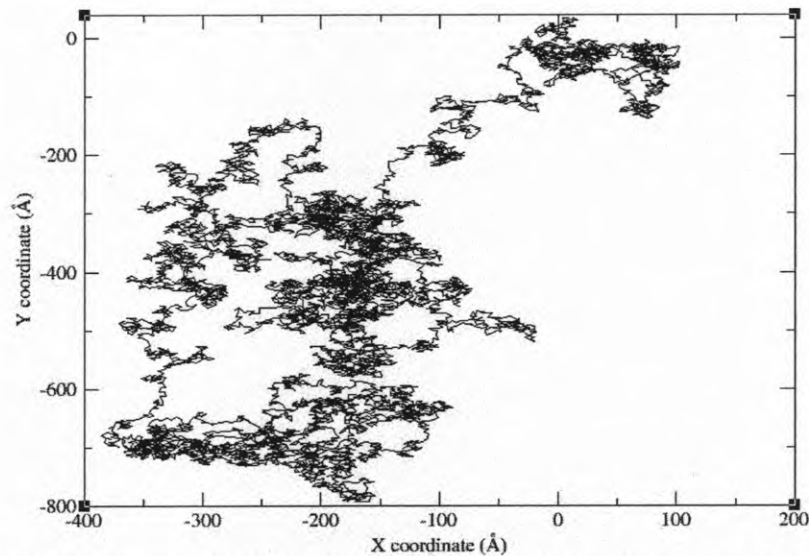


Fig. 7.4(a) Trace of CM for a 10 atom cluster at 300K for 100 million MC steps.

The 18 atom island (Fig. 7.4(b)) also shows a large area covered of about 30 by 25 nm. Note that in this case one can see some dark areas separated by thin paths

indicating a sort of stick slip motion, but appear to be random. Both these islands belong to the general category.

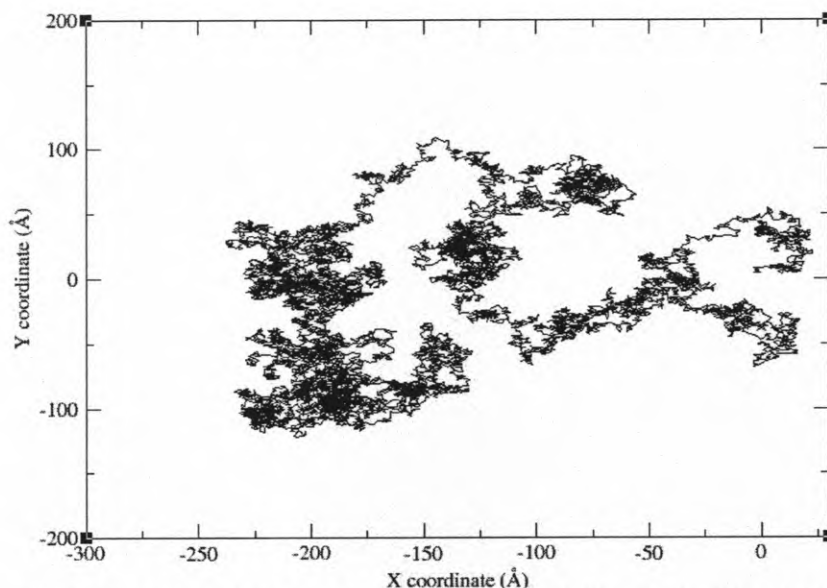


Fig. 7.4(b) Trace of CM for a 18 atom cluster at 300K for 100 million MC steps.

The 19 atoms island belongs to the compact hexagon category and one can see from Fig. 7.4(c) that the center of mass hardly moved during the 100 million MC steps corresponding to 2291 secs. The center of mass clearly experiences a stick slip motion but with a very long residence time during the stick phase. The trace of the center of mass is regular and is close to a hexagon. The difference between the 18 and the 19 atoms islands is only one atom, which will make the detachment/attachment of atoms very important in the diffusion of these islands. One can imagine a scenario when a 19 atom island starts to diffuse very rapidly because of loss of a peripheral atom, and inversely, a rapidly diffusing 18 atom island may be brought to a halt by incorporation of a diffusing single atom.

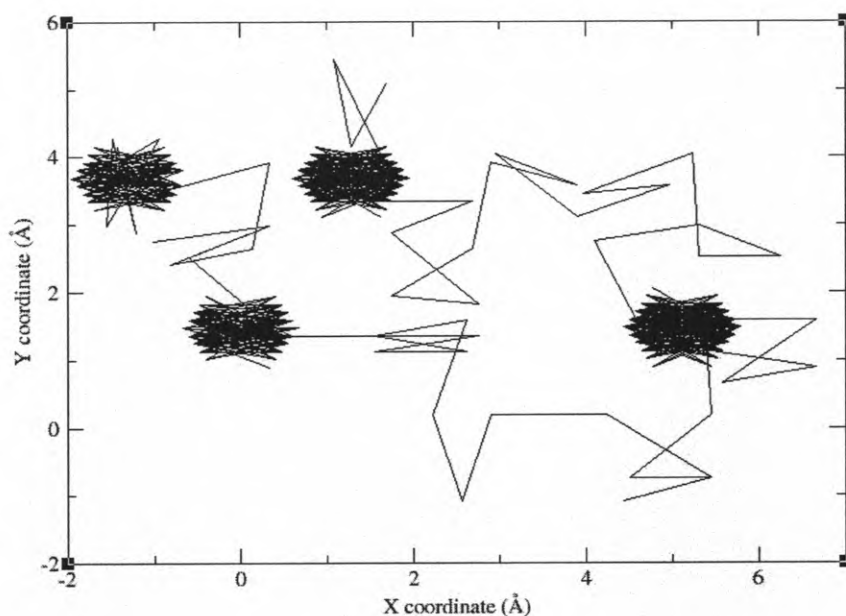


Fig. 7.4(c) Trace of CM for a 19 atom cluster at 300K for 100 million MC steps.

Another case of slowly diffusing island is the 21 atoms one (category $6n+3$) as illustrated in Fig. 7.4(d). Here again, the stick slip motion is obvious with a very long stick residence time. The trace of the CM during the stick phase present a 6-sided star and the area covered during these 3753 secs (100 million MC steps) is only about 1 by 1 nm.

The slow diffusion of these islands is not due to their large size as one would expect, but is rather due to the fact islands with magic numbers diffuse slowly. The 26 atoms (with category “general”, meaning no magic number) is larger than the 19 and the 21 atom ones but diffuses much more rapidly as one can see qualitatively in Fig. 7.4(e) The area covered by this island during the 3854 secs is about 10 by 10 nm, considerably larger than the 1 by 1nm covered by the 19 and 21 atom islands. It can also be noted that the trace is made of densely

packed dark spots indicating stick-slip motion but with a very short stick residence time. But the overall trace is like a random walk.

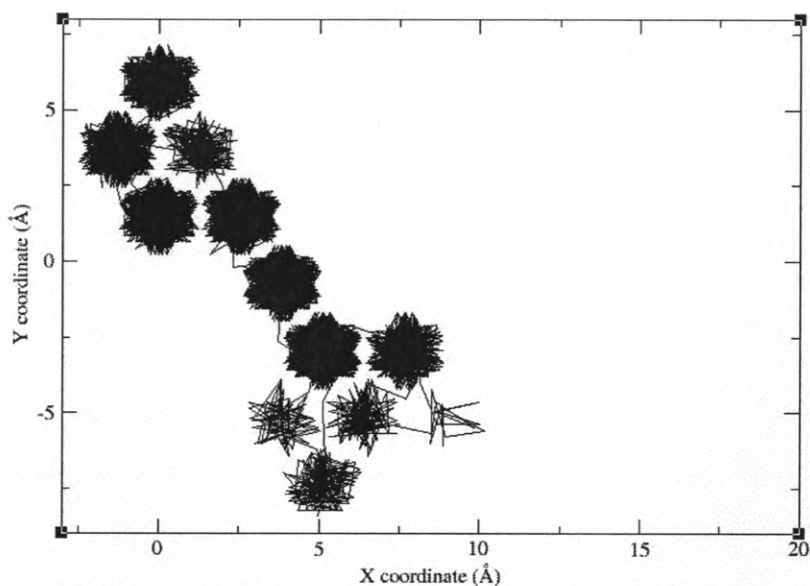


Fig. 7.4(d) Trace of CM for a 21 atom cluster at 300K for 100 million MC steps.

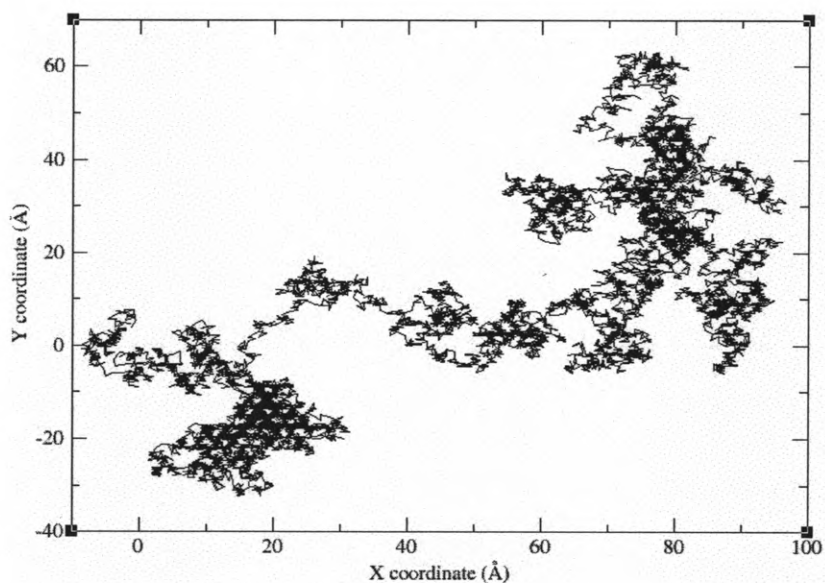


Fig. 7.4(e) Trace of CM for a 26 atom cluster at 300K for 100 million MC steps.

7.4.2.2 Mean square displacement and Diffusion coefficient

Since our KMC simulation scheme has a very high speed of performance and can run for several hundreds of millions of Monte Carlo steps in about one day of CPU time on a 2 GHz chip, we have performed simulations in the range of 500 million timesteps at different temperatures.

Since the physical time elapsed at each timestep is governed by the rate of the process, they are unequal in length. Thus, to calculate the mean square displacement of the center of mass, we filter our data to a set of almost equidistant timesteps along with the corresponding center of mass coordinates. This filtration is easily possible, due to the large number of iterations (100 to 500 million) that we perform in the simulations, which enable us to extract enough data points that are almost equidistant in time. From this new filtered data set we calculate the mean square displacement using correlations between these time intervals. We find that if we consider an overlap between the time intervals in order to obtain better averaging, the plots of MSD vs. time appear as a soft parabola. This indicates that overlap in the time intervals can lead to certain dependency effects of data points with their previous values. To rectify this problem, we performed our MSD calculations without an overlap in the time intervals. These plots clearly show a linear behavior.

The following figures (Figs. 7.5 (a),(b),(c),(d),(e),(f),(g)) show the plots of the mean square displacement (MSD) versus time, for some cases of clusters at different temperatures.

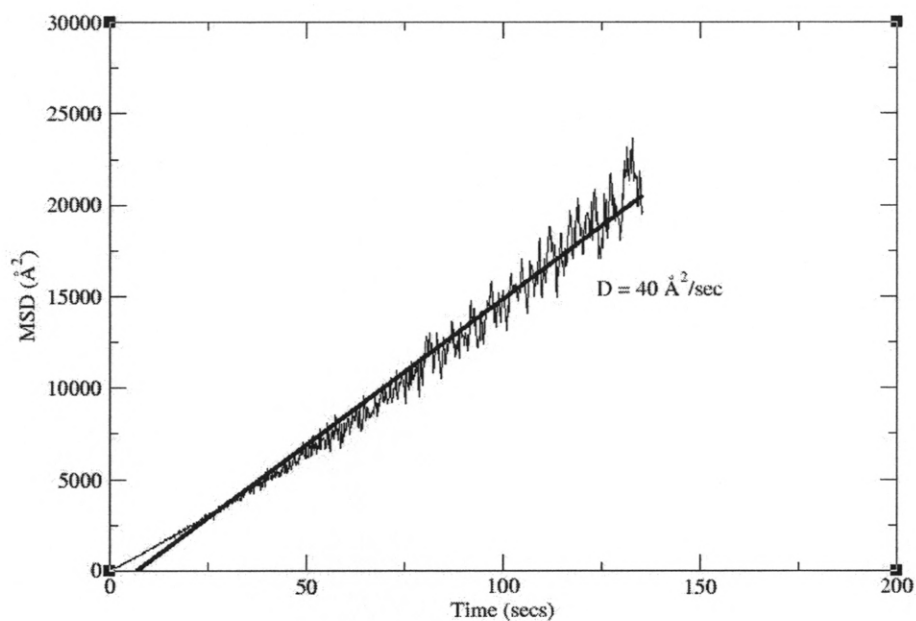


Fig. 7.5(a) MSD vs. Time for a 10 atom cluster at 300K

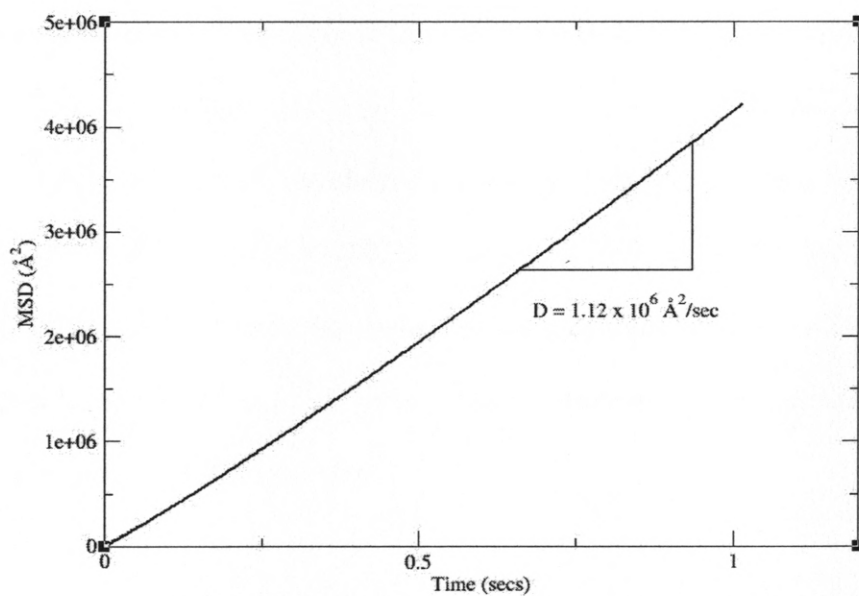


Fig. 7.5(b) MSD vs. Time for a 10 atom cluster at 500K

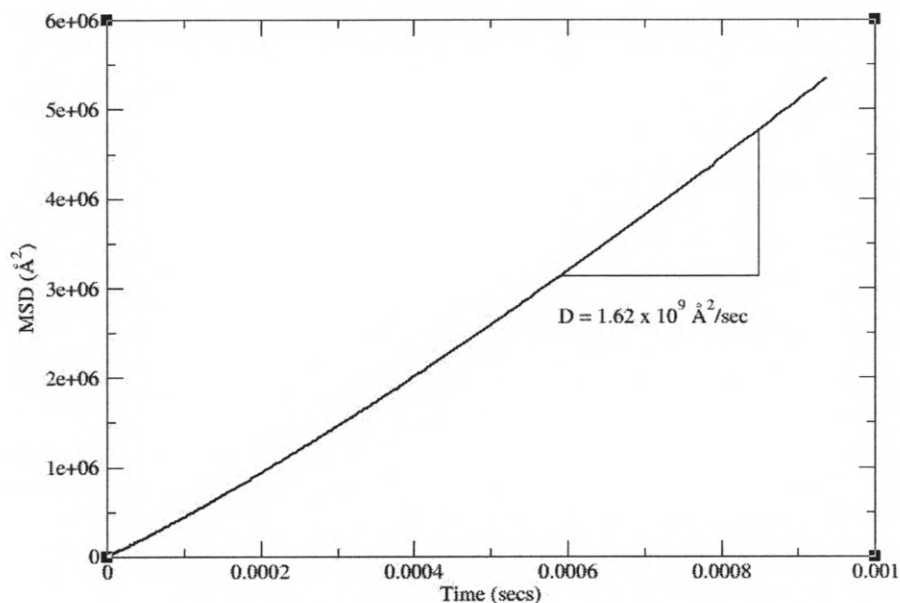


Fig. 7.5(c) MSD vs. Time for a 10 atom cluster at 1000K

For the cases of the magic cluster sizes, which are the 19, 21, and 38, we have already seen from the plots of their traces that they hardly move at 300K. Thus, we cannot extract the MSDs at this temperature. But at higher temperatures the diffusion coefficient has been extracted. Table 7.2 shows the diffusion coefficients of the different cluster sizes at different temperatures. Here, we have also included a case for a 100 atom compact cluster, so that we can obtain a scaling in terms of size. As compared to a 10 atom cluster, we find that the diffusion coefficient of a 100 atom cluster is three orders of magnitude slower at temperatures of 500 K and 1000 K.

