Preface

This thesis is submitted to the Faculty of Science, University of Aarhus, Denmark, in order to fulfil the requirements for obtaining the PhD degree in physics. The work that is presented has been carried out in the Scanning Tunneling Microscopy group at the Institute of Physics and Astronomy during the time-period from summer 1993 to summer 1997.

Throughout this period, it has been a pleasure and a privilege to be part of the STM group. This group thrives tremendously from a synergy between high scientific goals and a very pleasant atmosphere at the personal level. For these reasons, it is a pleasure to thank the three senior members and founding fathers of the group: Flemming Besenbacher, Ivan Stensgaard and Erik Lægsgaard for providing this possibility. Especially, I should like to thank Flemming for his never-ending encouragement and support in his role as my supervisor, and to express my admiration for his ceaseless optimism, enthusiasm and energy. Also, Erik’s ingenious technical solutions, not least the numerous software developments facilitating the data-analysis tremendously, have been a key-factor in obtaining the results presented in this thesis and are greatly appreciated.

The work concerning the Pt/Pt(100) system, presented in chapter 4 of this thesis, is the result of a fruitful collaboration between experiment and theory. Consequently, it is a pleasure to acknowledge Jens Jørgen Mortensen and Karsten W. Jacobsen at the Technical University of Denmark who approached the problem from the theory side.

During the work on the Pt/Pt(110) system presented in chapters 5–7, it has been a pleasure to collaborate with Sebastian Horch on experiments and data-analysis. Also the contribution by Lars Petersen in the form of computer simulations as presented in chapter 7 is very much appreciated.

The number of people that have passed through the STM group in the time-period during which I have been part of it is too numerous that everybody can be mentioned. You all know yourself who you are, however,
and in one way or another it has been rewarding and a pleasure to interact with each and every one of you.

With a number of people the overlap has been more extensive, and I should like to mention Lars Pleth Nielsen, Lars Olesen, Phil Sprunger, Morten Østergaard Pedersen, Kim Hansen and Paul Murray from all of whom I have received advice, encouragement and countless humorous remarks.

Finally, it is a great pleasure to acknowledge Lone Niedziella for reading large parts of this manuscript and providing much linguistic assistance.

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Chapter 1

Introduction

The present chapter provides an introduction to the work presented in this thesis. First, a general motivation is provided, aiming at placing the work in a larger perspective. Then, the investigations carried out are outlined in general terms. This is done partly for the benefit of the interested non-expert reader who does not wish to read the whole thesis, but not least to provide a concrete overview from the outset for those who wish to endure. Finally, the structure of the thesis is described.
1.1 General motivation

One of the most important long-term goals of surface science is to be able to synthesize “advanced materials” with a desired functionality at the microscopic scale, such as specific electronic, magnetic, optical or chemical properties. During the last 10 years or so, the Scanning Tunneling Microscope (STM) has provided scientists with a remarkable real space view of surfaces at length-scales ranging from, in principle, the atomic level and up to micro-meters. This possibility has spurred a tremendous activity within the field of crystal and thin film growth.

Although it has remarkably been demonstrated that the STM is also capable of manipulating matter at the atomic level in a controlled way, the serial nature of such a process and the enormous number of atoms within even the smallest macroscopic sample, make the ultimate perspective within materials synthesis of atom-by-atom construction still very remote.

A more likely avenue to success within this field of nano-structuring is that materials can be tempted to self-organize into desired structures at the nano-scale. This perspective derives from the fact that the growth of crystals and thin films is typically controlled not by the thermodynamic equilibrium configuration of the system but by the kinetic pathway taken by the adatoms arriving from the gas-phase as they meander about on the surface and eventually incorporate into the solid phase. It is by now well established that small changes to the possible microscopic processes can produce radical differences in the resulting growth morphology at the mesoscopic scale.

Intelligent manipulation of the microscopic atomic-scale processes underlying crystal growth by suitable control of deposition parameters requires that the processes are known and quantified and that the consequences of their existence for the resulting growth morphology are understood. Fundamental questions include: How and how fast do adatoms move around on the surface (diffusion), how well do adatoms stick together when they meet (nucleation), what structures result from these processes (growth), and are these structures stable at all?

The work presented in the present thesis aims at answering some such fundamental questions utilizing the STM to monitor growth morphologies and dynamic processes at the atomic level occurring when Platinum (Pt) adatoms are deposited onto two different surfaces of Pt single crystals under Ultra High Vacuum (UHV) conditions. Such idealized cases can be considered as model systems for the way growth occurs in more “real”
1.2. OVERVIEW

situations. Although the work is basic science in nature and as such has no direct impact whatsoever on deriving technologically "better" films it can, in a larger perspective, definitely be seen as part of a unified effort aiming at the goals outlined above.

1.2 Overview

The work to be presented in greater detail in the subsequent chapters of this thesis concerns homo-epitaxy and self-diffusion on two reconstructed surfaces, Pt(100)-hex and Pt(110)-(1×2).

The work carried out in the former case of Pt/Pt(100)-hex belongs to the conventional "evaporate-quench-look" category, where STM is used to taking "snapshots" of the growth islands resulting from Pt deposition in the sub-monolayer coverage regime with systematically varied deposition parameters. For the latter case of Pt/Pt(110)-(1×2), on the contrary, we have been able to zoom in on the microscopic processes and by acquiring "STM movies"¹, follow the dynamics of adatom diffusion, nucleation and growth directly at the atomic level as it occurs.

Aside from the fact that both surfaces are Pt, there are two important common themes among the work carried out in these two cases. The first is that both surfaces are reconstructed in a way that makes them highly anisotropic. While epitaxial growth on simple isotropic surfaces has been extensively studied in the past, much less is known about the anisotropic case. One of the principal interests of surface physics is the reduced dimensionality compared to bulk 3-D - the study of anisotropic surfaces can be seen as taking this one step further. The second common theme is that in both studies quantitative information is extracted from thorough statistical analysis of large quantities of STM images, thereby avoiding the potential pitfall of a local probe technique as STM (sometimes termed tunnel-vision), namely that of focusing on singular interesting observations. In this respect, the work illustrates a general current development within STM studies of progression from analysis of individual images towards detailed quantitative investigations.

¹The terms "snapshot" and "movie" are not only meant literally, they also provide very well the right intuition as to what the differences are between these two ways of using STM. If you have a snapshot of a car and there is someone behind the steering wheel, then the car is probably moving; if you have a movie, however, you immediately know a lot more, such as whether it is going forward or backwards and at what speed.
Figure 1.1: Atomically resolved STM image of the reconstructed Pt(100)-hex surface. The reconstruction consists of a quasihexagonal topmost layer resting on top of the quadratic bulk-truncation, resulting in a characteristic anisotropic height-modulation in the hexagonal layer. The "reconstruction channels" mentioned in the text run approximately diagonally in the image from lower left to upper right corner. In the inset, a submonolayer amount of Pt has been deposited, resulting in mono-atomically high, rectangular islands oriented along the reconstruction channels. Note that the images are of very different sizes (180 × 190 Å² and 1310 × 1350 Å² for the large image and the inset, respectively).
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reference to these two images we provide in the following an overview of the investigations carried out in these two cases. The aim is to outline the methods of investigation, also for the benefit of the non-expert reader, rather than to emphasize the results.

1.2.1. Pt/Pt(100)-hex

As mentioned, the work carried out in the Pt/Pt(100)-hex system belongs to the "quench-and-look" category. Pt was thus deposited at submonolayer coverage with different deposition rates and at substrate temperatures in the range from 45 to 220 °C. The resulting growth islands, as shown in the inset in fig. 1.1, were subsequently imaged with the STM after the surface was cooled down to room temperature.

The fundamental principle in this type of investigation is that information may be inferred from an analysis of the resulting growth morphology about the microscopic processes involved as the deposited adatoms migrate over the surface, nucleate and grow into the observed islands. The clean Pt(100) surface exhibits a "hex" reconstruction resulting in a characteristic anisotropic height-modulation in the topmost layer with 6-atom wide "reconstruction channels" (see fig. 1.1). The main question in the described investigation was — how does the reconstruction affect the diffusion, nucleation and growth and, especially, are there anisotropic effects?

From quantitative analysis of large numbers of STM images, the positions, areas and number densities (islands/unit surface area) of the resulting rectangular growth islands have been extracted. These data have subsequently been analysed within the framework of nucleation and growth theory.

For instance, within this theory a scaling law exist for the variation of island density with deposition rate and temperature. By comparison of the attained data to this relation, information has been inferred on the activation barrier for surface diffusion. Furthermore it has been determined that two adatoms are required to form a stable growth nucleus on the surface. Information can also be derived from the size-distribution of the islands. From such analysis it is for instance found that the two-adatom large growth nuclei (dimers) do not diffuse on the surface.

A specialty in the described study is an autocorrelation analysis of the island positions, revealing that the islands are distributed with long/short correlation lengths along/perpendicular to the reconstruction channels. The way in which the growth islands are distributed on the surface bears information on the migration speed of the adatoms. The autocorrelation
analysis therefore reveals that the adatom diffusivity is strongly influenced by the anisotropic surface reconstruction and allows us to quantify the degree of anisotropy in adatom diffusion.

In general, the investigation has benefited greatly from the interplay between experiment and theory, the latter in particular providing Kinetic Monte Carlo simulations aimed at elucidating the effects of anisotropic surface diffusion in combination with finite island sizes.

The described investigation of the Pt/Pt(100)-hex system demonstrates the amount of information that can be inferred from various statistical methods of analysis of the resulting growth morphology in the submonolayer coverage regime, the main novelty being the autocorrelation analysis of the island positions.

1.2.2 Pt/Pt(110)-(1×2)

While the Pt adatom diffusivity on the Pt(100)-hex surface is fast at temperatures above room temperature, allowing for the creation of large growth islands, the situation is very different in the Pt/Pt(110)-(1×2) system. Here, adatoms are completely immobile (on a time-scale of hours) at temperatures slightly below room temperature. Diffusion sets in just as the temperature is increased above room temperature. For this reason the Pt/Pt(110)-(1×2) system is very well suited for a direct investigation of adatom dynamics since problems related to the requirement of low temperatures can be avoided.

The difference to the Pt(100)-hex case is illustrated by the STM image shown in fig. 1.2, depicting the Pt(110)-(1×2) surface after a submonolayer amount of Pt has been deposited. The Pt(110) surface forms a (1×2) missing-row reconstruction where every second close-packed row is removed. In the image, the resulting monatomically deep troughs are shown in black, separated by close-packed Pt rows which are imaged with atomic resolution. The deposited Pt adatoms are found in the one-dimensional (1-D) troughs, both as single adatoms and in the form of dimers, trimers and longer chains of agglomerated adatoms. The image is acquired after the sample has been held at the deposition temperature of 40 °C for more than four hours.

From such a single image alone, a considerable amount of information may be inferred concerning the Pt adatom dynamics at temperatures slightly above room temperature. There are too many adatom islands that they can be caused by the random impingement of deposited adatoms on neighbouring sites. This means that there must be some thermal adatom
Figure 1.2: Atomically resolved STM image of the Pt(110)-(1×2) surface obtained after deposition of a sub-monolayer amount of Pt. This surface exhibits a missing-row reconstruction where every second close-packed row is removed, resulting in a channelled surface with monoatomically deep troughs separated by close-packed rows. The deposited Pt atoms can be seen in the troughs as individual adatoms, dimers and larger one-dimensional islands (230×244 Å²).
mobility allowing for the adatoms to meet, nucleate and grow into the 1-D islands. On the other hand, the fact that single adatoms are still left on the surface, indicates that the mobility is sufficiently low for the nucleation and growth process not to have ceased even after several hours.

Many questions are not readily answered from such an isolated image, however. Exactly how fast is the adatom migration and is it entirely 1-D or do the adatoms traverse between adjacent troughs? Are dimers stable towards dissociation and/or are they mobile - and what about the larger islands? Some progress along these lines could be made through statistical analysis of individual images, somewhat similar to the Pt/Pt(100)-hex case. A much more direct way to investigate the dynamic processes occurring on the surface, however, is to monitor the surface with the STM by acquiring large amounts of consecutive images (typically several hundreds over a time-scale of an hour). When such STM movies are played back they directly reveal the changes occurring on the surface.

From the acquired STM movies we are able to follow directly at the atomic level how the individual adatoms migrate and interact. This has been done at temperatures in the interval from room temperature and up to \( \sim 110 \, ^\circ\text{C} \). The adatoms are found to be confined to the missing-row troughs at the investigated temperatures and migrate in a fully 1-D fashion along these channels. Adatoms that meet in the troughs form dimers for a short while, but then break apart again. Longer adatom chains situated in the troughs, trimers and above, are much more stable towards dissociation. Interestingly, these 1-D adatom islands are found to be mobile, however, and are occasionally observed to shift position in the troughs by a single lattice spacing.

The information on adatom diffusion contained in the STM movies is quantified by determining the displacement (in lattice spacings) of the individual adatoms between consecutive images. The resulting displacement distributions are compared to the predictions of a simple 1-D random walk model. The large amount of statistical material obtained from the movies allows for a very detailed analysis of the adatom diffusion. The key result from this investigation is that the adatom migration is comprised of not only "single jumps" between adjacent sites but also incorporates significant amounts of long jumps or "double jumps" where the adatom makes a direct transition covering two lattice spacings. By determining the rates for these double jump transitions over a range of temperatures it is shown, for the first time, that the rate for such double jumps has an Arrhenius dependence on temperature. The activation barrier determined for these double jump transitions is slightly larger than that for the single jumps.
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Not only adatom diffusion but also aspects of nucleation and growth are directly revealed from the movies. Thus, from an analysis of the observed kinetics for dimer dissociation and formation, we derive a value for the binding energy of a Pt-dimer situated in the missing-row trough.

The described work based on STM movies shows how variable-temperature STM can be used to directly investigate dynamic processes at the atomic level in a detailed and quantitative way.

The final work carried out in the Pt/Pt(110)-(1×2) system is aimed at investigating coarsening or, in other words, how a non-equilibrium growth morphology relaxes towards thermodynamic equilibrium. Here, we revert to some degree to the "quench-and-look" approach. In the experiments, a submonolayer amount of Pt was deposited, creating a distribution of islands, i.e., one-dimensional chains of adatoms situated in the missing-row troughs. Such configurations were subsequently annealed to temperatures in the range from 96 to 122 °C, followed by cooling and STM imaging at lower temperatures where all mobility is frozen out.

From these annealing experiments, we observe two phenomena (i) the islands become larger (coarsening) and (ii) the islands restructure and become covered in the second layer\(^2\), signifying an ascending motion of adatoms from their position in the troughs and up on top of the islands.

The detailed analysis of these latter experiments is still in progress, and the understanding is consequently less developed than for the other investigations described. In short, the attraction is to combine the information from the annealing experiments with that obtained from the STM movies revealing how dynamic processes occur. The overall aim is to be able to account for the observed coarsening phenomena in terms of known rates for the involved microscopic processes: adatom diffusion, dimer dissociation, adatom detachment from islands, etc. derived from direct observations. Especially interesting in this respect is the observation that the 1-D adatom islands are mobile. While the original motivation for this work was to investigate ripening in a 1-D system, the current understanding is that certain quite subtle mechanisms cause the Pt/Pt(110)-(1×2) system not to be completely 1-D at the higher coverages used in the annealing experiments.

\(^2\)Meaning that in eg an x atom long island situated in the trough, \(\sim x/2\) atoms shift from their position in the trough and move up to the adsorption sites formed by the remainder of the original island and one of the adjacent close-packed rows.
1.3 How this thesis is structured

The thesis is structured in the following way.

The work carried out and the conclusions it gives rise to are presented in detail in chapters 4 to 7. These four chapters, which constitute the most important part of the thesis, are written largely in the format of articles. In this way, it is the intention that these four chapters can be read independently.

The work with respect to the Pt/Pt(100) system is treated in chapter 4, which is practically identical to paper (II). The investigations in the Pt/Pt(110) system are treated in chapters 5–7. Chapter 5 is devoted to the analysis of adatom diffusion leading to the identification of Arrhenius behaviour of the rate for long jumps. This chapter is based on paper (III), but has extended this paper to a significant degree. The dissociation kinetics of adatom dimers in the missing-row troughs is treated in chapter 6. This chapter will eventually turn into paper (V). Finally, the work on island mobility and coarsening is treated in chapter 7. As mentioned, this work is still at a premature state, but will form the basis of paper (VI).

Before these four chapters, two chapters containing background information are provided. In chapter 2, the STM technique is treated. First, elementary theory of STM imaging and the design of the Aarhus STM are briefly outlined. The remainder of the chapter is devoted to a discussion of the use of STM within the field of diffusion, nucleation and growth. In this discussion, STM is compared to other selected techniques, and it is especially emphasized how the work presented in this thesis has utilized the qualities of STM and to a certain degree has acted to extend the scope of STM studies.

The subsequent chapter 3 serves two purposes: First, to provide background information that may place the work presented in the latter four chapters in perspective and, secondly, to mention and discuss some relations between the work carried out in the two separate systems, Pt/Pt(100) and Pt/Pt(110). To meet these needs, chapter 3 is structured as follows. The first section contains a very broad introduction to diffusion, nucleation and growth with little specific reference to the work in the subsequent chapters. This section is especially intended for the benefit of the non-expert reader. After this, three sections follow, each aimed at one of the chapters 4 to 6 (chapter 7, which describes work in progress, has no such section). Since these later chapters are written in the form of articles, they only contain a brief introduction. The main purpose of the three sections in chapter 3 is to provide a more elaborate introduction to previous related
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studies or relevant theory. At the end of each of these three sections, the work described in the related chapter is briefly outlined. Finally, towards the end of chapter 3, certain relations between the work carried out in the Pt/Pt(100) and Pt/Pt(110) systems are discussed.

The thesis is concluded by a summary in chapter 8, where the most important results that have been reached are emphasized and a brief outlook is provided.

A comment regarding the structure of the thesis is warranted. The advantage of constructing the thesis in the described fashion is that the most important chapters 4–7 can be read independently with only a short introduction to other relevant work. The disadvantage is that some redundancy between the introductory chapter 3 and the following chapters necessarily results. It should be remarked that the thesis is not necessarily read best from cover to cover, one may also choose to read each of the chapters 4–6 following the relevant section in chapter 3.
Chapter 2

Scanning Tunneling Microscopy

The present chapter describes the experimental technique that has been utilized in obtaining the data discussed in this thesis. First, the principle of STM operation is briefly outlined. This is followed by a short introduction to the theory of STM imaging. After this, the most important design features of the Aarhus STM are described. In the final part of the chapter, the use of STM in investigations of nucleation and growth is discussed, and a comparison to other selected techniques is provided.
2.1 Principle of STM

Scanning Tunneling Microscopy (STM) is a local probe technique that, on conducting surfaces, allows for the imaging in direct space of features extending in size from the micrometer range to atomic dimensions [1–3].

Conceptually, the principle behind STM is strikingly simple. A sharp conducting tip is brought into such close proximity (\(\sim 5 \text{ Å}\)) of the surface under scrutiny that an overlap occurs between the parts of the wave functions for tip and sample that are exponentially decaying into the vacuum gap separating the two. For electrons at the Fermi level, the vacuum gap constitutes an energy barrier of roughly the same height as the average work function of tip and sample and with a width corresponding to the tip-sample separation. By applying a small bias voltage (mV) between tip and sample, their Fermi levels are shifted relative to each other by the corresponding amount of energy, allowing for the elastic tunneling of electrons from filled tip states to empty sample states or vice versa depending on the sign of the bias. The magnitude of the resulting quantum-mechanical tunneling current depends strongly (exponentially) on the tip-sample separation. A rule-of-thumb states that a variation of the tip-sample distance of 1 Å will result in an order of magnitude variation in tunnel current. Thus, a tip-atom extending, by chance, half a bondlength further towards the surface than any other tip-atom should carry virtually all the current running between tip and sample, making the capability of STM to achieve atomic resolution intuitively plausible.

Usually, STM imaging is executed in the so-called constant current mode, where the tip is raster-scanned over the surface at a fixed bias voltage while a feedback circuit regulates the vertical position of the tip in correspondence to features in the surface in such a way that the tunnel current is kept constant at some fixed (nA) value. During this procedure, the vertical position of the tip (or, in reality, the feedback signal) is stored as a function of the lateral coordinates of the tip, yielding a topographic STM image.

2.2 STM theory

While the principle underlying STM is simple, a full theoretical appreciation of the imaging process is extremely complicated since STM images represent a complicated convolution of the electronic states for tip and sample. In principle, a characterization of the electronic states of tip and sample as well as a description of the decaying wave functions for tip and
sample and the electron-potential in the tunnel-gap region are required. This is a formidable task, not least because the tip is poorly characterized, and tip-sample interactions may be so pronounced that the full quantum-mechanical problem of finding solutions to the Schrödinger equation for the combined system of tip, tunnel-junction and sample has to be addressed.

A simplified treatment of the STM problem has been provided by Tersoff and Hamann [4] relying on the “perturbative-transfer Hamiltonian” formalism introduced by Bardeen [5].

The formalism of Bardeen applies to the case where tip-sample interactions are sufficiently weak to be neglected and calculates the tunnel current $I_t$ from the overlap in the tunnel gap region of the wavefunctions $\Psi_\mu$ and $\Psi_\nu$, with eigenenergies $E_\mu$ and $E_\nu$, evaluated for the separate tip and sample systems, respectively. The tunneling current is obtained as a sum over states of tip and sample,

$$I_t = \frac{2\pi e}{\hbar} \int_{\nu,\mu} f(E_\mu)[1 - f(E_\nu + eV_t)]|M_{\mu\nu}|^2 \delta(E_\mu - E_\nu), \quad (2.1)$$

where the delta-function ensures that the electron tunnels between states of the same energy (elastic tunneling) and the two Fermi-Dirac functions ($f(E)$) take into account that tunneling occurs, for instance, from a filled tip state into an empty sample state. The energy shift $eV_t$ results from the bias voltage $V_t$ between tip and sample. The tunneling matrix element $M_{\mu\nu}$ is evaluated from an integral over a surface $S_0$ lying entirely within the barrier region:

$$|M_{\mu\nu}| = \frac{\hbar^2}{2m} \int_{S_0} dS \cdot (\nabla \Psi_\mu^* \nabla \Psi_\nu - \Psi_\mu^* \nabla \Psi_\nu^*). \quad (2.2)$$

To evaluate the tunneling matrix element, Tersoff and Hamann in their treatment [4] modelled the tip as a spherical potential well centred at a point $r_t$, in which case the tip can be described simply by spherically symmetric s-wave functions. Within this simplifying assumption and in the limit of small $V_t$, the Tersoff-Hamann formalism yields the following expression for the tunnel current (a number of constants have been left out for brevity)

$$I_t \propto V_t \sum_\nu |\Psi_\nu(r_t)|^2 \delta(E_\nu - E_F), \quad (2.3)$$

where the sum extends over states of the sample, and the delta-function ensures that only states at the Fermi energy, $E_F$, contribute.
From the decay of the sample wave functions into the tunneling gap, an approximate estimate for the tunneling conductance, $G_t$, can furthermore be obtained as

$$G_t = \frac{I_t}{V_t} \propto \exp[-\frac{(8m\phi)^{1/2}}{\hbar}d],$$

(2.4)

where $m$ is the electron mass, $\phi$ is the tunneling barrier height and $d$ is the tip-sample distance. The tunneling current thus decreases exponentially with increasing tip-sample distance. For typical values of $\phi$ (4 eV), the rule-of-thumb previously mentioned of an order of magnitude reduction in the current upon increasing the tip-sample distance by 1 Å follows.

Returning to the important expression (2.3) for the tunneling current, it shows that $I_t$ is proportional to the local density of states at the centre, $n_z$, of the tip resulting from sample-states at the Fermi level. Thus, within the simplifying assumptions of the Tersoff-Hamann formalism, the tip follows contours of constant local density of states on the surface during constant-current STM imaging, and the resulting STM topographs reflect the properties of the sample rather than the combined tip-sample system.

On metals, in contrast to semiconductors where localized states and dangling bonds are important, it is usually possible to interpret atomic-scale corrugations in the STM topographs directly as surface atoms.

The fact that STM images in general depict electronic rather than geometric effects is underscored in calculations by Lang addressing how the local density of states is affected by the adsorption of foreign atoms on the surface [6–8]. If the local density of states is depleted (enhanced) at the position of the adatom, the tip will have to move towards (away from) the surface as it passes the adatom in order to keep the current at a constant level, and the adatom is imaged as a depression (protrusion).

### 2.3 The Aarhus STM

The main obstacle faced when constructing an STM is the need to position and stabilize the tip with sub-Ångström precision at a distance of only a few Å away from the sample surface using construction elements in the centimetre range, i.e., a size-mismatch over approximately 9 orders of magnitude with associated problems concerning vibrations and thermal drift.
2.3. THE AARHUS STM

Figure 2.1: Cross-sectional sketch of the Aarhus STM. The meaning of the symbols is explained in the text. The described heating/cooling stage is not shown on the figure, but is connected to the isolated top-plate (C) via two Cu-braids. Figure courtesy of L. Olesen.

A cross-sectional sketch of the Aarhus STM [3] used in the present study is shown in fig. 2.1. The key features of this instrument are a compact, high resonance-frequency design and the use of two piezo-electric ceramic tubes, one for positioning the tip during scanning and one for coarse approach of the tip towards the surface.

The sample-holder (A) with the sample (B) is inserted into the instrument in-situ and is held rigidly against the top-plate (C) of the STM by two springs (D). The top-plate of the STM is insulated (electrically and thermally) from the remainder of the instrument by 3 quartz balls (E). The tip (F) is made from single-crystalline W wire, etched to form a sharp apex, and is mounted on the scanner-tube (G), which again is glued to a ceramic rod (H) that runs through the second piezo-electric tube (I), which, together with the rod, constitutes a linear motor for coarse approach of the tip and scanner tube assembly towards the sample. The linear motor is mounted on the STM housing via the disc (J).

The whole STM is mounted on a cradle that, during scanning, is sus-
pended by soft springs from support rods mounted directly onto a flange of the UHV chamber. The compact high-resonance frequency design of the STM in combination with the suspension from soft springs is the only vibration damping employed.

**Scanning and coarse approach**

The piezo-electric tubes used for scanning and coarse approach are covered on the inside and outside by conducting material (silver). For the scanner tube, the inside constitutes one electrode whereas the outside is segmented into four equally sized electrodes by cutting parallel to the tube axis. By biasing two oppositely placed outer electrodes antisymmetrically with respect to the inner electrode, one side is made to expand while the other contracts, resulting in an overall bending of the tube towards the shortened side. Similarly, by biasing the inner electrode with respect to the four outer ones, a contraction/expansion of the tube along the tube axis is obtained. In this way three spatial degrees of freedom are achieved, allowing the tip to be raster-scanned while following the contours of the surface.

For the piezo-tube used in the linear motor for coarse approach, the outer electrode is segmented into three axial sections, and on the inside of the tube the two end-sections are equipped with bearings that give a near-perfect fit to the ceramic rod running through the tube. By appropriate biasing with respect to the central electrode, the two end-sections of the tube can be made to clamp/unclamp around the central rod, and the centre-section can be made to expand or contract along the tube axis. The motor brings the tip/scanner-tube assembly towards the surface in the following “inchwormish” way. Imagine to start out with the bottom end (farthest away from the scanner tube) clamped and the mid-section expanded. Now, contract the mid-section (thereby bringing the tip towards the surface), clamp the upper end, unclamp the lower end, expand the midsection again, clamp the bottom end, unclamp the upper end, and repeat. The process is terminated as soon as a tunneling current is detected, thereby allowing the tip to be brought into a distance of a few Å from the surface while preventing it from being buried in the sample.

Scanning and coarse approach are achieved fully automated and computer controlled.
2.3. **THE AARHUS STM**

**Temperature control**

While the STM used for studying the Pt/Pt(100) system did only allow for imaging at room temperature, the work on the Pt/Pt(110) system was carried out using a variable temperature version of the instrument that allows the sample to be scanned at temperatures in the range from ~140 and up to at least 400 K.

In the variable temperature version of the STM, temperature control is achieved in the following fashion. The thermally isolated top plate of the STM (where the sample is introduced) is connected via Cu braids to an Al block, which is attached to the cradle and is suspended together with the STM during imaging. When temperatures below room temperature are required, the Al block is cooled by pressing a liquid nitrogen cooled dewar against it. Once the desired temperature has been achieved, the dewar is removed in order to eliminate vibrations from boiling nitrogen, and the cradle containing STM and Al-block is left to hang freely. Due to the large thermal reservoir provided by the Al block, the temperature of the top plate is fairly stable with a drift of only a few degrees per hour. In the opposite case, typical for the measurements in the Pt/Pt(110) system, where temperatures above room temperature are desired, the Al block (and thus the top plate of the STM) is heated by passing current through zener diodes mounted on the block. In contrast to the low-temperature case, this heating can continue also during measurement and the large thermal mass of the Al-block (which implies fairly long time constants during warm-up, on the order of an hour) is thus not strictly required. However, the large thermal mass implies that once a steady-state has been achieved, the temperature of the sample is very stable and can be maintained constant to within 1 K.

**Drift-compensation**

The STM is of a cylindrical design that is intended to minimize lateral thermal drift. During acquisition of individual images with the instrument thermally equilibrated, drift does not constitute a problem. With respect to STM movies, however, several hundred consecutive images are acquired over a time-scale of hours. In that case even a slight thermal drift (typically on the order of 0.3 Å/sec) results in the final STM movie imparting the impression that it is taken panning over the surface and, as a consequence, interesting features quickly drift out of the field of view. This problem has been practically removed, however, by the implementation of an active drift-compensation routine described in the following.
The lateral thermal drift of the instrument can be compensated for by changing the offset voltages on the scanner-tube for each new image in an attempt to keep the same field of view on the surface. Two drift-compensation coefficients determine the amount by which the offsets along the lateral x and y directions are changed between images. Until the active drift-compensation routine was implemented, these coefficients had to be manually adjusted, resulting in inevitable fluctuations in the field of view during a movie.

With the new automated routine, however, a characteristic feature on the surface is initially pointed out. The position of this feature in the image is determined and the pixel-information in an area surrounding it is stored as a template. Following the acquisition of each new image, the position in the image of the characteristic feature is automatically determined by sliding the defined template over the image, maximizing the cross-correlation between the template and the actual image. If this pattern-recognition routine finds that the position of the characteristic feature has changed from the setpoint initially determined, the drift-compensation coefficients are updated in such a way that the feature is brought closer to the initial setpoint in the following image. By locking-in on an immobile feature in this way, it is possible to keep the exact same field of view for many hours under favourable circumstances with a precision of ±1 pixel of the image.

2.4 Use of STM and comments on related techniques

Since its invention in the early eighties by Binnig and Rohrer [9], STM has developed to become an extremely widespread and versatile surface science technique that has provided a revolutionary insight into surface phenomena in real space. One of the main factors that makes STM unique is its large dynamic range for observation, extending from the atomic level and into the micro-meter range allowing both atomic-level structure and large-scale surface morphology to be revealed.

From its infancy and up to the present point, STM has matured considerably with a tendency of STM studies to become increasingly more quantitative by averaging observed properties over large numbers of acquired STM-images rather than focusing on singular observations. Within the field of metal-on-metal growth this tendency is especially illustrated by experiments of the “quench-and-look” type, where the growth morphology resulting from deposition under specified conditions of anywhere from
a few per cent of a monolayer up to many monolayers is observed subsequent to deposition and at temperatures where the dynamic processes are frozen out. From analysis of the resulting STM images with respect to number densities, sizes, shapes, positions, etc. of the resulting growth islands, information on dynamic processes occurring during the growth may be inferred by comparison to the predictions of nucleation and growth theory or simulations. This type of experiments will be reviewed extensively in the following chapter, and the work on the Pt/Pt(100) system presented in chapter 4 of this thesis constitute an excellent example of the amount of information that can be derived from thorough statistical analysis of large quantities of STM images.

During recent years, the utility of STM has been greatly expanded by the development of variable temperature instruments. This is of special importance in relation to the study of dynamic phenomena, which may be monitored with STM by acquisition of large numbers of sequential images (STM movies). This approach was used fairly early in our group (at room temperature) to investigate pronounced surface restructuring occurring during gas-surface interaction [10]. In the context of metal-on-metal growth, STM has been used to monitor dynamic phenomena involving larger-scale structures such as island diffusion and decay [11] or step fluctuations by sequential observations.