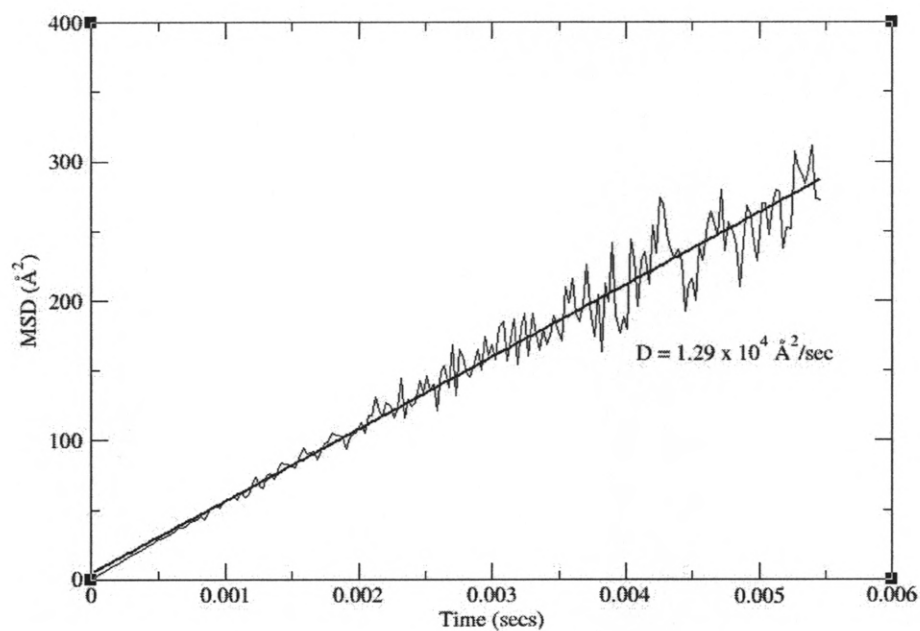


Fig. 7.5(d) MSD vs. Time for a 19 atom cluster at 500K

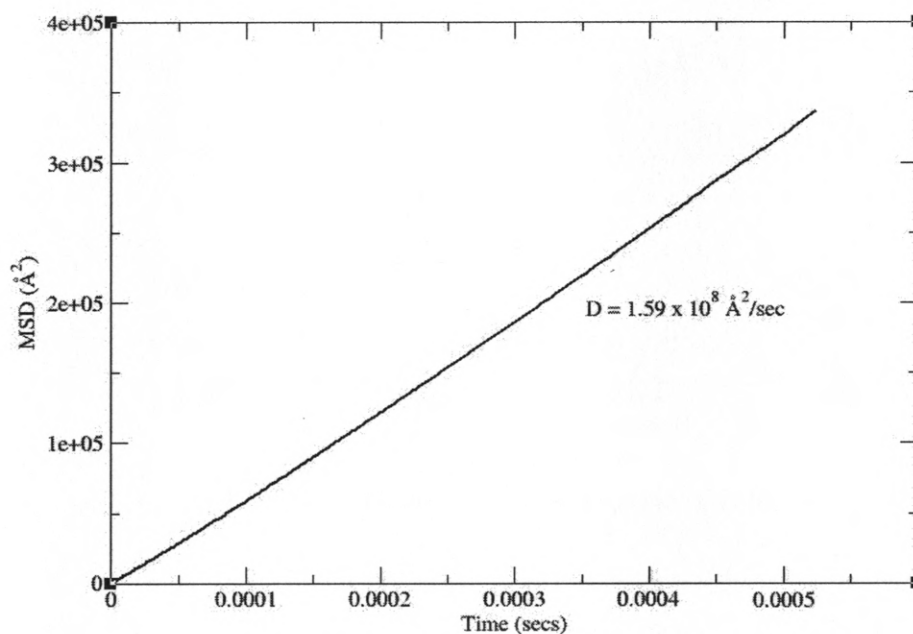


Fig. 7.5(e) MSD vs. Time for a 21 atom cluster at 1000K

Table 7.2 Diffusion coefficient for different clusters at different temperatures

Cluster size (atoms)	Diffusion Coefficient D ($\text{\AA}^2/\text{sec}$)		
	Temperature of simulation		
	300 K	500 K	1000 K
10	40	1.12×10^6	1.62×10^9
14	6.0	2.0×10^5	4.35×10^8
18	3.8	1.09×10^5	2.32×10^8
19	-	1.29×10^4	3.08×10^8
21	-	9.49×10^3	1.59×10^8
26	0.48	2.24×10^4	1.54×10^8
38	-	2.22×10^4	7.61×10^7
100	-	3.2×10^3	4.7×10^6

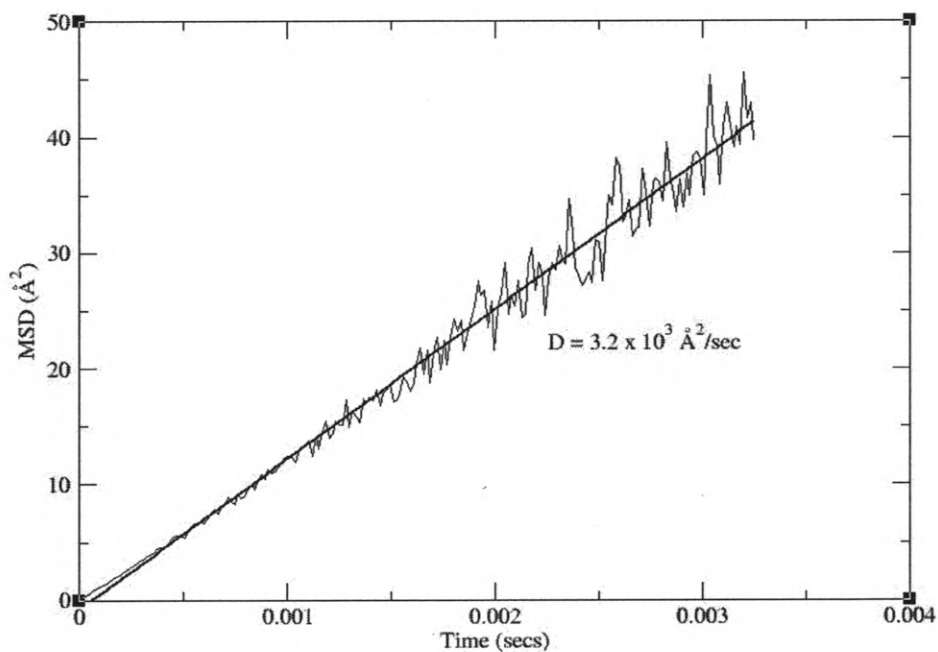


Fig. 7.5(f) MSD vs. Time for a 100 atom cluster at 500K

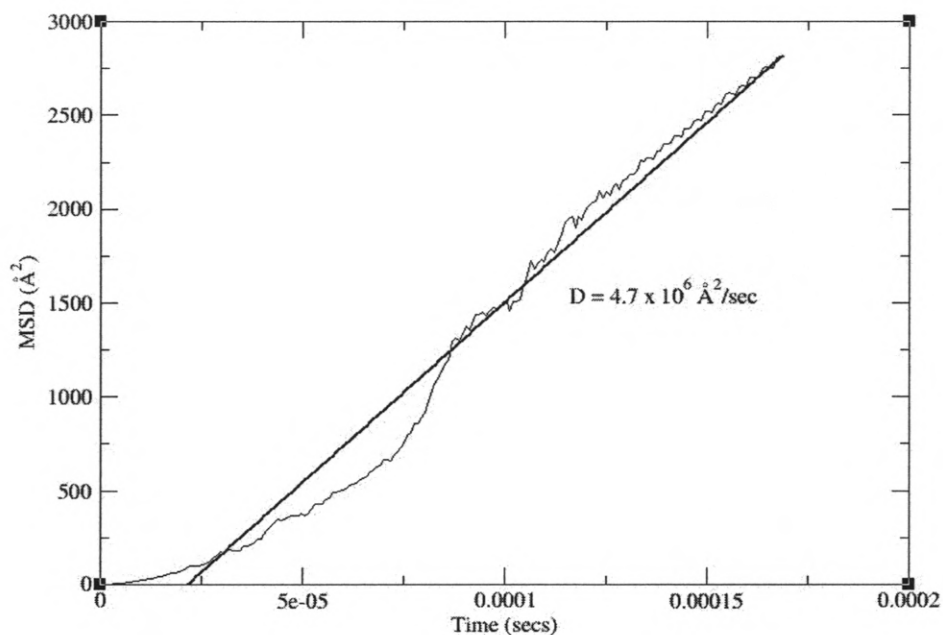


Fig. 7.5(g) MSD vs. Time for a 100 atom cluster at 1000K

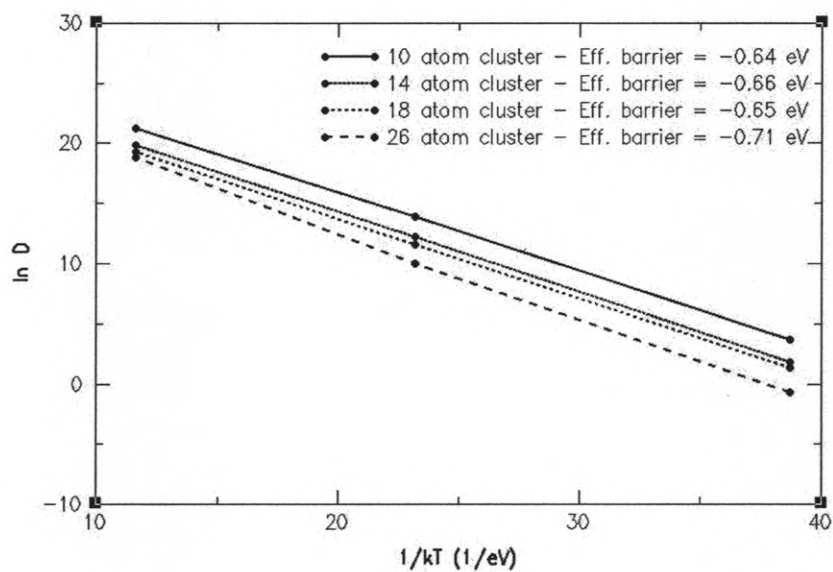


Fig. 7.6 Arrhenius plot with the effective barriers for the 10 atom, 14 atom, 18 atom and 26 atom clusters

The above Arrhenius plot (Fig. 7.6) for the general clusters gives us the values of the effective barriers. The 10, 14, 18 and 26 atom clusters have effective barriers of 0.64 eV, 0.66 eV, 0.65 eV and 0.71 eV respectively. As can be observed, there is a slight increase in the effective barrier for the 26 atom cluster as compared to the 10, 14 and 18 atom clusters which have almost the same value. We cannot make a definite conclusion from this result.

The tables below show the frequencies of the processes that are executed at different temperatures by these clusters. It is clearly observed that the corner rounding processes show a higher count in the highly diffusive clusters and increase count for the magic clusters as the temperature is increased. Also note that the frequency of the motion against step A is between 60-70% at 300K for all clusters. Even at higher temperatures, the frequency decreases to 45% at 500K and to 25% at 1000K but still remains as the maximum compared to the other processes. This can be explained by looking at the barriers for the corner roundings at the AB and BA junctions, where we can see that the barrier to go from the tip of the corner towards Step A (BA stage 2) is much lower than that from tip of corner towards Step B (AB stage 2). Due to this, the atom prefers to diffuse along the Step edge A, which is the reason for the high frequency count of process Step Edge A.

Table 7.3(a) Comparison of Frequency of Processes in the 4 cluster categories – 300K

Cluster Type Processes	Energy Barrier (eV)	10 atom (General)	19 atom (Hexagon)	21 atom (6n+3)	38 atom (Hexagon+1)
Step Edge A	0.252	0.63	0.62	0.71	0.72
Step Edge B	0.295	0.13	0.17	0.14	0.20
Kink Detach along Step A	0.519	0.0	0.0	0.0	0.0
Kink Detach along Step B	0.556	0.0	0.0	0.0	0.0
Kink Detach along Step (small) A	0.608	0.0086	0.026	0.017	0.0
Kink Detach along Step (small) B	0.680	0.0	0.0016	0.0010	0.0
Kink Incorp. A	0.220	0.0	0.0	0.0	0.0
Kink Incorp. B	0.265	0.0	0.0	0.0	0.0
Kink Incorp. (small) A	0.0075	0.0081	0.025	0.017	0.0
Kink Incorp. (small) B	0.0810	0.0	0.0	0.0	0.0
Kink Detach out of Step A	0.658	0.0	0.0	0.0	0.0
Kink Detach out of Step B	0.590	0.0	0.0	0.0	0.0
Kink Fall into Step A	0.074	0.0	0.0	0.0	0.0
Kink Fall into Step B	0.0069	0.0	0.0	0.0	0.0
Kink Rounding A	0.656	0.0	0.0	0.0	0.0
Kink Rounding B	0.678	0.0	0.0	0.0	0.0
KESE A	0.374	0.0	0.0	0.0	0.0
KESE B	0.402	0.0	0.0	0.0	0.0
Corner Rounding at AA stage 1	0.313	0.033	0.0	0.0031	0.0
Corner Rounding at AA stage 2	0.143	0.0	0.0	0.0	0.0
Corner Rounding at AA stage 3	0.0096	0.031	0.0	0.0031	0.0
Corner Rounding at BB stage 1	0.374	0.0033	0.0	0.0	0.0
Corner Rounding at BB stage 2	0.038	0.0024	0.0	0.0	0.0
Corner Rounding at BB stage 3	0.052	0.0012	0.0	0.0	0.0
Corner Rounding at AB stage 1	0.317	0.066	0.066	0.045	0.029
Corner Rounding at AB stage 2	0.0839	0.0042	0.0053	0.0029	0.0021
Corner Rounding at BA stage 1	0.396	0.0043	0.0047	0.0027	0.0021
Corner Rounding at BA stage 2	0.0148	0.066	0.067	0.045	0.029
Rounding a chain A	0.0626	0.0030	0.0	0.0	0.0
Rounding a chain B	0.0191	0.0023	0.0	0.0	0.0

Table 7.3(b) Frequency of Processes for the 10 atom cluster (General) at different temperatures

Temperature Processes	Energy Barrier (eV)	300K	500K	1000K
Step Edge A	0.252	0.63	0.38	0.19
Step Edge B	0.295	0.13	0.14	0.11
Kink Detach along Step A	0.519	0.0	0.0	0.0072
Kink Detach along Step B	0.556	0.0	0.0	0.0044
Kink Detach along Step (small) A	0.608	0.0086	0.019	0.031
Kink Detach along Step (small) B	0.680	0.0	0.0035	0.013
Kink Incorpor. A	0.220	0.0	0.0	0.0059
Kink Incorpor. B	0.265	0.0	0.0	0.0035
Kink Incorpor. (small) A	0.0075	0.0081	0.017	0.027
Kink Incorpor. (small) B	0.0810	0.0	0.0026	0.010
Kink Detach out of Step A	0.658	0.0	0.0	0.0
Kink Detach out of Step B	0.590	0.0	0.0	0.0
Kink Fall into Step A	0.074	0.0	0.0	0.0
Kink Fall into Step B	0.0069	0.0	0.0	0.0
Kink Rounding A	0.656	0.0	0.0	0.0
Kink Rounding B	0.678	0.0	0.0	0.0
KESE A	0.374	0.0	0.0020	0.0051
KESE B	0.402	0.0	0.0	0.0039
Corner Rounding at AA stage 1	0.313	0.033	0.049	0.054
Corner Rounding at AA stage 2	0.143	0.0	0.0025	0.011
Corner Rounding at AA stage 3	0.0096	0.031	0.042	0.041
Corner Rounding at BB stage 1	0.374	0.0033	0.013	0.028
Corner Rounding at BB stage 2	0.038	0.0024	0.011	0.025
Corner Rounding at BB stage 3	0.052	0.0012	0.0059	0.014
Corner Rounding at AB stage 1	0.317	0.066	0.11	0.12
Corner Rounding at AB stage 2	0.0839	0.0042	0.023	0.055
Corner Rounding at BA stage 1	0.396	0.0043	0.023	0.055
Corner Rounding at BA stage 2	0.0148	0.066	0.11	0.12
Rounding a chain A	0.0626	0.0030	0.010	0.018
Rounding a chain B	0.0191	0.0023	0.0086	0.017

Table 7.3(c) Frequency of Processes for the 19 atom cluster (Hexagon) at different temperatures

Temperature Processes	Energy Barrier (eV)	300K	500K	1000K
Step Edge A	0.252	0.62	0.42	0.23
Step Edge B	0.295	0.17	0.24	0.15
Kink Detach along Step A	0.519	0.0	0.0020	0.019
Kink Detach along Step B	0.556	0.0	0.0	0.012
Kink Detach along Step (small) A	0.608	0.026	0.012	0.043
Kink Detach along Step (small) B	0.680	0.0016	0.0023	0.019
Kink Incorp. A	0.220	0.0	0.0020	0.018
Kink Incorp. B	0.265	0.0	0.0	0.011
Kink Incorp. (small) A	0.0075	0.025	0.011	0.037
Kink Incorp. (small) B	0.0810	0.0	0.0012	0.012
Kink Detach out of Step A	0.658	0.0	0.0	0.0013
Kink Detach out of Step B	0.590	0.0	0.0	0.0027
Kink Fall into Step A	0.074	0.0	0.0	0.0016
Kink Fall into Step B	0.0069	0.0	0.0	0.0023
Kink Rounding A	0.656	0.0	0.0	0.0011
Kink Rounding B	0.678	0.0	0.0	0.0
KESE A	0.374	0.0	0.0011	0.0078
KESE B	0.402	0.0	0.0	0.0066
Corner Rounding at AA stage 1	0.313	0.0	0.0	0.014
Corner Rounding at AA stage 2	0.143	0.0	0.0	0.0050
Corner Rounding at AA stage 3	0.0096	0.0	0.0	0.012
Corner Rounding at BB stage 1	0.374	0.0	0.0	0.0079
Corner Rounding at BB stage 2	0.038	0.0	0.0	0.012
Corner Rounding at BB stage 3	0.052	0.0	0.0	0.0049
Corner Rounding at AB stage 1	0.317	0.066	0.11	0.11
Corner Rounding at AB stage 2	0.0839	0.0053	0.024	0.055
Corner Rounding at BA stage 1	0.396	0.0047	0.023	0.051
Corner Rounding at BA stage 2	0.0148	0.067	0.12	0.11
Rounding a chain A	0.0626	0.0	0.0	0.0053
Rounding a chain B	0.0191	0.0	0.0	0.0054

Table 7.3(d) Frequency of Processes for the 21 atom cluster ($6n + 3$) at different temperatures

Temperature Processes	Energy Barrier (eV)	300K	500K	1000K
Step Edge A	0.252	0.71	0.48	0.24
Step Edge B	0.295	0.14	0.19	0.15
Kink Detach along Step A	0.519	0.0	0.0018	0.021
Kink Detach along Step B	0.556	0.0	0.0	0.012
Kink Detach along Step (small) A	0.608	0.017	0.029	0.046
Kink Detach along Step (small) B	0.680	0.0010	0.0054	0.020
Kink Incorp. A	0.220	0.0	0.0018	0.019
Kink Incorp. B	0.265	0.0	0.0	0.011
Kink Incorp. (small) A	0.0075	0.017	0.026	0.039
Kink Incorp. (small) B	0.0810	0.0	0.0029	0.013
Kink Detach out of Step A	0.658	0.0	0.0	0.0016
Kink Detach out of Step B	0.590	0.0	0.0	0.0033
Kink Fall into Step A	0.074	0.0	0.0	0.0019
Kink Fall into Step B	0.0069	0.0	0.0	0.0032
Kink Rounding A	0.656	0.0	0.0	0.0017
Kink Rounding B	0.678	0.0	0.0	0.0012
KESE A	0.374	0.0	0.0027	0.0086
KESE B	0.402	0.0	0.0020	0.0071
Corner Rounding at AA stage 1	0.313	0.0031	0.0063	0.014
Corner Rounding at AA stage 2	0.143	0.0	0.0	0.0050
Corner Rounding at AA stage 3	0.0096	0.0031	0.0062	0.012
Corner Rounding at BB stage 1	0.374	0.0	0.0016	0.0081
Corner Rounding at BB stage 2	0.038	0.0	0.0019	0.011
Corner Rounding at BB stage 3	0.052	0.0	0.0010	0.0052
Corner Rounding at AB stage 1	0.317	0.045	0.090	0.10
Corner Rounding at AB stage 2	0.0839	0.0029	0.019	0.050
Corner Rounding at BA stage 1	0.396	0.0027	0.018	0.046
Corner Rounding at BA stage 2	0.0148	0.045	0.09	0.10
Rounding a chain A	0.0626	0.0	0.0011	0.0052
Rounding a chain B	0.0191	0.0	0.0013	0.0054