At present, a rapidly increasing interest in utilizing STM to monitor dynamic phenomena at the atomic level, especially surface diffusion, by use of variable temperature, time-lapse STM is developing. The effort in this field has hitherto mainly focused on the behaviour of semiconductor systems and gaseous adsorbates. In the semi-conductor case, an interesting development is provided by Swartzentuber [12], who has used “atom-tracking” STM to make the tip follow the motion of Si adatoms on Si(001) rather than acquiring full STM images. Recent examples (by conventional STM) from the latter gas-category include studies of the diffusion of N on Ru(0001) [13] and O on Ag(110) [14] by Ertl and co-workers. For metal-on-metal systems, the atomic corrugations are smaller and it is generally recognized to be more difficult to resolve the individual atoms. The work on adatom diffusion and dimer dissociation in the Pt/Pt(110) system described in chapters 5 and 6 of this thesis establishes that STM can be used as a quantitative probe of adatom dynamics at the atomic scale also for such metal-on-metal systems.
Field Ion Microscopy

The ability to resolve individual (metal) adatoms is not unique to STM, but has been provided for several decades by the Field Ion Microscope (FIM) [15,16]. The extensive and often very careful and detailed studies carried out using this instrument have provided a considerable inspiration during the work on the Pt/Pt(110) system presented in this thesis, and most of the experimental examples that this work is compared to in the following have been carried out using FIM. For these reasons we describe the technique briefly. The following concise introduction to FIM has been provided by Feibelman [17]:

"This instrument consists of an ultra-sharp needle pointing toward a fluorescent screen, in a chamber filled with inert gas atoms. When a high voltage is applied between the needle and the screen, the inert gas atoms are preferentially ionized, positively, at the locations near the needle’s apex where the field is highest. This, via the “lightning rod effect” is where the atoms protrude from the crystal planes that comprise the needle’s surface. A positive ion, formed when an atom loses an electron to the tip, is accelerated in a straight line to the screen. The record of ion arrival positions thus constitutes a map of where atoms have lost electrons. After numerous ionizations one obtains an atomic resolution picture of the tip. It typically shows protruding atoms surrounding single crystal planes, and also the positions of atoms adsorbed on these planes."

Under normal FIM operation, the imaging is done at low temperatures, where adatom mobility is frozen. The adatom motion occurs during intermittent intervals (with the electric field off), where the FIM tip is heated to a given temperature. By sequential observations in this way, dynamic phenomena can be monitored, and the diffusion of single adatoms as well as the dynamic behaviour of small clusters have been extensively studied using FIM [16].

The FIM has certain limitations with respect to STM, the main ones being that (i) the FIM tips have to be made from materials of high mechanical strength restricting the choice of substrate (common tip-materials are W, Ir or Pt), (ii) gasous adsorbates can not be studied since they are desorbed by the imaging field and, especially, (iii) the terraces formed at the apex of the FIM tip are very limited in size.

With respect to the points (i) and (ii), the work on adatom diffusion in the Pt/Pt(110) system, which is presented in chapter 5 of this thesis, is important in the sense that it demonstrates that the STM can be used to acquire a very large statistical material on single adatom diffusion compa-
rable in quality to that attained by FIM. Concerning the point (iii), the
fact that extensive terraces are imaged with the STM clearly allows for
more realistic growth phenomena to be studied. In this regard, STM has a
truly unique ability in that it allows for the combination of information on
microscopic dynamic processes on one hand with observations of growth
phenomena occurring on larger terraces on the other. This ability is illus-
trated in the work on coarsening and island mobility in the Pt/Pt(110)
system that is presented in chapter 7 of this thesis.

**Diffraction Techniques**

The surface morphology resulting from growth experiments can also be
monitored using diffraction techniques. Thus Spot-Profile Analysis Low
Energy Electron Diffraction (SPA-LEED) [18] allows for average island
shapes and island-island separations to be determined, while intensity osc-
cillations in Reflection High Energy Electron Diffraction (RHEED) [19]
or Thermal Energy He Atom Scattering (TEAS) [20] can reveal whether
growth occurs in a smooth layer-by-layer fashion or not during multi-layer
growth.

In comparison to a local-probe real-space technique as STM, such
diffraction techniques have the advantage of providing directly the av-
eraging over a large statistical material that must tediously be obtained
in the case of STM by recording large quantities of images. On the other
hand, the averaging nature clearly implies that also the contribution from
unwanted features are included in the signal, such as impurities, defects,
steps, etc. The interpretation of measurements obtained by such tech-
niques is also considerably less straightforward than with STM. Compa-
rison to STM-data may therefore provide an important qualitative input
to the understanding and, perhaps especially, act to rule out an incorrect
model.

With respect to adatom diffusion, information may be obtained with
Quasi-elastic He Atom Scattering (QHAS) [21]. To yield a signal, this
technique requires a large proportion of adatoms to be in the process of
making a transition between adsorption sites at any given time. It there-
fore operates at high temperatures where diffusion occurs at a time-scale
that is not accessible with FIM or STM.

**A final comment**

A final comment is warranted before the description of STM is complete.
While STM has some magnificent qualities as outlined above, it is also
unique in the sense that the actual probe, the outermost apex of the tip, is in reality fairly ill-defined. To work at its optimum, STM requires a favourable tip-condition. A well etched tip is a pre-requisite for this situation to occur, and gentle indentations into the surface or the application of voltage pulses to induce field-desorption or restructuring may act to improve tip-performance, but there are certainly no guarantees. The main challenge in obtaining STM movies lies in acquiring not one, but several hundred consecutive images of sufficient quality. From an operational point of view, experience, patience and to some extent luck (the latter not being unrelated to the two former) are required on behalf of the operator in order to obtain optimum results with STM.

References

REFERENCES


Chapter 3

Background

The aim of the present chapter is to provide background information that will aid the appreciation of the forthcoming chapters. First, a very broad overview of diffusion, nucleation and growth is presented. This overview is followed by three sections that describe theoretical and experimental results of specific relevance for the work presented in chapters 4 to 6. Each of these sections also contain a brief outline of the results reached in these corresponding chapters. At the end of the chapter certain relations between the work carried out in the two systems investigated, Pt/Pt(100) and Pt/Pt(110), are discussed.
3.1 An overview of metal-on-metal growth

3.1.1 Introduction

Adding atoms to a crystal from the vapour phase is the conceptually simplest possible form of crystal growth. Yet, growth of thin metal films by vapour deposition continues to provide intriguing new phenomena. This is largely due to the fact that at the temperatures where growth experiments are typically carried out, the rates for many atomic scale processes on the surface are too low for thermodynamic equilibrium to be established. The resulting growth morphology is thus dominated by the effects of kinetic limitations and does not represent thermodynamic equilibrium. The richness of attainable structures is therefore immense. As the temperature is increased, a hierarchy of different processes is gradually being allowed. Knowing what dynamic processes occur in a given temperature window under specific conditions and understanding the consequences for the growth morphology, in principle, open up the fascinating possibility of tailoring the surface structure by letting it self-organize in a way that meets specific needs.

The experimental techniques and methods of investigation that has provided the foundation for our current increasingly detailed understanding of the microscopic mechanisms underlying crystal growth were mentioned briefly in the previous chapter. The intention in the present section is to provide a very general introduction to the field of metal-on-metal growth. The presentation aims at emphasising how the rates for different processes determine the resulting growth structure. In a sense, elucidating such rates for different microscopic processes is the common denominator for the work presented in the present thesis.

The aim has been to write this section in such a way that it could provide a concise introduction to the field, relevant for instance for new students or interested readers from other branches of physics. A number of review-articles are recommended for a more extensive introduction to the field of diffusion, nucleation and growth [1–14].

3.1.2 Surfaces

The growth experiments that will concern us in the following are carried out on surfaces of single crystals under clean Ultra High Vacuum (UHV) conditions. Although growth on such near-perfect surfaces constitute highly idealized cases, it is by now generally accepted that they can be
3.1. AN OVERVIEW OF METAL-ON-METAL GROWTH

used as model-systems to investigate the microscopic processes that may decide how more “real” systems develop.

The sample crystals are typically cut along the basic crystal planes. This commonly produces terraces with the corresponding atomic structure such as hexagonal fcc(111), quadratic fcc(100) or two-fold symmetric fcc(110), the terraces being separated by steps that lead from one crystal plane to the next.

Reflecting the fact that part of the crystal has been removed, the atoms in the surface have a lower coordination than their counterparts in the bulk. In a few metals, the positions of the atoms in the surface layer rearrange dramatically to compensate for this, and such surfaces where the atomic arrangement is different from that which would result from a simple truncation of the bulk structure are said to be reconstructed. Generally, the rearrangements involved in reconstruction on metal surfaces tend to produce a more densely packed surface layer [12]. The two open surfaces of Pt being considered in the present thesis are examples of this; Pt(100) produces a contracted hexagonal topmost layer, while on Pt(110) every second close-packed row is removed creating close-packed (111) microfacets.

3.1.3 Condensation

Adatoms are deposited on the surface from a thermal evaporation source, such as a hot filament. The kinetic energy of the adatom as it impinges on the surface, $k_B T_{\text{source}}$, amounts to a few tenths of an eV and is small compared to the condensation energy, on the order of a few eV, gained by the adatom as it adsorbs on the surface. Although the possibility has been considered that the adatom may be able to convert some of this released energy into transient motion along the surface [15,5], this seems to be a small effect\(^1\), and in general the adatom becomes bound at the position on the surface where it lands. Due to the large value of the condensation energy, there is a negligible chance that the adatom re-evaporates at moderate temperatures and in typical growth experiments the adatom adsorption is irreversible.

3.1.4 Adatom diffusion

The adatom resides in a minimum energy adsorption site on the surface, typically a position corresponding to a continuation of the bulk stacking

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\(^1\)Transient mobility may have some influence at low temperatures where thermal motion is not effective [1,5].
Figure 3.1: Schematic illustration of the processes involved in crystal growth.
sequence (at least for unreconstructed surfaces), such as a fourfold hollow on quadratic fcc(100), a threefold hollow on hexagonal fcc(111), etc. Compared to the energy-cost of desorbing the adatom, the amount of energy required to momentarily move it from the adsorption site and place it at another position on the surface, such as a bridge-site separating two adsorption sites, is not very large (from a few tenths up to 1 eV). This raises the possibility that at temperatures where the adatom is bound to the surface it may occasionally be energized by the thermal fluctuations of the lattice to surmount this activation barrier and make a transition between adjacent adsorption sites. At moderate temperatures the time spent in making such a transition is short compared to the intervening time-periods where the adatom sits in the adsorption site interacting with the lattice. Between jumps, the adatom therefore loses all memory of which direction it came from, and a jump is as likely to take the adatom back to the position it came from as in any other possible direction. The resulting random migration of the adatom on the surface is known as surface diffusion [4,10,11].

Interestingly, on certain surfaces, such as unreconstructed Pt(100) [16], diffusion originates from an exchange-mechanism where the adatom in a concerted motion dives into the substrate simultaneously expelling a lattice atom. Calculations [17] show that the activation barrier for such a process is lower than that for bridge-hopping because the atoms are able to keep a high coordination during the transition. The phenomenon of exchange diffusion underscores how the diffusion process results from an interaction with the dynamic lattice and signifies that it is not a correct intuitive picture, nor in the case where diffusion occurs by ordinary hopping, to think of the adatom as moving simply on a corrugated potential energy surface defined by the checker-board like static lattice. It also emphasizes that it is appropriate to think of diffusion and other processes on surfaces in terms of chemical reactions where bonds are broken and new are formed [18].

The hopping rate, \( h \), by which the adatom makes site-to-site transitions is strongly dependent on the substrate temperature, \( T \), and the activation barrier, \( E_A \). These quantities are related through the Arrhenius expression \( h = \nu \exp\left(-\frac{E_A}{k_B T}\right) \), where \( k_B \) is the Boltzmann constant and \( \nu \) is a prefactor of the same magnitude as the vibration frequency in the adsorption well, typically \( \nu \sim 10^{12} \text{sec}^{-1} \). A similar relation applies to the rate for other kinetic processes, such as dimer dissociation or adatom detachment from a step, which are also characterized by barriers and prefactors. The general trends [4] for the magnitude of diffusion barriers are that (i)
they tend to be higher for higher melting point materials and (ii) barriers on close-packed surfaces like fcc(111) are lower than on open surfaces as fcc(110). If the diffusion barriers separating neighbouring sites are identical in all directions, as eg for fcc(100) or fcc(111) surfaces, the adatom diffusion will be isotropic, whereas if the barriers are different, as it may for instance be the case for site-hopping on a fcc(110) surface from a simple coordination argument, there will be a preferred direction of adatom motion and diffusion will be anisotropic.

3.1.5 Nucleation and growth scenario

The growth of a crystal during adatom deposition is a highly non-equilibrated phenomenon, and the resulting growth morphology is determined by a complicated interplay between the rate, $R$, by which adatoms are deposited from the vapour and the rates by which different processes occur on the surface, by far the most important among these being the rate for adatom diffusion. The following conceptual description of a nucleation and growth scenario proves extremely useful in rationalizing observed growth phenomena [1–3, 7–9].

As more and more adatoms impinge on the surface after deposition is initiated, an increasing density of migrating adatoms builds up. When this supersaturated lattice gas becomes sufficiently dense, an appreciable likelihood exists that such diffusing adatoms meet and bind to each other (for now, assume that two adatoms that bind to each other form a stable dimer). The formation of stable entities on the surface leads to a substantial decrease in the number of diffusing adatoms since these may now be lost by attachment to the formed nuclei resulting in the growth of larger islands. In the subsequent nucleation and growth regime, the density of diffusing adatoms is lower than the density of stable islands and nuclei (see fig.3.2).

An adatom deposited after this point has been reached may suffer two destinies - either it is incorporated into an existing island or nucleus (growth) or it meets another diffusing adatom and binds to it (nucleation). Which of the two will be realised depends largely on where the adatom lands. If it is deposited in the vicinity of an existing island or nucleus, there is a high probability that, during its random motion on the surface, it will find this entity and become incorporated into it. Since the adatom density is low, the requirement for the diffusing adatom to participate in a new nucleation event is largely that, before it is lost to such a growth event, another adatom is deposited close to it and the two find each other.
3.1. AN OVERVIEW OF METAL-ON-METAL GROWTH

Figure 3.2: The development of the numbers of adatoms and islands during a nucleation and growth simulation. The ratio between adatom hopping and deposition rate is $h/R = 10^3$. Note the small number of adatoms that are present on the surface during the period where most of the islands are nucleated. Data courtesy of J.J. Mortensen.

This will happen predominantly if the initial adatom is deposited outside the capture zone that can be imagined to surround each island or nuclei and within which a deposited adatom is more likely to be lost to growth than to new nucleation (see fig. 3.3).

An important consequence of this scenario is that the positions of the islands that form during the nucleation and growth regime are not random, but mutually correlated. When the island density becomes sufficiently large that the capture zones start overlapping, new nucleation practically ceases and all deposited adatoms are lost to growth. The extent of the capture zones is determined by an interplay between the two rates in the problem, that for adatom mobility (which is again determined by the temperature) and that by which atoms are supplied from the vapour. If eg the deposition rate is low, adatoms will have long time to find existing islands and the resulting capture zones will be large compared to those for a higher rate. Similar arguments apply if the temperature is varied. This allows for an intuitive understanding of the parameter dependence of the island density on $R$ and $T$: at low $T$ and high $R$ many and, at a fixed coverage, subsequently small islands result, while for high $T$ and low $R$, few and large islands are formed.

By measuring the island densities in this submonolayer coverage regime
resulting from experiments where $R$ and $T$ are systematically varied, quantitative information on eg the activation barrier for surface diffusion may be inferred. This principle forms the basis of a number of recent experimental studies including that for Pt/Pt(100)-hex presented in this work. Such studies are reviewed later in this chapter where quantitative nucleation and growth theory is also discussed.

If deposition is continued in the growth regime, islands continue to grow in size and eventually the borders of islands will meet and the islands will coalesce, that is merge together into one. This will lead to a decrease in the island density. Since the positions of the islands are correlated, the onset of coalescence occurs at a higher coverage than it would if the islands were randomly placed.
3.1. AN OVERVIEW OF METAL-ON-METAL GROWTH

Inter-layer mass transport

In the same way as the intra-layer mass transport, given by the surface diffusivity, is decisive for the surface morphology with respect to sizes and densities of islands in the submonolayer coverage regime just described, the inter-layer mass transport, determined by the rates for adatoms to cross steps, dictates the three-dimensional morphology of the growing surface [2].

As an adatom descends a step-edge, it passes through a low-coordinated transition state, which suggests that this process may have an energy barrier larger than that for adatom diffusion on terraces\(^2\). If this is the case, adatoms that are deposited on top of existing islands may be trapped there because they are prevented from descending the steps at the island perimeter. This greatly enhances the probability that a new island is nucleated on top of the old one. With continued deposition, the islands will pile up in pyramidal fashion leading to 3-D growth and a very rough growth front [21–23]. Alternatively, if there is no extra barrier associated with crossing a step, adatoms deposited on top of an island may descend the step and become incorporated in the step-edge. In this case, the crystal grows in a smooth layer-by-layer fashion where at most a couple of layers are exposed at any given time. Interestingly, it has proven possible to induce layer-by-layer growth by the addition of impurities or "surfactants" to the surface thereby modifying the barrier for crossing the step [22,23].

Other scenarios

As stressed several times above, crystal growth is determined by an interplay between the different rates for the processes involved. The described scenario therefore belongs to a certain window of relative time-scales for the deposition and diffusion. Different scenarios will be appropriate for different such windows [1,2,7,8].

If the temperature is raised to a level where the diffusion length defining the extent of the capture zones becomes comparable to the terrace width, nucleation on the terraces will be suppressed and instead the crystal will grow in a step-flow mode where the deposited adatoms diffuse towards and become incorporated into existing step-edges.

\(^2\)Adatoms probably often descend steps through an exchange-mechanism rather than "rolling over" the edge as suggested [5]. The additional barrier for descending a step compared to diffusion on the terrace is often termed the Schwoebel-barrier [19], or the Schwoebel-Ehrlich barrier [20] (the abbreviation SE-barrier may then as well be taken to mean the Step-Edge barrier!).
In the opposite regime, where the temperature is low, adatom mobility will not be sufficient to rapidly remove deposited adatoms by incorporating them into islands. In that case, the nucleation and growth will continue after the deposition flux has been turned off, a regime termed post-nucleation or post-growth [24]. In the extreme case where there is no thermal mobility, and adatoms simply stick where they land, so-called statistical growth results [1].

Depending on the system investigated and the choice of deposition parameters \( R, T \), very different scenarios can therefore be realized. The investigation in the Pt/Pt(100)-hex system described in chapter 4 belongs, as mentioned, to the nucleation and growth scenario with high adatom mobility and island formation. In contrast, diffusion on the Pt(110)-(1x2) surface is sufficiently slow (at the temperatures investigated) for the adatom diffusion and nucleation to persist for a long time after the deposition flux has been turned off. This fact is what enables us to follow the atomic-scale processes at this surface directly as described in chapters 5–7.

Several factors may serve to complicate the nucleation and growth scenario outlined earlier. Dimer formation may not be irreversible, or the nucleated dimers may in principle be mobile and able to diffuse on the surface at temperatures where they do not dissociate. These factors are now discussed.

### 3.1.6 The critical island size

The assumption of irreversible dimer formation is bound to break down in all systems at sufficiently high temperatures. In that case, larger clusters, where the participating adatoms have more inter-adatom bonds to be broken, may be stable towards thermal dissociation. In nucleation and growth terminology, this phenomenon is discussed in terms of the concept of a critical island size, \( i \). This quantity may be defined by saying that addition of an extra adatom to a critical cluster of size \( i \) produces a “stable” island of size \( i + 1 \) that is more likely to grow than to decay during the course of deposition\(^3\) [1–3,7,8]. Thus, if a dimer is in fact stable, the

\(^3\)The concept of a critical island size originates from thermodynamic considerations of the free energy of a cluster with a certain surface to volume ratio interacting with a gas phase of a given supersaturation [7]. While small clusters are unstable due to their large surface to volume ratio, the free energy goes through a maximum with increasing cluster size, and clusters larger than the position of this maximum (which defines the critical island size) are more prone to grow than to decay. Hence the somewhat strange definition of the critical island size, \( i \). For low supersaturations (which could occur by deposition at high substrate temperatures where the thermal ejection of adatoms
3.1. AN OVERVIEW OF METAL-ON-METAL GROWTH

Critical island size is $i = 1$; if a dimer is unstable, but a trimer does not
dissociate, $i = 2$, etc. Clearly, the idea of a sharp critical island size, above
which clusters are stable and below which they are not, represents a crude
and averaging way to account for the stability of small clusters.

An increase in the critical island size does not radically alter the nu-
cleation and growth scenario, but the details will change. For instance,
as we will return to later, the distribution in sizes of the grown islands
becomes more narrow with increasing $i$. Also, the variation in island den-
sities with rate and temperature changes. This illustrates how the onset of
some microscopic processes may affect the resulting growth morphology.

From simple bond-counting arguments, some expectations for transi-
tions in critical island size with increasing temperature may be arrived at
[27]: On a square fcc(100) substrate, a trimer is not expected to be stable if
a dimer is not since the end-atoms in a trimer will be able to detach by the
breaking of a single bond. Adding an extra atom to produce a quadratic
quadrimmer (4 atoms in a square), however, will produce a “closed-shell”
structure where two bonds have to be broken to detach an adatom. Thus
on fcc(100) surfaces, a transition from $i = 1$ to $i = 3$ may be expected.
On hexagonal fcc(111), in contrast, every atom in a triangular trimer has
two adatom-adatom bonds to be broken. It is therefore expected to be
more stable than a dimer, and an $i = 1$ to $i = 2$ transition may result.
Transitions in critical island size from $i = 1$ to $i = 3$ have indeed been
identified for fcc(100) surfaces, examples will be discussed in detail later.

In the general case, however, it is not at all clear how the binding
strength in a small cluster adsorbed on a surface will depend on its size.
Many-body effects and next-nearest neighbour interactions may serve to
produce deviations from expectations based on simple bond-counting argu-
ments and pair-wise interactions [4]. As nucleation is such a central
step in the growth process, a detailed understanding of the forces that
hold small clusters together is clearly desirable.

3.1.7 Cluster diffusion

If dimers become mobile at temperatures where they do not dissociate,
the $i = 1$ nucleation scenario may also in principle be altered by dimer
mobility. Simulations have shown that for instance the size distribution of
from steps and kink-sites produces an appreciable adatom density), the critical island
size can be large [25]. At the highly non-equilibrium growth-conditions considered here,
however, where the supersaturation resulting from deposition is large, the critical island
contains only few atoms, and it seems more appropriate to think of nucleation in terms
of the rates for cluster decay and formation [26].
the grown islands changes if dimers have significant mobility [28–30]. Clear
effects of dimer mobility have not been identified in growth experiments,
however [1,29].

Some information on the mobility of dimers and other small clusters is
provided by FTM as it may be seen from the review by Kellogg [4]. The
observations are highly system specific, however, and few general trends
emerge. Although the detailed mechanism by which clusters diffuse has
been solved only for a few cases of dimers, it seems that the cluster motion
is due to a sequence of displacements of the individual adatoms forming
the cluster. No evidence has been obtained that simultaneous jumps of
two or more adatoms take place (recently a dimer shearing mechanism
has been proposed for clusters on fcc(100) surfaces [31], but it remains
to be confirmed experimentally). In some instances, dimers have been
found to have a mobility comparable to or even larger than that of a
single adatom. Examples include systems with exchange diffusion such
as unreconstructed Pt(100). Here the presence of an extra atom lowers
the barrier for the exchange process, and consequently the dimer flip-
flops across the surface exchanging an atom with the surface for each
displacement [32]. For fcc(100) surfaces where diffusion occurs by ordinary
hopping, the barrier for dimer diffusion seems to be higher than that for
single adatoms [1]. Dimer mobility on a hexagonal surface has very recently
been observed for Pt dimers on the Pt(111) surface by Ehrlich and co-
workers [33].

An effective activation energy for cluster motion can be obtained from
observed cluster displacements without elucidating the mechanism by which
the cluster migrates. Interestingly, such measurements have revealed that
the effective activation barrier for cluster diffusion need not be monoto-
nously increasing with increasing cluster size [4,34,35].

3.1.8 Island shapes

Probably no single phenomenon better than that of island shapes illus-
trates how the appearance of mesoscopic structures resulting from crystal
growth may be radically affected by kinetically controlling factors.

In growth experiments carried out on hexagonal substrates, it has been
identified how dramatic changes in island structure result from deposition
at different substrate temperatures and with different deposition fluxes
[1,2]. Generally, at low temperatures islands that are either randomly
ramified or dendritic with triangular envelope develop [36,37]. At higher
temperatures, in contrast, the result is compact islands that have a trian-
3.1. AN OVERVIEW OF METAL-ON-METAL GROWTH

regular or hexagonal shape reflecting the substrate symmetry. These changes reflect the onset with increasing temperature of different microscopic processes involved in mass transport along step-edges and around corners of the islands as well as the interplay between the rate of deposition and the speed by which microscopic rearrangements at the island perimeter occurs.

3.1.9 Island mobility and ripening

The dynamic evolution of the surface morphology does not necessarily cease as deposition is stopped. The non-equilibrium structure resulting from the growth will relax towards thermodynamic equilibrium provided the necessary atomic-scale processes can occur with a sufficient rate. Clearly, from the perspective of synthesizing some nanostructure through intelligent manipulation of relevant kinetic parameters, an understanding of how, and especially if, such a meta-stable structure decays towards equilibrium is equally important. For instance, a growth morphology involving many small islands has an excess free energy associated with the unsaturated bonds at the island perimeters. The equilibrium structure that minimizes the free energy for such a partially filled layer is essentially a single large island. The approach towards equilibrium therefore necessarily involves coarsening, an increase in the typical size of the islands.

Microscopically, the redistribution of mass within and among islands involved in such ripening phenomena requires the breaking of adatom-adatom bonds. If atoms can detach from edges and corners of an island, they may diffuse over the surface and attach to other islands. During such Ostwald ripening, small islands gradually decay through loss of material while larger ones grow, leading to an increase in the average island size.

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4 It is often stated that at high enough temperatures, an “equilibrium shape” of the island is reached which reflects boundary free energies of the different edges of the island. Pointing out that, at the microscopic level, being in equilibrium does not at all mean being static, Metis has recently discussed how thermodynamic information can be obtained from observations of a dynamically fluctuating island (as could be attained with STM).

5 The thermodynamic driving force for this behaviour is the Gibb-Thomson effect. The Gibb-Thomson relation expresses that the pressure of a vapour that is in equilibrium with its condensed phase depends on the curvature of the interface between the phases, being larger for smaller curvature. On a surface with islands of different sizes, the adatom density is therefore largest in areas surrounding small islands, establishing a concentration gradient leading to mass transport from small to large islands. A microscopic understanding of this phenomenon, however, is only beginning.
[13,41,1]. This process has been shown to result in size-distributions that are considerably more narrow than those which result from the nucleation and growth scenario [1,42], and ripening can therefore be a method to create equally sized (mono-disperse) islands.

Recently, it has been shown that large islands (or vacancy islands) containing hundreds of atoms may be quite mobile [43,44]. Islands that meander about on the surface can thus contribute to the coarsening process by coalescing upon encountering each other [45].

The displacement of the centre of mass of an island required for island diffusion to occur is believed to be brought about by essentially one (or both) of two channels\(^6\) [43,44]. An atom can evaporate from the island at one position, migrate on the surface for a while, and then re-condense at another position of the same island, resulting in a net displacement of the island. Alternatively, an atom may diffuse around the perimeter of the island, re-attaching somewhere on the same island. For both the evaporation-recondensation and the perimeter-diffusion mechanism, the requirement for significant island mobility is that higher-coordinated atoms incorporated in edges or at corner sites are able to detach. If not, the “core” of the island will remain immobile while only low-coordinated atoms at the perimeter contribute to the mobility.

3.1.10 Hetero-epitaxial systems

In this account, we have focused on homo-epitaxy and ignored the multitude of phenomena that become possible in hetero-epitaxy where adatoms are deposited on a crystal of different chemical identity [12,3]. We mention briefly surface alloying, opening up the possibility of manipulating the surface chemical reactivity on a microscopic scale [46].

In the hetero-epitaxial case, interface energies have to be considered, leading to questions as to whether the ad-layer “wets” the substrate or not\(^7\) [7]. Adlayers may be strained because they grow pseudomorphically, to emerge [41].

\(^6\)Here we consider metal islands epitaxially grown on their own lattice. Large metal clusters deposited on graphite have been found to be extremely mobile, enabling them to agglomerate into fractal-like structures [47]. While the mechanism behind this is not understood, it has been suggested that the clusters are able to “glide” over the surface by thermal activation due to large lattice mismatch between cluster and substrate [48].

\(^7\)The original classification into three main “thermodynamic growth-modes” [7], layer-by-layer (Frank-van der Merwe), layer-plus-islanding (Stranski-Krastanov) and islanding (Volmer-Weber), dependent on the interplay between the surface free energies of the substrate and the adlayer and the interface free energy between the two, becomes more relevant in the hetero- than in the homo-epitaxial case. While applicable in many
accomodating to the lattice spacing of the substrate. Alternatively, lattice mismatch between adlayer and substrate may manifest itself in Moiré patterns, height modulations on a large lateral scale\(^8\) [46].

The question of diffusion, nucleation and growth on inhomogeneous and strained layers is highly interesting, not least from a nano-structuring point of view. Nucleation may be heterogeneous, occurring at preferential sites on the surface, leading to ordered arrays of islands [50], or adatoms may be confined by ordered dislocation networks that define the capture zones of the individual islands creating a mono-disperse island size distribution [1].

3.2 Quantitative nucleation and growth studies

As a result of interplay between experiment and theory, the understanding of quantitative aspects of nucleation and growth in the submonolayer pre-coalescence regime is by now well founded. The perspective of deriving microscopic information, such as the activation barrier for adatom diffusion and the critical island size, has been the impetus for a number of experimental investigations over the last years, utilizing STM to image the monoatomically high islands resulting from nucleation and growth. Although these types of investigations are often motivated by the possibility of deriving specific information on microscopic processes, the observed phenomena such as island size-scaling, island-island correlation, growth structures, etc, are clearly also interesting in their own right.

A quantitative treatment of the nucleation and growth scenario as outlined in the previous section can be attained through either the use of mean-field rate-equations describing the development of island and adatom densities [7] or through Kinetic Monte Carlo simulations [1]. Although refined in recent years, the rate-equation description of nucleation and growth was essentially developed long before STM provided the possibility of observing mono-atomic high adatom islands in the submonolayer coverage regime. With the advent of STM, it has become possible to test the predictions of nucleation and growth theory at the microscopic level.

By far the majority of experimental nucleation and growth studies situations, this distinction does not encompass the all-important role of kinetics in the growth process, however.

\(^8\)The problem of diffusion of adatoms on such Moiré-patterned layers is not unlike that of self-diffusion on the hex-reconstructed Pt(100) surface [49].
have focused on simple unreconstructed, isotropic surfaces. Surfaces where diffusion or growth may be anisotropic have been studied to much less extent. This has been a central motivation for the work presented in chapter 4 of this thesis, investigating nucleation and growth of Pt on the anisotropically reconstructed Pt(100)-hex surface.

This section is intended to provide background information with respect to quantitative nucleation and growth studies, placing special emphasis on the anisotropic case. First, relevant results from theory are treated, especially a scaling law for the island densities and the prediction of a scaling behaviour of the island size distributions. We then turn to describe selected examples of experimental investigations. First the isotropic case is treated, and subsequently we describe two investigations previously carried out on anisotropic surfaces which illustrate some of the additional complications met in this case. Finally, we provide a short summary of the results reached in chapter 4 for the Pt/Pt(100)-hex case.

### 3.2.1 Mean-field rate-equation treatment

In the mean-field rate-equation approach [7,51] the development of the adatom and island densities during nucleation and growth is described by birth-death type rate-equations. This allows for the derivation of a scaling relation for the dependence of the island density on deposition rate and temperature, which is central for quantitative nucleation and growth investigations. In the following, it is sketched how this relation is derived. We follow Evans and Bartel and cast the equations in a form that allows for a unified treatment of the one- and two-dimensional cases [51].