Table 7.3(e) Frequency of Processes for the 38 atom cluster (Hexagon+1) at different temperatures

Temperature Processes	Energy Barrier (eV)	300K	500K	1000K
Step Edge A	0.252	0.72	0.53	0.33
Step Edge B	0.295	0.20	0.25	0.42
Kink Detach along Step A	0.519	0.0	0.012	0.021
Kink Detach along Step B	0.556	0.0	0.0046	0.014
Kink Detach along Step (small) A	0.608	0.0	0.0098	0.032
Kink Detach along Step (small) B	0.680	0.0	0.0017	0.013
Kink Incorp. A	0.220	0.0	0.012	0.021
Kink Incorp. B	0.265	0.0	0.0044	0.014
Kink Incorp. (small) A	0.0075	0.0	0.0094	0.030
Kink Incorp. (small) B	0.0810	0.0	0.0010	0.014
Kink Detach out of Step A	0.658	0.0	0.0	0.0038
Kink Detach out of Step B	0.590	0.0	0.0013	0.0077
Kink Fall into Step A	0.074	0.0	0.0	0.0
Kink Fall into Step B	0.0069	0.0	0.0011	0.0072
Kink Rounding A	0.656	0.0	0.0	0.0
Kink Rounding B	0.678	0.0	0.0	0.0
KESE A	0.374	0.0	0.0012	0.0020
KESE B	0.402	0.0	0.0	0.0020
Corner Rounding at AA stage 1	0.313	0.0	0.0	0.0026
Corner Rounding at AA stage 2	0.143	0.0	0.0	0.0
Corner Rounding at AA stage 3	0.0096	0.0	0.0	0.0022
Corner Rounding at BB stage 1	0.374	0.0	0.0	0.0014
Corner Rounding at BB stage 2	0.038	0.0	0.0	0.0023
Corner Rounding at BB stage 3	0.052	0.0	0.0	0.0
Corner Rounding at AB stage 1	0.317	0.029	0.062	0.011
Corner Rounding at AB stage 2	0.0839	0.0021	0.013	0.0080
Corner Rounding at BA stage 1	0.396	0.0021	0.012	0.0064
Corner Rounding at BA stage 2	0.0148	0.029	0.063	0.013
Rounding a chain A	0.0626	0.0	0.0	0.0
Rounding a chain B	0.0191	0.0	0.0	0.0

Table 7.4 Diffusion coefficient for large clusters at 500 K

Cluster size (atoms)	Diffusion coefficient D ($\text{\AA}^2/\text{sec}$)
55	4.0×10^3
100	3.2×10^3
223	2.12×10^3
409	1.14×10^3
612	0.92×10^3
1003	0.69×10^3

Table 7.4 gives the diffusion coefficients for the larger clusters of sizes from 55-1003 atoms. As can be seen there is a decrease in the value of D with the size of the cluster. Calculations for a cluster size of 805 atoms shows an anomaly in the value of the diffusion coefficient. Calculations were performed using a different random number seeds and the average value of D is $1.30 \times 10^3 \text{ \AA}^2/\text{sec}$. We have not investigated the reason for this anomaly. Fig. 7.7 below shows a plot of $\text{Log } D$ vs. $\text{Log } N$, where D is the diffusion coefficient and N is the size of the cluster. The scaling exponent that we obtain for the larger cluster sized ranging from 55 atoms to 1003 atoms is close to -0.6. Values of the exponent from earlier work are found to be around, -1.5 [85,86,87]. Our exponent being a value less than 1.0 implies that the decay in the value of D with cluster size is slower than that found in earlier work. This could be attributed to the inclusion of a larger number of key processes in our database, having lower barriers due to which the atoms of the cluster could be fluctuating in a smaller region performing these low energy processes leading to lower diffusivity of the center of mass.

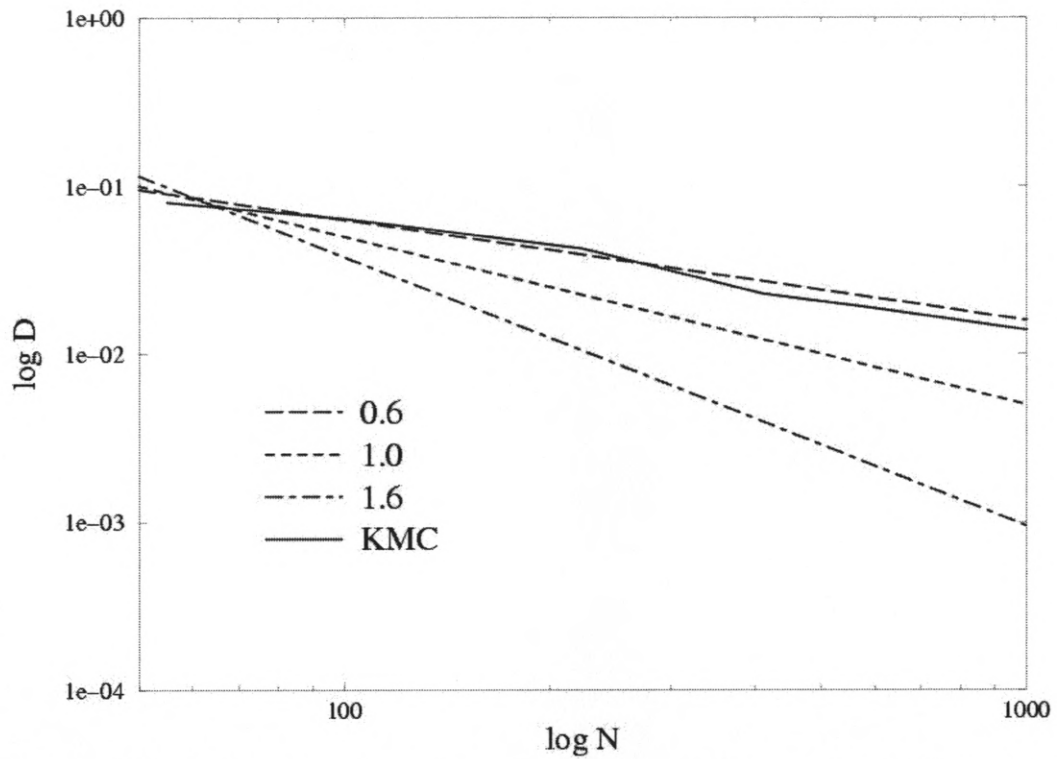


Fig. 7.7 Scaling of diffusion coefficient D with size of cluster N . The plot of the KMC simulation is for the larger cluster sizes ranging from 55-1003 atoms. The slope gives the scaling exponent as -0.6.

In Figure 7.8, it can be seen how a 1003 atom cluster evolves with time. It changes from a compact shape to a more triangular shape with longer step edges A than step edges B.

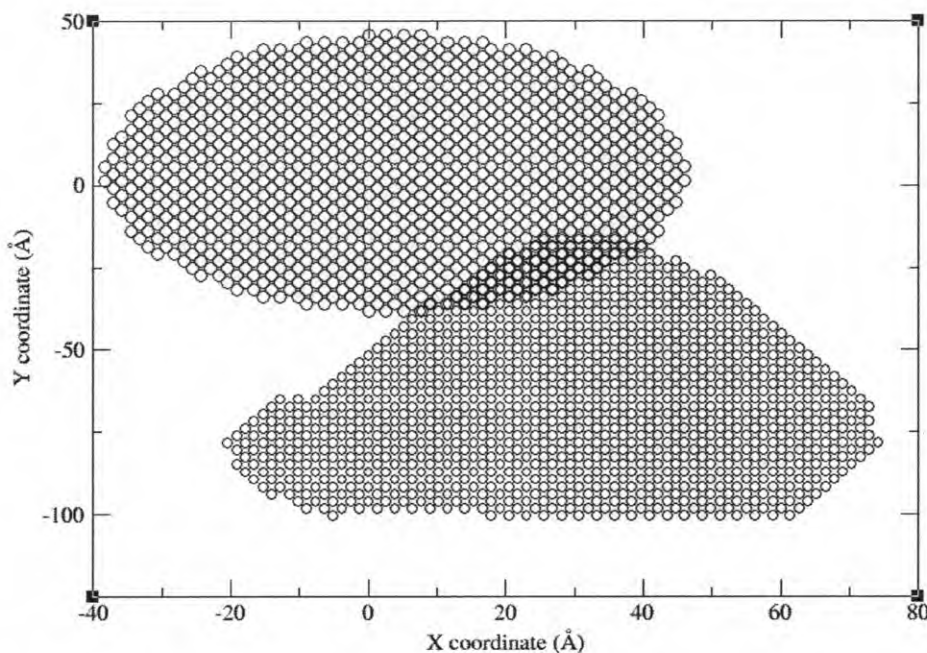


Fig. 7.8 Change in shape of a 1003 atom Cu cluster at 500 K. The upper compact shape is the starting configuration and the lower triangular shape is the configuration after 40 million Monte Carlo timesteps.

7.5 Conclusions

In summary, we have performed a kinetic Monte Carlo study of the diffusion of small Cu clusters on Cu(111) surface, using a unique pattern recognition scheme and allowing only single atom peripheral motion. A database of 49 key processes is used in the simulations and the range of MC steps is from 100 – 500 million. The temperatures used in the simulation are 300 K, 500 K and 1000 K. It is found that there exists types of magic clusters with sizes forming a perfect hexagon, $6n+3$ and hexagon+1, which exhibit a lower diffusivity as compared to the “general” category. However at higher temperatures, their diffusivity increases. This is attributed to the fact that many other processes are executed by the atoms at higher temperatures, thus enhancing their motion. The frequency list of the processes executed show that diffusion against Step edge A is the most frequently

executed process accounting for 60-70% of the total count at 300K, about 45% at 500K and about 25% at 1000K. This can be explained by looking at the barriers for the corner roundings at the AB and BA junctions, where we see that the barrier to go from the tip of the corner towards Step A (BA stage 2) is much lower than that from tip of corner towards Step B (AB stage 2). Due to this, the atom prefers to diffuse along the Step edge A, which is the reason for the high frequency count of process Step Edge A. We have also been able to confirm this by performing simulations for larger cluster sizes of 55 to 1003 atoms, which start with a circular shaped cluster and end up having a kind of triangular shape, with long step edges A and small step edges B. The corner rounding processes have a high count in the cases of general clusters and also for all clusters at elevated temperatures, especially the count at the AA and BB junctions increases with temperature and this could be a key factor for the enhanced diffusivities at these temperatures. We also find that the diffusion coefficient D shows a difference of 3 orders of magnitude in the diffusivities between a 10 atom and a 100 atom cluster. The shapes of the clusters during growth and post deposition are strongly dependent on the number of atoms in the cluster, whether they fall under any of the above mentioned magic categories or the general category. The clusters evolve with time and try to achieve a compact shape which is close to hexagonal, or an irregular hexagon. Larger cluster sizes tend to achieve a more triangular shape at 500 K, with larger step A edges as compared to step B edges. This is attributed to the anisotropy in the barriers for the corner roundings from the junction of step edge A to step edge B and vice versa. Experimentally, different

shape evolution has been observed at different temperatures and for different lattice geometry [161,162]. The scaling of the diffusion coefficient D , with size of cluster gives a scaling exponent of -0.6 for the larger cluster sizes. Earlier work [85,86,87] has found the scaling exponent to be -1.5. Thus, our results show that the decrease in D with the size of the cluster is slower than that in the earlier works. This could be due to the larger database of periphery mechanisms that we have included in our simulations. We have also found that at higher temperatures of 1000 K, vacancies begin to form within the cluster interior. This could lead to the locking of the CM of the cluster to within a few angstroms, since peripheral atoms in such a configuration have fewer options for motion. Another aspect of studying cluster diffusion can be to study the diffusion of vacancy islands. The advantage of doing so is that in vacancy islands, most of the mechanisms are peripheral. This detailed study and analysis has helped us in understanding the basic mechanisms which are important in nanocluster diffusion, scaling with respect to size, and existence of certain magic cluster sizes that show low diffusivity as compared to general clusters in the same size range.

Chapter 8

Future Directions

There has been extensive work in recent years on mound decay close to step edges on metal surfaces, where the decay of the islands is found to accelerate when in the vicinity of a step edge [20,163].

To try get an understanding of the mechanisms involved in fast island decay, we have performed MD simulations on Cu(111) and Ag(111) systems. As mentioned earlier, one of the drawbacks of MD simulations is its limited time scales which are orders of magnitude smaller than experimental timescales. However, we do get an idea of the behavior of the clusters at the initial stages. There are mainly two processes that occur when an atom is close enough to a step edge. It can either hop down the step, or exchange with a step edge atom. If there are vacancies in its vicinity, it is a little more complex, as the vacancies too participate in the diffusion mechanism. When there are a group of atoms (island) close to a step edge, it is difficult to nail down the processes that occur, because there are several mechanisms occurring simultaneously, concerted motion. This is one of the reasons to apply MD techniques, and observe how an island evolves with time at certain temperatures. This kind of theoretical simulation has also been performed earlier [163], where the most likely mechanism to occur, was found to be a two-atom exchange at a B-type step edge, having a barrier of 0.38 eV and around 0.35 eV if a kink existed at the lower step. This was for a Ag(111) system.

A more efficient way to perform simulations to study island decay would be to use a combination of MD and KMC. This would point to the various important processes that occur at different temperatures which could then be incorporated into the KMC to simulate large timescales. We are also working on developing the KMC technique for diffusion of 3D islands.

A summary of the observations obtained from various simulations performed using MD, is listed below. For the snapshots, refer to Appendix I.

8.1 Decay of small clusters on Cu/Cu(111) and Ag/Ag(111) systems

8.1.1 Cu/Cu(111) stepped and kinked surfaces at 500K

For the case of a 6 atom Cu cluster on a kinked Cu(111) surface, it is found that the cluster moves away from the kinked edge onto the terrace after 20 ps and reorients itself. This is also found for a 4 atom and a 2 atom cluster, and also for a single adatom.

For a 7 atom cluster on a 22 atom cluster on a Cu stepped surface, there is no decay observed even after 100 ps.

For the same case but with vacancies around the cluster, some atoms (more than one, as was earlier found for a single layer cluster) of the lower cluster decay after 20 ps itself, and fill in the vacancies. A step edge atom fills in a vacancy to form a kink. This configuration remains without any significant change till the end of 100 ps.

8.1.2 Cu/Cu(111) stepped and kinked surfaces at 700K

- For a 10 atom Cu cluster in the vicinity of a single vacancy, on a stepped Cu(111) surface, there is no decay, but an atom from the step edge moves in to fill the vacancy, thus forming a kink on the step edge.
- For the same case but in the vicinity of a divacancy, two atoms from the Cu cluster fall into the vacancies.
- For the cluster in the vicinity of many vacancies, one atom from the cluster detaches and falls into a vacancy after 20 ps, and even after 100 ps, no other cluster atoms are found to decay. However the vacancies diffuse around and the cluster reorientations.
- For the case of a 22 atom Cu cluster on a stepped Cu(111) surface, without vacancies, there is no decay of the cluster at all even after 100 ps, except for a slight reorientation.
- For the same case but in the vicinity of a divacancy, the stepped edge atoms move in to fill the vacancies, thus forming a kink at the stepped edge. There is no decay of the cluster, but reorientation is observed.
- For the same case but for a kinked Cu(111) surface with no vacancies, there is no decay but a slight reorientation after 100 ps.
- For a similar case on a stepped Cu(111) surface and in the vicinity of many vacancies surrounding the cluster, there is no decay, but a slight reorientation of the cluster. The vacancies are found to diffuse and some form divacancies by joining. Some step edge atoms move in to form kinks at the step edge and after 100 ps, two kinks that were formed at the step edge join to form one kink.

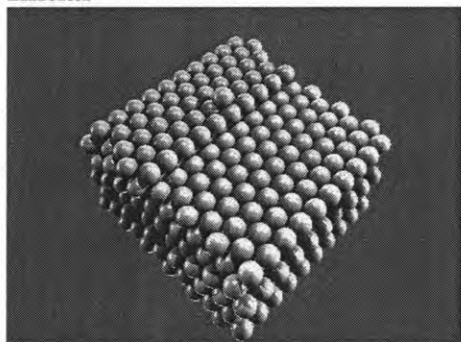
8.1.3 Ag/Ag(111) stepped and kinked surfaces at 500K

- For a 10 atom Ag cluster on a stepped Ag(111) surface with many vacancies surrounding it, it is found that one atom of the cluster detaches and falls into a vacancy. Some vacancies diffuse around. The cluster reorients itself. After 80 ps, a step edge atom fills a vacancy to form a kink at the step edge. There is not much movement seen even after 140 ps.
- For a 22 atom Ag cluster on the same system, we find that after 20 ps, one cluster atom detaches and falls into a vacancy and a step edge atom fills a vacancy to form a kink on the step edge. At the end of 100 ps too, there is just a slight reorientation of the cluster and no other significant changes.

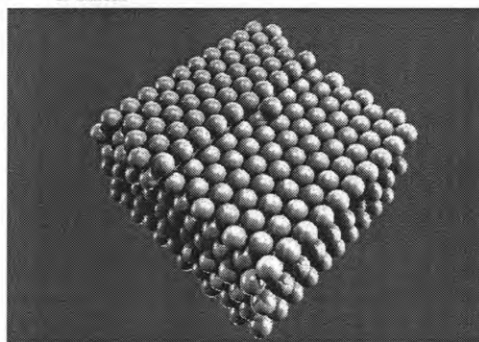
8.2 Barriers for Cu/Cu(111)

Some of the important island decay barriers that were calculated using the NEB technique are listed below:

Initial



Final

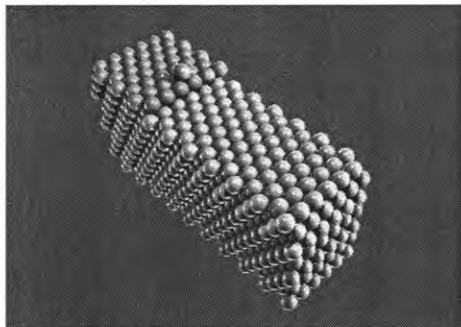


Barrier = **0.284 eV** (Exchange from an fcc site)

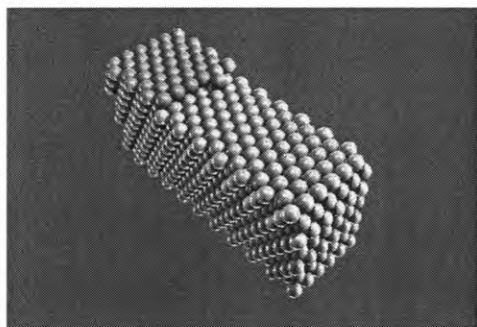
Barrier = **0.3248 eV** (Exchange from an hcp site)

Fig. 8.1(a) Adatom exchange from above step A with step edge atom.