Let $N_1$ and $N_s$ denote the density (per adsorption site) of adatoms and clusters of size $s$, respectively. Then $N_s = \sum_{s>1} N_s$, where $i$ is the critical island size, becomes the density of stable clusters (islands), while $N_T = \sum_{s>1} N_s$ is the total density of any adatom or cluster on the surface. An adatom may be lost to either (i) nucleation if it encounters a critical cluster of size $i$, or (ii) growth if it meets an island of size $s > i$. The probabilities for each of these two processes to occur we denote by $F_i \approx N_i/N_T$ and $F_s \approx N_s/N_T$, respectively. If adatoms are deposited at a rate $\dot{R}$, and $\tau$ is the average time an adatom spends on the surface before being lost to either of the two processes, then

\[
\frac{dN_1}{dt} = R(1 - \theta) - F_s \frac{N_1}{\tau} - (i + 1) \frac{dN_x}{dt},
\]

\[
\frac{dN_x}{dt} = F_i \frac{N_1}{\tau},
\]
where \( \theta \) is the deposited coverage.

These equations express that the island density, \( N_1 \), is increased due to deposition on the fraction \((1 - \theta)\) of the surface not covered by islands and depleted through adatom aggregation with stable clusters and new nucleation events, respectively, the latter each costing \((i+1)\) free adatoms. The island density \( N_x \) is increased whenever an adatom meets a critical cluster of size \( i \).

If it is assumed that a steady state exists for the density of critical and subcritical clusters \( (\frac{dN_i}{dt} = 0 \text{ for } j \leq i) \) then the density of critical clusters can be shown to be given by the quasi-equilibrium Walton relation \[32\]

\[
N_i \sim N_1^i \exp(E_i/k_B T),
\]

where \( E_i \) is the binding energy gained upon forming the critical cluster from \( i \) separate adatoms \((E_i = 0 \text{ for } i = 1)\).

To close the equations, an expression for the adatom lifetime \( \tau \) is needed. The number of hops executed by an adatom during this time-period is \( h \tau \), where \( h = \nu \exp(-E_d/k_B T) \) is the adatom hopping rate. To find a critical cluster or an island, the adatom needs to visit on the order of \( 1/N_T \) distinct sites assuming that the islands have no extent.\(^9\) Here a difference between the one- and two-dimensional cases arises. From random walk theory, expressions are known for the number, \( S_n \), of distinct sites visited during a random walk (RW) of \( n \) steps \[53\]. \( S_n \) depends crucially on the dimensionality of the RW. A random walker moving on a line has to perform vastly more jumps to visit a certain number of distinct sites compared to the case where it migrates in two dimensions. More precisely, \( S_n^{1-D} \approx (8n/\pi)^{1/2} \), while \( S_n^{2-D} \approx \pi n/\ln n \). From these expressions, \( \tau(N_T) \) can be found for the 2-D and 1-D cases, corresponding to isotropic and totally anisotropic diffusion, respectively, allowing for the rate equations to be solved in these two cases.

In the limit of large adatom hopping to deposition rate, \( h/R \), the rate-equation treatment produces the following scaling law for the island densities, \( N_x \), in the low coverage pre-coalescence regime \[7,51\],

\[
N_x \sim \eta(\theta) \left( \frac{R}{\nu} \right)^{\chi} \exp \left( \frac{\chi(E_d + E_i/i)}{k_B T} \right),
\]

This relation is the singularly most important result of nucleation theory. The scaling parameter \( \chi \) depends on the critical island size, \( i \), and is \( \chi = \)

\(^9\)Importantly, it is shown in chapter 4 that this assumption is not valid in the anisotropic case when islands have a finite extent.
\(i/(i+2)\) for the 2-D case and \(\chi = i/(2i+2)\) for the 1-D case. The function \(\eta(\theta)\) accounts for the rise in island density with increasing coverage and is independent of \(R\) and \(T\).

The result (3.4) provides the perspective of extracting information on the microscopic processes participating in diffusion and nucleation from measurements of the island density resulting from deposition experiments where rate and temperature are systematically varied. From the scaling parameter \(\chi\), the critical island size can be derived (in the small \(i\) limit typically encountered). In the \(i = 1\) case, the adatom diffusion barrier can be determined from the Arrhenius slope when \(N_z\) is plotted against deposition temperature. In the case where the critical island size is larger than one, the situation is more complicated since the diffusion barrier and the binding energy in the critical cluster are not trivially separable.

The scaling relation (3.4) should be applied with caution in interpreting experimental data, however. It is only strictly valid in the \(h/R \rightarrow \infty\) limit, and the scaling parameter \(\chi\) will gradually approach its asymptotic value as \(h/R\) is increased [54]. Therefore precautions must be taken to ensure that data are acquired at values for \(T\) and \(R\) where convergence has been reached, preferably one should measure \(\chi\) (from the variation of \(N_z\) with \(R\)) rather than rely on the asymptotic results. In the case where the critical island size changes, there will be transient behaviour separating the regions where the result (3.4) holds, and application of the law in these transient regimes may lead to erroneous results [55]. In such transient regimes and for low \(h/R\), one must resort to numerical integration of the rate-equations or to simulations as described below [1].

The influence of mobility of small clusters on the scaling behaviour (3.4) has recently been investigated by Metiu and co-workers [56] as well as Evans and co-workers [29]. In the 2-D \(i = 1\) case with only dimers mobile, a scaling exponent of \(\chi = 2/5\) is found for the flux-dependence.

The adatom density in the rate-equation treatment is described within a mean-field approximation, meaning that the density of adatoms is assumed to be the same at all positions of the surface, independent of the presence of islands or other sinks for the adatoms. Essentially, it is assumed that an adatom deposited at a given site on the surface is as likely to attach to an island far away as one nearby.

Accordingly, the mean field rate-equation approach largely fails in accounting for phenomena that are dependent on island-island correlation such as island size-distributions and coalescence [57]. To study such phenomena theoretically, as well as to test the predictions of nucleation theory, one must resort to simulations.
3.2.2 Kinetic Monte Carlo simulations

The dynamic evolution of a system that depends on a limited number of processes with known (or assumed) rates can be investigated with Kinetic Monte-Carlo (KMC) simulations [58,1].

In a nucleation and growth simulation, a lattice is defined and a number of processes to occur on this lattice as well as their rates are decided upon. Processes could include adatom hopping between sites, adatom detachment from a dimer, adatom hopping along a step-edge, deposition of a new adatom on the lattice, etc. For each simulation step, a single process is carried out for a single adatom. The processes are chosen with probabilities according to their relative rates, such that processes with a high rate have a high probability of occurring while low-rate processes occur less frequently. Following the simulation, quantities such as island density, island sizes, etc., can be evaluated. The theoretical foundations of KMC, such as the question of how to correctly propagate time in such simulations, have been treated by Voter [58] as well as Fichtorn and Weinberg [59].

In KMC simulations the effects of island-island and adatom-island correlations are automatically included since these follow intrinsically from the evolution of the system.

Scaling of the island size-distribution

One of the central results predicted from KMC simulations of nucleation and growth is a scaling behaviour for the island size distribution [51,27]. In agreement with the general picture of nucleation and growth outlined earlier in this chapter, simulations with different ratios, $h/R$, between the rates for adatom hopping and deposition result in very different size-distributions. It is found, however, that these distributions become congruent, that is collapse onto a single universal curve, $f(s/s_{av})$, if they are scaled according to the expression

$$f(s/s_{av}) = \frac{s^2}{\theta} N_s,$$

(3.5)

where $\theta$ is the coverage, $N_s$ is the density (per adsorption site) of islands of size $s$, and $s_{av}$ is the average island size (the relation (3.5) trivially implies that $\int f(x)dx = 1$ [51], the scaling therefore essentially amounts to normalizing the distributions and measuring the island sizes relative to the average island size).

Recent work by Bartelt and Evans [57] as well as Mulheran and Blackman [60,61] has demonstrated that the correlation among the island po-
sitions introduced by the nucleation and growth scenario lie at the origin of this scaling behaviour. To understand this, imagine that the surface is divided into cells, each cell surrounding an island and being defined as the part of the surface closer to this island than to any other island. The key point demonstrated by these authors is that an island predominantly captures adatoms from its own cell, introducing a correlation between the island sizes and the cell areas. The island size distribution is therefore related to the distribution of cell areas which again reflects the way islands are distributed over the surface. If \( h/R \) is changed, a different typical length-scale for the island separations results. The distribution of cell areas does not change, however, if these are re-normalized to this new length-scale, and hence the scaling of the island size distribution.

The scaling behaviour of the island size distribution is of significant practical value since the shape of the scaled size distribution may serve as a fingerprint for the presence of different atomic-scale mechanisms. Simulations by Amar and Family [27], Ratsch et al. [26] as well as Bartelt and Evans [51] show that when the critical island size is increased the scaled island size-distributions become more narrow and peaked. Analysing the island size-distribution therefore provides a method, independent of the scaling law analysis for the island densities, to assess the critical island size in experiments (we show in chapter 4 that the scaled distribution may also contain information on other processes, such as dimer mobility or island coalescence).

### 3.2.3 Experimental Examples

We now describe selected examples of quantitative experimental investigations of nucleation and growth. First, the isotropic case is treated illustrating the use of the results described in the previous section. Subsequently, we discuss the additional complications that arise in the anisotropic case.

#### Isotropic surfaces

The first\(^{10}\) example where nucleation and growth was extensively studied in a metal-on-metal system by STM is that of Fe on Fe(100)\(^{11}\) by Stroscio and Pierce [63–65]. From deposition experiments at a coverage of 0.07 monolayers and at temperatures ranging from 293 to 629 K, these authors

\(^{10}\)The first authors to derive a diffusion barrier from STM data on the variation of island density with temperature were Mo, Kleiner, Web, and Lagally in the Si/Si(100) system [62].

\(^{11}\)Fe is bcc not fcc, but the (100) face is still quadratic and isotropic.
were able to determine island densities, island sizes and island positions of the formed quadratic islands. An analysis of the island-island separation distribution revealed that the positions of the islands were indeed correlated in an isotropic fashion. The scaled island size distribution corresponding to depositions at \( T \leq 480 \) K showed collapse with a shape consistent with \( i = 1 \) behaviour as simulated by Bartelt and Evans [51]. For two experiments at \( T \geq 574 \) K, the scaled distributions were more peaked, which was interpreted as a change to higher critical island size with increased temperature. The measured island densities in the low-\( T \) regime were on a straight line in an Arrhenius plot, allowing for determination of a diffusion barrier of \( E_d = 0.45 \pm 0.04 \) eV via (3.4), assuming validity of the \( \chi = 1/3 \) result for the 2-D \( i = 1 \) case (the flux-dependence of the island density was not measured). Consistent with the observation of different size-distributions, the island densities for the two higher temperature points diverged from the Arrhenius fit to the points obtained at lower \( T \). Taking into account the absolute values for the island densities, \( i = 3 \) was inferred, and the cluster binding energy was estimated to be \( E_b = 1.1 \pm 1.0 \) eV from the Arrhenius slope in this high \( T \) regime. This was done assuming that the diffusion barrier was the same as that determined at lower temperatures.

The results of Stroschio and Pierce have subsequently been modelled using KMC simulations by Bartelt and Evans [51], Amar and Family [27] as well as Ratsch et al. [26], confirming the change to larger \( i \) from the size-distributions and deriving values for the bond-energy of \( E_b = E_d/2 \approx 0.65\text{eV} \) [51] and \( E_b = 0.60 \pm 0.1 \) eV [27].

Feibelman has later argued [66] that the derived values for the energy per bond in the Fe trimer of \( \sim 0.5 \) eV/bond are unreasonably large. We will return to this discussion later in this chapter.

Recently, a well-defined transition from \( i = 1 \) to \( i = 3 \) behaviour has been reported by Müller et al. [24] in the Cu/Ni(100) system, observed both from changes in \( \chi \) obtained from flux-variation and from the island size-distributions [1]. From the slopes of the Arrhenius plot in the \( i = 1 \) and \( i = 3 \) regimes respectively, a diffusion barrier of \( E_d = 0.351 \pm 0.017 \) eV and a bond-energy of \( E_b = 0.46 \pm 0.19 \) eV are determined.

An experimental test of the predictions of nucleation theory was provided by Brune et al., from deposition of Ag on Pt(111) at low temperatures. By comparing the observed density of clusters to the known coverage in the initial stages of nucleation, a critical island size of \( i = 1 \) was directly inferred [67]. A scaling parameter of \( \chi = 0.32 \pm 0.05 \) was later determined in agreement with the prediction \( \chi = 1/3 \) from (3.4) [1].
Figure 3.4: Data from the study of Fe/Fe(100) by Stroscio et al. [64]. This figure illustrates many of the concepts discussed in this section. (a) and (b) show scaled island size distributions obtained in the low and high temperature regime, respectively as discussed in the text. The inset in (a) show scaled size distributions simulated by Bartelt and Evans [51]. Note the difference between the \( i = 1 \) and \( i = 2 \) case and the corresponding difference between the two distributions obtained from measurement. The inset in (b) depicts an Arrhenius plot of the measured island densities. Note the break in slope which is interpreted as a change is critical island size. Reproduced from [64].
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An alternative method, independent of the relation (3.4), for deriving diffusion parameters from nucleation data was proposed by Bott et al. [68]. These authors used KMC simulations to model island densities for Pt/Pt(111), which were obtained in the temperature regime following the onset of adatom mobility where adatom motion was the only relevant process. The diffusion barrier obtained in this way (0.26 eV) was consistent with that derived by applying the relation (3.4) to data attained at slightly higher temperatures, thereby providing an experimental test of the applicability of (3.4).

Anisotropic Surfaces

The examples discussed above serve to demonstrate that for simple isotropic surfaces, and especially for the simplest \( i = 1 \) case, the understanding of the quantitative aspects of nucleation and growth is by now well-developed.

The additional complications in the case of anisotropic surfaces are those introduced by directional diffusion and, possibly, directional bonding or sticking to islands and step-edges. In observing anisotropic phenomena in growth, such as elongated island shapes, it is not a priori clear how to discern which of these two effects lie at the origin. The rate-equation treatment of Bartelt and Evans sketched above predicts in a purely one-dimensional model that the scaling parameter \( \chi \) is different from the result for 2-D (isotropic) diffusion, i.e. for \( i = 1 \) one obtains \( \chi^{1D} = 1/4 \) while \( \chi^{2D} = 1/3 \).

The first\(^{12}\) observation of 1-D islands in metal-on-metal growth was reported by Kern and co-workers for the heteroepitaxial Cu/Pd(110) system [70,1]. Deposition below 265 K resulted in 1-D monoatomically wide islands oriented along the closepacked direction, while deposition at higher temperatures produced elongated but 2-D islands. This behavior was originally interpreted as resulting from a transition from 1-D to 2-D adatom diffusion on the terraces. Recently, however, the Cu/Pd(110) system was revisited by Li et al. [71] who emphasize the importance of mass transport along the island perimeter and especially that of anisotropy in the corner- rounding process bringing adatoms from long to short edges of the islands and vice versa. In the KMC simulations of Li et al., it is shown that 1-D islands can result even if diffusion is isotropic, provided there is a large anisotropy in sticking between the two island edges. A re-measurement

\(^{12}\)For Si/Si(100), one-dimensional islands have also been observed [69]. The situation in this semi-conductor system is complicated by strong directional bonding effects, however, and the islands are oriented with their long direction perpendicular to the direction of fast diffusion.
[71] of the scaling behaviour of $N_z$ with $R$, however, revealed a scaling exponent $\chi \approx 0.2 - 0.28$, indicative of anisotropic rather than isotropic diffusion. In the final modelling of the data on Cu/Pd(110), it was therefore assumed that diffusion is anisotropic, but 1-D only for temperatures well below the transition from 1-D to 2-D island growth, and the key mechanism responsible for the transition from 1-D to 2-D islands is that mass transport from the short to the long island edge becomes possible.

Nucleation and growth in the Au/Au(100)-hex system has been described by Behm and co-workers [72] (Au(100) exhibits a hex reconstruction very similar to that of Pt(100)). Upon deposition at $T = 315 - 435$ K, regular rectangular islands are formed. Denuded zones\textsuperscript{13} are observed for steps perpendicular to the reconstruction channels, but not for parallel steps. From the variation of $N_z$ with $R$ at $T = 315$ K, a value of $\chi = 0.37 \pm 0.03$ is determined. The Arrhenius plot for $N_z$ exhibits a break at $\sim 400$ K separating regions with different slopes.

The observation of denuded zones suggests that diffusion is anisotropic, but the authors did not a priori rule out anisotropic sticking at different step-edges as the origin. The $\chi = 0.37$ result is marginally consistent with $i = 1$ and isotropic diffusion, but on the basis of a comparison of the absolute values for the island densities to those derived from simulations this possibility was ruled out. The authors then turned to anisotropic diffusion using the 1-D result $\chi = i/(2i + 2)$. Here, the found value for $\chi$ is consistent with $i = 2 - 6$ since $\chi$ varies slowly with $i$. To discriminate between these possibilities, and to disentangle the contributions from $E_d$ and $E_t$ in the Arrhenius slope, the authors resorted to careful analysis of the full rate-equations arriving at the conclusion that $i = 3$ with $E_d \approx 0.2$ eV and $E_t \approx 0.6$ eV. The break in the Arrhenius slope was interpreted as a transition to $i = 5$ at higher temperatures although values for $i$ between 4 and 9 were not ruled out.

Metiu and co-workers later suggested that isotropic diffusion with $i = 1$ but with significant dimer mobility, in which case $\chi = 2/5$ is expected, could fit the data obtained for Au/Au(100) [56]. An experimental size-distribution subsequently published [29] was shown by Behm and co-workers to differ from the one they obtained from simulations in a point-island model using the parameters suggested by Metiu et al. This was interpreted in favour of their initial model (a simulated distribution for their initial model with $i = 3$ and anisotropic diffusion was not shown for comparison, however).

\textsuperscript{13}Denuded zones are regions extending from steps where the island density is depleted. They originate from the same effect as the capture zones discussed previously.
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Although the suggestion of isotropic diffusion by Metiu and co-workers was probably prompted by an incomplete appreciation of the microscopic structure of the hex-overlayer, the related discussion underscores the difficulties in elucidating whether diffusion is anisotropic or not from the scaling of the island densities alone, this being especially true if the critical island size is larger than \( i = 1 \). The described investigation in the Cu/Pd(110) system, on the other hand, illustrates the problems related to distinguishing anisotropic effects in anisotropic diffusion and island growth.

Outline of the Pt/Pt(100)-hex case

Chapter 4 of this thesis is devoted to a detailed quantitative investigation of homo-epitaxial nucleation and growth on the anisotropic hex-reconstructed Pt(100) surface in the temperature interval \( T = 318\text{–}497 \) K.

The main novelty in this work is that it is demonstrated how information on the anisotropy in adatom diffusion can be derived from the spatial correlation among the positions of the islands. From the concept of capture zones outlined earlier, islands are expected to be distributed in an anisotropic fashion on the surface if diffusion has a preferred direction (as is suggested for the Pt(100)-hex surface from the anisotropic reconstruction channels). From a thorough autocorrelation analysis of the island positions, we indeed find that the islands are positioned with long/short correlation lengths along/perpendicularly to these channels, respectively. By comparison to the results of KMC simulations, we use this observation to quantify the degree of anisotropy in the adatom diffusion. This method is shown to distinguish between the effects of anisotropic diffusion and anisotropic sticking.

In addition to this new method of analysis, the island size distributions and the scaling of the island density with \( R \) and \( T \) are investigated.

The island size-distributions, which are shown to exhibit scaling also in this anisotropic case, reveal that \( i = 1 \) and also exclude the possibility of dimer mobility. From the scaled distributions, we furthermore find evidence that a significant amount of island coalescence has occurred despite the fact that the measurements are acquired at low coverage. This effect derives from the reduced island-island correlation length resulting from the diffusional anisotropy.

From the scaling of the island densities, we obtain an effective activation barrier for diffusion of \( E_d = 0.43 \text{ eV} \) and a scaling parameter of \( \chi = 0.27 \), the latter in fair agreement with the 1-D result for \( \chi \) in the \( i = 1 \) case (\( \chi = 1/4 \)). Importantly, however, we show that this 1-D re-
result is not generally applicable to 2-D surfaces with diffusional anisotropy. The 1-D assumption is not valid if islands have a finite extent since the cross-section for adatom capture then becomes proportional to the island width enabling an island to block more and more “diffusion channels” as it grows. The 1-D result for $\chi$ remains valid for string-like islands, however (eg as observed for Cu/Pd(110) at low temperatures). The reason for the apparent agreement in the Pt/Pt(100) case is sought in the detailed structure of the reconstructed surface.

### 3.3 Diffusion

The diffusion of atoms and molecules adsorbed on surfaces is central for a large class of dynamic phenomena occurring on surfaces, comprising not only crystal growth, but also eg. catalysis or oxidation. Although the extraction of diffusion parameters from nucleation and growth experiments using STM is by now a fairly well-established method, the bulk part of our knowledge on single metal-atom diffusion on metal surfaces stems from FIM which allows for the observation of the displacements of individual atoms. The work on Pt adatom diffusion on the Pt(110)-(1×2) surface presented in chapter 5 of this thesis shows how the STM can be used similarly to FIM as a quantitative probe of metal adatom diffusion at the atomic level. In the work presented in chapter 5 it is demonstrated that the diffusion in this system not only consists of adatom jumps between nearest neighbour sites, but also comprises long jumps where the adatom traverses two lattice spacings.

The present section is intended as a further introduction to adatom diffusion with special emphasis on the question of long jumps in diffusion.

#### 3.3.1 Transition state theory

In the simplest picture of surface diffusion, the adatom moves on a corrugated potential energy surface defined by the static lattice. In the jump-diffusion regime that is accesible with experimental techniques as FIM or STM, there is a clear separation of time-scales between the short time-scale on which the actual transition between sites occur (pico-seconds) [73] and the much longer times that the adatom resides in the adsorption well between transitions (on the order of seconds). In this rare event regime the rate for such transitions to occur can be described within transition state theory [11]. Within this theory a dividing surface separates initial and final states, in the present case two adsorption wells on the surface. The
3.3. DIFFUSION

A dividing surface is situated at the highest energy point on the potential energy surface along the minimum energy path connecting initial and final states. It is assumed that the adatom only crosses the dividing surface once as it moves from the initial to the final state. From this theory the well-known Arrhenius dependence for the rate, \( h \), by which the adatom crosses between initial and final states is obtained,

\[
h = \nu \exp \left( -\frac{E_d}{k_BT} \right)
\]  

(3.6)

where the activation barrier, \( E_d \), is the energy difference between the minimum energy at the dividing surface and the energy at the initial state. The prefactor, \( \nu \), is related to the curvatures of the potential energy surface in the adsorption well and at the transition state and is independent of temperature within a harmonic approximation for these curvatures [11].

3.3.2 Molecular dynamics simulations

In reality, diffusion occurs through a complicated interplay with the dynamic lattice. It is the thermal vibrations of the lattice that act to excite the adatom to the transition state separating two adsorption sites, and it is at the same time the energy dissipation to the lattice that acts to de-excite the adatom causing it to be trapped in an adjacent well. A more detailed insight into the way in which diffusion occurs can be obtained through the use of molecular dynamics simulations [58,74,73,75]. Here, the classical equations of motion (Newtons second law) are integrated for the involved particles. The interaction between the atoms is described by potentials that can range from simple Lennard-Jones type expressions [74] to more advanced semi-empirical potentials [76]. This type of simulation provides information on adatom dynamics on the short time-scales of adatom transitions (and can for instance be used to evaluate the rates that are input to KMC simulations [58]). Such simulations reveal details of the diffusion process, and for instance show how there can be re-crossings of the dividing surface, where the adatom returns to the original well after crossing the dividing surface once. Such effects have been described as dynamic corrections to transition state theory [74].

3.3.3 Long Jumps in diffusion

The diffusing adatom moves on a periodic potential energy surface. It is therefore a possibility that transitions can occur between non-adjacent sites. This raises the question — how does diffusion in fact occur at the
microscopic scale, does the adatom only perform transitions between nearest neighbour sites, or does it also perform long jumps where it traverses directly between non-adjacent sites? Note that due to the separation of time-scales mentioned earlier, such a long jump is distinctly different from two successive single jumps as illustrated in fig. 3.5. In the case of two successive single jumps the adatom comes to rest in the intermediate well on the long timescale that separates transitions, whereas in the case of a long jump the transition between non-adjacent sites occur directly on the short time-scale of site-to-site transitions.

To obtain guidelines as to when long jumps occur, Ferrando et al. [77] as well as Pollak and co-workers [78,79] have modelled adatom diffusion as the Brownian motion of a particle on a periodic potential using a generalized Langevin equation analysis. In such a treatment the lattice vibrations that excite the adatom to make transitions are modelled as a random fluctuating force, and the interaction with the lattice that acts to de-excite the adatom is described by a friction coefficient. The factors that in the theory of Ferrando et al. determine whether long jumps occur are (i) the ratio between the activation barrier for diffusion and the thermal energy, $E_d/k_B T$ and (ii) the mean energy dissipation due the work done by the frictional force as the adatom traverses one lattice spacing. For $E_d/k_B T < 1$ diffusion does not occur by discrete jumps but becomes quasicontinuous. A jump-diffusion regime with participation of long jumps is expected for more moderate temperaturas in the limit of low energy dissipation. However, it is not entirely clear how the results of Ferrando et al. should be related in a quantitative fashion to a given experimental case.

The issue of long jumps has been investigated in molecular dynamics simulations by several authors. Dobbs and Doren have studied the dif-
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fusion of CO adsorbed on Ni(111) [73], and Metiu and co-workers have investigated the diffusion of H on Ni(100) [75]. In both these cases of light adsorbates significant amounts of long jumps were found. For metal-on-metal systems the coupling to the lattice can be expected to be stronger [75] and the energy dissipation therefore more effective. In simulations for Rh on Rh(100) by Voter and Doll [74] long jumps became effective only for high temperatures above 1000 K.

**Experimental evidence for long jumps**

The most extensive\(^{14}\) experimental investigations of the question of long jumps, in the jump-diffusion regime at moderate temperatures, have been carried out by Ehrlich and co-workers relying on the FIM to reveal the displacements of the individual adatoms [81,82].

In diffusion experiments with the FIM, where the motion of individual isolated adatoms is followed, one usually focuses on the tracer or intrinsic diffusion coefficient, \(D\) [4]. This quantity is obtained from the observed mean square displacement, \(\langle r^2 \rangle\), of the adatom during diffusion intervals of time \(\tau\) as

\[
D = \langle r^2 \rangle / 2m\tau
\]  

(3.7)

where \(m\) is the dimensionality of the diffusion \((m = 1\) or \(2\)). The diffusion coefficient is expressed as

\[
D = D_0 \exp(-E_d/k_BT)
\]  

(3.8)

where the prefactor, \(D_0\), is given by

\[
D_0 = (\nu l^2 / 2m) \exp(\Delta S/k_B)
\]  

(3.9)

in which expression \(l\) is the mean length of the adatom jumps and \(\Delta S\) is the entropy of activation.

From an Arrhenius plot of diffusion coefficients obtained from (3.7) at different temperatures, the diffusion barrier, \(E_d\), and the diffusion prefactor, \(D_0\), can be obtained.

A contribution from long jumps should in principle be revealed in the prefactor, \(D_0\), [81,4] since such transitions would act to produce a mean jump length, \(l\), larger than one lattice spacing. However, it is not likely

\(^{14}\) Evidence for long jumps has also been obtained by STM in the Pb/Ge(111) system [80]. This system is very special, however, in that the Pb adatoms are embedded in the reconstructed Ge surface and it is not at all clear how the actual site-to-site transitions occur.
that such a method of analysis can be used to identify a contribution from long jumps since (i) it is difficult to determine prefactors very precisely and (ii) there is no independent way to assess the magnitude of the two other quantities in the prefactor, $\nu$ and $\Delta S$.

To obtain information on long jumps in diffusion, Ehrlich and co-workers have shown that one should extend the analysis of the adatom displacements beyond the usual evaluation of only the mean square displacement. By focusing instead on the detailed distribution over adatom displacements, it should be possible to derive the rates by which long jumps occur.

In this respect, the authors have shown [83] that for diffusion in one dimension, the probability, $P_x(t)$, of an atom, initially at position $x = 0$ at time $t = 0$, to be at lattice site $x$ at some later time $t$ is given by

$$P_x(t) = \exp[-(h_1 + h_2)t] \sum_{j=-\infty}^{\infty} I_j(h_2 t)I_{j-2}(h_1 t)$$  (3.10)

where $I_n$ are the modified Bessel functions of the first kind of order $n$, and $h_1$ and $h_2$ are the rates by which the adatom leaves an adsorption site by single and double jumps, respectively.

By comparing this stochastic relation to distributions derived from experiment, a possible contribution from long jumps can be identified (provided that a sufficient statistical material is available [81]). In chapter 5 this is discussed in depth, and it is also shown how the relation (3.10) is derived, consequently we do not discuss it in further detail here.

By using this described approach, Ehrlich and co-workers have investigated several systems with respect to identifying a possible contribution from long jumps in diffusion. In an initial investigation [81], the diffusion of Re, Mo, Ir, and Rh on the channelled W(211) plane was examined. In these cases diffusion was found to consist of single jumps between nearest neighbour sites only, although a slight contribution from double jumps could not be ruled out for the Ir and Rh adatoms. In a subsequent publication, the diffusion of W and Pd on the same W(211) surface was investigated [82]. In this case the self-diffusion of W was found to occur by single jumps only. For the Pd case, however, significant amounts of double and triple jumps were identified at 133 K (which was close to the highest temperatures the authors could investigate). In this case the ratio between the rates for double and single jumps was found to be 21 % and the corresponding triple to single jump ratio was found to be 14 %. Interestingly, however, the contribution from long jumps disappeared completely by only a slight lowering of the temperature by 11 K, and at 122 K no evidence for long jumps
was found. This rapid temperature variation led the authors to speculate that the long jumps arise in an activated process over an activation barrier roughly twice as large as that for a single jump.

There are several questions that arise from the investigation of Ehrlich et al. Is the diffusion of Pd on W(211) a singular case where long jumps occur in metal-on-metal diffusion at moderate temperatures and, especially, is it so that long jumps do not occur for self-diffusion (as it was suggested by the authors themselves in their motivation for choosing W as a reference system)? What behaviour would have been found if the authors had been able to investigate the Pd/W(211) system at higher temperatures — would the rapid increase in the proportion of long jumps have persisted? More generally, this latter question can be phrased: What temperature dependence is to be expected for the rate for such long jump transitions — do they follow a simple Arrhenius behaviour on temperature, and in this case what is the activation energy?

The Pt/Pt(110)-(1×2) system

In the work presented in chapter 5 of this thesis, we investigate the diffusion of Pt adatoms in the missing row troughs of the Pt(110)-(1×2) surface. The adatoms are monitored using STM movies and are found to migrate in a 1-D fashion in the troughs. The STM movies allow for a large statistical material on the adatom diffusion to be acquired. From this investigation we are able to provide answers to some of these fundamental questions. By analysis of the displacement distributions by the method discussed above, evidence for significant amounts of long (double) jumps are found in this self-diffusion system. The rates for these long jump transitions have been determined over a range of temperatures from slightly above the onset of diffusion at ~300K and up to 380 K. The rates for the long jumps are found to follow an Arrhenius dependence on temperature. The barrier determined for the long jump transitions (0.89 eV) is slightly larger than that derived for jumps covering only a single lattice spacing (0.81 eV).

3.3.4 Comment by Pollak et al.

Finally in this section we mention a criticism that has been put forth by Pollak et al, concerning the analysis of the long jump results by Ehrlich and co-workers based on the equation (3.10). This criticism has also occasioned these authors to submit a comment [84] on our paper (III), which is the main motivation for the following brief discussion.
Based on a generalised Langevin equation analysis, Pollak et al. have derived an alternative expression for the adatom displacement distribution [78,79]. In their theory this distribution is uniquely defined by two quantities, the hopping rate for single jumps and the energy loss due to the frictional force experienced by the adatom as it traverses one lattice spacing. The rates for jumps of different lengths are thus related to each other within this theory.

Consequently, the main point of these authors is that it is too simplistic to use an expression of the form (3.10) since it only incorporates jumps covering a limited number of lengths, and the rates for these different jumps are independent. Based on this idea they have attempted in a paper [79] to account for the results of Ehrlich and co-workers [82] within their own model. While this, in itself, is appreciable, the arguments are not entirely clear, and the paper seems to be motivated by a very strong desire to make their theory fit to the results of Ehrlich and co-workers.

The main point in their submitted comment on our paper (III) is similarly a criticism that only the possibility of single and double jumps are included in the analysis. They provide a displacement distribution obtained from their theory which they claim to be as good a fit as ours to the distribution published by us in (III). The distribution provided by Pollak et al. suggest that triple jumps with a rate that is 0.8 % of that for single jumps should participate in the diffusion.

In brief, our reply to their comment was that: (i) the comment is partly based on a misunderstanding. We did in fact (as discussed in chapter 5) include rates for jumps up to a length of four lattice spacings. The rates for the transitions of length larger than two (double jumps) were however determined to be insignificant based on careful considerations of the statistics in the measurements (a triple jump fraction of 0.8 %, as suggested, is not detectable in the measurements). Regrettably, this was not discussed in the paper (III). (ii) The procedure used in obtaining the distribution claimed by Pollak et al. to fit to the distribution measured by us is doubtful (they use as input the rate for single jumps obtained from our Arrhenius fit to all the measured single jump rates, rather than the actual rate for the particular distribution and, furthermore, they seem to use the wrong lattice constant for the Pt(110) surface in evaluating the energy loss!).

In general, it is worth making the following remark about the analysis based in the equation (3.10). This equation is purely stochastic and involves no physical assumption as to the underlying mechanism of long jumps. In judging in an unbiased way from the experimental data whether
or not long jumps occur, using this expression therefore seem to be a better procedure than to use a theory based on assumptions about the mechanism for long jumps that may or may not be correct. At the time of writing it is not clear whether the comment of Pollak et al. will be accepted.

3.4 Adatom-adatom interactions

The formation of bonds between adatoms that meet as they migrate on the surface is the fundamental step that leads to nucleation in thin film growth. In this respect, a detailed understanding of the binding strength between adatoms in small clusters is clearly desirable. Information on adatom-adatom interactions has been derived in two instances in the work presented in this thesis. Most explicitly by quantifying the dissociation kinetics of Pt dimers on the Pt(110)-(1 x 2) surface as described in chapter 6, but also through the observation of a critical island size of i = 1 for nucleation of Pt island on the Pt(100)-hex surface.

These investigations illustrate the two different methods by which such information can be derived — either directly from atomic-scale observations or indirectly through nucleation and growth studies. The present section serves two purposes. First, it provides an introduction to the direct methods and thereby to chapter 6. This is done in the following subsection. Secondly, it addresses an interesting question raised by the two investigations in Pt/Pt systems mentioned above. While in the Pt/Pt(110) case we observe directly that dimers dissociate quite readily at temperatures following the onset of diffusion (right around room temperature), we find on the other hand from the nucleation and growth investigation in the Pt/Pt(100) case that i = 1 up to temperatures of ~ 500K, suggesting that dimers are much more strongly bound in this system. A related question has previously been raised by Feibelman who, as mentioned earlier, has commented that binding energies derived from a nucleation and growth investigation in the Fe/Fe(100) case seem unreasonably large. Motivated by this, we provide in the second part of this section a general discussion of results obtained by the nucleation and growth method. It should be emphasized that this discussion is very tentative and is intended mainly to put the question raised by the present findings for Pt/Pt into a broader perspective.

Finally, in the end of this section, we discuss the possibility of using the methods of nucleation and growth investigations in the Pt/Pt(110) system.
Figure 3.6: Sketch of a potential energy surface modified by attractive adatom-adatom interactions. The interaction potential is superposed on the periodic potential of the substrate (black) producing the potential energy surface (grey) that define the dynamic behaviour of the adatoms in the vicinity of each other. The periodic substrate potential (black) can be thought upon as the potential energy of the system consisting of substrate and adatoms when atom B moves between the sites shown and atom A is placed on the surface but too far away for the adatoms to interact, whereas the distorted potential energy surface (grey) is the potential energy when atom B moves in the vicinity of atom A. The binding energy $E_b$ of the dimer AB is defined on the figure.

3.4.1 The direct approach

Introduction

The interaction potential for two adatoms at a given separation on the surface may be defined as the difference in potential energy between the configuration where the adatoms are at this particular separation and the situation where both adatoms are still adsorbed on the surface but placed so far apart that their mutual interactions are negligible [4,85]. The interaction potential is thus an effective pair potential that encompasses not only all the changes in the direct adatom-adatom interaction that follow upon bringing the adatoms into proximity of each other, but also changes to the lattice and especially changes in the strength of the adatom-surface interaction. The adatom-adatom interactions include short range interactions arising from mutual overlap of the adatom atomic orbitals (i.e., bond formation in the case where interactions are attractive) or dipole-interactions as well as possible longer-range indirect interactions mediated through the substrate electrons.

A principal sketch of a distorted periodic potential energy surface caused by an attractive adatom-adatom interaction potential is shown in
3.4. ADATOM-ADATOM INTERACTIONS

If the behaviour of the adatoms as they move on such a potential energy surface can be monitored, information on the adatom-adatom potential can be derived. Previously, a number of experiments relying on the FIM to resolve the individual adatoms have been carried out. These experiments can be divided into two classes, referred to as equilibrium and kinetic experiments. Extensive reviews of such experiments are given by Kellogg [4] and Tsong [85], here we sketch the methods and mention some important results.

Equilibrium experiments

These types of experiments rely on the fact that at equilibrium the probability, $P(r)$, of finding two adatoms in adsorption sites of a given separation $r$ is weighted by a Boltzmann factor in the adatom-adatom interaction potential, $U(r)$, and thus

$$P(r) = CP_0(r) \exp(-U(r)/k_BT),$$  \hspace{1cm} (3.11)

where $C$ is a normalization constant and $P_0(r)$ is a geometric factor that takes into account the probability of finding the adatoms at separation $r$ in the absence of adatom-adatom interactions. Experiments of this type consist of observing the relative positions of a pair of adatoms a large number of times following intermittent heating intervals to the temperature $T$ during which the adatoms are allowed to "equilibrate", that is perform a reasonably large [86] number of jumps between different sites. In practice, this procedure is greatly helped by the fact that during the "equilibration" intervals the adatoms are confined to a small terrace on the FIM tip by the step-edge (Schwoebel) barrier at the terrace edge and do therefore move on a fairly limited number of sites. From the probabilities of observing adatoms at given separations, values for the adatom-adatom potential can be derived from the relation (3.11) taking due account of the geometric coefficients $P_0(r)$ for the particular terrace under consideration.

Experiments utilizing this procedure have centred on a number of adatom pairs adsorbed on the W(110) surface. This surface has a semi-hexagonal structure with a large density of possible adsorption sites allowing adatom-adatom interactions to be probed at many different distances.

Casanova and Tsong have investigated the behaviour of Re-Re, W-Re, W-Ir, and Ir-Ir [87,88] focusing on the radial distribution function for these adatom pairs, i.e. ignoring any directional dependence of the interaction. Except for the Re-Re pair which appear to repel each other, the general trends observed from these studies are an attractive interaction at closest
separation with a dimer binding energy below 0.1 eV (eg. 82.0 ± 2.5 meV for Ir₂) followed by a slightly repulsive interaction at larger distances and some indication of a weak oscillatory behaviour in the interaction potential out to distances of ~20-30 Å.

By mapping the sites visited by a Pd adatom when moving in the vicinity of a stationary W or Re adatom placed at the centre of the W(110) terrace, Watanabe and Ehrlich have later extended this type of study [89,86] beyond the assumption of isotropic interactions, demonstrating that there can be a strong directional dependence to the adatom-adatom interaction, which in this case was found to be primarily attractive along one direction and repulsive along others.

**Kinetic experiments**

In kinetic experiments, the rate of change of an adatom between different adsorption sites is observed, and this quantity is subsequently related to the corresponding activation barriers through a simple Arrhenius dependence. From an experimental point of view, the difference compared to the equilibrium experiments is that in the kinetic case sampling is done more often, allowing one to resolve what occurs during the “equilibration intervals”. In principle, kinetic experiments may therefore provide additional information, compared to equilibrium experiments, on the dynamic behaviour of the adatoms and may allow one to determine not only the adatom-adatom interaction at the adsorption sites but also how the potential energy surface is modified at the saddle points passed by an adatom as it makes transitions between these adsorption sites. In reality, however, the kinetic approach has been pursued to a fairly limited degree due to the fact that this type of experiment becomes complicated if information on adatom-adatom interactions beyond the nearest neighbour distance is desired.

The most extensive experiments on adatom-adatom interactions by the kinetic approach were performed very early by Basset and co-workers [90] for a number of transition metal dimers (Ta, W, Re, Ir, Pt) adsorbed on the W(110) surface. These experiments in fact constitute the first direct determination of the strength of adatom-adatom interactions. By recording the number of heating cycles at a given temperature necessary to dissociate a dimer, the dimer lifetime, τ, was deduced, and the dimer binding energy E_b was then derived from the relation

\[
\frac{1}{\tau} = \nu \exp[-(E_d + E_b)/k_B T],
\]

(3.12)
assuming a reasonable value for the prefactor $\nu$ and using a diffusion barrier, $E_b$, determined in an independent experiment.

The binding energies derived from these early experiments for dimers on W(110) are endowed with a considerable uncertainty due to limited statistics, but range from $0$ (Re) to $0.6$ eV (Ta), being e.g. $0.3 \pm 0.1$ eV for W$_2$ and $0.15 \pm 0.05$ eV for Pt$_2$ [90,85].

The magnitude of the dimer binding energy

On the basis of the fact that an atom situated in the bulk of an fcc crystal has 12 nearest neighbours or, equivalently, that there are 6 “bonds” per atom in the bulk, one would naively assume that the energy required to break the bond between the two adatoms in a dimer should amount to, or at least be roughly of the order of, 1/6 of the cohesive energy per atom for the corresponding material\textsuperscript{15}. The surprising result derived from experiments of the type described above is that the energy required to separate an adatom dimer into two adatoms adsorbed on the surface is in general considerably smaller than this estimate. For Ir for instance, the cohesive energy per bond is 1.16 eV while $E_b$ for an Ir$_2$ dimer on W(110) is determined to be only $0.082$ eV [88]. Similarly a value of $E_b = 0.285 \pm 0.018$ eV is determined for W$_2$ on W(110) [91] while the cohesive energy of W is 2.18 eV per bond.

The question of the weak adatom-adatom separation energy has been addressed by Feibelman in total-energy ab-initio calculations for Al pairs adsorbed on Al(100) [92]. For Al, the cohesive energy per bond is 0.556 eV, yet the calculations predict the dimer binding energy in the Al/Al(100) system to be only 0.07 eV, i.e. a result in line with the experimental findings for the more complicated case of transition metals on W surfaces. The work by Feibelman explains the weak dimer dissociation energy as a result of the interaction of the adatoms with the surface and the corresponding bond-order-bond-length correlation. An atom in the Al adatom dimer has five nearest neighbours and its bonds to the surface are therefore weaker than those of an isolated adatom for which the number of nearest neighbours is only four. Thus, as a dimer dissociates, the electrons that participated in the adatom-adatom bond reallocate and strengthen the adatom-surface bonds, which become shorter. As a consequence, the energy cost of breaking the adatom-adatom bond in the dimer is compensated by the energy gained when the now isolated adatoms move closer.

\textsuperscript{15}In bcc crystals, as Fe and W, there are 8 nearest neighbours or 4 “bonds” per atom.
towards and rebond to the surface, providing an explanation for the low value for the dimer binding energy.

**Dissociation of Pt dimers on Pt(110)**

In chapter 6 of this thesis, we present an STM based study of the dissociation and formation dynamics of Pt dimers situated in the missing-row troughs of the Pt(110)-(1×2) surface. The dimer kinetics is monitored using STM movies. The movies are acquired with a time-separation between images that is at least comparable to, and often considerably shorter than, the mean dissociation time for the adatom dimers. Since the adatom dynamics can thus be followed almost directly from these movies, the STM-data acquired in this way is well suited for analysis by the kinetic approach\(^{16}\). The attraction in kinetic experiments compared to those of the equilibrium type is that the direct observation of the adatom dynamics allows one to probe also the saddle points on the potential energy surface that separate the adsorption sites.

In the experiments on dimer dynamics in the Pt/Pt(110) system, we quantify not only the kinetics of dimer dissociation, but investigate also dimer association, i.e. the process where a dimer is formed from a pair of adatoms separated by an empty lattice site. The observations of dimer association kinetics suggest that the potential energy surface is reduced at the saddle point passed during dimer dissociation or association. Since such a saddle point reduction has implications for the joint dynamic behaviour of the two adatoms constituting the dimer, the finding is of principal interest in the context of dimer mobility.

The central result from the investigation of dimer dissociation/association kinetics is an evaluation of the dimer binding energy for a Pt dimer situated in the missing row troughs. For this quantity, a value of \(E_b = 0.07 \text{ eV}\) is determined. This fairly low value is in line with the general trend from the previous determinations by direct methods of binding energies for dimers adsorbed on W surfaces.

From the dynamic STM observations, it is furthermore found that

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\(^{16}\)Performing experiments of the equilibrium type in this system is hampered by the fact that after a few "equilibration intervals", the two adatoms whose interactions one wishes to study have simply diffused away from each other. In this particular respect, the limited terrace size with reflecting edge-barriers found in FIM experiments is actually advantageous over the extended terraces monitored with STM. Tricks could be envisioned for circumventing this problem, however, such as studying the behaviour of adatoms on a limited number of sites in a missing-row trough where they could be confined by two adatom islands, but this has not been pursued.
longer adatom chains in the missing-row troughs, trimers and above, are considerably more stable towards dissociation compared to dimers.

3.4.2 The nucleation and growth approach

Nucleation and growth experiments provide, through the concept of a critical island size, a different means from the direct experiments described above of obtaining information on the binding strength in dimers and small clusters.

As alluded to in an earlier section, there has been some criticism by Feibelman [66] of bond energies derived by this approach in the Fe/Fe(100) case [64]. The argument is based on the assumption that cluster binding energies should scale as the corresponding bulk cohesive energies. With this expectation the derived bond-energy for an Fe-Fe bond of $\sim 0.5$ eV seems unreasonably large compared to the binding energy determined from FIM experiments for a W dimer on W(110) of 0.285 eV since the cohesive energy for Fe (4.3 eV/atom) is only half of that for W (8.7 eV/atom) (furthermore, adjacent adatoms on a bcc(100) surface are not even nearest neighbours).

The nucleation and growth approach based on the scaling law (3.4) requires that the critical island size is larger than $i = 1$ in order for the binding energy in the critical cluster to be determined, and in that case the dimer binding energy and the diffusion barrier have to be separated. Thus, the bond energy for Fe mentioned above is derived by Strucic and Pierce [64] from the Arrhenius slope for the island density, $N_d$, in the $i = 3$ regime using a diffusion barrier determined at lower temperatures in the $i = 1$ regime to disentangle the contribution from $E_d$ and $E_a$ (and assuming a nearest-neighbour pair-bonding model to obtain the bond-energy as $E_a/2$). Accordingly, the assumption that the diffusion barrier for Fe/Fe(100) is the same in the high-$T$ regime as that determined in the low-$T$ regime is questioned by Feibelman, who suggests that two different diffusion mechanisms with different barriers and different prefactors, allowing for a cross over between the two mechanisms in going from low to high $T$, could produce a more satisfactory binding energy. Thus, if e.g. a diffusion mechanism with a barrier of 0.8 eV prevailed at the higher temperatures, a binding energy of 25 meV would result.

However, the case of Fe/Fe(100) does not seem to be an isolated case where bond energies derived from nucleation and growth experiments are larger than the typical values of a few tenths of an eV determined by more direct methods from FIM experiments of the type described above. Thus,
recently a bond-energy of 0.46±0.19 eV for the Cu-Cu bond in a Cu trimer on Ni(100) was determined by Müller et al. [24] in a similar fashion as for the Fe case, but from a considerably larger dataset.

The requirement of \( i > 1 \) for bond energies to be accessible from nucleation and growth measurements is perfectly reasonable since in the \( i = 1 \) case bond-breaking does not occur to a significant degree. Observation of \( i = 1 \) behaviour in a deposition experiment at a given temperature and with a given deposition rate, however, should enable one to place a lower bound on the dimer lifetime, and consequently through (3.12) on the dimer dissociation energy. In the \( i = 1 \) case, it is usually stated that “dimers are more likely to grow than to decay” and “dimer formation is irreversible at the time-scale of the deposition experiment”. It is not entirely clear how such notions should be quantified in a requirement for the dimer lifetime. Based on the fact that most nucleation occurs during the early stages of deposition, however, it is probably sufficient for \( i = 1 \) behaviour to occur that the dimer lifetime is a small fraction of the deposition time.

Motivated by these considerations, we can attempt at estimating dimer binding energies from nucleation and growth experiments in the \( i = 1 \) regime based on the relation (3.12), taking the dimer lifetimes, \( \tau \), to be (rather arbitrarily\(^\text{17}\)) \( 1/10 \) of the deposition time and assuming an attempt frequency of \( \nu = 10^{12} \text{ sec}^{-1} \).

In the cases of Fe/Fe(100) [64] and Cu/Ni(100) [24], well-defined transitions from \( i = 1 \) to \( i = 3 \) have been identified, and the maximum temperature where \( i = 1 \) holds is therefore known. For the Fe case, the transition occurs at \( \sim 520 \text{ K} \), the deposition time is 6 seconds and \( E_d = 0.45 \text{ eV} \). From (3.12) this yields \( E_b = 0.76 ± 0.1 \text{ eV} \), where the stated error bar corresponds to one order of magnitude variation in the product \( \tau \nu \) and should be viewed mainly as an indication of the sensitivity to the assumptions stated above for these two quantities. Correspondingly for the Cu/Ni(100) case, \( i = 1 \) up to 320 K, \( E_d = 0.35 \text{ eV} \) and the deposition time is 74 seconds, yielding \( E_b = 0.46 ± 0.07 \text{ eV} \). These estimates for \( E_b \) are in fair agreement with the bond-energies stated earlier, which were derived in the \( i = 3 \) regime, giving some confidence to the crude method. Especially, the result for Fe seems to rule out the suggestion by Feibelman that the determined large value for the bond energy originates from erroneously applying the diffusion barrier obtained in the \( i = 1 \) regime to extract the binding energy in the \( i = 3 \) regime at higher temperatures.

\(^{17}\)This is clearly a zeroth order approximation. It could be improved by considering the interplay between the deposition rate and the adatom diffusion rate. K. Jacobsen is thanked for pointing this out.
3.4. ADATOM-ADATOM INTERACTIONS

We now move on to consider two cases where \( \dot{i} = 1 \) behaviour has persisted up to the highest temperatures investigated. For Pt homoepitaxy on Pt(111), data published by Bott et al [68] indicate that \( \dot{i} = 1 \) at least up to \( \sim 250 \) K. The diffusion barrier in this case is \( E_d = 0.26 \) eV. The deposition times are not provided in [68], but if we assume 60 seconds, a lower bound on the dimer binding energy of \( E_b \geq 0.37 \pm 0.05 \) eV is obtained. Finally, for the case of Pt/Pt(100)-hex, which is described in this thesis, we find that \( i = 1 \) at least up to 497 K, the maximum deposition time is 1800 seconds and \( E_d = 0.43 \) eV. With these values a very large binding energy of \( E_b \geq 1.0 \pm 0.15 \) eV is obtained.

The discussion above shows that nucleation and growth measurements in several cases seem to suggest higher values for the bond strength in adatom-adatom pairs than the direct FIM measurements (an extensive review of bond-energies derived from STM data is given by Bartelt et al. in [93]). The origin of this difference is at present unclear. Two suggestions seem to be possible. First, the previous interpretation of \( \dot{i} = 1 \) behaviour in terms of a dimer lifetime roughly an order of magnitude lower than the deposition period could be incorrect, and a much shorter lifetime could be sufficient to ensure \( \dot{i} = 1 \) behaviour in eg island density scaling or size-distributions. With regard to the fact that the crude method gave some agreement with binding energies derived from the \( \dot{i} = 3 \) regime, it is worth remarking that the extraction of binding energies from the scaling law (scalaw) in the \( \dot{i} > 1 \) regime is hinged on the quasi-equilibrium Walton relation (walton). Whether the assumptions underlying this relation are fulfilled in the growth experiments, and thereby how well this method of determining binding energies works quantitatively, has to the present authors’ knowledge not been tested eg in simulations. Secondly, it is worth noting that the explanation by Felbelman for the low values for dimer binding energy stresses the importance of the adatom-surface interaction, and the previous FIM experiments on adatom-adatom interactions have all been carried out on surfaces of W. Measurements by direct methods of binding energies for dimers adsorbed on a wider variety of substrates especially those used in the nucleation and growth experiments is therefore evidently desirable.

The measurement reported in chapter 6 of the binding energy of a Pt dimer in the missing row troughs of the Pt(100)-(1x2) surface is in line with the previous FIM results. Very recently the Pt/Pt(111) system has been investigated by FIM by Ehrlich and co-workers [33]. These authors mention that Pt dimers are stable on this surface up to at least 210 K (without reporting a time-scale, however). This result suggests a larger
dimer binding energy for the Pt dimer on this surface, close to the one estimated above from the nucleation and growth measurements of Bott et al. in the Pt/Pt(111) system.

3.4.3 The nucleation and growth approach for Pt/Pt(110)

Using the nucleation and growth approach in the Pt/Pt(110) system could in principle be interesting from two perspectives. First, motivated by the discussion above, it would be interesting to elucidate what result for the critical island size one would obtain from this method of investigation given that a value for the dimer binding energy is determined beforehand and dimers and longer adatom chains are in addition known to have very different stability. Secondly, in relation to the discussion of the scaling parameter \( \chi \) in the 1-D and 2-D cases presented in chapter 4, the Pt(110) surface could be believed to constitute a completely 1-D system far simpler than the anisotropic Pt(100)-hex surface.

Certain problems seem to be associated with using the traditional nucleation and growth approach in the Pt/Pt(110) system, however. The scaling law (scalaw) is, as mentioned, only strictly valid in the limit where the ratio \( h/R \) between adatom hopping and deposition rate becomes very large. This is especially important in the anisotropic case as discussed in chapter 4, where it is shown how the scaling parameter \( \chi \) only converges towards its asymptotic value for \( h/R \sim 10^9 \). In the Pt/Pt(110) system at the temperatures investigated, this situation is not at all realized. With a hopping rate on the order of \( h = 1 \text{ sec}^{-1} \) and a deposition time of 10 seconds to deposit a coverage of 10% of the available sites, \( h/R \sim 10^2 \) results, i.e. a fundamentally different regime. Clearly, one could attempt investigating the system at higher temperatures. However, as shown in chapter 7, where island mobility and coarsening in this system are discussed, the dynamic evolution of the system becomes quite complicated at higher coverages even when the temperature is increased merely to \( \sim 400 \text{ K} \). It is therefore doubtful that the Pt/Pt(110)-(1 \times 2) system can be used as a simple test-case of the traditional nucleation and growth method.

References


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Chapter 4

Pt/Pt(100)-hex: Nucleation and growth

The present chapter describes the investigation of sub-monolayer nucleation and growth in the Pt/Pt(100)-hex system. The chapter is identical to the submitted version of the paper (II) (except for the omission of one figure). In this respect it should be remarked that the results reported in this chapter represent a collaboration between experiment and theory.
4.1 Introduction

Nucleation and growth during metal-on-metal deposition have been studied for decades both experimentally and theoretically. From a fundamental point of view, this interest follows from a desire to understand the underlying microscopic processes such as the diffusion of adatoms on terraces and across steps, the nucleation caused by the formation of bonds between adatoms, and the subsequent growth and coalescence of islands. A quantitative understanding of such processes may prove rewarding also from a more applied point of view, since presently a large effort is being devoted to growing thin films with novel physical and chemical properties. This goal may be better accomplished with an increased ability to control the growth conditions.

Fundamental nucleation and growth studies are typically carried out at such low substrate temperatures that re-evaporation of deposited atoms is negligible. In that case, the following general picture describes the events occurring on the surface [1–4].

The deposition of adatoms from the vapor phase drives the system to a non-equilibrium supersaturated state with a high adatom density. This facilitates the random encounter of adatoms diffusing on the ideally flat and defect-free substrate, leading to the formation of small clusters. The stability of these clusters depends on the temperature and their binding energy. Usually a sharp critical island size $i$ is assumed, where $i + 1$ is the size of the smallest cluster that is stable on the time-scale of the deposition period. This means that if, e.g., $i = 2$, a dimer tends to dissociate whereas a trimer does not.

Following the initial formation of a few nuclei, a competition for the adatoms sets in since these may now be lost either to the growth of the existing nuclei into larger islands or to new nucleation events. In this nucleation and growth regime, the island density $N_i$ increases with coverage. Since adatoms deposited close to existing islands are most likely accommodated into these before other adatoms with which they can nucleate arrive from the vapor, the nucleation probability is diminished in the vicinity of existing islands. This effect leads to correlations in the island positions and causes the island density to saturate when the mean island-island distance becomes equal to a characteristic length determined by the adatom mobility and the deposition rate. When the islands have grown to a size comparable to the island-island separation distance, coalescence sets in and the island density decreases.

The surface morphology resulting from a nucleation and growth sce-
4.1. INTRODUCTION

nario, as described above, is to a high degree controlled by kinetic effects and therefore reflects the rates of the different processes involved; the rates again being determined by activation barriers and the substrate temperature. Quantitative information about the involved processes can thus be deduced from systematic observation of the surface morphology resulting from nucleation and growth experiments with different deposition rates $R$ and substrate temperatures $T$ followed by comparison to the predictions derived from mean-field rate-equations and/or kinetic Monte Carlo (KMC) simulations. Of particular importance in this respect is the existence of simple scaling laws relating the variation in island density $N_z$ with $R$ and $T$ to, e.g., the activation barrier for surface diffusion $E_d$ and the critical island size $i$ [1–4]. Recently, there has also been a prediction from KMC simulations of a scaling behavior in the island size distribution allowing for the extraction of a universal scaling-function, the shape of which depends on the atomistic processes occurring during nucleation and growth [3,5].

Quantitative nucleation and growth studies have over the last years attracted considerable attention since it has become possible with unprecedented real space resolution to study the surface morphology by means of Scanning Tunneling Microscopy (STM). One of the great advantages of STM in this respect is the large dynamic range for spatial resolution from the atomic scale up to several micrometers. The atomic-scale resolution is important for directly revealing aspects of the growth kinetics reflected in the shapes and detailed atomic structure of the islands, such as whether they are compact/fractal or reconstructed/unreconstructed. Scans over larger regions, on the contrary, give information on island density, island sizes, island-island correlations, influence of defects, and steps on nucleation, etc. An alternative means of data-acquisition is provided by diffraction techniques (RHEED [6], SPA-LEED [7], and He atom scattering [8]). The average nature of these techniques implies that the time-consuming work involved in collecting sufficient statistics with STM can be avoided, but at the same time means that also areas with defects and steps are included. Furthermore, the interpretation of data acquired with these techniques is far less straightforward than with STM.

For simple isotropic surfaces, the last few years have yielded a considerable improvement in the understanding of nucleation and growth for homoepitaxial systems (e.g., Fe/Fe(100) [9], Cu/Cu(100) [7], and Pt/Pt(111) [10]) as well as heteroepitaxial (e.g., Cu/Ni(100) [11] and Ag/Pt(111) [12]). The scaling relations for $N_z$ resulting from mean-field nucleation and growth theories have been verified on the atomic scale, allowing for the determination of activation energies for surface diffusion and critical
island sizes \[9,11,13,14\]. Variations with temperature in the critical island size have been observed \[9,11,13\] and has been directly determined from a comparison of island sizes and coverage in the small island regime \[12\]. The predicted scaling of the island size distribution has been confirmed experimentally \[9\], and correlations in island positions have been revealed with STM \[9\] as well as SPA-LEED \[7\].

For anisotropic surfaces, where the surface diffusion is expected to be anisotropic, the number of experimental investigations is on the contrary still fairly limited.

Kern and co-workers have studied Cu on Pd(110) \[15,16\]. With respect to homoepitaxial systems, measurements of Au/Au(100)-hex have been reported by Behm and co-workers \[17,18\] and Si/Si(001) has been investigated by Mo et al. \[19\].

On the theoretical side, a scaling relation for \(N_x\) has been derived by Bartelt and Evans from a mean-field rate-equation treatment of the case of infinitely anisotropic (i.e., strictly one-dimensional, or 1-D) diffusion and point-islands \[3,20\]. However, it is unclear what importance it would have if the surface diffusivity is only moderately anisotropic. The consequences of having islands of a finite width comparable to the extent of the fast diffusion channel have not been investigated. In this latter case, one may expect the islands to block an increasing number of diffusion channels as they grow, thereby reducing the nucleation probability by capturing an increasing number of adatoms. It is also natural to ask how a diffusional anisotropy affects the correlations in island positions and what the consequences are for the shape and scaling of the island size distribution. Furthermore, not only the terrace diffusion of the adatoms but also the sticking of diffusing adatoms to already existing islands and island edge diffusion may be anisotropic, and it may be difficult \textit{a priori} to discern these effects.

The purpose of the present work is to investigate such questions through an experimental study of the homoepitaxial nucleation and growth on an anisotropic surface, Pt(100)-hex, combined with KMC simulations and rate-equation theory incorporating anisotropic diffusion and finite island sizes.

The Pt(100)-hex surface exhibits a fairly complicated reconstruction in which a topmost quasi-hexagonal close-packed (111) layer rests on top of the quadratic (100) bulk truncation \[21\]. The resulting Moiré pattern gives rise to a large-scale anisotropic height modulation with six atom wide "channels" on the surface running along a close-packed direction of the substrate. Diffusion, nucleation, and growth on this surface is interesting in
4.1. INTRODUCTION

several respects. Since the Pt atoms in the topmost layer have a hexagonal isotropic arrangement, one might intuitively have anticipated the diffusion of Pt adatoms to be isotropic. However, as will be shown below, the large-scale height modulation does in fact lead to strong anisotropic effects in the Pt adatom diffusion. Furthermore, the hex-reconstruction is known to be lifted by the adsorption of various reactive atoms and molecules [22–24]. Thus a natural question to raise is if a supersaturated lattice gas of Pt adatoms will lift the Pt(100)-hex reconstruction as well.

By means of STM, the positions, sizes, and densities of Pt islands formed in the monolayer coverage regime have been determined over a wide range of deposition temperatures and rates. These experimental data are compared to the results of KMC simulations in a simple model incorporating anisotropic diffusion and finite island sizes.

An autocorrelation analysis of the experimentally determined island positions reveals that the islands are anisotropically distributed. This observation allows us to quantify the degree of anisotropy in the surface diffusivity of Pt adatoms.

The island size distributions obtained for different deposition conditions are found to collapse onto a single scaling curve, also in the present case of strongly anisotropic diffusion. By comparing this curve to the results of simulations, the anisotropy in diffusion is seen to imply a surprisingly early onset of coalescence. Furthermore, it is shown that the critical island size is \( i = 1 \), i.e., the dimer is stable towards dissociation, and that the mobility of these dimers is negligible compared to that of the adatoms.

From the scaling of the saturation island density \( N_z \) with \( R \) and \( T \), an effective barrier for Pt adatom diffusion of \( E_d = 0.43 \) eV is determined. The observed scaling of \( N_z \) with \( R \) is found to be in agreement with the prediction of Bartelt and Evans for the case of point-islands and 1-D diffusion [3]. This result, however, is shown to be partly coincidental, and a detailed theoretical investigation of the scaling expected for systems with moderate diffusional anisotropies and finite island sizes is presented. If the finite extent of the different islands is taken into account, it is shown that the obtained scaling differs from the scaling in a point-island model.