Initial



Final

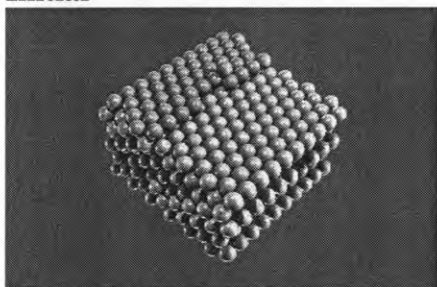


Barrier = **0.0611 eV** (Exchange from an fcc site)

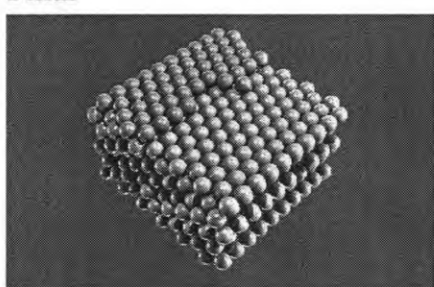
Barrier = **0.0954 eV** (Exchange from an hcp site)

Fig. 8.1(b) Adatom exchange from above step B with step edge atom.

Initial



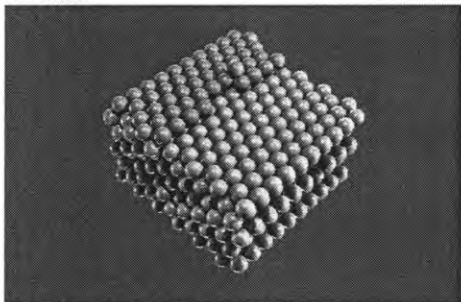
Final



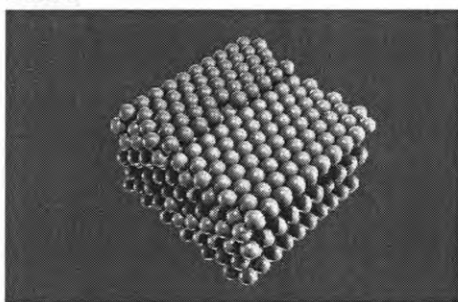
Barrier = **0.3659 eV**

Fig. 8.2(a) Adatom above kink A exchange with kink atom

Initial



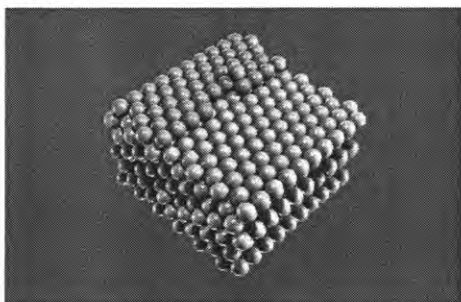
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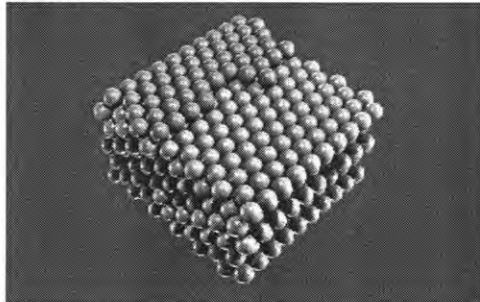
Barrier = **0.3889 eV**

Fig. 8.2(b) Adatom above kink A hop into kink

Initial



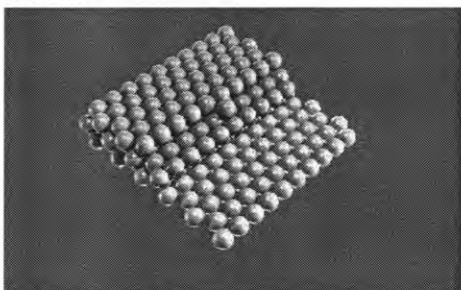
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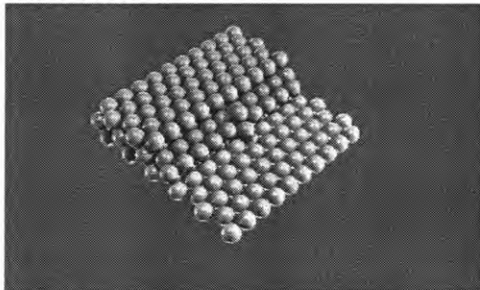
Barrier = **0.4825 eV**

Fig. 8.2(c) Adatom above kink A hop over kink

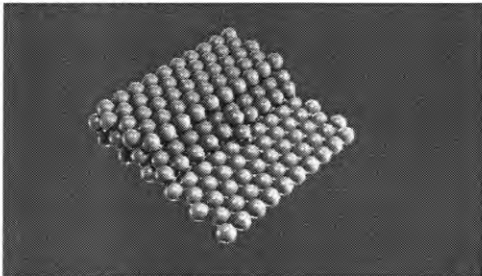
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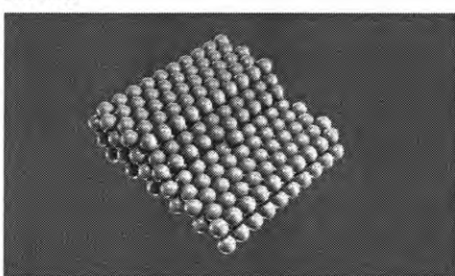
Intermediate



Intermediate



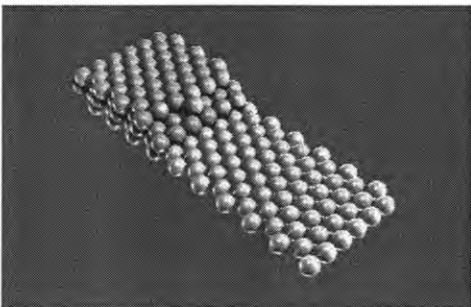
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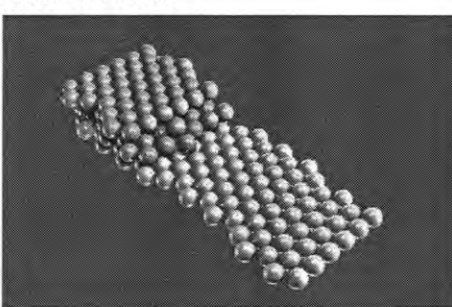
Barrier = **0.8167 eV**

Fig. 8.3(a) Adatom against upper step A exchange with lower step atom

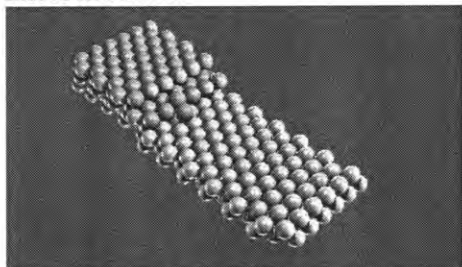
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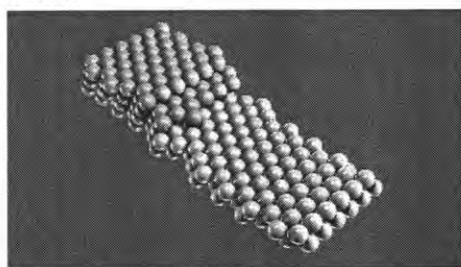
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Intermediate



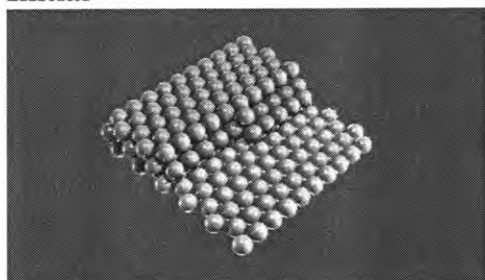
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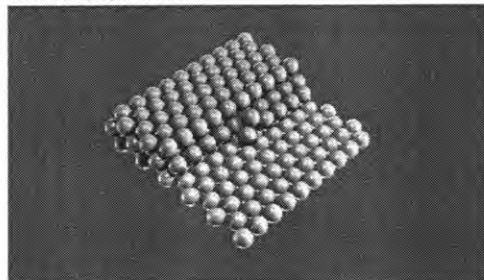
Barrier = **0.3147 eV**

Fig. 8.3(b) Adatom against upper step B exchange with lower step atom

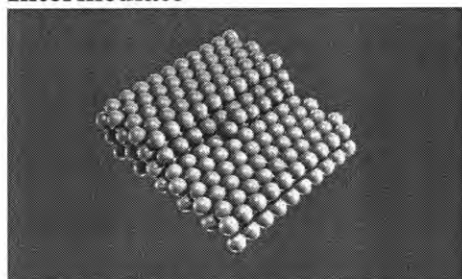
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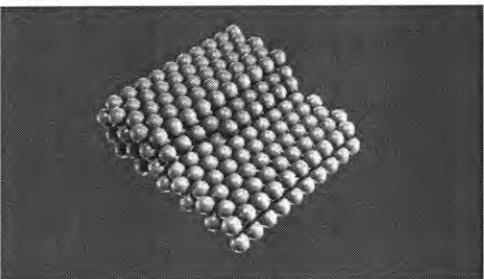
Intermediate



Intermediate



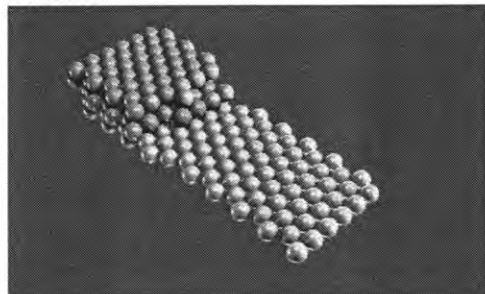
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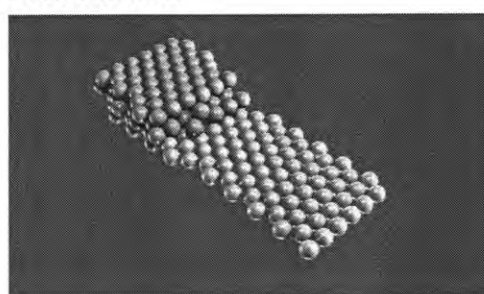
Barrier = **0.6405 eV**

Fig. 8.4(a) Adatom against upper step A exchange with lower kink atom

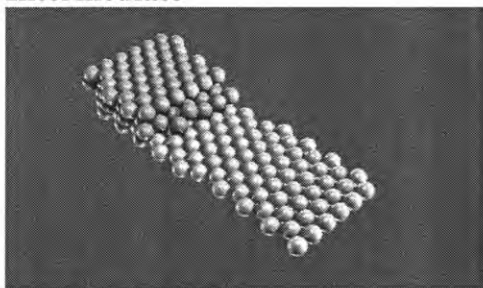
Initial



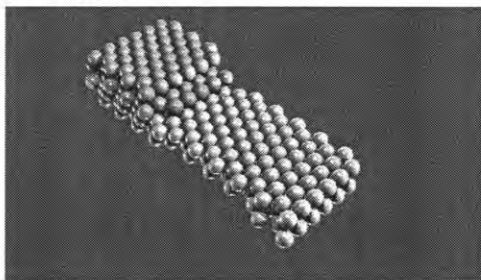
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Intermediate



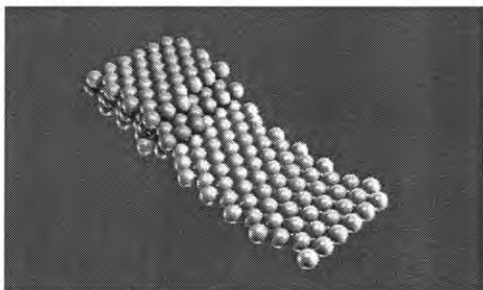
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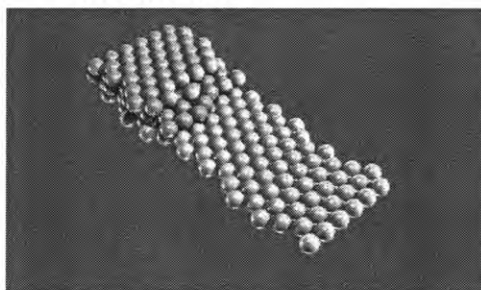
Barrier = **0.5117 eV**

Fig. 8.4(b) Adatom against upper step B exchange with lower kink atom

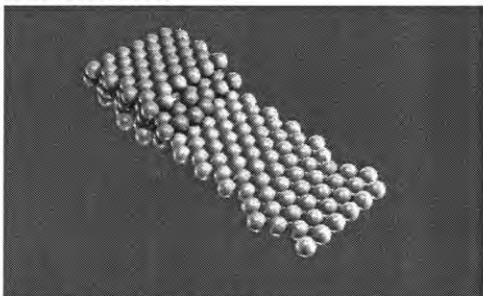
Initial



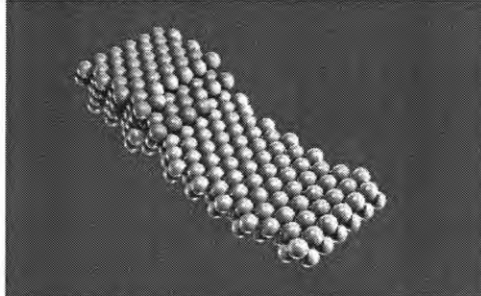
Intermediate



Intermediate



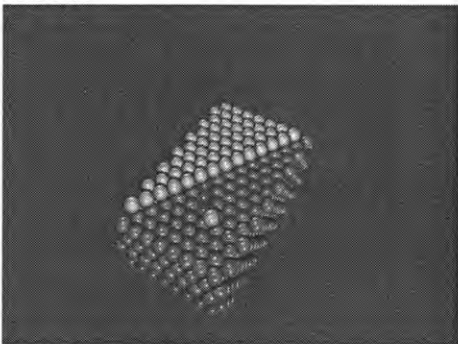
Final



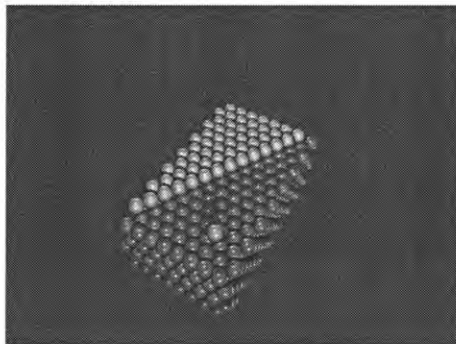
Barrier = **0.7374 eV**

Fig. 8.5 Adatom against upper kink A exchange with lower kink atom

Initial



Final



Barrier = **0.033 eV**

Fig. 8.6 Terrace Diffusion – from FCC to HCP to FCC site

8.3 Barriers for Ag/Ag(111)

For similar barriers in the case of Ag/Ag(111), look at Table 8.1 below. For all detailed figures refer to Appendix II

Table 8.1 Barriers for Ag/Ag(111)

No.	Process description	Barrier in eV	
		Step A	Step B
1	Terrace diffusion	0.061	---
2	Diffusion along Step edge	0.294	0.338
3	Exchange with Step atom	0.436	0.209
4	Exchange with Kink atom	0.396	0.269
5	Kink Rounding	0.570	0.582
6	Kink detachment	0.471	0.540
7	Hopping from upper to lower terrace	0.407	0.663
8	Hopping over Kink site onto lower terrace	0.395	0.330
9	Small outward detachment from Step	0.758	0.691
10	Small outward detachment from Kink	0.571	0.527
11	Outward detachment from Step onto terrace	1.135	0.963
12	Outward detachment from Kink onto terrace	0.759	0.766
13	Attaching from terrace to the step edge	0.043	---
14	Hopping from terrace fcc site to adjacent fcc site away from step edge	0.56	---
15	Hopping from terrace fcc site to adjacent fcc site parallel to step edge	0.58	---
Multilayer Processes (2 step/kink system)			
16	Exchange of adatom along upper step with lower step atom	0.859	0.535
17	Hop of adatom along upper step onto lowest terrace	0.832	1.219
18	Exchange of adatom along upper step with lower kink atom	0.650	0.601
19	Hop of adatom along upper step onto lower kink	0.519	0.374

Chapter 9

Conclusions

In this dissertation we have presented a comprehensive and comparative study of adatom manipulation on fcc(111) metal surfaces using tips of (100) and (111) crystal orientations. We find that during lateral manipulation the barrier for the adatom to move in the direction of the tip is considerably lowered due to the shift in the saddle point. Use of a fine grid in the calculations, which was not employed in the earlier work [93] provided the necessary resolution to see this shift in the saddle point. The lowest barriers are reached at lateral separations between $2.0\text{\AA}$ - $3.0\text{\AA}$. The results show that the qualitative changes in the potential energy surface are independent of the shape and geometry of the tip but a quantitative difference is seen when considering the tip details. We have also examined the trends in six different metal systems, and two special cases of heterogeneous systems having a Cu tip and a Pt adatom/substrate and a Pt tip on a Cu adatom/substrate. Among the homogeneous systems studied, Ag is found to have the lowest barrier of 50 meV. However, even though Cu had the next lowest barrier of 61.7 meV, it is Cu that is the easiest to manipulate. This is concluded from the ratios of the opbarrier to the barrier in the presence of the tip and also the ratios of difference in the opbarrier and barrier to the cohesive energy and to the barrier in the absence of the tip. Since the cohesive energy of an element is defined as the energy to extract an atom out of the bulk, we have made a direct comparison of this with the energy barriers for the different metals studied. The ratios of the barriers and opbarriers to the cohesive energy help in explaining this

interesting result of the changes in the potential energy surface due to the interatomic potentials. In the case of the Pt homogeneous system, we find an anomaly in the value of the barrier in the presence of the tip. It is higher than the value in the absence of the tip, indicating that the presence of a Pt tip on a Pt surface with an adatom hinders the motion of the adatom along the step edge instead of assisting it, as in the other 5 homogeneous metal systems. It is an interesting result which requires deeper investigation. For the heterogeneous systems, the lowering of the barrier is found to be due to the interaction between the adatom, its nearest neighbors and the tip atoms. This is concluded from the binding energies of the individual atoms. For the case of a Cu(100) tip on a Pt(111) stepped surface with an adatom, the barrier is reduced as compared to the case of a Pt tip on a Pt surface. However, when a Cu tip on a Cu surface is replaced by a Pt tip, it is not effective in lowering the barrier to a value lower than the Cu tip.