In the following, we first present the experimental data and subsequently discuss these in relation to the results of our theoretical investigations. Part of this work has previously been presented briefly in letter form [25]. Results for nucleation and growth of Au on Au(100)-hex, which have some similarities to the system Pt/Pt(100)-hex studied in the present work, have been reported by Behm and co-workers [17,18].
4.2 STM Experiments

4.2.1 Experimental details

The experiments were performed in an ultra-high-vacuum (UHV) system equipped with a compact, stable STM, the prototype for the Rasterscope UHV-STM [26], as well as standard facilities for sample cleaning and characterization. The experimental set-up is described in detail elsewhere [27].

The Pt(100) crystal was spark cut from a single crystal rod, mechanically polished with diamond paste down to 1 μm, and subsequently electropolished in a solution of H$_2$SO$_4$, H$_3$PO$_4$, and HNO$_3$. After insertion into the UHV chamber, initial crystal cleaning consisted of Ne sputtering at 1.2 keV followed by prolonged heating in vacuum at 1300 K and in an atmosphere of $10^{-7}$ Torr of oxygen at 1000 K. After repeated cycles of this procedure, the surface was clean as determined by Auger electron spectroscopy, LEED, and atomically resolved STM images. Day-to-day cleaning consisted of 1.2 kV Ne sputtering followed by annealing at 970 K. This led to large terraces with a width of several thousand Ångström.

The Pt evaporation was performed by passing current through a 0.4 mm diameter Pt wire wound to a small coil to ensure a homogeneous heating. The sample was heated by electron bombardment from the back, and the temperature during deposition was measured by a thermocouple mounted directly to the back of the sample, implying an accurate temperature determination.

After Pt deposition, the Pt(100) sample was cooled to room temperature within minutes and transferred to the STM. All the STM images were acquired at room temperature. The Pt evaporation rate was determined from the evaporation time, precisely controlled by a shutter, and from the deposited coverage as determined from the STM images. The experiments were performed at a fixed coverage of $\theta = 0.075 \pm 0.016$ monolayers [28]. The Pt depositions were performed at five temperatures between 318 K and 497 K. At each temperature, several rates were used, corresponding to deposition periods ranging from 10 to 1800 sec.

For each set of deposition parameters ($T$, $R$), approximately 2000 individual islands on large step-free terraces were analyzed. A software routine was developed which could automatically analyze the STM images for number of islands as well as find, for each individual island, its area and the coordinates of its center of gravity.
4.2. STM EXPERIMENTS

4.2.2 The Pt(100)-hex surface

Together with Au and Ir, Pt belongs to the class of late 5d fcc metals, the clean (100) surfaces which reconstruct by forming a close-packed quasihexagonal (111) layer on top of the quadratic (100) bulk truncation [21,29]. These "hex" reconstructions have been studied extensively by diffraction techniques [21,30–34].

Figure 4.1(a) depicts an atomically resolved STM image of the Pt(100)-hex surface. The structure in the topmost layer is clearly seen to be hexagonal, superposed however, with a large-scale height modulation. The origin of this height modulation can be understood by considering the schematic ball-model depicted in fig. 4.1(c). Here, a hexagonal topmost layer is placed on top of a substrate layer of quadratic symmetry and oriented such that there is alignment between a close-packed direction in the hexagonal layer and the close-packed [1\bar{1}0] direction in the substrate. In the model, the hexagonal layer is isotropically contracted with a 3.8% reduction in nearest neighbor distance compared to the bulk value (2.78 Å for Pt). This contraction allows for a perfect commensurability along the [110] direction, where six close-packed rows of the topmost hexagonal layer fit over five close-packed rows of the underlying square substrate. Along the [\bar{1}0] direction, the isotropic contraction in the topmost layer does not lead to commensurability, but an approximate matching exists for every \approx 26 top-layer lattice spacings, or equivalently for every 25 atoms in the quadratic layer below. For this reason, the reconstruction has often been referred to as (5 \times 25) [21]. Due to the contraction, the topmost quasihexagonal layer accommodates \approx 25% more atoms than the underlying (100) layer (compared to the 15.5% excess density in an uncontracted (111) layer).

A comparison to the STM image in fig. 4.1(a) reveals that the model accounts qualitatively for the hex-reconstruction if the height modulation is ascribed to a simple geometric distortion caused by the misfit between the two layers. The periodicity along the [110] direction is very distinct in the STM image, whereas the lack of matching in the [\bar{1}0] direction causes slight fluctuations in the periodicity along this direction, something even more clearly revealed in larger-scale images which are not shown here.

The hex-reconstruction of Pt(100) causes the surface morphology to be highly anisotropic. Qualitatively this can be described in terms of channels running along the [1\bar{1}0] direction, each channel consisting of 6 close-packed rows of the quasihexagonal layer. In the following, the [1\bar{1}0] direction will be referred to as the direction of the reconstruction channels. In fig. 4.1(b) are shown the corrugation amplitudes as measured from the STM image...
Figure 4.1: (a) Atomically resolved STM topograph of the Pt(100)-hex surface ($180 \times 190 \, \text{Å}^2$). The "reconstruction channels" referred to in the text run parallel to the line (iii). The corrugation measured along the lines marked (i)–(iii) is shown in (b). A hard-ball model to account for the height-modulation seen in the STM topograph is depicted in (c). The model assumes that a hexagonal layer (filled circles) which is isotropically contracted by a factor $\frac{5}{(3\sqrt{3})}$ reduction in nearest-neighbour distance is placed on top of an unperturbed quadratic layer (indicated by empty circles). The hex-layer is oriented with a close-packed direction along the [1\overline{1}0] direction of the substrate. In this case the isotropic contraction ensures that there is commensurability along the [1\overline{1}0] direction where 6 rows of the hex-layer fit over 5 rows of the substrate. The height above the substrate of the atoms in the hex-layer is calculated assuming hard-ball stacking and the filled circles representing these atoms are gray-shaded accordingly. The dark atoms at the corners of the shown approximate ($5 \times 25$) unit cell are placed at four-fold hollow positions of the quadratic layer. The area of the surface to be compared to the ball-model within the approximate ($5 \times 25$) unit cell is marked by the white rectangle in (a).
along the lines (i)–(iii) in fig. 4.1(a), parallel and perpendicularly to the reconstruction channels.

One of the central aims of this investigation is to illuminate how the anisotropic surface morphology affects the diffusion of Pt adatoms on the Pt(100)-hex surface. It is clear from the STM image in fig. 4.1(a) that the detailed diffusional properties will be highly complex since all transitions between adsorption sites will occur in slightly different environments and therefore, presumably, with different activation barriers for diffusion. As will be shown below, the diffusion is found to be highly anisotropic, occurring preferentially along the reconstruction channels.

In addition to the Pt(100)-hex structure described above, LEED studies have revealed the existence of a slightly different reconstructed phase, referred to as Pt(100)-hex-R(0.7°) [31]. This structure forms when the crystal is annealed to temperatures above ∼1100 K. The Pt(100)-hex-R(0.7°) structure is believed to have a similar quasihexagonal topmost layer, but in this case with the close-packed direction of the hexagonal topmost Pt layer rotated by 0.7° away from the closed-packed [1T0] direction of the substrate. STM images of the Pt(100)-hex-R(0.7°) phase acquired in the present study do indeed reveal a Moiré pattern which is distinctly different from that of the Pt(100)-hex phase and which can be accounted for by such a 0.7° rotation. In the present study, Pt evaporation was performed on the Pt(100)-hex phase exclusively.

4.2.3 Island morphology

Deposition of a submonolayer amount of Pt on the Pt(100)-hex surface results in the formation of monoatomic islands as shown in fig. 4.2(a) and (b). The island shape depends on the temperature during deposition. For the higher temperatures used, regular rectangular islands are formed whereas the shape is somewhat more irregular while still compact for the lowest temperature.

The Pt islands are observed to exhibit the same characteristic height modulation as the reconstructed Pt(100)-hex surface, implying that the islands are also reconstructed. This is confirmed by atomically resolved images as shown in fig. 4.2(c). Occasionally, part of an island close to its perimeter is not hex-reconstructed, and the atoms there assume a quadratic, (1×1), arrangement. This suggests that the reconstruction is lifted under the islands, which are assumed to be resting on a (1×1) inclusion in the hex-layer [35]. We observe that the ridges of the reconstruction channels on the islands predominantly end at the troughs of the channels
Figure 4.2: STM topographs showing monoatomically high Pt islands formed after deposition of \(~0.07\) ML of Pt on the Pt(100)-hex surface. (a) Irregular but compact islands obtained at the lowest deposition temperature of \(T = 318\) K. The islands are reconstructed. \((R = 3.2 \times 10^{-4}\) site\(^{-1}\) sec\(^{-1}\), \(930 \times 960\) Å\(^2\)). (b) Rectangular islands obtained by deposition at \(T = 389\) K \((R = 3.2 \times 10^{-5}\) site\(^{-1}\) sec\(^{-1}\), \(930 \times 960\) Å\(^2\)). The height-modulation caused by the hex-reconstruction (the reconstruction channels) is seen at the substrate as well as on top of the islands. The islands are oriented with their long edge parallel to the direction of the reconstruction channels. In the small darker areas at the boundary of some of the islands, the atoms assume a quadratic \((1 \times 1)\) arrangement. The reconstruction of the islands is clearly revealed in (c), where the edge of an island is depicted with atomic resolution \((90 \times 90\) Å\(^2\)).
4.2. STM EXPERIMENTS

on the substrate. If the height modulation is due to a geometric effect, this would not occur if the islands were resting on an unperturbed hex-layer since the opposite relation is then expected. The observed correlation between the hex-reconstruction on top of the islands and in the surrounding substrate may be established at the island edges during the growth of the islands as the reconstruction is lifted under the islands.

The observations described here indicate a pronounced restructuring during the growth of an island, involving rapid edge diffusion and inter-layer mass transport to expel the excess atoms under the islands. The regular rectangular shape with an aspect ratio (length/width) \( \sim 1-2 \) and the orientation of the islands with the long edges parallel to the direction of the reconstruction rows reflect both the kinetics of island growth and restructuring as well as edge-energies and the energies of the misfit-boundaries under the island [35].

4.2.4 Correlation among island positions

In the following, we will investigate the spatial correlation among the island positions. STM images, as shown in fig. 4.3(a), reveal regions in the vicinity of step edges with a reduced island density. Such depleted regions, often referred to as denuded zones [2,19], occur because the step-edge acts as a sink for adatoms, thereby reducing the nucleation probability close to the step. A comparison of images (a) and (b) of fig. 4.3, which depict steps perpendicular and parallel to the reconstruction channels, respectively, reveals that denuded zones exist on both the upper and lower terraces for the former case, whereas no island depletion is visible on either of the adjoining terraces for steps running parallel to the rows. The observation of a denuded zone on the upper terrace side of a perpendicular step is evidence that an adatom can descend the step and become incorporated at the step-edge.

The asymmetry in the widths of denuded zones for steps along orthogonal directions shows that the adatom depletion is only effective for steps perpendicular to the reconstruction channels. This suggests that diffusion occurs preferentially along the reconstruction channels rather than across them.

Let us for a moment consider the consequences of an anisotropic surface diffusion for the correlations among island positions. If the nucleation probability in the vicinity of an existing island is diminished in a region which is elongated along the direction of fast diffusion, the islands are expected to be distributed with long/short correlation lengths parallel and
perpendicularly to this direction, respectively.

To investigate this, we have performed an autocorrelation analysis of the island positions. From all the determined island positions corresponding to a single set of deposition parameters \((R,T)\), an autocorrelation function is obtained as a two-dimensional histogram over the inter-island vectors. An example of such an autocorrelation plot is shown in fig. 4.4 together with one of the \(\sim 25\) STM images from which it has been derived. The autocorrelation plot clearly reveals a strong anisotropy in the spatial distribution of the Pt islands. The common origin, from which all inter-island vectors are superposed, is in the center of the plot surrounded by a slightly elongated region void of inter-island vectors. Extending from this central region are two thin arms in which the density of inter-island vectors is also significantly reduced. As may be verified by reference to the orientation of the islands in the STM image, these arms point exactly in the direction of the reconstruction channels, thereby directly demonstrat-
4.2. STM EXPERIMENTS

Figure 4.4: Autocorrelation analysis of the island positions. All inter-island vectors as indicated in the STM-image (a) are superposed in a 2-D histogram to yield the autocorrelation function depicted in a gray-scale representation in (b). The length-scales in the image and the autocorrelation plot are identical, allowing for direct comparison. The plot is based on ~ 25 images similar to (a), all obtained for \( T = 380 \) K and \( R = 2.3 \times 10^{-4} \) site \(^{-1} \) sec \(^{-1} \). The reduced density of inter-island vectors towards the edges of the plot (b) is due to the finite image sizes. Both images are 1500 \( \times \) 1500 Å \(^2\).

In the direction perpendicular to the reconstruction channels, the distance from the origin of the plot and out to the edge of the central region, where no inter-island vectors occur, is seen to be quite comparable to the typical width of an island in the STM image. Thus, there is little or no correlation between the island positions in this direction. Islands that may have nucleated closer than what has become the island width at the coverage where the images are acquired will have coalesced. It will indeed be shown later that a significant amount of coalescence has occurred. Evaluating a correlation length in the direction along the reconstruction channels by a similar direct inspection of the plot is difficult due to the overall low density of inter-island vectors. The limited statistics occur despite the fact that the autocorrelation plot shown is based on ~ 1500 island positions. In a later section of this chapter, however, we will intro-
duce a method of integrating the autocorrelation functions, allowing us to quantify the degree of anisotropy in the island positions and to relate this to the anisotropy in adatom diffusion.

The observed asymmetry in the width of demarcated zones depicted in figs. 4.3(a) and (b) could in principle also occur if the diffusion was isotropic, but the sticking of diffusing adatoms to the two types of step-edges proved to be different [17]. It will be shown from KMC simulations, however, that no significant anisotropy in the spatial distribution of islands occurs in this case, and the autocorrelation analysis is thus a superior means of revealing anisotropy in diffusion.

4.2.5 Variation of \( N_x \) with \( R \) and \( T \)

In this section, the dependence of the saturation island density \( N_x \) on deposition rate and temperature is investigated. In fig. 4.5 are shown STM images revealing how \( N_x \) decreases with increasing \( T \) for depositions carried out at fixed \( R \), resulting in fewer and larger islands at higher temperatures. At fixed \( T \) the island density is similarly found to decrease with decreasing deposition rate. This behavior clearly shows the effects of the competition between island growth and nucleation of new islands as described in the introduction. As the adatom mobility increases with increasing temperature, existing islands can capture adatoms from a larger area. Consequently, longer island-island correlation lengths or, equivalently, a lower island density results. Similarly, new nucleation becomes less probable with decreasing \( R \) since adatoms are supplied less frequently from the vapor phase.

From mean-field rate-equation descriptions of the nucleation and growth process, the following scaling law for the variation of \( N_x \) with \( R \) and \( T \) has been derived [1-3]

\[
N_x \sim \eta(\theta) \left( \frac{R}{\nu} \right)^{\chi} \exp \left( \frac{\chi(E_a + E_b/i)}{k_B T} \right),
\]

(4.1)

where \( E_a \) and \( \nu \) are the activation barrier and prefactor for diffusion, respectively, \( k_B \) is the Boltzmann constant, and \( \eta(\theta) \) is a coverage dependent function. In the derivation of Eq. (4.1), a sharp critical island size \( i \) is assumed, meaning that a cluster consisting of \( i \) or less atoms is considered unstable on the time-scale of the deposition whereas a cluster of \( i+1 \) atoms forms a stable, immobile nucleus. \( E_b \) is the binding energy gained when \( i \) adatoms are combined to form the critical island of size \( i \). The scaling law has been derived both for isotropic [1] and infinitely anisotropic diffusion
4.2. STM EXPERIMENTS

Figure 4.5: Series of STM topographs showing how the increase in adatom mobility brought about by raising the substrate temperature during deposition leads to a lowering in the island density and a corresponding increase in the island sizes. All images are 1310 × 1350 Å² and for $R \approx 2.7 \times 10^{-4} \text{site}^{-1} \text{sec}^{-1}$. The deposition temperatures, $T$, are: (a) 318 K, (b) 389 K, (c) 439 K and (d) 497 K. The different orientations of the islands are due to rotations of the crystal between measurements. The faint lines seen on the substrate in (c) and (d) should be ignored; they are an artefact caused by interference between the pixel-resolution of the images and the height-modulation of the reconstruction.

[3] and is found to differ only in the exponent $\chi$, which is determined to be $\chi^{2-D} = i/(i + 2)$ and $\chi^{1-D} = i/(2i + 2)$, respectively. Thus, one expects $\chi^{2-D} = 1/3$ and $\chi^{1-D} = 1/4$ for $i = 1$ [20]. The exponent $\chi^{1-D}$ is derived assuming point-shaped islands. The effects of including the finite extent of the islands and finite degrees of anisotropy in diffusion will be discussed later in this chapter, where we will investigate how these factors affect the scaling exponent $\chi$.

When investigating the variation in the island density $N_2$ with $R$ and $T$, the measurements should be performed at fixed coverage to ensure that the function $\eta(\theta)$ has a constant value. This coverage should on one hand be chosen below the point where coalescence sets in since otherwise the number of islands will no longer represent individual nucleation events. On the other hand, it would be advantageous to have as high an island density as possible since this yields better statistics for a given number of acquired STM images. In practice, however, there is a gradual cross-over with increasing coverage from the nucleation and growth-regime to the regime where coalescence occurs. In the experiments, island densities have been determined at a fixed coverage of $\theta = 0.075 \pm 0.016 \text{ML}$ [28]. We shall later see that some coalescence has actually occurred at this fairly low coverage, but also that this has no consequence for the scaling of $N_2$.

Values for $N_2$ have been determined for thirteen different combinations
of rate and temperature; \( T \) is varied between 318 K and 497 K and \( R \) between \( 4 \times 10^{-5} \) site\(^{-1} \) sec\(^{-1} \) and \( 7 \times 10^{-3} \) site\(^{-1} \) sec\(^{-1} \). To convert from the measured island densities (islands/area) to islands per site, the density in the isotropically contracted topmost layer of \( 1.61 \times 10^{15} \) atoms/cm\(^2\), or equivalently an area of 6.2 Å\(^2\) per site, is used.

The typical way of presenting data for \( N_z(R, T) \) is through an Arrhenius plot for \( N_z \) versus \( 1/T \) at fixed \( R \) and a double-log plot for \( N_z \) versus \( R \) at fixed \( T \) [17]. The critical island size can in principle change to a higher value with increasing temperature, and this should be observed as a change in the \( \chi \) obtained from such plots for various temperatures. No such change is found in the present case, however, and it is therefore reasonable to merge all data onto a single plot. By fitting the data for \( N_z(R, T) \) to Eq. (4.1), we obtain \( E = E_d + E_i/i = 0.43 \pm 0.03 \) eV and \( \chi = 0.27 \pm 0.01 \). The exact value of the function \( \eta(\theta) \) is not known. As suggested by Venables (fig. 6(c) in [1]), this function increases with increasing coverage approaching \( \sim 0.25 \) at saturation coverage. As seen from Eq. 1, a small variation in \( \eta \) has a strong influence on the determined value for the prefactor, \( \nu \). A value of \( \eta = 0.1 \) yields a reasonable prefactor of \( \nu = 10^{13} \) sec\(^{-1} \), which will be used in the following.

The data for \( N_z \) are presented in fig. 4.6 by plotting this quantity versus the parameter \( \nu \exp(-E/k_B T)/R \), which is calculated from the experimental values for \( R \) and \( T \). The fitted value of \( E = 0.43 \) eV, and \( \nu = 10^{13} \) sec\(^{-1} \) for the prefactor. The data are seen to collapse excellently onto a straight line, demonstrating that \( \chi \) is constant over the probed parameter space. The choice for \( \nu \) has no effect on this collapse. It merely serves to provide a scale for the ordinate that may be interpreted (in the \( i = 1 \) case) as roughly the ratio \( h/R \) between the rates for adatom hopping and deposition. If values of \( E \) different from 0.43 eV are used in calculating the values along the ordinate, the collapse of the data for \( N_z \) onto a single curve is not observed.

The critical island size may be determined from the scaling parameter \( \chi \). Among the expressions given above for \( \chi \), the determined value of \( \chi = 0.27 \) is best reconciled with the scaling for anisotropic diffusion in the \( i = 1 \) case, \( \chi^{1-D} = 1/4 \). Also, the measured island size distributions (to be discussed in the next section) disagree with those obtained from simulations for \( i > 1 \). As mentioned, we will return to a discussion of the scaling parameter \( \chi \), but the conclusion that \( i = 1 \) remains valid. Thus, the dimer is found to be stable in the temperature interval examined. In the expression \( E = E_d + E_i/i \), \( E_i \) is by definition zero for \( i = 1 \), meaning that the fitted value for \( E \) may be interpreted directly as an effective
activation energy for diffusion. In the present case of highly anisotropic diffusion, the island densities are determined by the diffusivity along the fast direction. Thus the effective barrier for diffusion, which is most likely to be interpreted as the activation barrier for the rate-limiting step in adatom diffusion along the reconstruction channels, is $E_{\|} = 0.43 \pm 0.01$ eV.

For self-diffusion on the Pt(111) surface, a diffusion barrier of $0.26 \pm 0.01$ eV is found from an analysis of nucleation and growth data [10], in agreement with a result derived from Field Ion Microscopy observations [36]. The limiting barrier for diffusion along the fast direction on the buckled quasihexagonal topmost layer of Pt(100)-hex is thus $\approx 0.2$ eV higher than the barrier on an unperturbed (111) layer. On the unreconstructed Pt(100) surface, diffusion occurs through an exchange-mechanism with a barrier of 0.47 eV [37].
4.2.6 Island size distribution

In addition to positions, also the sizes (areas) of the individual islands are determined from the STM images. In order to determine the island size distribution, we need to know the density of islands containing \( s \) atoms, \( N_s \), for all sizes \( s \). Since the images are obtained with finite resolution, this quantity cannot be directly obtained. However, from the number of islands with sizes in the interval \([s - \Delta s/2; s + \Delta s/2]\), denoted by \( N(s, \Delta s) \), found in the total area examined for a given set of \((R, T)\) (covering \( N_{\text{tot}} \) sites), approximate values for \( N_s \) can be calculated for a range of \( s \)-values:

\[
N_s \simeq \frac{N(s, \Delta s)}{N_{\text{tot}}} \frac{1}{\Delta s}
\]  

(4.2)

Five such size distributions, which were obtained from experiments carried out for fixed \( R \) but at different \( T \), are shown in fig. 4.7(a). The tendency of islands to become fewer and larger at higher temperatures is once again clearly revealed.

A scaling behavior of the island size distribution has been proposed by Bartelt and Evans based on KMC simulations [3]. They find that the size distributions collapse onto a single scaling-curve if they are normalized and the island sizes are measured relative to the average island size, \( s_{\text{av}} \). The scaled size distribution may be obtained as \( f(s/s_{\text{av}}) = N_s s_{\text{av}}^2 / \theta \). This definition ensures that \( \int_0^\infty f(x)dx = 1 \) and \( \int_0^\infty x f(x)dx = 1 \). For isotropic diffusion, such a scaling behavior has been confirmed experimentally for the case of Fe on Fe(100) [9], but it has not previously been addressed experimentally in the case of anisotropic diffusion [25]. The origin of the scaling behavior has been rationalized in terms of the concept of capture zones by Mulheran and Blackman [38,39] as well as Bartelt and Evans [40].

In fig. 4.7(b), we show the size distribution from fig. 4.7(a) scaled according to the above-mentioned proposal, i.e., \( f(s/s_{\text{av}}) \). The scaled distributions are indeed seen to collapse onto a single curve, also in the present case of strongly anisotropic diffusion. From the shape of this experimentally derived scaling curve, a considerable amount of information regarding the diffusion, nucleation, and growth can be deduced. This requires comparison to similar curves obtained from KMC simulations, and for this reason a detailed discussion is deferred until these simulations have been presented in the next section.
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Figure 4.7: The scaling behavior of island size distributions derived from experiment. (a) Unscaled island size distributions showing the density $N_s$ of islands of size $s$ for five different temperatures (as indicated in the figure) and a common rate of $R \approx 8 \times 10^{-3}$ site$^{-1}$ sec$^{-1}$. (b) The same distributions as in (a), but scaled and normalized according to the ansatz $f(s/s_{av}) = N_s s^2_{av}/R$. The distributions are seen to collapse onto a single curve. The slight deviation of the 439 K result may be ascribed to fluctuations in the deposited coverage. The distributions are evaluated using a sliding window of $\Delta s = 0.3 s_{av}$. The smoothing introduced by this procedure does not significantly alter the shape of the distributions.
4.3 Simulations

As has been shown in the previous sections, diffusion, nucleation, and growth of Pt on Pt(100)-hex are strongly influenced by the complicated, anisotropic reconstruction exhibited by this surface. To aid in the interpretation of the scaling of island densities, autocorrelation functions and island size-distribution derived from the acquired data, we have performed KMC simulations. Due to the complexity of the Pt/Pt(100)-hex system, however, it is not feasible to carry out simulations that incorporate a realistic set of atomistic diffusion, nucleation, and growth processes. In the approximate (5×25) unit cell alone, there are on the order of ∼ 100 inequivalent adsorption sites, and the transitions between these presumably occur over a wealth of different energy barriers. Similarly the growth of the islands involves a complicated restructuring including ejection of atoms from the hex-layer as well as edge- and corner-diffusion processes to achieve the compact shapes. Instead of attempting the hopeless task of reproducing all these processes, we adopt the simplest possible model that exhibits the key characteristics found in the real growth system: Strongly anisotropic diffusion, nucleation with a critical island size of i = 1 and growth of compact islands that are not extremely elongated.

A central issue that we wish to explore with the simulations is the importance of finite island sizes in a system with highly anisotropic diffusion. In a simulation with point-islands, an island will only block the channel in which it was nucleated and possibly the two neighboring channels. Islands of finite extent, on the contrary, block an increasing number of diffusion channels as they grow, thereby increasing their ability to capture adatoms. For isotropic diffusion, a similar effect is not expected due to the space-filling properties of a 2-D random walk which ensures that the ability of an island to capture adatoms is fairly independent of its size. Furthermore, with the reduced correlation length along the direction of slow diffusion, island coalescence may be of greater importance in the anisotropic case than in the isotropic case, and this can only be explored by considering islands of a finite extent.

In our simulations, the substrate is modeled by a square lattice where each lattice site can accommodate one atom. Adatoms are deposited at a rate R. The anisotropy in diffusion is described through the use of two adatom jump-rates: \( h_\parallel \) for jumps in the x-direction (to the left or right, respectively) and \( h_\perp \) for jumps along the y-direction. Isotropic, anisotropic and 1-D diffusion (on a 2-D lattice) may then be modeled with \( h_\parallel = h_{1,1} \), \( h_\parallel > h_\perp \), and \( h_\perp = 0 \), respectively. Once an adatom jumps to a site where
one of the four nearest neighbor sites is occupied by another adatom, a
new island is nucleated and the resulting dimer is not allowed to dissociate
\((i = 1)\). Unless otherwise stated, the dimer is immobile. Once an adatom
jumps to a site that is nearest neighbor to an island, the size of this island
is incremented by one.

We apply two different schemes for the growth of the islands. In the
first case, an island occupies just one site at the position where it was
nucleated. Adatoms captured by the island are removed from the lattice
and a number is incremented to keep track of the island size. These islands
are referred to as point-islands. Alternatively, we take into account the
finite sizes of the islands. This is done by letting the island grow from
the nucleation site and outwards in a spiral manner such that the shape
is always compact and as close to a square as possible. If two or more
islands growing in this way meet (coalesce), we do not shape-equilibrate
to one square island, but keep account of the respective sizes of the two
islands and increment it if one of the islands is hit by an adatom. For both
methods of island growth, no additional parameters are introduced. The
simulations will therefore only depend on the two ratios \(h_\parallel/R\) and \(h_\parallel/h_\perp\).
The simulations are stopped at a coverage of 0.07 ML similar to that used
in the experiments. The algorithm we use to do KMC simulations is the
one proposed by Voter [41]. Periodic boundary conditions and lattice sizes
up to \(6000 \times 1200\) sites are employed.

The number of distinct sites that an adatom has to visit before it en-
counters another adatom or an existing island is in the order of \(1/(N_x + N_1)\), where \(N_1\) is the density of adatoms. This number increases with
increasing \(h_\parallel/R\) because of the reduced island density, and thus the com-
puter time used for diffusion of adatoms rises with increasing \(h_\parallel/R\). The
computing time is also severely affected by the degree of anisotropy in
diffusion. To see this, consider the extreme case of infinitely anisotropic
\((1-D)\) diffusion. Here the \(1/(N_x + N_1)\) distinct sites have to be visited
in one dimension, meaning that an adatom will traverse longer distances
and perform vastly more jumps before it is captured as compared to the
isotropic case where it may diffuse in two dimensions and a much smaller
fraction of the performed jumps will bring the diffusing atom to a site
that has already been previously visited [42]. This effect requires the use
of very large lattice sizes to avoid errors due to periodic boundaries in
the anisotropic case. In order to finish the simulations in a reasonable
amount of time, we do not go beyond \(h_\parallel/R = 10^{10}\). In the experiments,
\(h_\parallel/R\) is estimated to lie at somewhat higher values in the range from \(10^9\)
to \(10^{13}\) as can be seen from fig. 4.6. However, the features in which we
are interested, such as autocorrelation functions, island size distributions, and island densities, show a scaling behavior that allows us to perform meaningful comparisons between experiment and simulations in spite of this.

To exemplify the difference between the possible scenarios, it is shown in fig. 4.8(a) how the island and adatom densities develop as a function of deposited coverage in simulations with infinitely anisotropic diffusion; one with square islands (full line) and one with point-islands (dotted line). For comparison, the dashed line shows the results for isotropic diffusion and

![Graph showing island and adatom densities as a function of deposited coverage.]

Figure 4.8: (a) The development of adatom and island densities, $N_1$ and $N_x$ respectively, as a function of deposited coverage during simulations carried out under different conditions. Full line: square islands and anisotropic diffusion ($h_\perp = 0$). Dotted line: Point-islands and anisotropic diffusion ($h_\perp = 0$). Dashed line: Square islands and isotropic diffusion ($h_\perp = h_\parallel$). In all cases $h_\parallel/R = 10^3$. (b) The importance of coalescence in the anisotropic case relative to the situation where diffusion is isotropic is illustrated by plotting the relative difference between the observed island density $N_x^{\text{true}}$ (including coalescence) and the density of nucleated islands $N_x^{\text{nuclei}}$. 
square islands. At low coverage an adatom density \( N_1 \) builds up whereby initiating nucleation of islands. When an appreciable amount of islands has formed, the adatom density starts decreasing. This point is reached much earlier for the isotropic case than for the anisotropic case, again reflecting how the adatom lifetimes are longer when diffusion is anisotropic. At higher coverages, the two simulations with \( h_\perp = 0 \) begin to deviate. Due to their smaller size, the point-islands capture less adatoms leading to a larger nucleation probability and subsequently a higher island density as compared to the square island case. For the square islands, coalescence may be important. When evaluating the island density, coalesced islands may be counted as two distinct islands to obtain the density of nucleated islands \( N_{x}^{\text{true}} \) or as one island to obtain the true island density \( N_{x}^{\text{true}} \). In fig. 4.8(b), we plot the relative difference between these two quantities as a function of coverage for isotropic and infinitely anisotropic diffusion. It is clearly revealed how coalescence is much more pronounced for the anisotropic case than for the isotropic case. At a coverage of 0.07 ML, where the simulations are stopped, \( \sim 20\% \) of the nucleated islands in the anisotropic case have coalesced with other islands. As a result, the true island density of \( 6.9 \times 10^{-4} \) is \( \sim 10\% \) lower than the density of nucleated islands, which is \( 7.7 \times 10^{-4} \). The difference between \( N_{x}^{\text{true}} \) and \( N_{x}^{\text{true}} \) is too small to be discerned in panel (a) of fig. 4.8, where \( N_{x}^{\text{true}} \) is plotted.

### 4.3.1 Island-island correlations

We now wish to quantify how the anisotropy in the spatial distribution of islands depends on the degree of anisotropy in the adatom diffusion. In fig. 4.9(a)-(d), we show autocorrelation functions derived from simulations with square islands and different degrees of anisotropy in the adatom diffusion, \( h_{\parallel}/h_{\perp} \), of 1, \( 10^2 \), \( 10^3 \), and \( 10^4 \), respectively. These plots very clearly reveal how the anisotropy in the island-island correlations develop, reflected in the increasing length of the "arms" with a reduced density of inter-island vectors.

Such plots obtained from simulations with the same degree of anisotropy in diffusion but different \( h_{\parallel}/R \) are different due to the variation in island density. For isotropic diffusion, the characteristic length-scale for the island-island separation is \( L = 1/(N_{x})^{1/2} \). We find that the autocorrelation functions are invariant with respect to \( h_{\parallel}/R \) if they are scaled with this characteristic length, also in the case of anisotropic diffusion. Applying this scaling to autocorrelation plots obtained from experimental data should then allow for a direct comparison to those derived from simula-
Figure 4.9: Top row (a)-(d) shows autocorrelation functions derived from simulations with square islands and anisotropies in diffusion, $h_{||}/h_{\perp}$, of $1$, $10^2$, $10^3$, and $10^4$ respectively (from left to right). The development of anisotropic island-island correlations is clearly revealed. The distance from the origin at the center of the plots to their edge is $3L$, where $L = 1/(N_x)^{1/2}$ is the characteristic lengthscale for the island separations. The same scale is used in (f), where the accumulated autocorrelation plot from all experiments at different $R$ and $T$ is shown. The plot has been rotated to make the direction of the reconstruction channels horizontal and compares well to (c), where $h_{||}/h_{\perp} = 10^3$. The number of inter-island vectors within 4-cell wide bands running through the center of the $128 \times 128$ cell histogram (f) has been evaluated along the horizontal and vertical directions and are shown in (g). The density of inter-island vectors in the direction perpendicularly to the reconstruction channels decays towards the edges of the plot due to the finite sizes of the STM images. In the direction parallel to the channels, there is depletion in the density of inter-island vectors out to a distance of $\sim 2.5L$, where the density along the two orthogonal directions becomes indistinguishable. The mean width of rectangular islands at a coverage of 0.07 ML is $\sim 0.22L$ if the island aspect ratio is 1.5. This width is very similar to the distance along the perpendicular direction from the center of the plot and out to the point where the depletion in inter-island vectors stops. Panel (e) shows an autocorrelation function obtained from simulations where diffusion is isotropic but adatoms are only allowed to stick to two opposite edges of the islands. As it may be seen, this does not lead to anisotropic correlations in the island positions.
4.3. SIMULATIONS

tions. However, in this respect it is problematic that the statistics in the autocorrelation plots obtained from the experiments are so low that it is difficult in many cases to discern the exact dimensions of the regions with a reduced density of inter-island vectors. In order to circumvent this problem, we have introduced an integration method to try to quantify the information on anisotropy in island positions contained in the autocorrelation functions.

The method, which we refer to as the box-method, is based on the following principle. Consider an area \( A \) containing \( N \) islands (either an STM image or the lattice used in the simulations). Determine the island positions and place a rectangle with area \( A/N \) centered on each island, all rectangles having the same aspect ratio \( \alpha \) (length/width) and being rotated by the same angle \( \phi \) with respect to a fixed direction. Then determine the area of overlap between the rectangles and divide this by \( A \) to obtain a scaled overlap, \( O(\alpha, \phi) \). The hypothesis is that \( O(\alpha, \phi) \) will attain a minimum when \( \alpha \) and \( \phi \) are given by values that describe the anisotropy in the island positions. To examine this idea, test-images are created with island positions determined by three methods: i) Points are chosen at random. ii) The image area is divided into quadratic cells and a point is chosen at random in each cell. iii) Similar to the previous, but with rectangular cells. In the first approach there is no correlation between island positions. The latter two approaches are assumed to mimic isotropic and anisotropic correlations in island positions. When these test-data are analyzed, we obtain \( O(\alpha, \phi) \) that shows for the three cases: i) No minimum. ii) A minimum at \( \alpha = 1 \) and in general a lower value than for the uncorrelated points. iii) A minimum at values of \( \alpha \) and \( \phi \) equal to the aspect ratios and orientation of the original rectangles, respectively. Thus, the ratio between island-island correlation lengths, \( l_{\parallel}/l_{\perp} \), and the preferred direction of diffusion may apparently be determined as the values for \( \alpha \) and \( \phi \) yielding a minimum in \( O(\alpha, \phi) \).

We have applied this procedure to the island positions obtained from simulations with square islands and different degrees of anisotropy in diffusion. In fig. 4.10 it is shown how the anisotropy in island-island correlations depends on the anisotropy in adatom diffusion.

The correlations in island positions is mediated by diffusing adatoms and thus, as a guideline, one may consider the Einstein relation in 1-D

\[
\langle x^2 \rangle = a^2 2ht
\]

for the mean-square displacement after time \( t \) of a particle which jumps with the rate \( h \) (to the left or right, respectively) on a grid with spacing \( a \). This relation suggests that the correlation lengths \( l_{\parallel} \) and \( l_{\perp} \) may be expected to vary as
\[(l_\parallel/l_\perp)^2 = (h_\parallel/h_\perp) \tag{4.3}\]

Scaling of this form is indeed found for low values of \(h_\parallel/h_\perp\) as may be seen from fig. 4.10.

When evaluated for the STM data, \(O(\alpha, \phi)\) is determined as an average over all images for a given set of \(R, T\). As expected, \(O(\phi)\) shows a clear minimum at exactly the angle defined by the direction of the reconstruction channels. When evaluated for this angle, \(O(\alpha)\) yields a curve with a broad shoulder instead of a clear minimum. This behavior is attributed to limited

![Graph](image_url)

**Figure 4.10**: Values of the aspect ratio \(\alpha\) found to give minimum overlap \(O(\alpha)\) when the box-method is applied to island positions obtained from simulations with different degrees of anisotropy in adatom diffusion, \(h_\parallel/h_\perp\) and \(h_\parallel/R = 10^3\). The line represents the relationship \(\alpha \sim (h_\parallel/h_\perp)^{1/2}\), which is seen to hold for small values of \(h_\parallel/h_\perp\). The determined \(\alpha\) are not significantly affected by the value of \(h_\parallel/R\). In evaluating \(O(\alpha)\), island coalescence is taken into account when determining the island positions. The detailed behavior of \(\alpha(h_\parallel/h_\perp)\) is influenced by the spatial extent of the islands since this places a limit on how close separate islands can be positioned (as it may also be seen in the central region of the autocorrelation plots). Also finite size effects with respect to image dimensions are important. This is illustrated for \(h_\parallel/h_\perp = 10^3\), where \(\alpha\) has been determined from segments of the simulation lattice containing different numbers \(N\) of islands as indicated in the figure (since periodic boundary conditions have been applied, \(\infty\) refers to the full lattice). The points shown for other values of \(h_\parallel/h_\perp\) have been evaluated for \(N = 60\), which is a typical value for the number of islands in one STM image.
image dimensions since it is also found from the simulation results if the evaluation of $O(\alpha)$ is based on a reduced number of islands comparable to that found in a single STM image. To proceed further, test images with areas and island numbers as the real images, but with uncorrelated island positions, are generated and $O(\alpha)$ is evaluated for these. By subtracting the curve for the uncorrelated points from the curve for $O(\alpha)$ obtained from the STM images, a curve with a clear minimum is obtained, and the position of this minimum is the desired measure of $l_\parallel/l_\perp$. Again, applying the same procedure to the simulation results supports this idea.

When analysing the whole STM dataset for different $R$ and $T$ in this fashion, we find that $\alpha = 10 \pm 2$ in all cases without any systematic variation. By comparison to fig. 4.10, this value for the anisotropy in island positions translates into approximately a factor 1000 for the anisotropy in adatom diffusivity.

Since no variation in anisotropy can be detected between the different experiments, we scale the autocorrelation functions to the characteristic length $L$ and combine all data onto a single plot. The result, shown in fig. 4.9(f), is very similar to the autocorrelation plot derived from simulations with $h_\parallel/h_\perp = 1000$, consistent with the result just obtained from the box-method. In fig. 4.9(g) linescans through the accumulated autocorrelation plot, along and perpendicularly to the direction of the reconstruction channels, are shown. The depletion in inter-island vectors in the direction parallel to the channels can be seen to extend to a distance of $\sim 2.5L$.

If the mean hopping rates on the hex-reconstructed surface can be described by effective activation-barriers and prefactors, then

$$\frac{h_\parallel}{h_\perp} = \frac{\nu_\parallel}{\nu_\perp} \exp(\Delta E/k_B T) \tag{4.4}$$

where $\Delta E = E_\perp - E_\parallel$ is the difference between the effective barriers for diffusion perpendicularly to and along the reconstruction channels. Since the anisotropy of the diffusion does not vary (within the error bars) in the temperature range $T = 318-497$ K, we estimate that the energy difference $\Delta E$ must be smaller than $\sim 0.2$ eV. A larger $\Delta E$ than this would result in a change in $h_\parallel/h_\perp$ by more than a factor of 10 as the temperature is changed from 318 K to 497 K and this is not consistent with $\alpha = 10 \pm 2$ at all temperatures (see fig. 4.10). A value for $\Delta E$ of 0.2 eV is consistent with a ratio of the prefactors $\nu_\parallel/\nu_\perp \sim 1$. For smaller $\Delta E$s, the ratio between the prefactors must be larger in order to reproduce the obtained anisotropy $h_\parallel/h_\perp \sim 1000$. It may be that transitions between the reconstruction channels can only occur at few places, but with activation barriers for
crossing these transition paths similar to the limiting barrier for diffusion along the reconstruction channels. If such a geometric effect is the source of the anisotropy in diffusion, this would be manifested in the prefactors, and a temperature variation of the anisotropy is not expected.

As noted earlier, the observation of denuded zones of different widths near steps along orthogonal directions may in principle be due to different sticking of adatoms to different types of step-edges. One may therefore ask what influence such an effect would have on the correlations within island positions. To examine this problem, we have performed simulations where diffusion is isotropic but the adatoms only stick on two (opposite) edges of the islands. The resulting autocorrelation plot, which is shown in fig. 4.9(c), reveals only marginal evidence of anisotropy in the island positions. This behavior probably reflects that an adatom which hits one of the reflecting sides of an island will simply diffuse around on the substrate for a short while and then with large probability hit one of the other sides of the same island rather than migrate to some other island further away. In this way, anisotropic sticking does not have much effect on the reduced nucleation probability in the vicinity of an island.

4.3.2 Island size distribution

We now return to a discussion of the scaled island size distributions. By averaging over the five scaled distributions of fig. 4.7(b) corresponding to different deposition temperatures, we obtain the curve represented by circles in fig. 4.11. This experimentally derived scaling function is characterized by a maximum of 0.85 at $s/s_{cr} = 0.8$. The scaling properties of island size distributions have been extensively studied in the literature based on KMC simulations of island nucleation and growth [3,5,25,38,44,45]. The shape of the scaling function has been found by several authors to vary with the critical island size $i$. Bartelt and Evans [3] as well as Amar and Family [5] have performed simulations incorporating sharp critical island sizes of up to $i = 3$, whereas Ratsch et al. [45] have studied a model with a gradual onset of bond-scission. In all cases it emerges that with increasing $i$, the scaled size distributions become more narrow with a corresponding increase in maximum-value. Thus Amar and Family [5] find maxima of 0.85, 1.1, and 1.4 for $i = 1$, 2, and 3, respectively. When compared to these results, the obtained scaling function for Pt/Pt(100)-hex can only be reconciled with $i = 1$ behavior, consistent with the conclusion drawn from the observed scaling of $N_i$ with $R$ and $T$.

The experimentally derived scaling function attains its maximum at
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Figure 4.11: Comparison of scaled island size distributions. Circles: Average over the five scaled distributions derived from experiment shown in fig. 4.7(b). Full line: Scaled size distribution from simulations with anisotropic diffusion ($h_\parallel/h_\perp = 10^3$) and square islands. Dashed line: Similarly for isotropic diffusion ($h_\parallel/h_\perp = 1$). Dash-dotted line: Scaled size distribution from simulations with mobile dimers and anisotropic diffusion ($h_\parallel/h_\perp = 10^3$ for both adatoms and dimers). In all simulations $h_\perp/R = 10^9$.

$s/s_{av} = 0.8$. This is a considerably lower value than what is found for the simulated size distributions of Evans and Bartelt [3] and Amar and Family [5], which generally attain their maximum for values of $s/s_{av}$ at or slightly above 1.

The origin of this difference is found to be the increased tendency towards coalescence in the case of anisotropic diffusion. Consider the scaled size distributions of fig. 4.11 shown with dashed and solid lines. These are derived from simulations using the square island model, incorporating isotropic ($h_\perp = h_\parallel$) and anisotropic diffusion ($h_\parallel/h_\perp = 10^3$), respectively. When evaluating the scaled size distributions, coalescence is taken into account as explained earlier. The distribution obtained for isotropic diffusion peaks at $s/s_{av} = 1.1$ whereas the distribution obtained for anisotropic diffusion is shifted considerably downwards towards lower $s/s_{av}$ and is generally in very good agreement with the distribution derived from experiment.

If instead we construct the island size distributions based on the sizes of the nucleated islands, i.e., neglect coalescence, the origin of the difference between the curves for isotropic and anisotropic diffusion is clearly
revealed. Both sets of distributions are depicted in fig. 4.12. The distributions obtained for isotropic diffusion and anisotropic diffusion with neglect of coalescence are almost identical. Including coalescence introduces only a marginal change to the distribution for isotropic diffusion whereas the average island size is increased in the anisotropic case, resulting in a pronounced downwards shift in value of $s/s_{ad}$, where the scaled distribution attains its maximum. It is worth remarking that the simulations are stopped at a low coverage of 0.07 ML, where the effects of coalescence on island size distributions are usually deemed unimportant. Evidently, this does not hold for highly anisotropic diffusion due to the reduced correlation length in the direction where diffusion is slow.

From Field-Ion Microscopy studies, dimers have in several cases been found to have a mobility comparable to that of adatoms [43, 46–48]. In the context of nucleation and growth studies, it has been pointed out by Liu et al. [49] that the possibility of dimer-mobility should be considered also in the present case of $i = 1$, where the dimer is stable towards thermal dissociation. The dash-dotted curve in fig. 4.11 shows the scaled island size distribution obtained from a simulation where adatoms and dimers are equally mobile and diffuse with the same degree of anisotropy $h_{ij}/h_{||} = 10^3$ [25]. Simulations by Bartelt et al. [18] with mobile dimers and isotropic diffusion give a very peaked scaling curve similar to the one shown here. The poor agreement with experiment leads us to conclude that the mobility of dimers in the probed temperature interval is negligible in comparison to that of the adatoms. Also, the scaling of the island density is expected to be different if dimers are mobile. Here a scaling exponent of $\chi = 2/5$ has been derived [18] for isotropic diffusion and $i = 1$, significantly different from the present finding of $\chi = 0.27$.

As mentioned earlier, a transition from hexagonal to quadratic arrangement of the atoms is believed to occur under the islands as they grow. Also, the hex-reconstruction is known from many studies to be unstable when molecules such as NO, H$_2$ or CO are adsorbed on the surface, resulting in a lifting of the reconstruction during which the excess atoms in the hex-layer are expelled [22–24]. One may therefore consider the possibility that the islands are nucleated by an activated process in which the presence of a Pt adatom leads to the ejection of an atom from the hex-layer, thereby initiating the lifting of the reconstruction under the islands. A similar spontaneous nucleation process has been observed in the surface alloying of Fe into the Cu(100) surface [50] and has been referred to as $i = 0$ behavior since it does not require two adatoms to meet. Reflecting the fact that new islands are continuously being nucleated in this scenario, the resulting
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Figure 4.12: The importance of coalescence for the scaled island size distributions in the case of simulations with isotropic and anisotropic ($h_{||}/h_{\perp} = 10^3$) diffusion, respectively. Full lines: Two or more coalesced islands are counted as a single island with a size equal to the sum of the individual sizes. Dashed lines: Each nucleated island contributes individually to the scaled island size distribution. The effect in the anisotropic case is seen to be considerable. In all simulations $h_{||}/R = 10^9$.

scaled island size distribution have been found (from simulations [5,51]) to be monotonically decreasing functions of island size. From the obtained island size distribution of Pt on Pt(100)-hex, this possibility can therefore be ruled out in the present case. A similar argument may be considered to argue that the nucleation is not caused by pinning of diffusing adatoms to defects or impurities on the surface [52].

4.3.3 Scaling of island densities

In fig. 4.6 we showed the scaling of the experimentally determined saturation island density $N_{s} \sim (h_{||}/R)^{-\chi}$ and obtained a value for the scaling
exponent of $\chi = 0.27$ quite close to the result $\chi^{1-D} = 1/4$ for the 1-D case [3,20]. We now compare these findings to results derived from the KMC simulations and from a rate-equation treatment of nucleation and growth in a system with anisotropic diffusion and finite island sizes. The results are summarized in fig. 4.13.

In the upper panel (a) of this figure, the dots and squares show the results for $N_I$ from simulations with infinitely anisotropic diffusion ($h_\perp = 0$) in combination with point and square islands, respectively. As was also seen in fig. 4.8(a), a higher island density is obtained in the point-island case. The simulated values for $N_I$ have a slight curvature when plotted

![Figure 4.13](image)

Figure 4.13: (a) Comparison of island densities obtained from simulations, rate-equation theory, and experiment, respectively, as a function of $h_\parallel/R$. (b) The behavior of the scaling exponent $\chi$ derived from the data in (a). For the KMC simulations the symbols correspond to: Dots: Point-islands and $h_\parallel/h_\perp = \infty$, triangles: Point-islands and $h_\parallel/h_\perp = 10^3$, squares: Square islands and $h_\parallel/h_\perp = \infty$. And for the rate-equation results: Dashed line: Point-islands and $h_\parallel/h_\perp = \infty$, full line: Square islands and $h_\parallel/h_\perp = \infty$. The circles show the experimental data from fig. 4.6 for reference. See text for details.
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versus \( h_{\|}/R \), meaning that they cannot be described by a single \( \chi \). In the bottom panel (b) are shown the local slopes (\( \chi = \frac{d \log N_x}{d \log (R/h_{\|})} \)) derived from the points in panel (a). The scaling exponent \( \chi \) is an increasing function of \( h_{\|}/R \), converging to a value for \( h_{\|}/R \rightarrow \infty \) that is characteristic for the nucleation and growth mechanism.

For the point islands, \( \chi \) converges to a value of \( \sim 0.24 \) in good agreement with the \( \chi = 1/4 \) result from the 1-D rate-equation treatment of Evans and Bartelt [3]. For the square island case, however, considerably larger values for \( \chi \) are found. \( \chi \) is seen to converge towards values above \( \sim 0.31 \) despite the fact that diffusion is infinitely anisotropic [53].

These findings raise the question of what scaling to be expected if diffusion is not totally 1-D. The triangles in fig. 4.13(b) depict the \( \chi \) obtained from simulations with point-islands and a finite degree of anisotropy of \( h_{\|}/h_{\perp} = 10^3 \). Surprisingly, we find that when we in this way add a small mobility in the \( y \)-direction 1000 times smaller than that in the \( x \)-direction, the exponent changes significantly towards higher values (from 0.24 to 0.29 at \( h_{\|}/R \approx 10^{10} \)) and actually approaches the value \( \chi = 0.33 \) expected for isotropic diffusion (this result, which is not shown in the figure, is confirmed in the simulations for both point islands and square islands). The conclusion from these findings is that the analytic result \( \chi^{1-D} = 1/4 \) is only applicable in the idealized case of infinite anisotropy in diffusion and point islands.

The question that now remains is how to reconcile the fact that diffusion in the Pt/Pt(100)-hex system is shown by the autocorrelation analysis to be highly anisotropic, the islands have a finite size, and yet a value of \( \chi = 0.27 \), quite close to the point-island result, is derived from the experimental data for \( N_x \). As may be seen from fig. 4.13(a), the data are acquired in the regime of \( h_{\|}/R \) where convergence is expected to be reached, so this may not explain the apparent discrepancy. Also, reducing the degree of anisotropy in the simulations with square islands from infinity to a finite value will bring about a higher value for \( \chi \) than the \( \sim 0.31 \) found in the described simulations since the situation of isotropic diffusion will then be approached. We tentatively ascribe the apparent discrepancy to originate from the detailed surface morphology of the Pt(100)-hex surface, which has been ignored in the simulations. If adatom diffusion takes place preferentially along one of the six close-packed atomic rows in the reconstruction channels, then islands may become quite large before the diffusion in the adjacent reconstruction channel is affected. Generally this effect would reduce the cross-section of the islands for adatom capture by a factor of up to \( \sim 6 \), making the nucleation and growth scenario effectively approach
that of the point-island case.

In the regime of $h_{||}/R$, where there is overlap between experiments and simulation, the absolute values of the island density derived from measurements, which are shown with circles in fig. 4.13(a), are not quite reproduced by any of the simulations (when discussing this it must be borne in mind that the value for $h_{||}/R$ for the experimental data is an estimate based on the assumption that $\nu = 10^{13}$ sec$^{-1}$). The closest approach to the measured values is achieved by the simulation with square islands and infinitely anisotropic diffusion where the obtained island densities are roughly a factor of 2 too high. Relaxing the anisotropy to a finite value would reduce the island density as it may be seen from fig. 4.8(a), where the island densities for 1-D and isotropic diffusion are compared, but would at the same time increase $\chi$ as it was previously discussed. In any case, given the crudeness of the simulation model, it is probably not reasonable to expect perfect agreement in the absolute numbers. For instance, if only a fraction of the sites on the hex-reconstructed surface is accessible for the diffusing adatoms, it may well be more appropriate to evaluate the island density with respect to this, unknown but reduced, number of sites only. This would increase the effective island density by a factor of $\sim 6$ if diffusion is limited to one atomic row for each reconstruction channel.

Since the scaling law, Eq. (4.1), can be derived without including coalescence of islands [3,54], island densities should in principle be measured at a constant coverage in the pre-coalescence regime. However, the scaled island size distribution has shown that some island coalescence has in fact occurred in the experiments, and the question remains whether this has any effect on the scaling of $N_{z}$. In evaluating the simulated island densities shown on fig. 4.13(a), coalescence was taken into account. We find, however, that the scaling exponents are not affected if we instead evaluate the island densities with respect to the number of nucleated islands. This is due to the fact that the fraction of coalesced islands is fairly independent of $h_{||}/R$. Thus, a limited amount of coalescence does not seem to constitute a serious problem when one uses the scaling laws for $N_{z}$ in the interpretation of experimental nucleation and growth data.

Mean-Field theory

From the KMC simulations, the scaling behavior of island densities for the case of anisotropic diffusion was found to be markedly different when point-islands and islands of a finite extent were used. To further elucidate this, we will now provide a mean-field rate-equation treatment of nucleation
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and growth incorporating the effect of the finite island sizes.

If $N_1(t)$ and $N_2(t)$ denote the density of adatoms and stable islands at time $t$, we can write the rate of change in the number of nucleated islands per area as follows

$$\frac{dN_2}{dt} = F_1 \frac{N_1}{\tau}. \quad (4.5)$$

Here $\tau$ is the average lifetime of an adatom and $F_1$ is the fraction of the adatoms that is captured by other adatoms and thereby nucleates new islands.

Island coalescence is not included in the rate-equations. In general, this is difficult to do since the mean-field approach does not incorporate the island-island correlations that have been shown here to strongly influence the importance of coalescence [1]. However, as explained above, neglecting coalescence is justified by the observation from the KMC simulations where the scaling exponent obtained from the true island density (including coalescence) is the same as that obtained from the density of nucleated islands.

We assume that all adatoms deposited on top of an island are incorporated in the edge of that island in the first layer. This gives a simple relation between time and coverage: $Rt = \theta$. The adatom density is increased by deposition on the part of the surface that is not covered by islands or adatoms. Adatoms captured by islands (growth) or other adatoms (nucleation) decrease the adatom density. Combining this, the equation of the change in adatom density is

$$\frac{dN_1}{dt} = R(1 - \theta) - F_2 \frac{N_1}{\tau} - 2 \frac{dN_2}{dt}, \quad (4.6)$$

where $F_2 = 1 - F_1$ is the fraction of adatoms captured by islands.

Equations (4.5) and (4.6) are quite general and can describe many nucleation and growth scenarios. In the appendix, the behavior of these equations in the limit of $h_0/R \to \infty$ is investigated for infinitely anisotropic diffusion. It is shown that the scaling of the island density depends crucially on the assumed model for the island shapes. We distinguish between two different cases, i) point-islands and ii) islands of a finite extent and a fixed shape. In this latter case, we denote the average width of the islands in the direction perpendicularly to the direction of fast diffusion by $b$. During deposition, the width varies approximately as $b \simeq (\theta/N_2)^{1/2}$.

We first note that the two-dimensional random walk occurring for isotropic diffusion is space-filling and the capture coefficient of an island
will therefore depend only weakly on its size (see also Ref. [40]). For this reason, the scaling exponent for isotropic diffusion $\chi^{2-D}$ is $1/3$ in both of the two cases, point-islands and islands of finite extent.

However, the situation is very different for anisotropic diffusion. With increasing size, the island is able to block an increasing number of diffusion channels, and thus the capture coefficient of a given island will be proportional to the width of the island, $b$. Therefore, for strongly anisotropic diffusion, the two cases lead to different scaling exponents. In the appendix, we find for the scaling exponent: i) $\chi = 1/4$ for point-islands and ii) $\chi = 1/3$ for square islands. The point-island result also applies to islands that are extremely elongated along the direction of fast diffusion and therefore, with respect to adatom capture, act as point-islands.

These results for the behavior of the scaling exponent in the limit $h_\parallel/R \to \infty$ are in good agreement with the simulation results for $\chi$ (obtained for finite values of $h_\parallel/R$), which are shown on fig. 4.13(b).

For finite $h_\parallel/R$, the rate-equations have been solved numerically in the case of infinitely anisotropic diffusion and point- and square islands, respectively. The results are shown in fig. 4.13, where they can be compared to the island densities and scaling exponents obtained from the KMC simulations. The rate-equation results of point-islands (dashed line) and for square islands (full line) agree qualitatively with the exact results from the simulations for these two cases, respectively. For instance, the exponent from the rate-equations with point islands increases with increasing $h_\parallel/R$ and converges slowly toward the analytic result of $1/4$. The KMC simulations with point-islands present almost exactly the same behavior for the dependence of $\chi$ on $h_\parallel/R$. For square islands, the rate-equations give slightly higher values for $\chi$ than the KMC simulations. This difference could be due to fluctuations in the island width $b$ that are not treated correctly in mean-field theory.

4.4 Summary

Homoeptaxial growth in a system with strongly anisotropic diffusion and finite island sizes, Pt/Pt(100)-hex, has been investigated and several differences have been revealed compared to the case where diffusion is isotropic. A quantitative analysis of STM topographs obtained after Pt deposition in the submonolayer coverage regime at a range of different temperatures and rates has yielded information on number densities, sizes, and positions of the islands formed. To aid interpreting these observations, KMC sim-
ulations have been carried out in a simple model giving special emphasis to the effects of anisotropic surface diffusion in combination with islands of a finite extent.

We have performed an auto-correlation analysis of the island positions and introduced a method of quantifying the anisotropy within island-island correlations. From this analysis, an anisotropy of $h_{||}/h_{\perp} \sim 1000$ is found for the adatom diffusivity. The reduced correlation length caused by the strongly anisotropic adatom diffusion leads to an early onset of island coalescence. It is shown how the scaled island size distribution may be used to reveal this. In general the scaled size distribution contains much information regarding the diffusion, nucleation, and growth, and we furthermore find that the critical island size for nucleation is $i = 1$ and that dimers have negligible mobility. The measured saturation island density scales as $N_x \sim (R/h_{||})^\chi$, and a scaling exponent of $\chi = 0.27$ and an energy of $E_{||} = 0.43$ eV are derived. The energy $E_{||}$ is interpreted as the limiting activation barrier for diffusion along the fast direction. The determined $\chi = 0.27$ is close to the $\chi = 1/4$ derived in a 1-D model for $i = 1$, apparently in agreement with the observation that diffusion is anisotropic and that dimers are stable. However, from the KMC simulations, the scaling exponent $\chi$ is found to be very dependent on the finite extent of the islands as well as on the degree of anisotropy in diffusion. From a mean-field rate-equation treatment of the case where islands are square and diffusion is infinitely anisotropic, the limiting behavior of the scaling exponent found for $h_{||}/R \to \infty$ is $\chi = 1/3$, which is in agreement with the simulation results. The fact that the measured $\chi = 0.27$ is closer to the $\chi = 1/4$ result valid only for point-islands and infinitely anisotropic diffusion is attributed to the detailed morphology of the reconstructed surface.

These findings underscore that caution should be exercised in drawing conclusions from the scaling of $N_x$ with rate and temperature alone and emphasize that it is preferable to combine information gained in this way with that obtained from other methods of analysis, such as the shape of the scaled island size distribution and the spatial correlations among islands.

Appendix

To solve Eqs. (4.5) and (4.6), we have to specify how $\tau$, $F_1$, and $F_2$ depend on $N_1$, $N_x$, and $\theta$. The probabilities $F_1$ and $F_2 = 1 - F_1$ are given by

$$F_1 \simeq \frac{N_1}{N_1 + bN_x},$$

(4.7)
For each site unoccupied by islands or adatoms, there will be a certain number of consecutive sites in the $x$-direction bounded by an island or an adatom at each end. The average length $L$ of such channels is obtained from the area not covered by islands:

$$bLN_x + 1LN_1 \simeq 1 - \theta \simeq 1. \quad (4.8)$$

The numbers $b$ and 1 on the left side are the cross-sections of islands and adatoms, respectively. A random walker put randomly on one of the $L$ sites in a line will on the average hit one of the two end-points in $\sim L^2$ jumps (when $L$ is large), and the lifetime $\tau$ is thus found using

$$h_{||}\tau \sim L^2. \quad (4.9)$$

Since each square island contains $b^2$ atoms, we must have

$$N_1 + b^2N_x = \theta. \quad (4.10)$$

To mimic the point-island model, $b = 1$ is used instead of Eq. (4.10).

It is convenient to introduce scaled variables:

$$\tilde{N}_1 = (h_{||}/R)^{1/3}N_1, \quad \tilde{N}_x = (h_{||}/R)^{1/3}N_x, \quad \tilde{\theta} = (h_{||}/R)^{1/3}\theta. \quad (4.11)$$

With these substitutions and the approximation $1 - \theta \simeq 1$ in Eqs. (4.5) and (4.6), we get the following equations that are independent of $h_{||}/R$:

$$\frac{d\tilde{N}_x}{d\tilde{\theta}} = \tilde{N}_1^2(\tilde{N}_1 + b\tilde{N}_x) \quad (4.12)$$

$$\frac{d\tilde{N}_1}{d\tilde{\theta}} = 1 - (b\tilde{N}_x\tilde{N}_1 + 2\tilde{N}_1^2)(\tilde{N}_1 + b\tilde{N}_x). \quad (4.13)$$

We want to find the scaling of $N_x$ in the limit $h_{||}/R \to \infty$. We therefore look for the asymptomatic solutions to Eqs. (4.12) and (4.13) ($\tilde{\theta} \to \infty$).

With $b = 1$, the solution to those equations is

$$\tilde{N}_x = \sqrt{2} \tilde{\theta}^{1/4}, \quad (4.14)$$

for $\tilde{\theta} \to \infty$. This gives the point island result

$$N_x \sim \left(\frac{R}{h_{||}\theta}\right)^{1/4}, \quad \chi = \frac{1}{4}. \quad (4.15)$$
REFERENCES

With \( b \) from Eq. (4.10), we get for \( \hat{\theta} \to \infty \)

\[
\hat{N}_z = \text{constant},
\]  

(4.16)

and the square island result is

\[
N_x \sim \left( \frac{R}{h_{||}} \right)^{1/3}, \quad \chi = \frac{1}{3},
\]  

(4.17)

References


REFERENCES


[26] The microscope is a prototype of the RASTERSCOPE 4000, DME A/S, Transformervej 12, DK–2730 Herlev, Denmark, Fax: +45 4284 9197.