For the study of vertical manipulation we find that at large ($>12\text{\AA}$) tip heights the energy required to pull an adatom from a flat surface (2.47eV) is lower than that from a stepped (3.21eV) and a kinked surface (3.53eV). As the tip is lowered to facilitate manipulation, the changes in the surface energetics of these surfaces are such that it is easier to extract an adatom from a stepped or a kinked surface than from a flat one, implying that the tip affects the low coordinated local environment of the adatom, which assists in its extraction. We also find that for specific tip heights, there is a floating region on the kinked and stepped surfaces

in which the adatom is found to be equally attracted to the substrate and to the tip apex atoms.

Since the local environment of the adatom plays a crucial role (also shown in [101]) in its extraction we have looked into the relaxations of the tip apex atoms, the adatom and the neighboring atoms, comparisons of the sum of displacements of the nearest neighbor atoms as the adatom is raised from the surface to the tip apex as well as the comparison of the sum of the individual energies of the nearest neighbor atoms as the adatom is raised from the surface to the tip apex. From this study, we have obtained useful and interesting information about adatom manipulations for homogeneous and heterogeneous systems, and relaxations of the atoms assisting in the process, thus providing us with important factors that can enhance the manipulation process.

We then move on to the examination of the ledge morphology during step flow growth in metal surfaces vicinal to (001). In earlier work, MC [Ref. 110] and the SOS [Ref. 111] simulations had proven that the KESE is the dominant mechanism behind the meandering instability and that it leads to the selection of the dominant wavelength determined by dimer nucleation at step edges. We have shown that the KESE also induces an invariant shape of the step profiles during in-phase growth. This occurs inspite of the overall roughness of the step structures $w(\theta)$ showing no signs of saturation. The value of the corresponding scaling exponent $\beta \approx 0.3$ is consistent with the case of an isolated step [120]. From the SOS model an exponent $\beta \approx 0.57$ [107] is obtained for the strong KESE, while for a collection of steps in the phase-locking regime $\beta = 1/2$ [113,114,133]. This

strange behavior of dynamical scaling is apparently related to the strict in-phase growth and consequent formation of the invariant shape of the profile. The invariance seen in the shape even though the roughness does not show any sign of saturation, indicates a subtle coupling of the step edge currents with the stationary morphology. By numerically integrating the continuum equation we have shown how the interplay between various surface currents determines the invariant step shapes.

Next we have performed a study to obtain the ratio of prefactors for interlayer diffusion on Ag/Ag(111). Prefactors play an important role in simulations. Usually a fixed value is chosen for the prefactor, for all mechanisms used in simulations. However, if we can understand the ratio of prefactors for different mechanisms, we could expect to obtain a difference in the results. Because of the large difference between the atom detachment and atom terrace diffusion rates for Ag/Ag(111), we have presented an alternative interpretation of the island versus vacancy decay experiments. We consider that the decay process consists of independent atom detachments, instead of continuous atom emission under steady conditions. With the new analysis one obtains that the probability for interlayer diffusion, $p \gg P_{RS}$, where, P_{RS} is the probability for an atom detached at R to be adsorbed at r after overcoming the reflecting boundary. This implies $v_s/v_t > 30$, where, v_s is the prefactor for step-edge diffusion and v_t is the prefactor for terrace diffusion, and a better agreement between the high and low temperature experiments. However further work is needed to specify detailed

experimental criteria for deciding the range of validity of the independent versus steady state model in island decay experiments.

Lastly we have done a detailed study of small Cu clusters on a Cu(111) surface using the KMC technique. This work is influenced by earlier experimental and theoretical works [70,154,85]. In this study we have used a unique pattern recognition scheme and allowed only single atom peripheral motion. A database of 49 key processes is used in the simulations and the range of MC steps is from 100 – 500 million. The temperatures used in the simulation are 300 K, 500 K and 1000K. We find the existence of certain magic clusters with sizes forming a perfect hexagon, $6n+3$ and hexagon+1, which exhibit a lower diffusivity as compared to the “general” category. However at higher temperatures, their diffusivity increases. This could be due to the many other processes that are executed by the atoms at higher temperatures, thus enhancing their motion. The frequency list of the processes executed show that diffusion against step edge A is the most executed process accounting for 60-70% of the total count at 300K, about 45% at 50K and about 25% at 1000K. The corner rounding processes have a high count in cases of the general clusters and for all clusters at elevated temperatures. The low barrier for the process to move from the junction of steps A and B towards step A is responsible for the higher count shown by the process motion against Step Edge A. The shapes of the clusters during growth and post deposition are strongly dependent on the number of atoms in the cluster, whether in the magic or general category. Evolution of the clusters with time, show a compact shape formation, which is close to hexagonal, or an irregular hexagon.

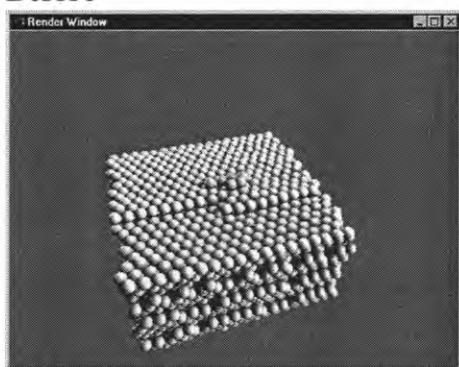
Larger cluster sizes tend to achieve a more triangular shape with larger step A edges as compared to step B edges. The scaling of the diffusion coefficient D , with the size of the cluster, gives a scaling exponent of -0.6 for the larger sized clusters. This study has helped us understand the basic mechanisms which are important in nanocluster diffusion, scaling between cluster sizes, change of diffusive behavior with temperatures, and the possibilities of existence of magic cluster sizes that show low diffusivity as compared to general clusters in the same size range. A summary of island decay results performed using MD simulations has also been presented, along with a list of barriers for interlayer diffusion calculated for Cu/Cu(111) and Ag/Ag(111) systems.

Appendix I

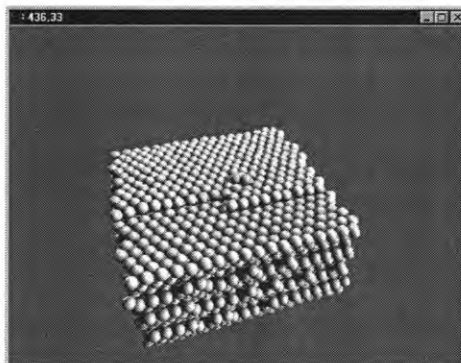
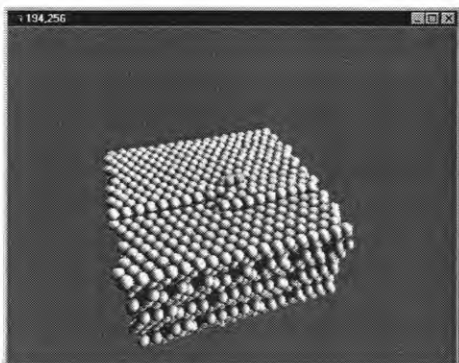
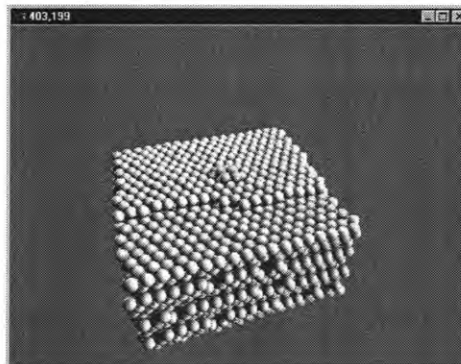
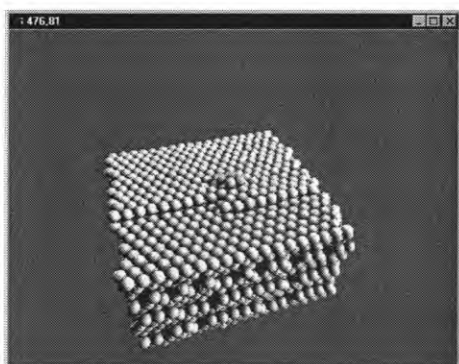
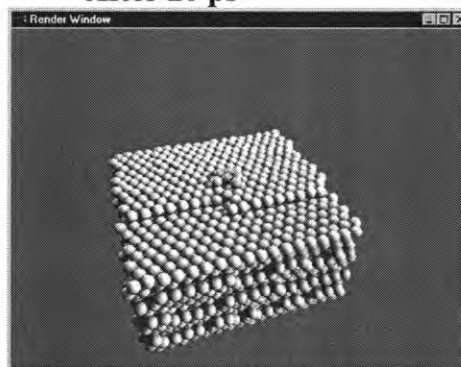
Decay of small clusters on Cu(111) stepped and kinked surfaces, 500K.

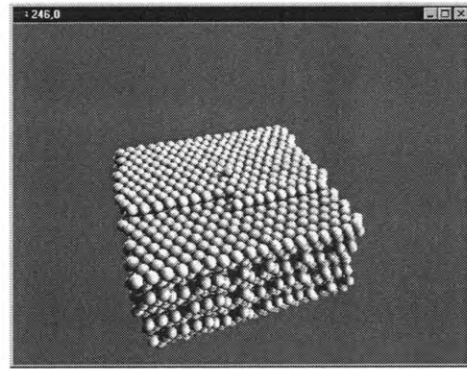
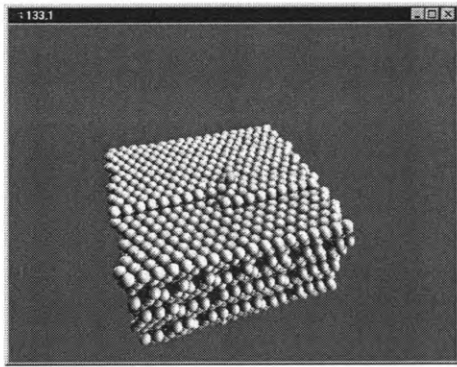
- For the case of a 6 atom Cu cluster on a kinked Cu(111) surface, it is found that the cluster moves away from the kinked edge onto the terrace after 20 ps and reorients itself. This is also found for a 4 atom and a 2 atom cluster, and also for a single adatom.

Before



After 20 ps



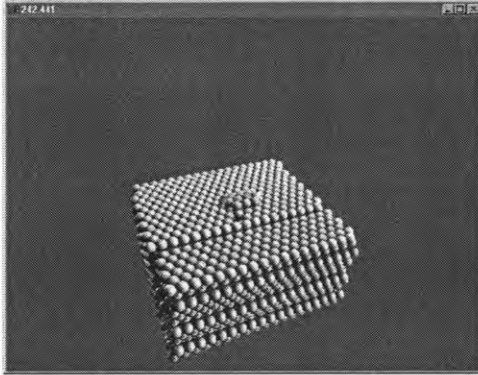


- For a 7 atom cluster on a 22 atom cluster on a Cu stepped surface, there is no decay observed even after 100 ps.
- For the same case but with vacancies around the cluster, some atoms (more than one, as was earlier found for a single layer cluster) of the lower cluster decay after 20 ps itself, and fill in the vacancies. A step edge atom fills in a vacancy to form a kink. This configuration remains without any significant change till the end of 100 ps.

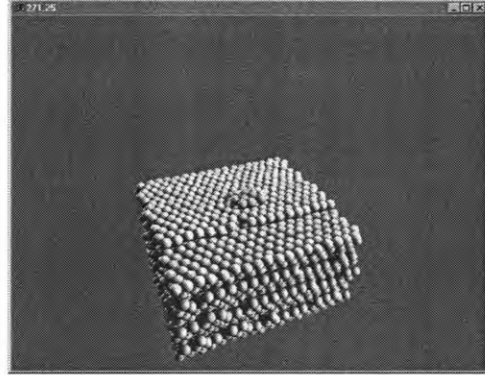
Decay of small clusters on Cu(111) stepped and kinked surfaces, 700K.

- For a 10 atom Cu cluster in the vicinity of a single vacancy, on a stepped Cu(111) surface, there is no decay, but an atom from the step edge moves in to fill the vacancy, thus forming a kink on the step edge.

Before

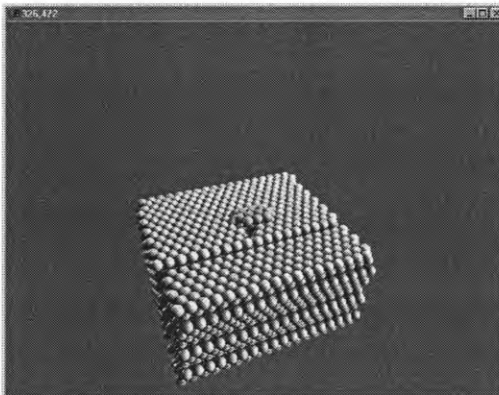


After 20 ps

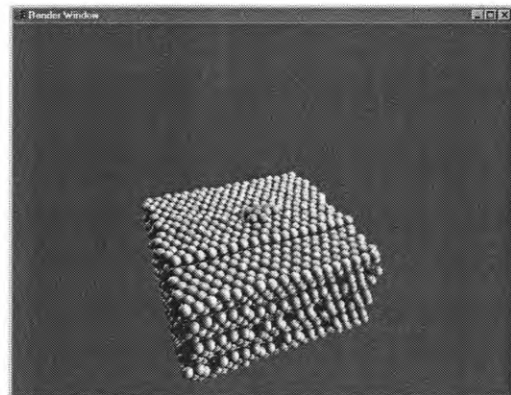


- For the same case but in the vicinity of a divacancy, two atoms from the Cu cluster fall into the vacancies.

Before

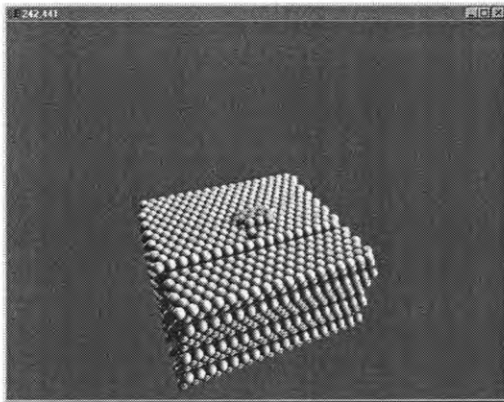


After 20 ps

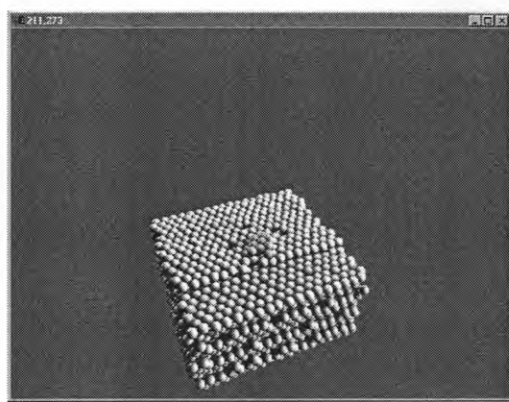


- For the cluster in the vicinity of many vacancies, one atom from the cluster detaches and falls into a vacancy after 20 ps, and even after 100 ps, no other cluster atoms are found to decay. However the vacancies diffuse around and the cluster reorientations.

Before

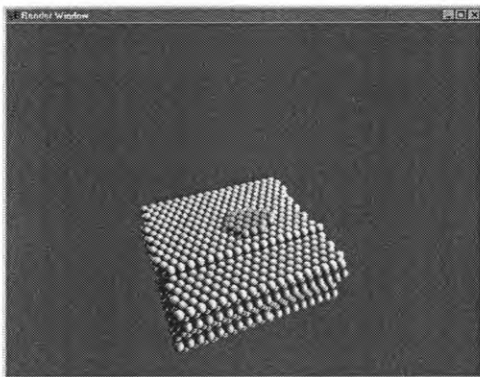


After 100 ps

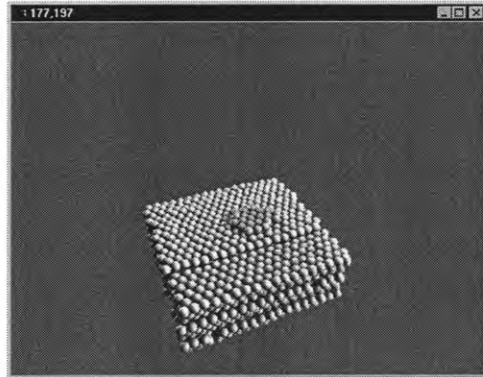


- For the case of a 22 atom Cu cluster on a stepped Cu(111) surface, without vacancies, there is no decay of the cluster at all even after 100 ps, except for a slight reorientation.

Before

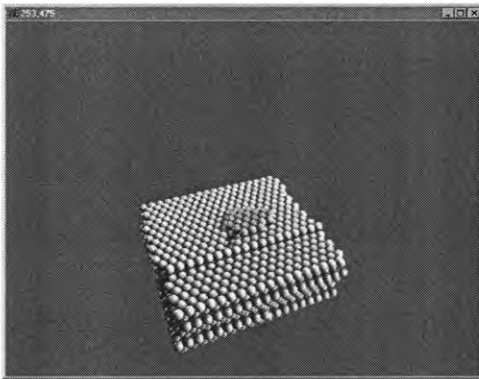


After 100 ps

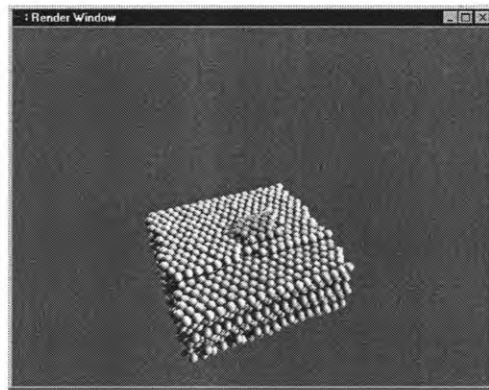


- For the same case but in the vicinity of a divacancy, the stepped edge atoms move in to fill the vacancies, thus forming a kink at the stepped edge. There is no decay of the cluster, but reorientation is observed.

Before

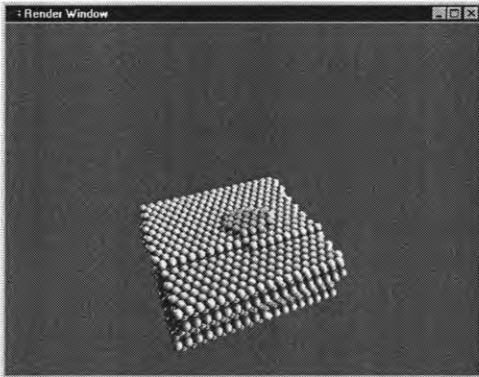


After 100 ps

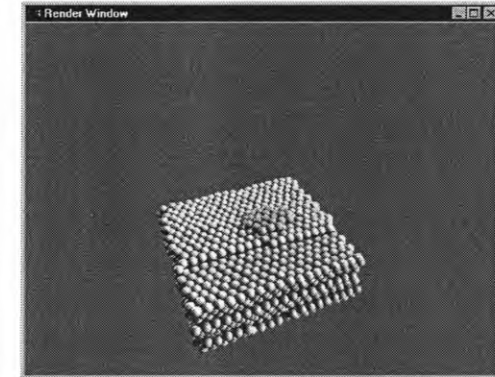


- For the same case but for a kinked Cu(111) surface with no vacancies, there is no decay but a slight reorientation after 100 ps.