[28] The stated coverage of $\theta = 0.075$ ML is the fraction of the surface area covered by islands as measured from the STM-images. What deposited amount of $Pt$ this corresponds to depends on whether or not the reconstruction is lifted under the islands since this process is
REFERENCES

associated with a mass-transfer from the substrate and into the islands of \( \sim 20\% \). In evaluating the deposition rates \( R \), the lifting of the reconstruction was not taken into account. Including it would reduce \( R \) by \( \sim 20\% \). This would have no effect on any of the conclusions drawn, however.


[42] The number of distinct sites visited in an n-step random walk, \( S_n \), is in 1D \( S_n \approx (8n/\pi)^{1/2} \), and in 2D \( S_n \approx \pi n / ln(n) \), E. W. Montroll and B. J. West, p.137 in Fluctuation Phenomena, eds. E. W.Montroll and J. L. Lebowitz, North-Holland (1976).


[52] It should be cautioned in this respect, however, that simulations by Blackman and Mulheran [60] where nucleation occurs at predefined pinning centers, yield scaling functions of the ordinary type exhibiting a clear maximum. The monotonically decreasing scaling function characteristic of \( i \approx 0 \) behavior therefore presumably only result, if the concentration of defects is so large that nucleation at these sites can persist during the whole deposition period.


Chapter 5

Pt/Pt(110)-(1×2): Adatom Diffusion

The present chapter describes the analysis of adatom diffusion in the Pt/Pt(110)-(1×2) system. The data presented are based on STM movies that directly reveal the migration of adatoms on this surface. Further analysis of these data with respect to dimer dissociation and island mobility are presented in chapters 6 and 7, respectively. The chapter is based on the paper (III), but has extended this paper to a significant degree.
5.1 Introduction

The diffusion of adatoms on metal surfaces is one of the most fundamental processes in surface science and is of crucial importance in such diverse areas as crystal and thin film growth, heterogeneous catalysis and oxidation. This has spurred a tremendous interest in understanding the nature of surface diffusion on the atomic scale. In the conventional picture of surface diffusion, the adatom migration occurs through a series of uncorrelated displacements over the minimum energy barrier between nearest neighbour binding sites on a static substrate. The time honoured technique for direct observation of surface diffusion processes is Field Ion Microscopy (FIM), where the migration of adatoms is followed on small terraces at the apex of very sharp FIM tips [1,2]. This technique has over the years led to the discovery of many novel atomic scale diffusion mechanisms [1–3]. More recently also Scanning Tunneling Microscopy (STM) has given valuable information about surface diffusion although in most cases in an indirect manner from nucleation and growth experiments [4–8]. In a few cases it has also been possible by means of STM to follow the diffusion processes directly at the atomic level [9–11], but so far attempts at studying metal on metal diffusion by tracking the individual atoms have not been successful [8].

In spite of the increased knowledge of diffusion processes, a number of fundamental questions still remain unsolved. In particular it has been speculated that long jumps may occasionally occur where a diffusing adatom, once promoted to a transition state, spans several lattice spacings before retrapping rather than migrates in the ordinary fashion between nearest-neighbor lattice sites. The presence of long jumps may for instance affect the activation barrier determined from measurements of the mean-square displacement of diffusing adatoms since a long jump would contribute strongly to this quantity [12–14]. Long jumps are believed to be common at high temperatures where $k_BT$ is comparable to the activation barrier for diffusion. At lower temperatures, long jumps are thought to occur if the energy dissipation to the substrate lattice is weak [15], and from Molecular Dynamics (MD) simulations they have been found to play a significant role in the diffusion of adsorbed gases on metal surfaces [14,16]. However, for metal on metal diffusion the coupling to the lattice is much stronger. This is especially true for self-diffusion where the equal masses of adsorbate and substrate atoms causes the energy transfer in collisions to be at a maximum [17]. Thus for self-diffusion long jumps are expected to be less likely. Experimental observations of long jumps are still very scarce.
5.1. **INTRODUCTION**

![Diagram of Pt(110) surface]

Figure 5.1: Ball-model illustrating the structure of the Pt(110)-(1×2) missing row reconstructed surface. In the uppermost missing-row trough a four-atom long island is shown, and in the bottom row an individual adatom is drawn. (1×1) and (1×2) unit cells are shown to the right and left, respectively.

In a FIM study by Senft and Ehrlich [13], a significant contribution from long jumps was revealed for the diffusion of Pd on W(211), whereas for self-diffusion of W on W(211) no long jumps were found to occur.

Several questions arise in this connection. Do these long jumps exist for other systems than Pd on W(211), and is it generally so that they do not exist for metal self-diffusion? Does the rate for long jumps follow a simple Arrhenius dependence with temperature? If so what is the activation barrier for long jumps, and does it differ from the activation barrier for single jumps? This chapter will address these fundamental questions by presenting results on the surprising finding that a significant proportion of long jumps participate in the self-diffusion of Pt on the Pt(110)-(1×2) surface.

The clean Pt(110) surface is known to form a (1×2) missing row reconstruction with every alternate close-packed row removed as illustrated in fig. 5.1 [18]. The result of this reconstruction is a channelled surface consisting of one-dimensional (1-D) troughs separated by close-packed rows of Pt atoms.

By using atomically resolved time-lapse STM movies we have monitored the migration of individual Pt adatoms deposited on this surface. From the onset of mobility at ~ 300 K and up to the highest temperature of 380 K investigated, the Pt adatoms are found to be confined to the troughs formed by the missing row reconstruction. The diffusion is thus
totally 1-D. By analysing distributions over the displacement of adatoms
between consecutive images, we find that 5 – 10% of the adatom jumps
are double jumps covering two lattice spacings. These results allow us for
the first time to construct an Arrhenius plot for the double jump rate,
demonstrating that it follows an Arrhenius dependence on temperature.
The activation barrier derived for the double jumps, $E_{d2} = 0.89$ eV, is
slightly larger than the barrier $E_{d1} = 0.81$ eV found for the single jumps.

The present chapter is structured as follows. After an account of rel-
levant experimental details in the next section 5.2, we focus in section 5.3
on the analysis of the time-lapse STM movies, explaining how the distrib-
ution over adatom displacements is derived. The rates for adatom single
and double jumps are determined by fitting an analytic expression for
the displacement distribution to the distributions obtained from experi-
ment. A derivation of this analytic expression, originally due to Ehrlich
[19,20], is presented in section 5.4. In this section we also describe Kinetic
Monte-Carlo simulations aimed at illuminating the important question of
the statistical significance with which it is possible in practise to identify
long jumps in diffusion by such a scheme. The results for the double jump
rates and the Arrhenius analysis are then presented in section 5.5. In this
section, we also discuss the obtained results in relation to a recent the-
oretical study by Jacobsen et al. [21] which was initiated by the results
presented in this chapter. In the final section before a concluding sum-
mary, we list a number of potential sources of error in the experiments,
and results regarding the way these have been dealt with are presented
and discussed.

5.2 Experimental procedures

The experiments were performed in a UHV chamber with a base pressure
around $5 \times 10^{-11}$ mbar equipped with a variable temperature STM as well
as standard facilities for sample preparation and characterization.

Initial cleaning of the Pt(110) crystal consisted of prolonged heating
in an oxygen atmosphere of $10^{-7}$ mbar at 900 K to remove residual car-on contaminants, combined with annealing in vacuum at 1200 K and
prolonged sputtering by 1.5 keV Ne ions at room temperature. Previous
studies have also found carbon to be the dominant impurity on Pt(110),
and observations of higher order reconstructions of the type (1×n) have
been ascribed to carbon contamination [22,23]. The described treatment
persisted till the crystal was clean as judged by AES and was in its (1×2)
5.2. EXPERIMENTAL PROCEDURES

reconstructed state as seen by LEED and STM. On a day-to-day basis, the Pt(110) crystal was sputter-cleaned with 1.5 kV Ne ion bombardment followed by annealing to 980 K with a ramp of 2 K/second.

The surface morphology of the clean Pt(110)-(1×2) surface is not found to consist of large flat terraces separated by occasional steps. Rather, we find alternating sequences of ascending and descending steps with step-edges primarily parallel to the close-packed direction. As a result, the surface is corrugated on a large scale and consists of elongated ridges oriented along the close-packed [110] direction. The amplitude of the modulation is of the order of 30 Å and the periodicity is judged to be of the order of 1000 Å. This mesoscopic surface self-organization has also recently been described by Hanesch and Bertel, who relate it to surface stress [23]. As a result of the described large-scale morphology, the typical terrace width is small. This makes it difficult to locate suitably large terraces for measurements to be carried out at. However, at the top of the ridges, terraces may occasionally be found with a width of sometimes up to ~1000 Å and a length of several thousand Å. The single atom diffusion is monitored on such perfect defect-free terraces.

The Pt adatoms were deposited on the surface by resistive heating of a thoroughly outgassed 0.4 mm diameter 99.995 % pure Pt wire, which was wound to a small coil to ensure homogeneous heating. There was no significant pressure rise in the chamber during deposition. The temperature of the sample during deposition was typically kept somewhat below the temperature at which the imaging was subsequently carried out.

After deposition, the sample was transferred to the STM for imaging at temperatures ranging from 280 K to 380 K. Temperature control was achieved by heating the top-plate of the STM as described in chapter 2. The temperature during scanning was measured with a Chromel/Alumel thermocouple mounted on the top-plate of the STM within a distance of approximately 1 cm from the sample. It was verified that the temperature measurement obtained in this way was consistent with the temperature measured by a thermocouple mounted directly to the back of the sample. During scanning the temperature of the sample was very stable and could be maintained constant to better than 1 K precision.

A typical time-lapse STM movie consists of on the order of 300-500 consecutive images. The images have 256×256 pixel resolution and usually show a 160×160 Å² area. To reduce adatom-adatom interactions as much as possible, all movies are acquired at very low coverages where only 5–20 adatoms are within this field of view at a time. For a given movie, the images are equidistantly spaced in time. In the following, we will denote
the time that elapses between the moments when the tip is at the same position in consecutive images by $t$. This time-period is a combination of the image acquisition time plus a possible waiting time between images, which typically amounts to $\sim 10\%$ of the acquisition time. The atomic mobilities vary greatly with temperature, and the image-to-image times, $t$, are varied accordingly. Values for $t$ range from 2 to 20 seconds. All STM movies are obtained in the constant current mode with $I_t = 1$ nA and $V_t = 100$ mV.

5.3 STM movies

In fig. 5.2 is shown an STM-image of the Pt(110)-(1×2) surface after a submonolayer amount of Pt has been deposited. The close-packed Pt rows separating the missing row troughs are imaged with atomic resolution. The deposited Pt atoms are found in the 1-D troughs, both as single adatoms and in the form of longer chains of agglomerated adatoms. The image is acquired after the sample has been held at the deposition temperature of 313 K for more than 4 hours.

From such a single image alone, a considerable amount may be inferred about the Pt adatom dynamics slightly above room temperature. The density of adatom islands is too large to be due to random impingement of deposited adatoms on neighbouring sites. This means that there must be some thermal adatom mobility allowing for the adatoms to meet, nucleate and grow into the one-dimensional islands. On the other hand, the fact that single adatoms are still left on the surface indicates that the mobility is sufficiently low for the nucleation and growth process not to have ceased even after several hours.

A direct insight into the adatom dynamics is attained by acquiring sequences of successive STM-images. When such time-lapse STM movies are played back, they reveal the changes that occur on the sample's surface from image to image. The migration of the adatoms in the troughs becomes immediately clear from such movies\(^1\). We never observe events where an isolated adatom travels from one missing row to another. The adatom diffusion is thus truly 1-D at temperatures up to at least 380 K.

As mentioned, a movie typically consists of several hundred images, each showing perhaps 5 or more isolated adatoms that should be analysed. Evidently, some sort of automation is needed to facilitate this process if the

\(^1\)Examples of movies can be found at our WWW site: http://www.dli.aau.dk/condensm/surface/stmlab/ptmovies/ptmovies.htm
information on surface diffusion contained in the movies is to be quantified. To meet this need, a tracking procedure has been developed that allows us to semi-automatically follow, or “track”, the position of an individual adatom through the movie.

Central to the tracking procedure is the following pattern-recognition routine that identifies the position of an adatom. Initially, a small area that contains the adatom to be tracked and part of the surrounding close-packed rows is defined in a given image. The pixel-information in this area, which we refer to as a template, is stored. In a subsequent image, where the adatom may have moved to another position, the appearance of the local environment of the adatom will still be very similar to that of the area stored in the template. Identifying the new position of the adatom therefore consists of finding the position of the template that minimizes the difference between the pixel-information in the template and in a similar area of the image. This is done automatically.

In practice, tracking of an adatom thus works by stepping through the images of a movie, in each step allowing the pattern-recognition routine to
identify the adatom position. In each new image, the old adatom position is taken as the starting point for the template search. As long as the adatom displacement between images is smaller than the extent of the template, the procedure works fairly automatically. The result is a record of the pixel-positions of a given adatom through a movie (i.e., the positions relative to the frame of the image).

To determine what adsorption sites these positions correspond to, distances have to be calibrated and a small lateral thermal drift in the movies has to be corrected for\textsuperscript{2}. The distance calibration is done from the atomically resolved close-packed rows separating the missing-row troughs\textsuperscript{3}. To correct for the drift, the position of an immobile feature on the surface, usually one of the one-dimensional islands, is tracked in a similar way. By relating the adatom positions to this fixpoint, it is possible to determine what lattice sites are occupied by an adatom through a movie.

From the determined adatom positions, the displacement (in lattice spacings) of adatoms between consecutive images can be derived. In fig. 5.3 we show examples of such distributions over adatom displacement attained at different sample temperatures. The number of observations, that is the number of times an adatom is observed in two consecutive images, displaced or not, typically amounts to several thousand.

Despite the fact that the distributions are acquired for slightly different times $t$ and therefore, strictly, are not directly comparable, the general trend that the distributions become broader (of larger mean square displacement) for higher temperatures is very apparent. At the low temperature, the adatoms are not very mobile and are typically observed to be at the same site through many images. At the higher temperatures, the mobility is increased and it is not uncommon to observe image-to-image displacement of an adatom over several lattice spacings.

### 5.4 Analysis of the displacement distribution

From the observed displacements of adatoms, we wish to derive the adatom hopping rate and identify a possible contribution from long jumps. The basic problem faced in interpreting the displacement distributions obtained from the STM movies is illustrated in fig. 5.4(a). The adatom occasionally

\textsuperscript{2}The drift problem was severely minimized after implementation of the automated drift compensation routine described in chapter 2, which utilizes the same pattern-recognition technique to lock-in on immobile features on the surface.

\textsuperscript{3}In contrast to FIM, we do thus not rely on a site-visitation map to determine the positions of the adsorption sites.
jumps from one lattice site to another along the one-dimensional trough. At equidistantly spaced moments in time, the position of the adatom is observed from the STM images. During the time-period \( t \) between consecutive observations, an adatom might perform several jumps which could be observed, for instance, as a displacement over several lattice spacings or, if the atom jumped back and forth, no displacement at all. Thus, due to the finite time-resolution, the observed displacement of adatoms between consecutive images cannot simply be equated with the actual adatom jumps. With this complication in mind, how are the observed distributions of adatom displacement related to the adatom hopping rate, and to what extent is it possible to derive from them information on a possible contribution from long jumps to the adatom mobility?

A detailed treatment of the problem of a 1-D random walk in continuous time, including the possibility that an adatom can make long jumps,
Figure 5.4: Schematic illustration of the random walk problem treated in the text. Panel (a) illustrates the position along the trough occupied by the adatom as a function of time (grey line). The random walk problem derives from the fact that the position of the adatom is only observed at equidistantly spaced moments in time (arrows) and the observed displacements can thus not be equated with the actual adatom jumps. Panel (b) illustrates single and double jumps during a 1-D random walk. Note the definition of the jump-rates.

has been carried out by Ehrlich and co-workers [19,20,12]. In the following section, we provide a derivation (very similar to that of ref. [19]) of an analytic expression for the adatom displacement distribution. By fitting the derived stochastic relation of the type (5.8) to an experimentally derived distribution of adatom displacement, the rates by which adatoms perform jumps covering one, two or, if need be, more lattice spacings may in principle be determined. The important issue as to what extent such a scheme may in practice be successful, given the inevitable statistical scatter in the measurements, is treated in the subsequent section. There we discuss results obtained by fitting the derived relation to displacement distributions obtained from KMC simulations of a 1-D random walk incorporating known amounts of single and double jumps.

5.4.1 Analytic random walk model

What we wish to obtain is an expression for the probability \( P_x(t) \) of an atom, initially at position \( x = 0 \) at time \( t = 0 \), to be at lattice site \( x \) at some
5.4. ANALYSIS OF THE DISPLACEMENT DISTRIBUTION

later time \( t \), given that it performs jumps covering one lattice spacing at a rate \( h_1 \), and double jumps covering two lattice spacings at a rate \( h_2 \) (see fig. 5.4(b)). For simplicity, we restrict the derivation of \( P_x(t) \) presented in the following to the case in which the adatom migration occurs by jumps covering a single lattice spacing only.

Consider first the case of a random walker moving on an infinite line of distinct sites, jumping to the left or to the right with equal probabilities. We denote the position of the walker by \( x \) (an integer) and assume that the random walk is started at position \( x = 0 \). The conditional probability, \( P(x|N) \), that the particle is found at position \( x \) after having performed a total of \( N \) jumps is straightforwardly \([24]\) given by the binomial expression

\[
P(x|N) = \binom{N}{x} \frac{N!}{(N-x)!} \left( \frac{1}{2} \right)^N
\]

(5.1)

Note that, trivially, after the particle has performed a total of \( N \) jumps, it has to be found at a position \(-N \leq x \leq N\), and also that if \( N \) is even, \( x \) also has to be even and, conversely, if \( N \) is odd, then so is \( x \). In accordance, the expression (5.1) is undefined (and \( P(x|N) = 0 \)) unless these criteria are fulfilled.

In the case we are considering experimentally, the number of adatom jumps between observations is low, typically on the order of or below unity. The mean number of jumps during the time \( t \) is \( \bar{N}_1 = h_1 t \). Since the adatom only makes a jump occasionally, however, fluctuations in the time between jumps are important for our observations. Inserting the expression for \( \bar{N}_1 \) in (5.1) will therefore not suffice to correctly describe a random walk in continuous time. The fluctuations in the number of jumps between observations, \( N \), are treated by making two very general assumptions about the jump processes: (i) in the limit of very short time intervals, the probability for more than one jump to occur approaches zero, and (ii) jumps occur independently of each other. Under these assumptions, the probability \( P(N) \) of having \( N \) jumps during the time \( t \) follows a Poisson distribution \([25]\), and

\[
P(N) = \exp(-h_1 t) \frac{(h_1 t)^N}{N!}
\]

(5.2)

Note that a Poisson distribution for the number of jumps implies that the waiting time before a jump occurs is exponentially distributed, i.e. the probability that a jump has not occurred after a time \( t \) is given by \( P(t) = \exp(-h_1 t) \).
The desired probability function $P_x(t)$ is now obtainable as

$$P_x(t) = \sum_{N=0}^{\infty} P(x|N)P(N). \quad (5.3)$$

The expressions (5.1) and (5.2) are inserted into (5.3). By substituting $N = 2n + x$ and summing over $n$, we avoid terms where $P(x|N) = 0$ and obtain

$$P_x(t) = \exp(-h_1 t)(\frac{h_1 t}{2})^x \sum_{n=0}^{\infty} \frac{(\frac{h_1 t}{2})^{2n}}{(n + x)!n!}. \quad (5.4)$$

The modified Bessel function of the first kind of order $\nu$ is given by [26]

$$I_{\nu}(z) = (\frac{z}{2})^{\nu} \sum_{n=0}^{\infty} \frac{(\frac{z}{2})^{2n}}{(n + \nu)!n!} \quad (5.5)$$

and consequently $P_x(t)$ may be more elegantly expressed as

$$P_x(t) = \exp(-h_1 t)I_x(h_1 t). \quad (5.6)$$

The probability function $P_x(t)$ is properly normalized, $\sum P_x(t) = 1$. The second moment of $P_x(t)$, which is equivalent to the mean square displacement of the diffusing adatom, is given in units of the lattice spacing by [19,20]

$$\langle \Delta x^2 \rangle = \sum_{x=-\infty}^{\infty} x^2 P_x(t) = h_1 t = N. \quad (5.7)$$

Thus, if only single jumps participate in the adatom diffusion, the adatom hopping rate may be directly determined from the mean square displacement, $\langle \Delta x^2 \rangle$, which is readily calculated from the observed displacement distribution.

The slightly more complicated problem of a 1-D random walk incorporating double jumps covering two lattice spacings in addition to single jumps has been treated by Wrigley, Twigg and Ehrlich using arguments similar to the ones presented above and also, more elegantly but physically less transparent, using a generating function approach [20]. The

\[\text{The relation } \langle \Delta x^2 \rangle = \frac{N}{N} \text{ between mean square displacement and mean number of jumps in a 1-D random walk is a well known result for large } N \text{ [24] (Einstein relation). Importantly, the treatment presented here shows that the result is also valid in the limit of small } N \text{ where jumps occur only occasionally.}\]
probability distribution equivalent to (5.6) obtained for this case is
\[ P_x(t) = \exp[-(h_1 + h_2)t] \sum_{j=-\infty}^{\infty} I_j(h_2 t) I_{x-2j}(h_1 t). \] (5.8)

Similar expressions extended to incorporate rates for jumps covering even longer distances may also be straightforwardly obtained [20].

For the case where both single and double jumps participate in the diffusion, the mean square displacement in units of the lattice spacing is [20]
\[ \langle \Delta x^2 \rangle = (h_1 + 4h_2) t. \] (5.9)

This relation shows that, for a given \( t \), the distribution function (5.8) is uniquely defined by the mean square displacement, \( \langle \Delta x^2 \rangle \), and the ratio \( h_2/h_1 \) between the rates for double and single jumps.

The mean square displacement is readily obtained from the displacement distributions derived from experiment or KMC simulations. In fitting the relation (5.8) to the probabilities obtained by normalisation of such distributions, we therefore need only vary the quantity \( h_2/h_1 \) until a best agreement is obtained. The rates \( h_1 \) and \( h_2 \) are subsequently obtained from the fitted \( h_2/h_1 \), the time \( t \) and the known mean square displacement using the relation (5.9).

Following Ehrlich and co-workers [12], we maximize a log-likelihood function, \( \ln(L(h_2/h_1)) \), to achieve best agreement between the distribution \( P_x^{\text{real}} \) derived from experiment or simulation and the trial function \( P_x(h_2/h_1) \). The likelihood estimator is given by
\[ L(h_2/h_1) = \prod_x P_x(h_2/h_1)^{x^{\text{real}}}. \] (5.10)

The evaluation of modified Bessel functions needed to calculate the probability function (5.9) is done most efficiently using routines from a suitable programme library [27] rather than the expression (5.5).

5.4.2 Statistical significance

In the previous section, an expression was derived for the distribution \( P_x(t) \) of probabilities for observing displacements of different lengths in a random walk incorporating single and double jumps. Under certain circumstances, the presence of long jumps may be quite apparent from the displacement distribution. For the sake of argument, consider the extreme case where
the mobility is due exclusively to double jumps. Here the distribution will consist of displacements covering an even number of lattice spacings only. In reality, of course, long jumps are expected to constitute only a small fraction of the total number of jumps. This section deals with the question of to what extent the existence of double jumps in diffusion may in practice be revealed under such circumstances by comparing the prediction (5.8) to distributions derived from experiment. This issue has previously been addressed in some detail by Wang, Wrigley and Ehrlich [12].

General consideration

An experimentally obtained displacement distribution, for which \( N_x \) denotes the number of observations of displacements covering \( x \) lattice spacings, is characterized by the total number of observations, \( M = \sum N_x \), and the mean square displacement, \( \langle \Delta x^2 \rangle = \frac{1}{M} \sum x^2 N_x \). A useful result is that the expected standard deviation on the number of observations of displacements of length \( x \), \( \sigma(N_x) \) is given by [12]

\[
\sigma(N_x) = \left[ N_x \left( 1 - \frac{N_x}{M} \right) \right]^{1/2}, \tag{5.11}
\]

It seems intuitively reasonable when comparing displacement distributions as those shown in fig. 5.3 that distributions with a larger mean square displacement should be “better” or “contain more information” than narrow ones with a small value for this quantity. This is, however, not entirely true.

In the limit of large \( \langle \Delta x^2 \rangle \), the probability distribution (5.8) becomes broad and approaches the Gaussian form usually expected from a random walk problem [19, 20, 12, 24]. In this case, all information on the detailed jump processes is smeared out, and it becomes more difficult to unravel the contribution of different jump-lengths to the mobility. This level seems to be reached already at \( \langle \Delta x^2 \rangle \sim 3 \sim 5 \). The time between observations should thus preferably be kept below, or at least comparable to the mean time between adatom jumps.

To consider the opposite limit of small mean square displacement, imagine that we choose a fixed total time to observe a system of diffusing adatoms and do this with increasing sampling frequencies (by scanning faster). In that case, we will obtain distributions with more observations, \( M \), but lower \( \langle \Delta x^2 \rangle \). Clearly, however, this does not diminish our ability to resolve whether long jumps occurred. The important question to ask in the limit of small mean square displacement is whether the integral
number of long jumps derived from the displacement distribution is in fact significant.

KMC simulations

General statements of the type presented above do not suffice, however, to reliably judge whether a double jump rate derived from a given measured displacement distribution is endowed with a reasonable degree of statistical significance. A very generally applicable tool in this respect is to perform simulations of a random walk incorporating given rates for double and single jumps, for instance those determined from a measured distribution, and then fit the resulting displacement distributions by the relation (5.8) to see how well the input rates may be regained. In this way, both the statistical scatter in the numbers of double and single jumps as well as the obscuring effect introduced by the random walk, as illustrated in fig. 5.4(a), are taken into consideration.

The Kinetic Monte-Carlo routine employed to simulate 1-D random walks works according to the following principles [28, 29]. The walker moves on a line of sites. In each step of the simulation, it moves to the left or to the right (with equal rates) by either one (rate $h_1/2$) or two (rate $h_2/2$) lattice spacings (see fig. 5.4(b)). Let $h = \sum h_i = h_1 + h_2$ denote the sum of the rates for these four processes. Which of the four processes is to be carried out at a given step of the simulation is chosen randomly but weighted according to the probabilities $P_i = (h_i/2)/h$ for each of the processes to occur. The time that elapses between successive jumps should on average be $\tau = 1/h$. However, since we wish to sample the position of the walker at time-intervals comparable to $\tau$, fluctuations in the time that elapses between jumps occur will be of importance. We therefore keep track of time in the simulation by incrementing it following each step where the walker has moved by an amount $\Delta t$, which is picked randomly\footnote{The time increments are obtained as $\Delta t = -\tau \ln(z)$, where $z$ is a uniform random number in the interval $[0; 1]$.} from an exponential distribution of times with mean $\tau$ [29]. The position of the walker is evaluated at time-intervals $t$, and the simulated displacement distribution is obtained as the displacements between such successive observations. The simulation is stopped after a predefined number of observations.

It is verified that if averaging is performed over a large number of displacement distributions calculated by the approach described above, then the result is indeed in agreement with the distribution given by (5.8). Similarly it is found that the standard deviations on the mean number of
observations of displacements of a given length, $N_x$, obtained from many such simulated distributions, comply very well with the relation (5.11).

An example

We now describe a general example that illustrates to what extent we may expect to be able to identify the presence of double jumps from the experimental data.

Displacement distributions with a desired mean square displacement, $\langle \Delta x^2 \rangle$, and a double to single jump ratio, $h_2/h_1$, (on average) may be obtained from simulations with input parameters, $h_1$ and $h_2$, calculated from (5.9). The time between observations, $t$, enters all relevant expressions in the form $h_2 t$ and serves therefore merely to define a scale for the rates $h_1$. For convenience, we may set $t = 1$. All distributions in the example discussed here are for $\langle \Delta x^2 \rangle = 1$ and have a number of observations of $M = 1000$. In the simulations, the ratio $h_2/h_1$ has been varied in the range from 0.01 to 1, and it is subsequently investigated to what extent this input ratio may be regained by fitting the expression (5.8) to the simulated displacement distributions. The results are illustrated in fig. 5.5.

In fig. 5.5(a) is depicted the correlation between the $h_2/h_1$ that is input to the simulation and the $h_2/h_1$ that subsequently results from the fitting. Each point on the curve is determined as an average over the results obtained by fitting to 50 simulations. The shown confidence intervals represent one standard deviation (in either direction) calculated from these fitted values for $h_2/h_1$. The correlation between input and output values is good for these averaged quantities, even down to the level of a few per cent double jumps. The identification of such low levels of double jumps thus appear to be possible.

In the experimental situation, of course, we are likely to have obtained only a single distribution at a given temperature. To further illustrate the magnitude of the inevitable statistical scatter, we focus on the case where $h_2/h_1 = 0.1$ is input to the simulations and examine the spread in output values for this quantity. It is also instructive to examine the case where $h_2 = 0$ and ask the question: If no double jumps are allowed in the simulation, to what extent does the random walk then conspire to make it look as if double jumps were present?

For each of these two cases, 1000 distributions have been simulated, and the averages over these distributions are shown in panel (b) in fig. 5.5. We stress the fact that the two distributions do not appear very different.
Figure 5.5: Results from KMC simulations aimed at elucidating to what extent double jumps can be reliably identified from analysis of displacement distributions. (a): Correlation between the fraction of double jumps that is input to the simulations and the fraction that is subsequently determined from fitting to the simulated distributions. (b): Comparison of averaged distributions obtained from simulations with and without double jumps, respectively. (c) and (d): Histograms over the determined double to single jump ratio derived from fitting to these simulated distributions. See text for further details.
This is to be expected – the only difference between the simulations leading to them is that in one case roughly every tenth jump covers two lattice spacings instead of one while in the other the migration proceeds by single jumps only.

In spite of this similarity, the results obtained by fitting to the two sets of displacement distributions are quite different as may be seen from panels (c) and (d) of fig. 5.5. Here histograms over the resulting fitted values for $h_2/h_1$ are shown. For the case without double jumps (c), the dominant result is that, indeed, no double jumps are found from the fitting (note the axis break). To the low extent to which double jumps are erroneously determined, the values found for $h_2/h_1$ are below $\sim 5\%$. From the simulations that do incorporate double jumps (d), the fitted values for $h_2/h_1$ are symmetrically scattered around the input value of $h_2/h_1 = 0.1$ with a Gaussian envelope\(^6\) from which a standard deviation of $\sigma = 0.03$ is determined. From the large difference between the histograms in fig. 5.5(c) and (d), it is evident that identification of double jumps at a level of $h_2/h_1 = 0.1$ is feasible. In general, the example justifies that double jumps down to a level of at least $\sim 4\%$ may be reliably identified.

5.5 Long jumps — Arrhenius behaviour

In the previous section, the tools necessary for analysing distributions of the type shown in fig. 5.3 were treated. We now describe the results of this analysis. After this we discuss the results briefly in relation to other experimental work, and thereafter we describe fairly extensively results from a recent theoretical investigation by Jacobsen et al. [21]. In this work, which was initiated by the experimental results presented in this section, these authors provide a valuable picture of the way in which long jumps occur, and develop what they term transition path theory in order to account for such processes quantitatively.

\(^6\)Parenthetically, it may be remarked that if we plot a similar histogram over the ratio between the numbers of double and single jumps that actually occurred in these simulations, we then find a Gaussian envelope with a width that is $\sim \frac{1}{3}$ of that found for the fitted $h_2/h_1$. Thus, for this particular case at least, the "smearing" introduced by the random walk process acts to increase the scatter on the determined values for $h_2/h_1$ by a factor of $\sim 3$ over the purely statistical scatter in the number of double jumps that occurs.
5.5. \textit{LONG JUMPS — ARRHENIUS BEHAVIOUR}

![Graph showing displacement distribution with experimental and theoretical fits.](image)

Figure 5.6: Comparison of experimentally derived displacement distribution and the best fits assuming only single jumps and both single and double jumps, respectively. The best fit (dark grey) is obtained with a double to single jump ratio $h_2/h_1 = 9.5\%$.

5.5.1 Results

In fig. 5.6 we show an example of an experimentally determined displacement distribution together with the best fits of the expression (5.8) for $P_x(t)$ when we allow for (i) only single jumps ($h_2 = 0$) and (ii) both single and double jumps. Keeping in mind the example of the previous section, the fit allowing for both single and double jumps is clearly seen to be superior. We thus conclude that it is imperative to include double jumps to account for the observed displacement distribution.