Before

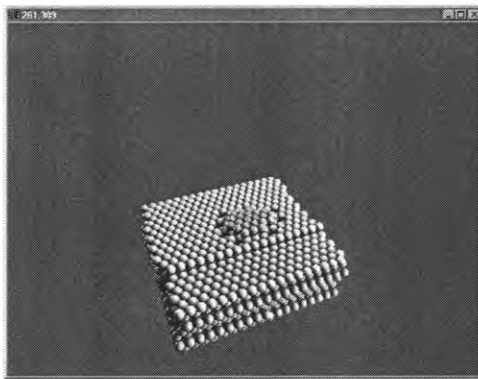


After 100 ps

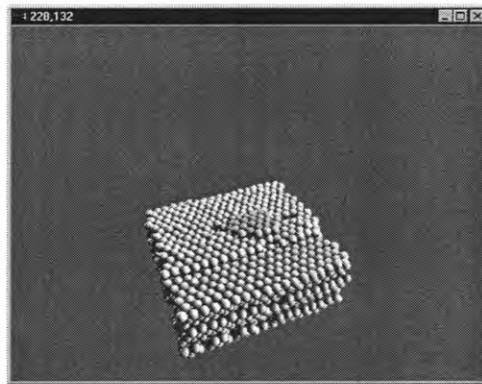


- For a similar case on a stepped Cu(111) surface and in the vicinity of many vacancies surrounding the cluster, there is no decay, but a slight reorientation of the cluster. The vacancies are found to diffuse and some form divacancies by joining. Some step edge atoms move in to form kinks at the step edge and after 100 ps, two kinks that were formed at the step edge join to form one kink.

Before



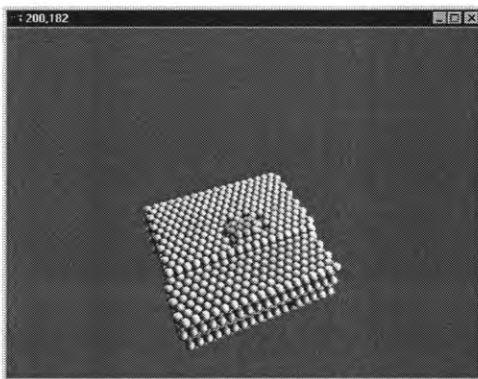
After 100 ps



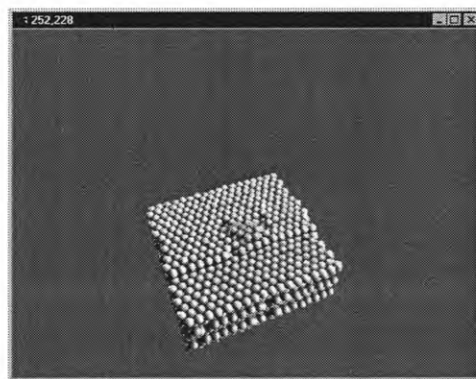
Decay of small clusters on Ag(111) stepped and kinked surfaces, 500K.

- For a 10 atom Ag cluster on a stepped Ag(111) surface with many vacancies surrounding it, it is found that one atom of the cluster detaches and falls into a vacancy. Some vacancies diffuse around. The cluster reorients itself. After 80 ps, a step edge atom fills a vacancy to form a kink at the step edge. There is not much movement seen even after 140 ps.

Before



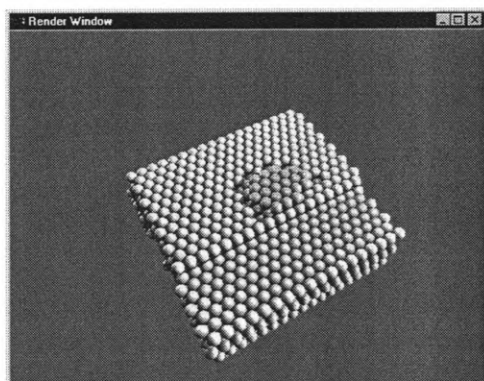
After 140 ps



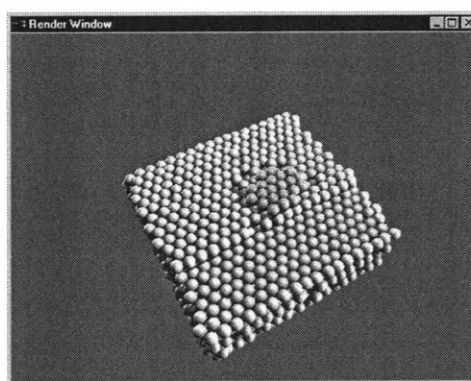
- For a 22 atom Ag cluster on the same system, we find that after 20 ps, one cluster atom detaches and falls into a vacancy and a step edge atom fills a vacancy to

form a kink on the step edge. At the end of 100 ps too, there is just a slight reorientation of the cluster and no other significant changes.

Before



After 100 ps

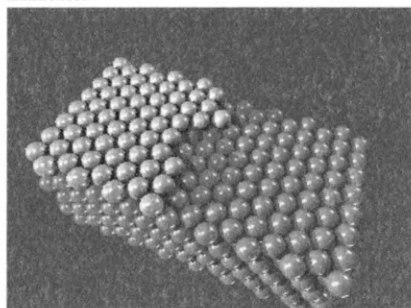


Appendix II

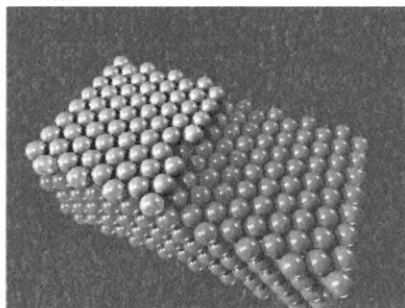
Barrier and Potential Energy Surface using the Nudged Elastic Band method for the Kink Ehrlich Schwoebel Effect (KESE) in a Ag/Ag(111) system having an A- type step face

The number of images between the initial and the final state are taken as 30.

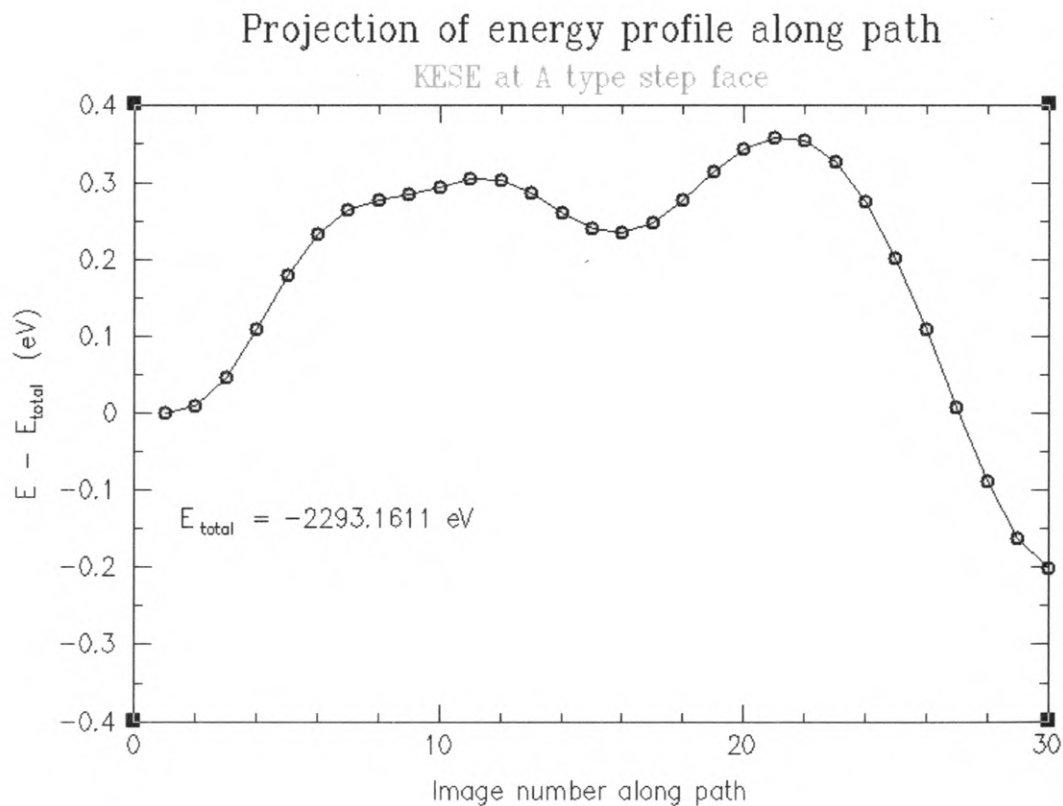
Initial



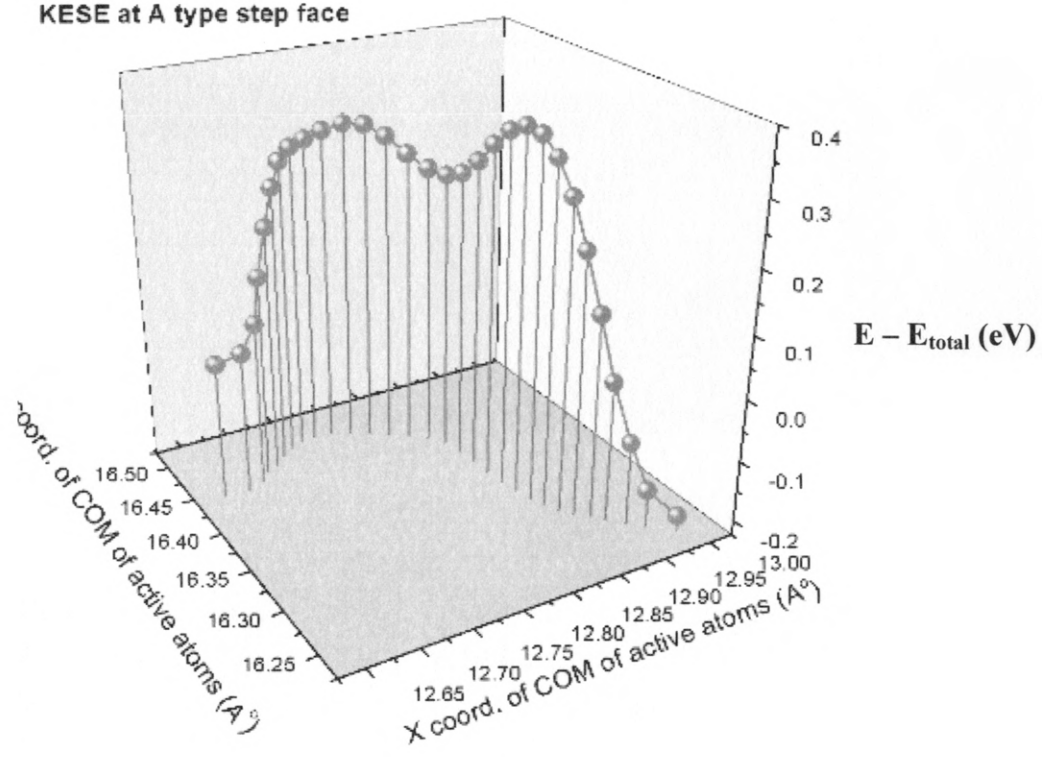
Final



Barrier = 0.358 eV

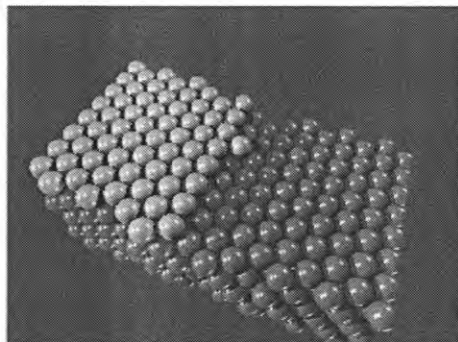
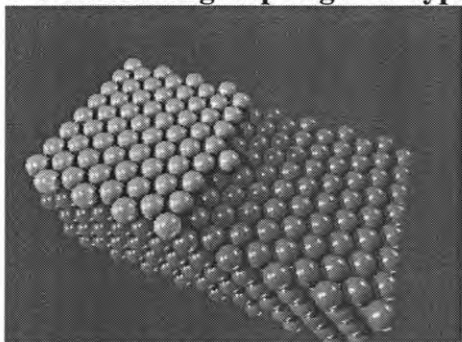


KESE at A type step face



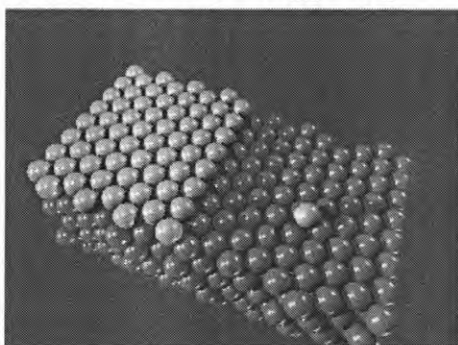
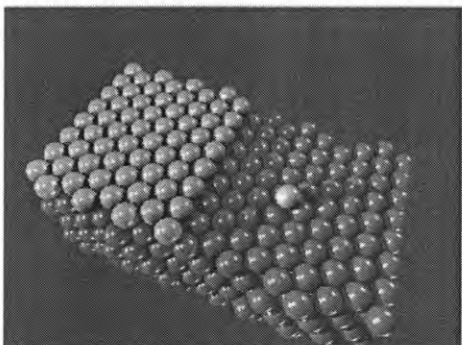
Barriers for Ag/Ag(111) using NEB

Diffusion along step edge – A type



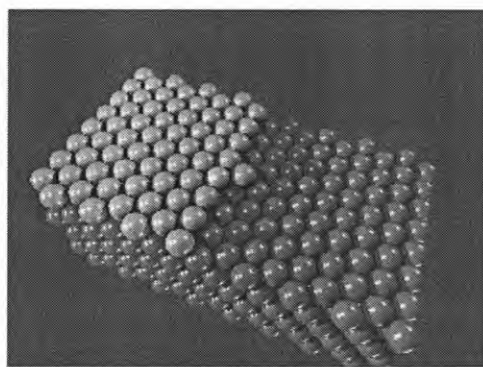
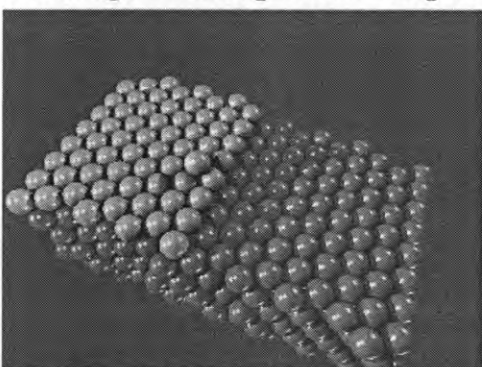
Barrier = **0.294 eV**

Diffusion on terrace-from FCC to HCP to FCC site– A type step



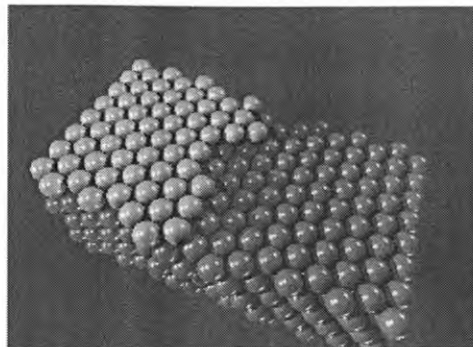
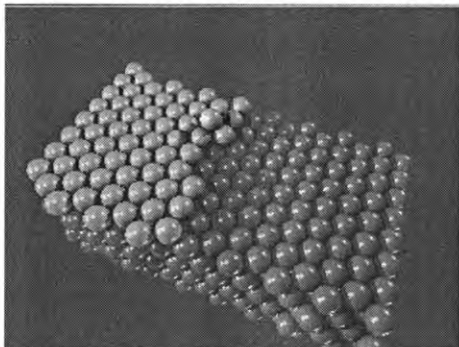
Barrier = **0.061 eV**

Exchange with Step atom – Step A



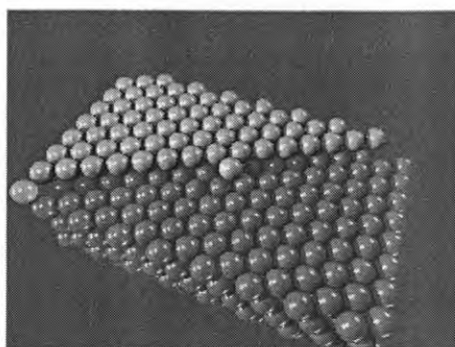
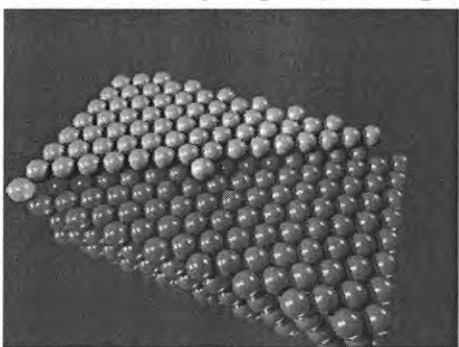
Barrier = **0.436 eV**

Exchange with Kink atom – Step face A



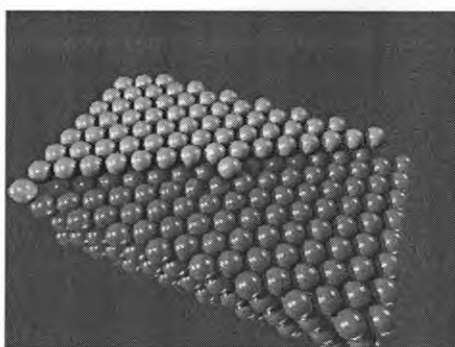
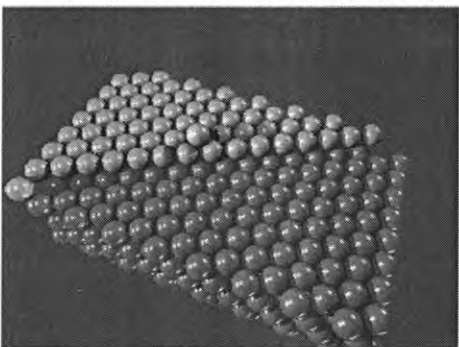
Barrier = **0.396 eV**

Diffusion along step edge – StepB



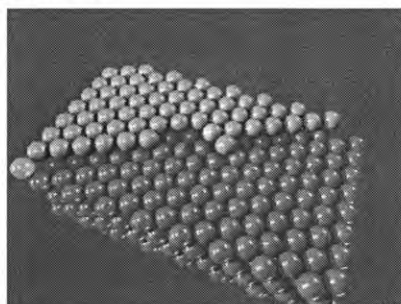
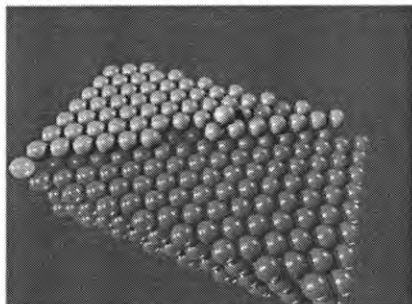
Barrier = **0.338 eV**

Exchange with Step atom – Step B



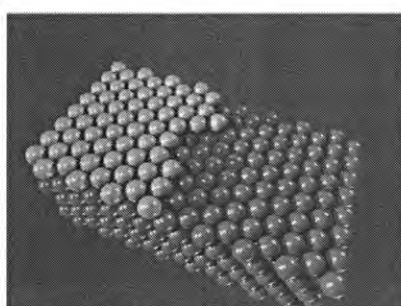
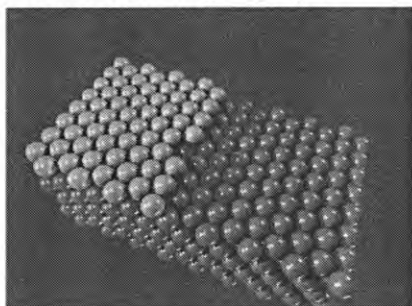
Barrier = **0.209 eV**

Exchange with Kink atom – Step face B



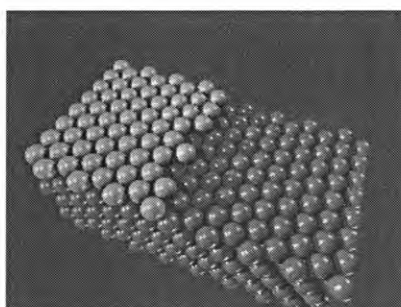
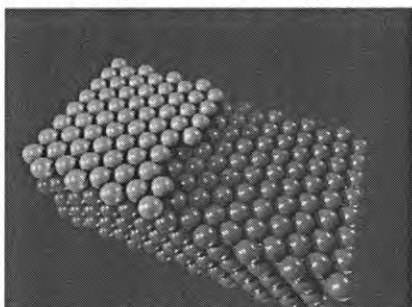
Barrier = **0.269 eV**

Kink Rounding – Step A



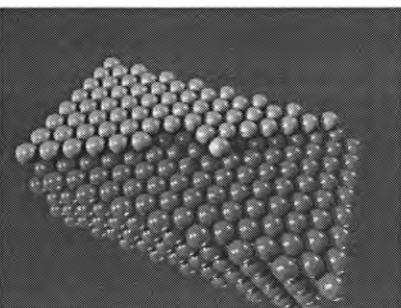
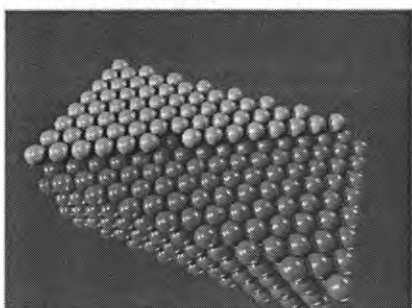
Barrier = **0.570 eV**

Kink Detachment – Step A



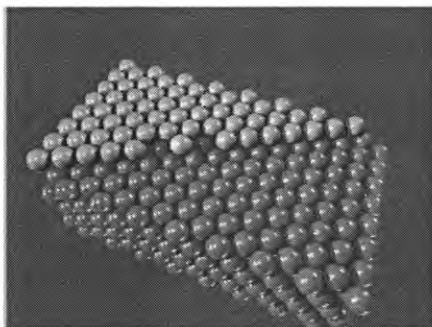
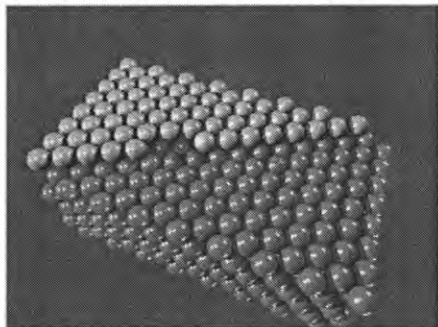
Barrier = **0.471 eV**

Kink Rounding – Step B



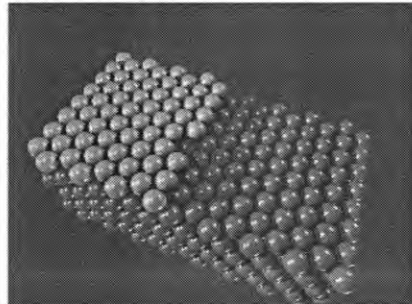
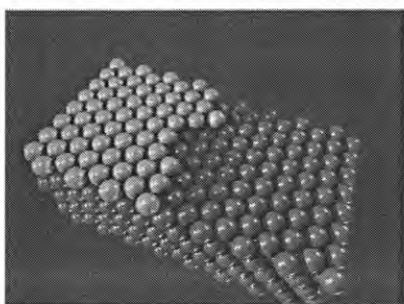
Barrier = **0.582 eV**

Kink Detachment – Step B



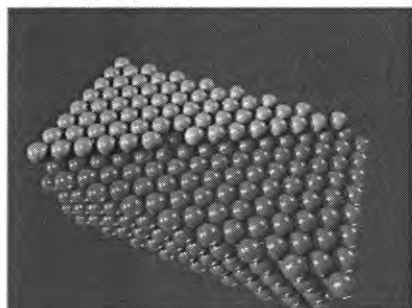
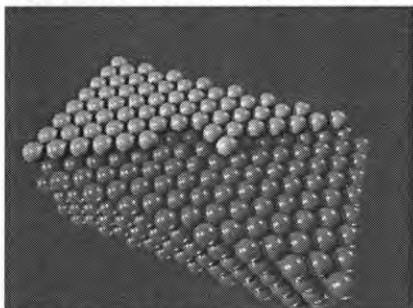
Barrier = **0.540 eV**

Kink Ehrlich Shwoebel Effect (KESE) – Step A



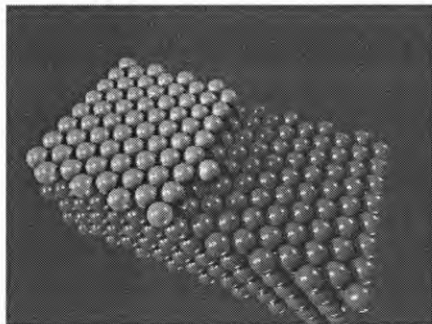
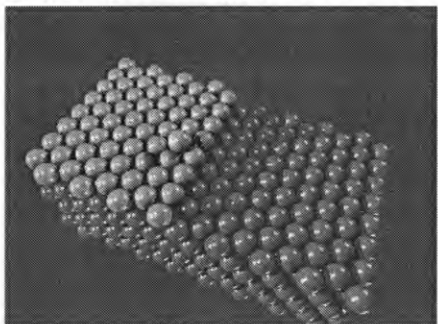
Barrier = **0.358 eV**

Kink Ehrlich Shwoebel Effect (KESE) – Step B



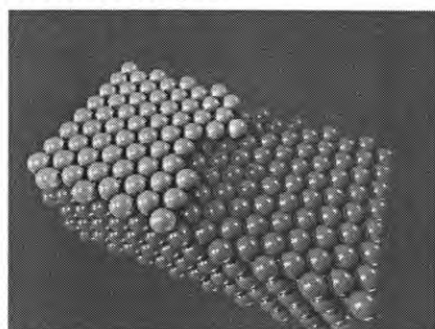
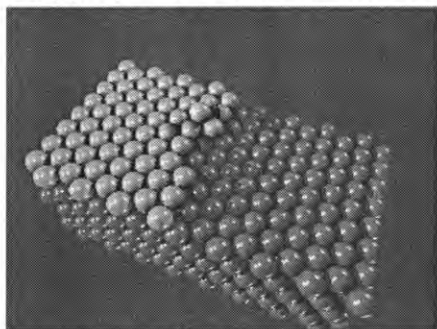
Barrier = **0.378 eV**

Hopping from upper to lower terrace – Step A



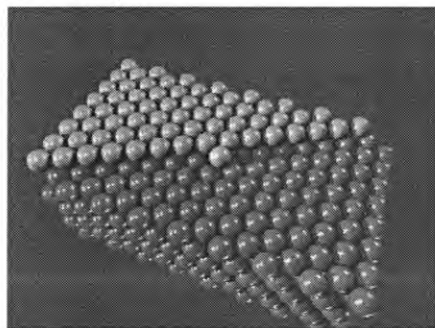
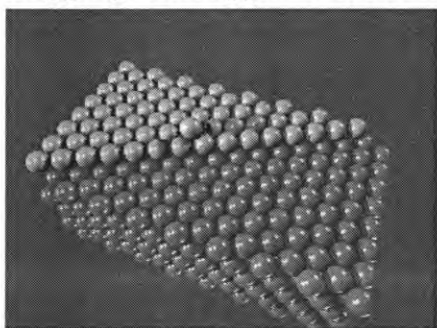
Barrier = **0.407 eV**

Hopping over Kink site onto lower terrace - Step A



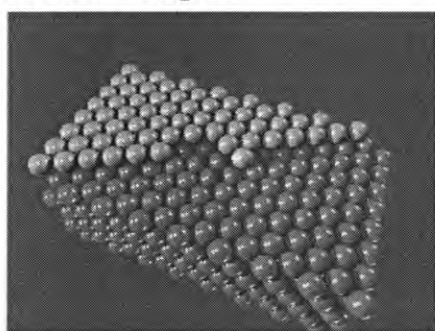
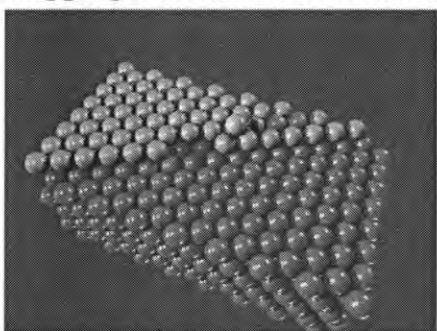
Barrier = **0.395 eV**

Hopping from upper to lower terrace – Step B



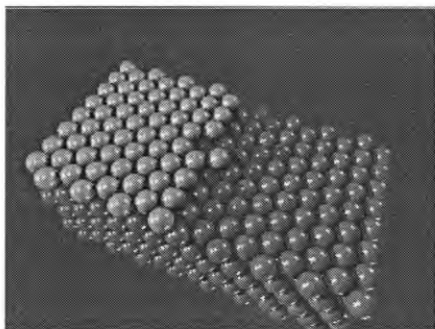
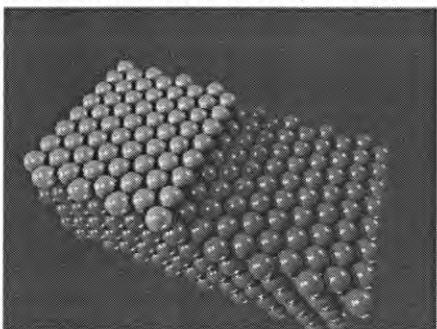
Barrier = **0.663 eV**

Hopping over Kink site onto lower terrace – Step B



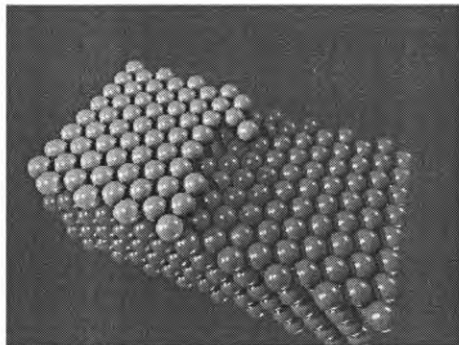
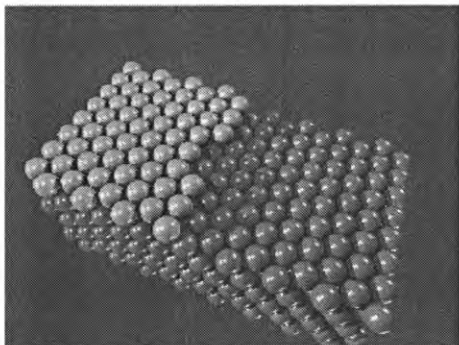
Barrier = **0.330 eV**

Detachment from Step – Step A



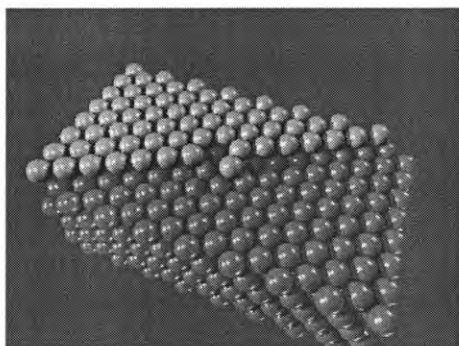
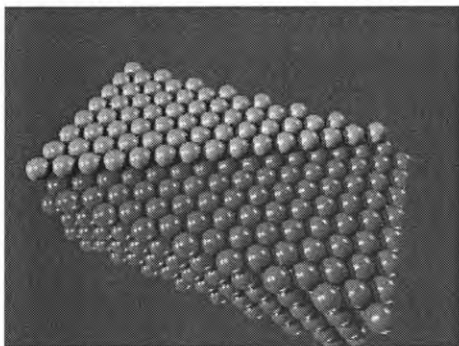
Barrier = **0.758 eV**

Detachment from Kink – Step A



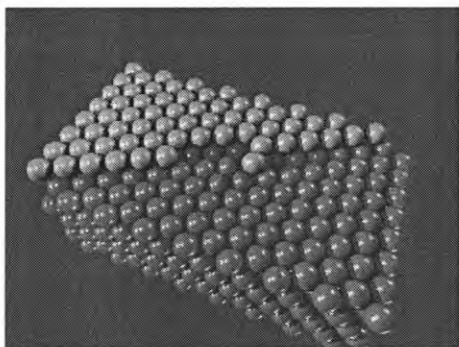
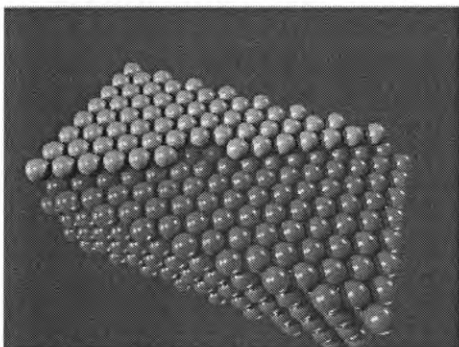
Barrier = **0.571 eV**

Detachment from Step – Step B



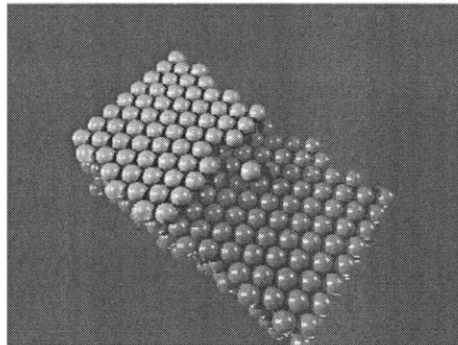
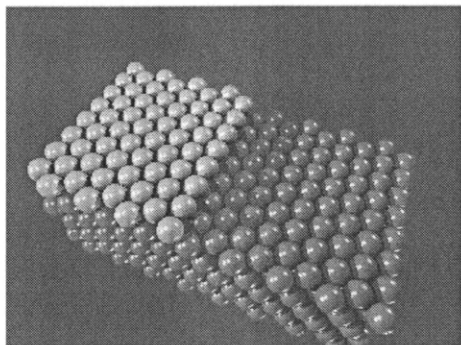
Barrier = **0.691 eV**

Detachment from Kink – Step B



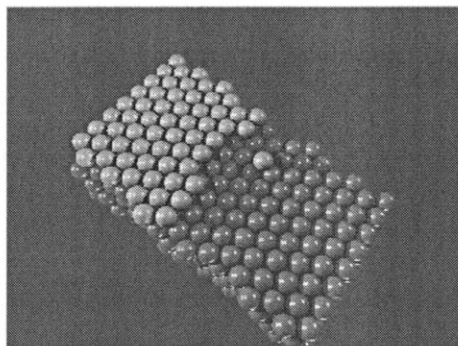
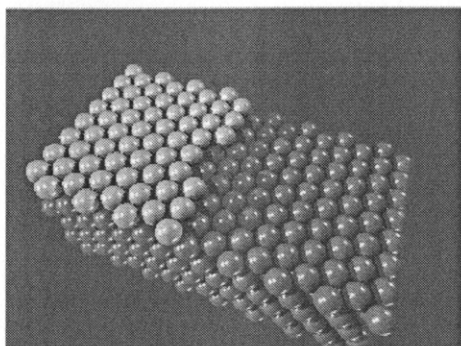
Barrier = **0.527 eV**

Detachment from Step onto terrace – Step A



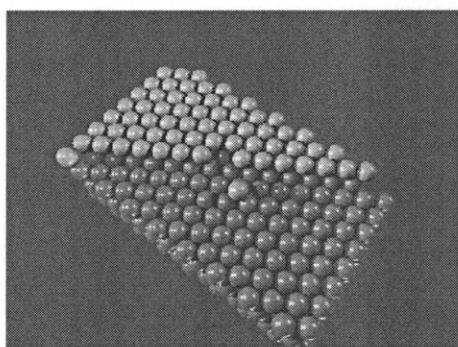
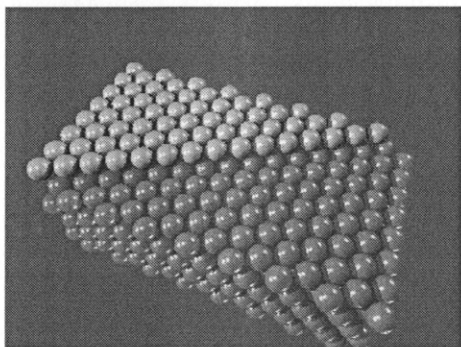
Barrier = **1.135 eV**

Detachment from Kink onto terrace – Step A



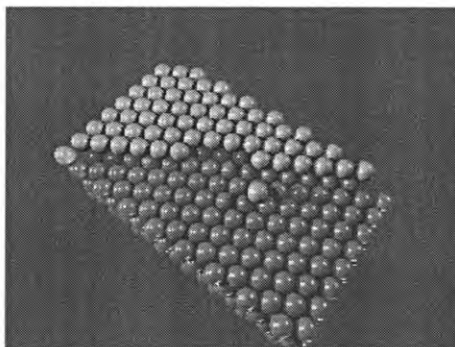
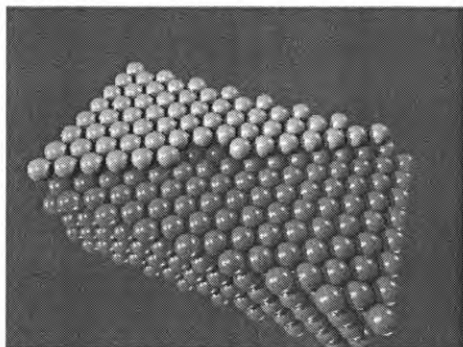
Barrier = **0.759 eV**

Detachment from Step onto terrace – Step B



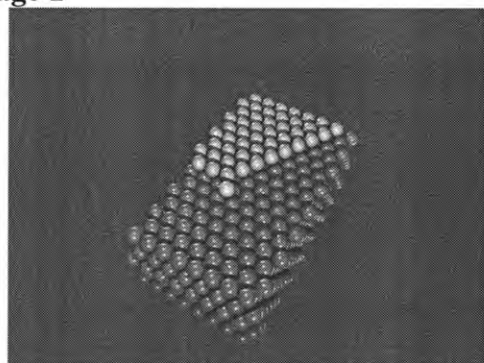
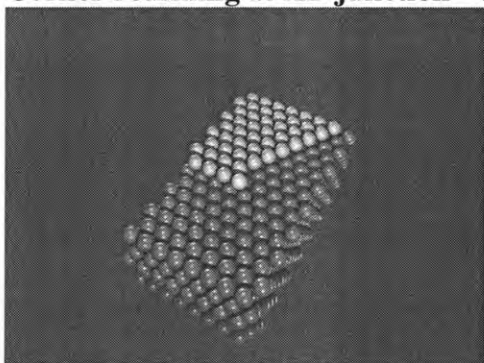
Barrier = **0.963 eV**

Detachment from Kink onto terrace – Step B



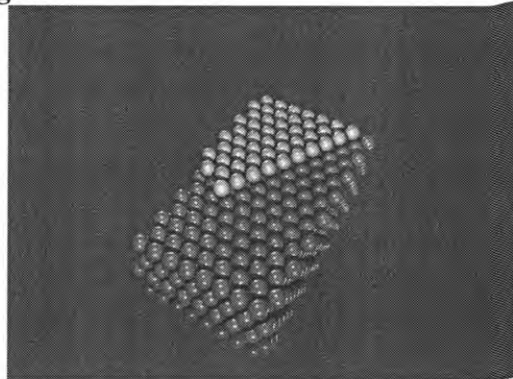
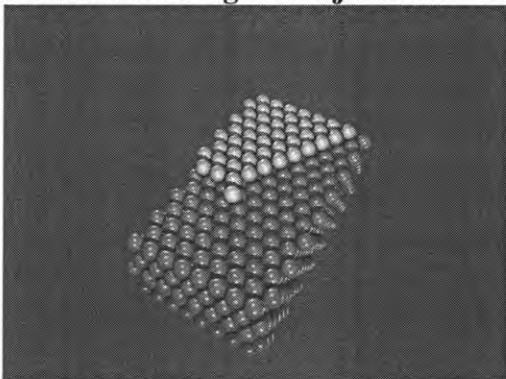
Barrier = **0.766 eV**

Corner rounding at AB junction – stage 1



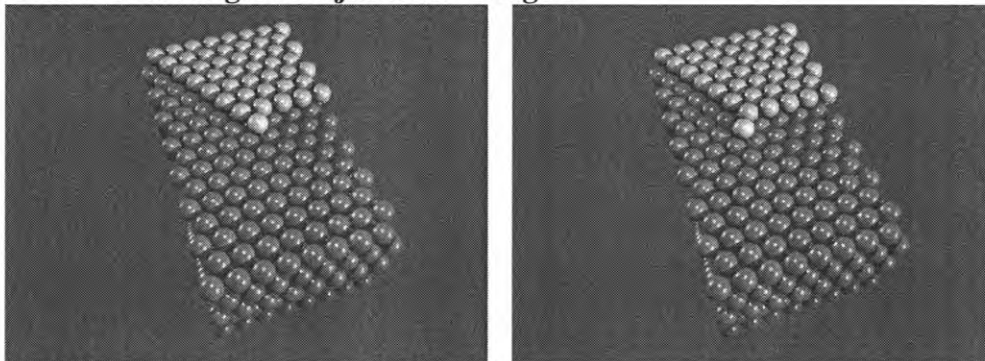
Barrier = **0.310 eV**

Corner rounding at AB junction – stage 2



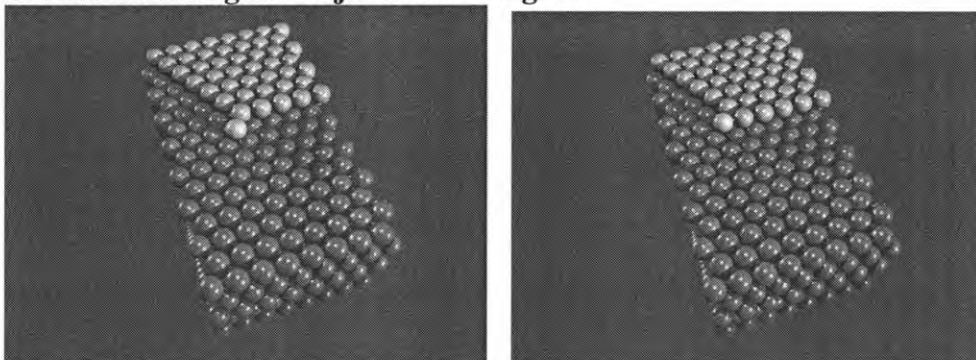
Barrier = **0.148 eV**

Corner rounding at BA junction – stage 1



Barrier = 0.387 eV

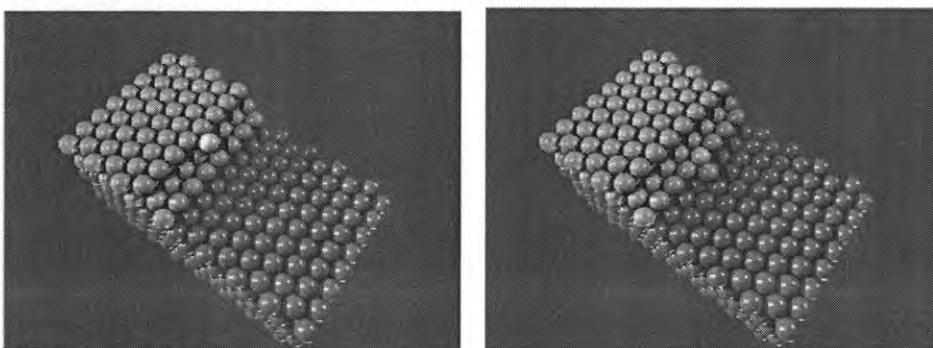
Corner rounding at BA junction – stage 2



Barrier = 0.077 eV

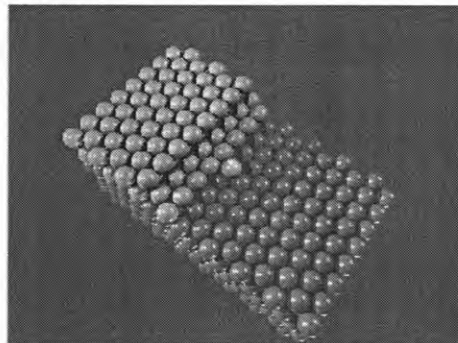
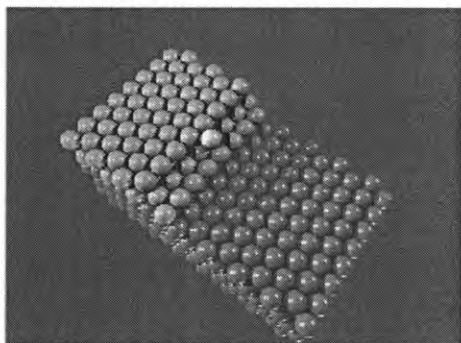
Multilayer processes

Exchange from upper step with lower step – Step A



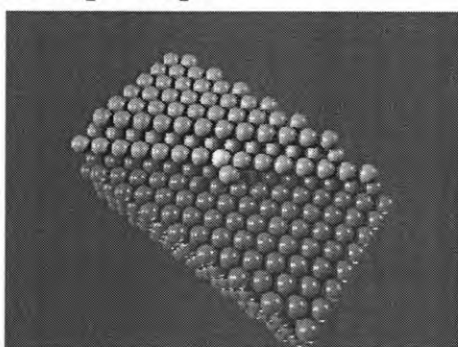
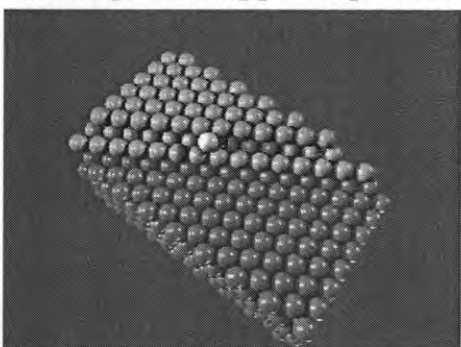
Barrier = 0.859 eV

Hop from upper step onto terrace – Step A



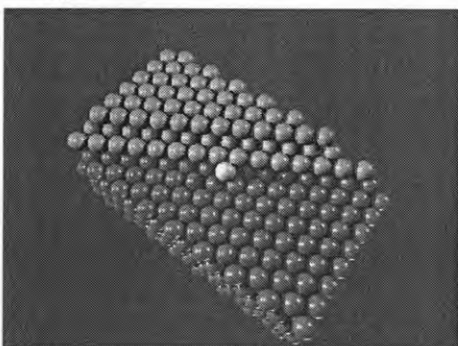
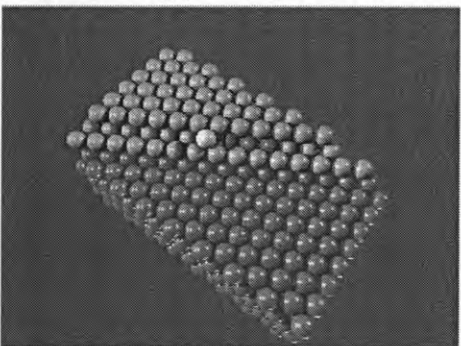
Barrier = **0.832 eV**

Exchange from upper step with lower step – Step B



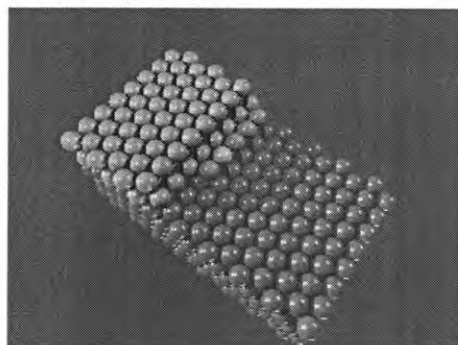
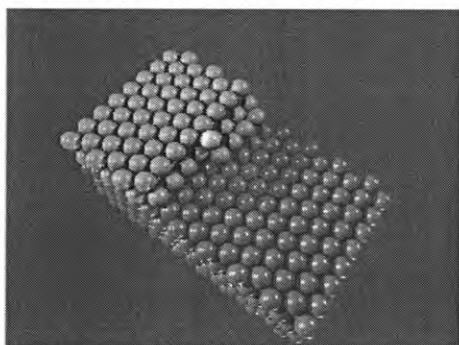
Barrier = **0.535 eV**

Hop from upper step onto terrace – Step B



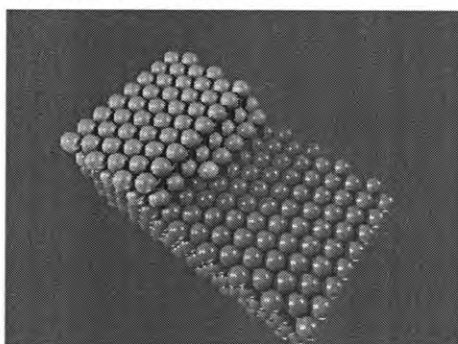
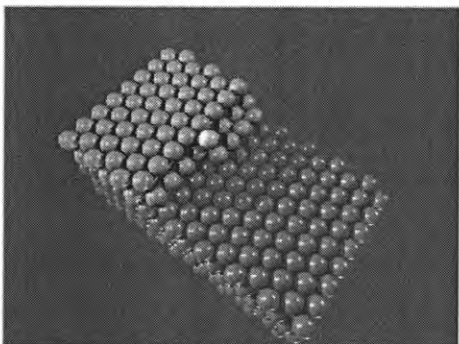
Barrier = **1.219 eV**

Exchange from upper Step with lower Kink – Step A



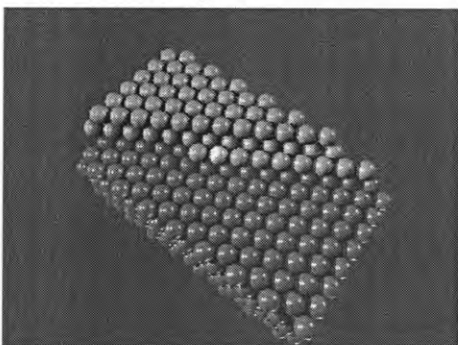
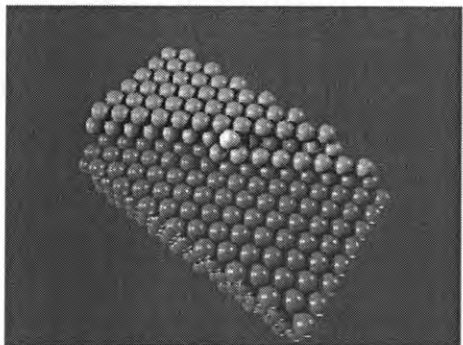
Barrier = **0.650 eV**

Hop from upper step over kink onto terrace – Step A



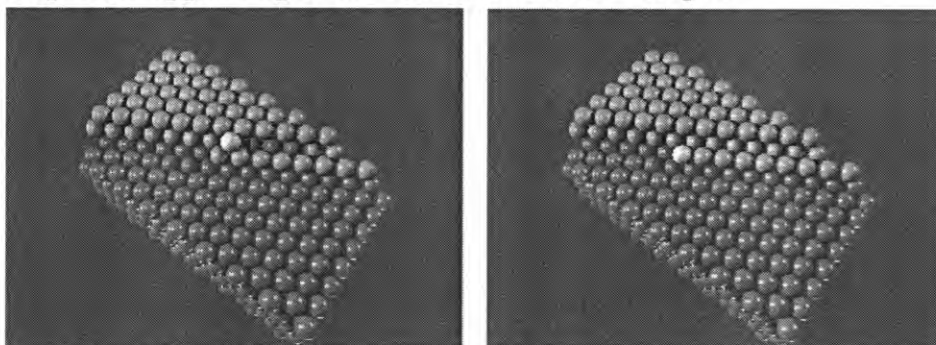
Barrier = **0.519 eV**

Exchange from upper Step with lower Kink – Step B



Barrier = **0.601 eV**

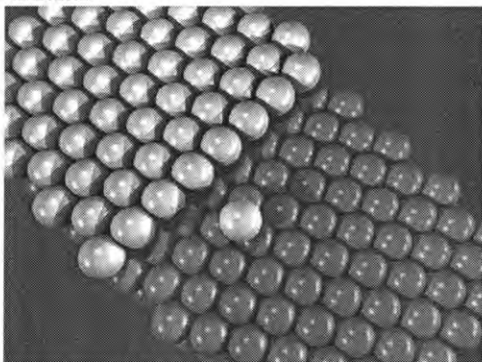
Hop from upper step over kink onto terrace – Step B



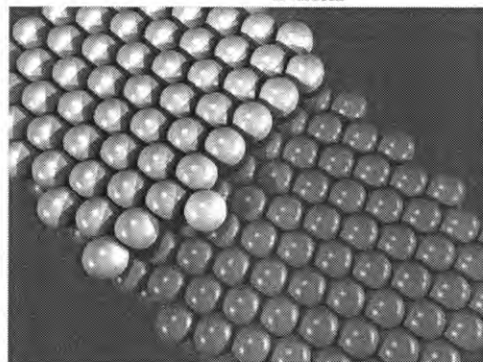
Barrier = **0.374 eV**

Terrace adatom close to Step edge A, attaching to the step edge

Initial



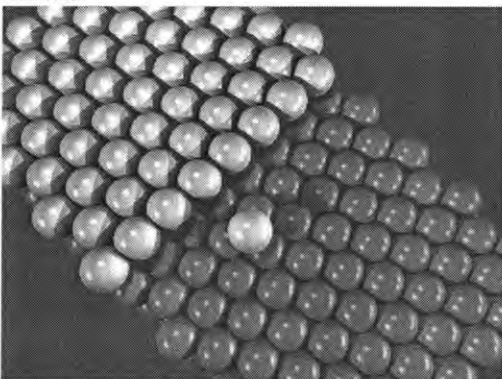
Final



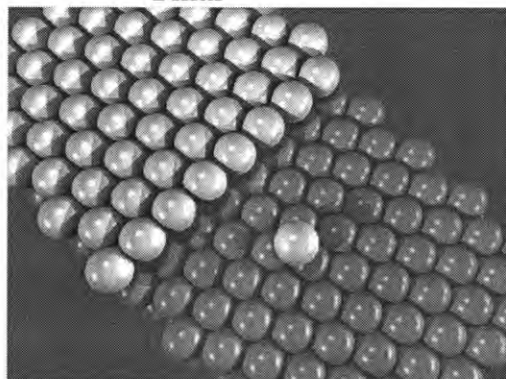
Barrier = **0.043 eV**

Terrace adatom close to Step edge A, hopping to adjacent fcc site, away from the step edge

Initial



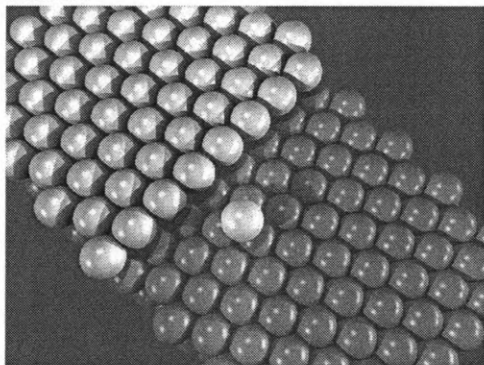
Final



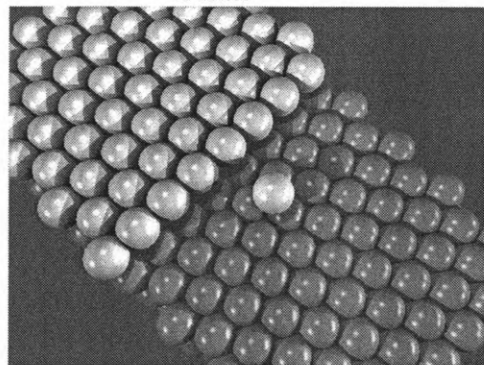
Barrier = **0.56 eV**

Terrace adatom close to Step edge A, hopping to adjacent fcc site, parallel to the step edge

Initial



Final



Barrier = **0.58 eV**

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