A similar analysis has been carried out for distributions attained at a range of temperatures, and in all cases double jumps have been identified, except for the lowest temperature considered where the integral number of jumps was too low for the question to be answered. The determined hopping rates for single and double jumps are plotted in fig. 5.7 versus $1/T$. The ratio between double and single jumps, that is $h_2/h_1$, increases slightly with temperature, but lies in the 5-10\% range.

The determined double jump rate is thus within the regime where the
Figure 5.7: Arrhenius plot of the derived rates for single \( h_1 \) and double jumps \( h_2 \), respectively.

The example treated in the previous section shows that it is possible to reliably identify a contribution from double jumps. In the general case, the ability to identify a contribution from double jumps depends on the parameters of the obtained displacement distribution (i.e., total number of observations and mean square displacement). While the choice of parameters in the example is typical for the experimental data acquired, variations exist between the distributions attained at different temperatures. To ascertain that the double jump rates derived from the experimental data indeed have statistical significance, simulations were performed for each distribution derived from the experiments with the relevant parameters for the particular distribution and rates identical to those obtained by fitting to this distribution. The confidence intervals shown on fig. 5.7 correspond to one standard deviation (in either direction) obtained from fitting to such simulated distributions. We conclude from the figure that the existence of long jumps is indeed statistically significant.

It should be remarked that in the analysis carried out, a possible contribution to the adatom migration from jumps covering three or four lattice spacings was also considered. This was done by extending the expression (5.8) to include the rates for such transitions. It was occasionally possible
to obtain a marginally better agreement with the experimentally derived distributions by including these processes. Such a behaviour is generally to be expected, however, from including more fitting parameters, and the determined contribution from such longer jumps was so low that it was concluded to be insignificant from arguments of the type presented in the previous section (the contributions were below $\sim 1\%$ for the triple jumps and substantially lower for the jumps covering four lattice spacings). We stress that these findings do not rule out that triple jumps with a rate below $\sim 1\%$ of that for the single jumps could occur, but the existence of such a contribution can not be ascertained with any significance from the performed experiments.

Returning to the Arrhenius plot of fig. 5.7, the hopping rate for the single jumps is seen to exhibit an Arrhenius dependence on temperature. More importantly, however, such an Arrhenius dependence is seen to hold also for the double jump rate. By fitting to the Arrhenius form, $h = \nu \exp(-E_a/k_BT)$, where $\nu$ is the prefactor, $k_B$ is Boltzmann's constant, $T$ is the temperature and $E_a$ is the activation barrier for diffusion, we obtain for the single jumps: $E_{a1} = 0.81 \pm 0.01$ eV, $\nu_1 = 10^{10.7\pm0.2}$ sec$^{-1}$ and for the double jumps: $E_{a2} = 0.89 \pm 0.06$ eV, $\nu_2 = 10^{10.9\pm0.8}$ sec$^{-1}$ (the error bars represent one standard deviation). The activation barrier determined for the double jumps is thus slightly larger than that for the single jumps by an amount $\Delta E = E_{a2} - E_{a1} = 0.08 \pm 0.06$ eV.

Comparison to other experimental results

The present findings can be compared to the FIM studies of Pd and W on W(211) by Ehrlich and co-workers [13] using the same method of analysis as described here. In this case no long jumps were found for the self-diffusion of W on W(211). For Pd on the other hand, significant amounts of long jumps were identified at a single temperature of 133 K. The long jumps disappeared completely, however, by a lowering of the temperature by only 11 K to 122 K. This led the authors to suggest that the barrier for a double jump in this system was roughly twice as big as that for a single jump.

The selfdiffusion of Pt on the unreconstructed Pt(110) surface has been investigated by Kellogg using FIM [30] (without addressing the issue of long jumps). Interestingly, the adatom diffusion rate along the close-packed [100] direction on this surface is found to be considerably higher, by roughly two orders of magnitude, than the rate determined in the present investigation for adatoms situated in the missing row troughs (the rates
determined by Kellogg are shown in chapter 7, fig. 7.6). The results of Kellogg appear to be in agreement with an earlier investigation by Basset and Webber [31]. The origin of this difference with respect to diffusion on the reconstructed surface is not known. It is worth noting, however, that diffusion along the orthogonal [001] direction is known to occur through an exchange mechanism on the unreconstructed surface [31.2]. In this respect it could be speculated that the close-packed rows on the reconstructed surface acted to change the diffusion mechanism along the close-packed [1\bar{1}0] direction.

5.5.2 Transition path theory

The data presented here constitute the first experimental demonstration that the rate for double jumps follow an Arrhenius dependence on temperature. Even though this result might have been expected from general considerations of activated processes, it has apparently never been shown explicitly\(^7\) in any of the previous theoretical papers on this subject.

Inspired by the results presented in this chapter, a theoretical investigation of the diffusion of Pt adatoms in the missing row troughs of the reconstructed Pt(110)-(1 \times 2) surface was initiated by Jacobsen et al. [21], especially focusing on the rates for double jump transitions. The key results that emerge from this work are: (i) a picture of how a double jump transition occurs and (ii) the development of what the authors term Transition Path Theory, showing that a thermally activated form is indeed to be expected for the rate for such correlated double jump transitions. In the following this is described in further detail, placing special emphasis on the simple picture provided by these authors, rather than on the technical details of the calculations.

To clarify, let us start by providing a picture of how an ordinary single jump occurs. Here, a thermal energy fluctuation acts to bring the adatom from the adsorption site and up into the transition state at the saddle point of the potential energy surface separating this site from an adjacent site along the troughs. From this position the adatom slides down into the adjacent well, transferring its energy to the nearby atoms, until finally it is at rest in this adjacent well. The minimum energy fluctuation for which this occurs is the transition state energy, \(E_{TS}\) (equivalent to the \(E_{\text{ad}}\) used earlier) and the associated rate is given by the usual Arrhenius expression from Transition State Theory, \(r_{1}^{TS} = \nu \exp(-E_{TS}/k_{B}T)\). The

\(^7\)Georgievskii and Pollak have remarked that the result is implicit in theory published by them [32,33] (E. Pollak, private communication).
question is, what is the equivalent minimum energy fluctuation that acts to bring the adatom over the initial saddlepoint, through the central well (without coming to rest there) and over the second saddle point, resulting in a double jump transition?

An appealing picture is the following: The adatom is excited over the initial saddle point with an extra energy compared to the minimum energy, $E_{TS}$. This allows the adatom to sustain some energy loss as it passes through the central well, and yet still be able to overcome the potential energy barrier of the second saddle point.

The authors show, however, that while such a scenario can occur, it is not the correct picture if one wishes to identify the minimum energy fluctuation of the system for which a double jump transition occurs. Instead, they show that one should rather focus attention on the adatom as it is in the central well which separates the starting and ending adsorption site, since it is at this point that the additional energy is most localized near the adatom. What happens is that energy, stored in degrees of freedom of the substrate lattice at the time the adatom crosses the first saddle point, radiates in and is localized near the adatom as it passes through the central well, thereby acting to bring it up on top of the second saddle point.

To further appreciate this picture, let us briefly consider the way in which the minimum energy fluctuation required for a double jump to occur is calculated by the authors, using molecular dynamics simulations within the effective medium theory.

They start with the adatom in the central well and all the lattice atoms at their relaxed positions. Let $p_x$ denote the momentum of the adatom at this position along the direction of the trough. By running the molecular dynamics simulation forward and backwards in time they determine the minimum momentum, $p_x^{\text{min}}$, that allow the adatom to perform a double jump, that is cross into the well on one side at large negative times and into the well at the other side at large positive times. They then optimize the degrees of freedom (that is, the positions and momenta) of the lattice atoms that are near to the adatom as it is in the starting configuration in the middle of the central well. By doing this they identify the configuration of the system with minimum total energy for which a double jump can still occur.

This optimum trajectory in phase space, which brings the diffusing adatom over the initial saddle point, trough the central well, over the second saddle point and into the final adsorption well with the minimum energy fluctuation of the system, is termed the Transition Path, and the associated energy fluctuation is the transition path energy $E_{TP}$. 
In the second stage of the investigation the authors develop what they term Transition Path Theory (in analogy to ordinary Transition State Theory). Here they show that the rate, \( r_2^{TPT} \), for such correlated double jump transitions depends on the energy fluctuation of the Transition Path according to the thermally activated form,

\[
    r_2^{TPT} = C_1 \sqrt{T} \exp(-E_{TP}/k_BT).
\]

That is, aside from the \( \sqrt{T} \) dependence of the prefactor, an Arrhenius dependence on temperature. For the ratio between the rates for double and single jump transitions the authors therefore find

\[
    \frac{r_2^{TPT}}{r_1^{TST}} \sim \sqrt{T} \exp(-(E_{TP} - E_{TS})/k_BT). \tag{5.13}
\]

In the final part of the study, molecular dynamics simulations are performed to directly determine the ratio between the rates for double and single jump transitions, and thereby test whether there is agreement with the theoretically derived expression (5.13) using the energy difference \( E_{TP} - E_{TS} \) obtained from the initial total-energy calculations. By focusing attention on the transition path it is possible to do these simulations in a numerically efficient way, allowing for a large temperature range to be probed. The agreement is indeed found to be good, confirming the thermally activated form and also the \( \sqrt{T} \) dependence of the prefactor.

The \( \sqrt{T} \) dependence of the prefactor is interesting for fundamental reasons, but less relevant from the experimental point of view, since the temperature range over which experimental data can be acquired is to limited that such an effect can be revealed (temperatures in the range from \( \sim 20 \) to \( \sim 1200 \) K are considered in the simulations that reproduce the \( \sqrt{T} \) dependence!).

In addition to providing a very valuable intuitive picture of the way in which a long jump occurs, the investigation by Jacobsen et al. therefore, for all practical purposes, confirm that an Arrhenius form is to be expected for the rate for the double jump transitions, in agreement with the experimental results presented earlier. We can thus interpret the energy \( E_{d2} \), derived from the experiment, as the energy of the transition path, and the energy difference \( \Delta E = E_{d2} - E_{d1} = 0.08 \pm 0.06 \) eV becomes the extra energy that has to be present in the system for a long jump to occur as compared to an ordinary single jump.

The agreement between experiment and theory is less good in the absolute numbers, however. The barrier for single jumps found from the
calculations by Jacobsen et al. is thus only $E_{TS} = 0.47$ eV in contrast to the $E_{d1} = 0.81$ eV. The additional energy fluctuation for a long jump to occur is determined to be $E_{TP} - E_{TS} = 0.12$ eV, i.e. a result quite close to that obtained from the experiment. Given the difference in the diffusion barriers this agreement should be interpreted with caution, however, and could be accidental. Also the ratio between the rates for double and single jumps is considerably lower in the simulations than what is found experimentally. Thus, at the highest temperature of 770 K probed in the simulation, a ratio of $r_2/r_1 \sim 2\%$ is determined, and the ratio decreases for lower temperatures.

5.6 Potential sources of error

This section is devoted to a discussion of a number of potential sources of error that could have influenced the results on Pt adatom diffusion presented in the present chapter. In the analysis of the experimental data, it is implicitly assumed that the adatom migration is a random walk between equivalent sites with jump-rates independent of time. A number of factors could affect the validity of this assumption. First, we have to consider the possibility that the adatom diffusivity is influenced by the presence of the STM tip. This question is addressed in the following subsection. The importance of adatom-adatom interactions and a possible influence of adsorbates are then discussed. Finally a more technical matter related to the time-separation, $t$, in the random walk analysis is briefly treated.

In two of the following subsections, those on tip-influence and adsorbates, further experimental results are presented.

5.6.1 Tip-influence

At present, a rapidly growing number of studies are emerging where STM is used to probe dynamic phenomena [10,11,34–36]. However, in several cases the STM has also been used successfully to manipulate atoms and molecules on surfaces [37–39,42]. The obvious question as to under what conditions STM may by used in a non-perturbative way to monitor dynamic processes therefore certainly deserves attention. In the following, we treat this important issue. First, a general introduction is provided. We then present experimental results aimed at identifying a parameter regime where the STM may be used in a non-perturbative way to study dynamic phenomena in the present system. Finally, these results are discussed.
CHAPTER 5 — Pt DIFFUSION ON Pt(110)-(1×2)

Introduction

Recall that the resistance, $R_t$, of the tunnel junction in STM can be expressed to simplest approximation as [40]

$$R_t = V_t / I_t \propto \exp(1.025 \sqrt{\phi d}),$$  \hspace{1cm} (5.14)

where $I_t$ and $V_t$ are the tunneling current and voltage, respectively, $\phi$ is the average barrier height (in eV) and $d$ is the tip-surface distance (in Å). The resistance therefore provides a simple measure of the tip-surface distance. Even though the tunneling voltage and current do not normally attain values that sound dramatic (mV and nA, usually), the electric field and the current density in the junction are substantial due to the small dimensions of the gap, on the order of some Ångström.

At low temperatures, where thermal mobility is excluded, adatoms have been manipulated by using directly the inter-atomic potential or chemical binding force between the adsorbate and the outermost tip atom or atoms. In these experiments, the tip is moved towards the adatom, which is then dragged along the surface followed by retraction of the tip. Examples include Xe on Ni(110) [37], the quantum corrals formed by Fe on Cu(111) [41] and very recently Cu on Cu(211) [42]. The threshold resistances reported for manipulating metal atoms on a metal surface by such a sliding process are low, implying very short tip-adatom distances. We mention 20 kΩ for manipulating Pt on Pt(111) [39] and 500-700 kΩ for moving Cu atoms across and along step-edges on Cu(211) [42].

At higher temperatures, thermal processes may be of importance. If the binding energy of an adatom, or the activation barriers for transitions between binding sites, are perturbed under the tip, the adatom dynamics here may be different from elsewhere on the surface. If the adatom is able to jump between sites under the tip, but unable to jump away from the tip-region, it may be made to follow the motion of the tip, moving on a time-evolving potential energy surface.

A change in the potential energy of an adatom under the tip may be caused by the electric field in the tip region, which can act on a permanent or induced dipole moment in the adatom [38,39]. The spatially inhomogeneous field, concentrated near the tip apex, can lead to a potential energy gradient, that is a force, along the surface which results in field-assisted directional diffusion of the adatom. Cs adatoms deposited on GaAs and InSb semiconductor surfaces have been found to migrate towards and accumulate under a stationary tip, a phenomenon that has been attributed to such a field-effect [38,39].
5.6. **Potential Sources of Error**

Even in the absence of an electric field, the sheer proximity of the tip may perturb the activation barrier for adatom diffusion under the tip, provided that the tip is close enough to the surface. In calculations by Sørensen et al. [13], the minimum energy path for diffusion of a Au adatom on a Au(100) surface when a tip (modelled as a Au(100) surface) was at short proximity has been determined using potentials derived from effective medium theory. For short tip-surface separations, a considerable decrease in the diffusion barrier is found. The effect is found to decay rapidly with increasing tip-sample separation, however, and at normal imaging separations it should be negligible (we will return to these results in more detail below).

Finally, it has been speculated that a heating effect could occur, where the current in the gap region acts by inelastic scattering of electrons off the adatom to promote this into a vibrationally hot state that may easier jump to an adjacent site [39].

Systematic experimental investigations of the influence of STM imaging on dynamic phenomena are scarce. Schneider and co-workers have reported an influence on step-dynamics observed on Ag(110) at room temperature, even under moderate scanning conditions normally used for imaging [44]. These findings are contrasted, however, by the work of Morgenstern et al., who have investigated the dynamics of adatom and vacancy islands on Ag(111) using STM and report that they are able to do so without any tip-influence [35,36]. With respect to single metal adatom diffusion, Comsa and co-workers were able to follow the motion of Pt adatoms on the flat Pt(111) surface, where self-diffusion occurs with a barrier of only $E_D = 0.26$ eV, but found that the adatom migration was influenced by the STM tip [8]. An increasing number of investigations concerning diffusion in semi-conductor systems [16] or gaseous adsorbates on surfaces [11,34], however, report that it is possible to study adatom dynamics in a non-perturbative manner using STM.

**Results**

In the following we will describe a number of investigations aimed at elucidating whether the STM imaging affects the observed adatom mobility. Motivated by the expression (5.7) we have used the diffusivity, $(\Delta x^2)/t$, as a measure of the adatom mobility.\(^8\)

\(^8\)In the case where there is tip-influence, the adatoms do not execute an unperturbed random walk, and it is not a priori clear how the data should be analysed. Essentially (except for constants of proportionality), the chosen measure for mobility, $(\Delta x^2)/t$, is
Figure 5.8: Diffusivities plotted versus tunnel junction resistance. (a) is for $T = 303$ K whereas (b) is for $T = 322$ K. The horizontal lines correspond to the Arrhenius fit on fig. 5.9 at these two temperatures, respectively. Representative error bars are shown.

Motivated by the expression (5.14) we focus on the resistance, $R_t$, in the tunnel-junction. By adjusting $I_t$ and $V_t$ to produce different resistances, we have acquired several STM movies where $R_t$ is varied through the movie to investigate how different resistances affect the diffusivities. At each value for $R_t$, 25 images have been acquired. In fig. 5.8 we plot the diffusivities, $\langle \Delta x^2 \rangle / t$, obtained for each such 25-image slot at fixed resistance versus $R_t$. Within the expected statistical scatter the diffusivity exhibits a plateau over a very wide range of resistances ranging up to the highest values probed of $R_t = 1000$ MΩ. At low resistances, however, a considerable increase in the diffusivity is observed for some of the datapoints.

Chronologically, these types of measurement were occasioned by our initial attempts at measuring adatom dynamics in the Pt/Pt(110)-(1×2) system. In these trial experiments, STM movies were acquired with tunneling parameters corresponding to fairly low resistances$^9$ since this approach usually maximizes corrugation and produces “good” images. The diffusivities derived from these initial low $R_t$ experiments are shown with squares

the ordinary tracer diffusion constant [2]. Directly addressing the issue of whether long jumps are affected by the imaging is in practise a hopeless task given the large statistical material required.$^9$

$^9$The tunneling parameters such as $I_t$ and $V_t$ are normally stored automatically with the data. Unfortunately this was not done correctly during acquisition of the described initial data due to a programming error. A conservative estimate for the resistance during these measurements is $R_t < 20$ MΩ. The resistances were probably often considerably below this value, however.
Figure 5.9: Comparison of diffusivities attained from experiments at different $R_t$. Circles: same data as shown previously in fig. 5.7, squares: initial data (see text), and triangles: the data also shown in fig. 5.10

In fig. 5.9, shown for reference (circles) are the diffusivities obtained from the later final dataset (ie the dataset used in producing fig. 5.7) which was acquired at $R_t = 100$ MΩ. The diffusivities obtained from the initial dataset show substantial scatter, and generally lie at higher values than those derived from the dataset acquired at $R_t = 100$ MΩ. This difference in diffusivity is attributed to an influence of the STM tip on the adatom mobilities in the low $R_t$ case, as was also evidenced in the curves of fig. 5.8 (although the increase is less pronounced for these data).

In the limit where the tip is far away from the surface (large $R_t$), any tip-influence must be negligible. We interpret the observation of constant diffusivities over a wide range of resistances extending up to $R_t = 1000$ MΩ as evidence that this non-perturbative regime has been reached. The value of $R_t = 100$ MΩ used in the final measurements is well within this regime of negligible tip-influence. In the final diffusivity measurements, the resistance of $R_t = 100$ MΩ was realized with tunneling parameters $V_t = 100$ mV and $I_t = 1$ nA. In addition to the experiments described above, it was verified that if the voltage was varied in the range from $V_t = 25$ to $V_t = 250$ mV, and the current was adjusted accordingly to keep $R_t = 100$ MΩ, then no change in the adatom mobilities resulted.

We now turn to describe measurements aimed at investigating fur-
ther the tip-influence found in the perturbative regime. Irrespective of the origin of the perturbation at low resistances, we expect it to be a local phenomenon that is effective for a given adatom only when the tip is in close proximity. Thus, when the tip is scanning the lower left corner of an image, for instance, it should have no effect on the mobility of an adatom situated in, say, the upper right corner of the field of view, perhaps more than 100 Å away. Loosely speaking, there must be some fairly small region of interaction around a given adatom, and only during the “interaction time” that the tip spends in this region, will it act to perturb the diffusivity of this adatom. The increased diffusivity, $(\Delta x^2)/t$, at low resistances (as shown on fig. 5.8) is an average measure that does not take these considerations into account. The true perturbative effect of the tip can only be ascertained if we know how large a fraction of the time $t$ this interaction time amounts to.

If a given area of the surface is scanned with different times, $t$, the fraction of the time spent in the interaction region does not change since this is determined solely by the ratio between the area of the interaction region and the total image area$^{10}$. Changing the size of the scanned area, on the other hand, changes the fraction of the time spent in the interaction region. Furthermore, it can not a priori be ruled out that the scanning frequency, i.e. the number of times per unit time that the tip passes over the adatom, may not also affect the diffusivities in the perturbative regime.

Given these considerations, movies were acquired in which the image size and the scanning time per image, $t$, where systematically varied. In these measurements, a resistance of $R_\text{i} = 10 \Omega$ ($I_\text{i} = 1 \text{nA}, V_\text{i} = 10 \text{mV}$) was used. The diffusivities derived from these measurements are shown in fig. 5.10 versus the image size and the acquisition time per image (the data are also included in fig. 5.9 as triangles). Unfortunately, the results obtained from these measurements are completely inconclusive. As may be verified by inspection of fig. 5.10, no systematic trend is found for the diffusivity by variation of either the image size or the scanning time. It may be remarked that the variations in diffusivity are too large to be ascribed to statistical scatter.

Finally, we mention that the displacement distributions derived from measurements carried out in the perturbative regime are often found to be asymmetrical as illustrated in fig. 5.11. This propensity of adatoms to move in one direction in some instances is the only immediately apparent indication in the movies that the adatom migration is influenced by the imaging process. Reasons for this asymmetry have not been identified.

$^{10}$This assumes that there is no waiting time between images
Figure 5.10: Results from experiments aimed at investigating whether the size of the scanned area or the image-to-image time has any effect on the adatom mobilities in the low resistance case ($R_t = 10 \, \text{M} \Omega$). The derived diffusivities are shown versus these two quantities (the area is given as the edge-length of the quadratic image). As it may be seen, no systematic trend with any of these parameters is found. Note that these datapoints are also included in fig. 5.9.

Discussion

We first discuss the results on tip-influence in relation to the aforementioned calculations by Sørensen et al. [43] showing that the barrier for diffusion of an adatom under the tip can be reduced if the tip comes sufficiently close to the surface.

Determination of the absolute tip-surface distance is a non-trivial problem in STM, despite the fact that the displacements of the tip are known with great precision. However, Olesen et al. have performed experiments\footnote{The experiments were performed in our laboratory at the same instrument used in the present work and were aimed at investigating the apparent barrier height in the tunneling junction.} [45] where the STM tip is moved towards the surface while the resistance in the tunneling junction is measured. This is done until the adhesive forces between tip and surface become so strong that a sudden transition occurs and the tip jumps into contact with the surface. In ref. [45] these phenomena are studied theoretically using essentially the same model as in the tip-perturbation calculations by Sørensen et al. This allows for a
quantitative comparison between our experiment and the calculations by Sørensen et al.

By comparing to the experimental results of Olesen et al., we estimate\(^\text{12}\) that for a tunneling junction resistance of \(R_t = 10 \, \text{M} \Omega\), the tip is \(2.5 \pm 0.6 \, \text{Å}\) away from the point where jump-to-contact occurs. Increasing the resistance to \(R_t = 100 \, \text{M} \Omega\) moves the tip further away from the surface by another \(1.2 \pm 0.2 \, \text{Å}\).

In the calculations by Sørensen et al. [43], the jump-to-contact occurs at a tip-surface (core) separation of \(3 \, \text{Å}\). In combination with the distances estimated above, this provides a scale for the tip-surface separation allowing for a quantitative comparison between calculations and experiment.

The perturbation to the barrier for adatom diffusion has in the calculations been evaluated for tip-surface separations between 3.3 and 4.1 Å. Over this range the barrier changes from being \(\sim 30\%\) to being \(\sim 90\%\) of the unperturbed value that it has in the absence of the tip [43]. The decay of the perturbation to the diffusion barrier caused by the proximity of the

\(^{12}\)Results for Pt(110) are not available, and accordingly we have used results obtained for a Pt(100) surface. Similar results obtained for Au(110) and Ni(100) surfaces are not very different, however, and consequently this approximation is not expected to change the resulting estimate very much.
tip is thus very rapid over this interval of 0.8 Å. We therefore conclude that at a tip-surface separation that is even 1.4 Å larger, where we estimate to be at $R_t = 10$ MΩ, this proximity effect has to be negligible and can not be the origin of the observed perturbation.

We next turn to the possibility of a field-induced effect. Suitable measurements to elucidate whether the perturbation depends on the field strength or the polarity still remain to be carried out. Based on the discussion above, we remark, however, that in increasing the resistance from 10 to 100 MΩ the tip-surface distance is apparently increased by $\sim 20\%$. This is accompanied by an increase in the potential drop over the junction by a factor of 10 (from 10 to 100 mV). In fact, the magnitude of the field therefore appears to be smallest in the low resistance case, where the perturbation is found.

In any case, the inconclusive measurements reported in fig. 5.10 serves to underscore that the problem of the dynamic behaviour of an adatom placed in the tunnel junction of an STM may be very complicated indeed. Key factors like the microscopic shape of the tip and the chemical identity of the apex atom are unknown to us and, largely, beyond our control at the present point.

To summarize this section, we have investigated how the observed adatom dynamics depends on the imaging parameters during acquisition of STM-movies. In general, the results reported in this section demonstrate that the question of tip-influence is highly relevant and should always be addressed when using the STM to investigate dynamic phenomena. In the treatment presented here, the main emphasis has been on identifying a parameter regime where a possible tip-influence is negligible. In short, we find two regimes for the interaction. At low resistances, the diffusivities can be considerably increased and the displacement distributions obtained under these conditions are often found to be skew. At higher resistances, the distributions are symmetrical, and we find constant values for the diffusivity over a wide range of resistances and also if the tunneling parameters are varied at constant resistance. The data on adatom diffusivity reported in earlier sections of this chapter are acquired at $R_t = 100$ MΩ in this latter regime, and we therefore conclude that these results are not affected by the STM-imaging.

### 5.6.2 Adatom–adatom interaction

The random walk executed by the individual adatoms will be affected if there are adatom-adatom interactions. This problem is discussed in the
present section. As mentioned earlier, all data are acquired in a regime of very low coverage to minimize this problem. In spite of this, it occasionally happens that two adatoms come into close proximity of each other. In that case we can divide adatom-adatom interactions into those that are between adatoms in the same channel and interactions between adatoms in adjacent troughs.

Adatoms that meet in the same channel form a dimer which is stable for a short while after which it dissociates. This is analysed in detail in the following chapter 6 on dimer dissociation. In the present context of adatom diffusion we treat these in-channel interactions by excluding the displacements of such two adatoms from the analysis as long as they are within a few (~ 3) lattice spacings from each other.

Adatoms in adjacent troughs diffuse past each other quite readily. Although this has not been quantitatively analysed, there seem to be no significant interaction between such two adatoms, and consequently their displacements are included in the analysis. In a test-case it was verified that if the relatively small number of such events were also excluded, no significant change in the determined jump-rates was found. The results on adatom diffusion do therefore not appear to be affected by adatom-adatom interaction.

5.6.3 Influence of adsorbates

As mentioned, the background pressure in the chamber during the measurements was ~ $5 \times 10^{-11}$ mbar, the dominant residual gas being $H_2$. Thermal desorption spectroscopy (TDS) measurements [46] show that hydrogen desorbs from the Pt(110)-(1×2) surface at temperatures around ~310 K. Despite the low background pressure it has to be considered that hydrogen could adsorb on the surface and affect the adatom mobilities$^{13}$.

To test for this possibility, experiments were performed where $H_2$ was deliberately introduced into the chamber during acquisition of an STM movie. Results from such an experiment are depicted in fig. 5.12. In the case shown, the sample was at 290 K, at which temperature the adatom mobility is practically negligible under normal conditions. The idea was to test whether the exposure to $H_2$ affected (increased) the adatom mobility. The mean square displacement for the adatoms, $\langle \Delta x^2 \rangle$, obtained by

$^{13}$In general, the question of adsorbate induced metal-adatom diffusion is highly interesting, and currently a very "hot" topic. Measurements of the type described in this section can be used to investigate this, something which is being pursued extensively in our group at present. It is not the topic of the present thesis, however.
5.6. POTENTIAL SOURCES OF ERROR

![Graph showing the effect of hydrogen on adatom mobility](image)

Figure 5.12: Measurements showing the effect of hydrogen on the adatom mobility. The determined mean square displacement of the Pt adatoms (black) is shown as a function of time in an experiment where the hydrogen pressure is gradually increased. The vertical lines separate regions of different $H_2$ pressure as indicated in the figure. The grey bars show the average over $\langle \Delta x^2 \rangle$ in these regions (scaled by a factor of 10 for clarity). The temperature was 290 K.

Averaging over two image-to-image observations are shown in black versus time. The vertical lines separate regions of different $H_2$ pressure as indicated. Finally, the grey bars represent an average over the $\langle \Delta x^3 \rangle$ obtained for the different regions of constant pressure (multiplied by a factor 10 for clarity).

As may be seen, exposing the surface to hydrogen increases the adatom mobility. The partial pressure of hydrogen has to be increased by roughly three orders of magnitude above the background level, however, before an increased mobility is found. Similar results were obtained when oxygen was introduced into the chamber. Based on this type of observations, we conclude that the adatom mobility in the diffusion measurements does not seem to be influenced by adsorbed gases on the surface.
5.6.4 Non-equidistant times

The analysis of the adatom displacement distributions by the expression (5.8) requires that a given distribution is acquired with a fixed time-interval \( t \). In the present case, \( t \) is the time that elapses between the moments when the tip is at the same position in consecutive images. Due to the gradual scanning of the image, however, an adatom is only imaged with precisely this time-separation provided that it does not move between images. In the present case the scan-lines are horizontal and the image is scanned from the bottom and upwards. Consequently, if an atom jumps “upwards” / “downwards” in the image, it is imaged with a time-separation that is slightly larger/smaller than the time \( t \). As a result, one side of the displacement distribution corresponds to time-separations that are longer than those for the other side and this in principle introduces a skewness to the distribution\(^{14}\). The question is whether this effect is of a magnitude that has any implications for the analysis.

This problem of non-equidistant times has been treated by considering the relation between the true distribution that we would obtain if imaging was done instantaneously at fixed time-separations, and the actual distribution that we obtain by gradual scanning of the image. The difference between these two distributions can be parametrized by the small probability, \( P^* \), for an adatom to make a jump during the short time it takes the scanning to proceed over one lattice distance in the vertical direction. Two important results are reached: (i) By comparing the determined difference to the expected statistical uncertainties obtained from the expression (5.11), it is found that for the parameters relevant for the present case, the change to the distribution introduced by the time-problem is always considerably smaller than these uncertainties. (ii) The changes to the two sides of the distribution are anti-symmetric and cancel to first order in the probability \( P^* \) if the two sides are averaged, making the effect even less significant.

It is thus concluded that the described time-problem is insignificant in the present case. It would be of importance, however, if very small images were acquired, since then the time to scan over one lattice spacing would constitute a larger fraction of the image acquisition time.

\(^{14}\)This has nothing to do with the skew distributions discussed in the section on tip-influence.
5.7 Conclusion

To summarize, we have investigated the diffusion of Pt adatoms in the missing row troughs of the Pt(110)-(1×2) surface using variable temperature STM to monitor the adatom displacements through the acquisition of STM movies.

The analysis of these data in the form of displacement distributions for the diffusing adatoms has been described. In particular it was shown how a random walk model previously put forth in the literature can be derived and, furthermore, KMC simulations aimed at investigating the question of the statistical significance of the results were presented. In the last section of the chapter a number of potential sources of error in the experiments were discussed.

In conclusion, the investigation shows that a significant amount of long jumps occur for self-diffusion of Pt on the Pt(110)-(1×2) missing row reconstructed surface. The hopping rate for the long jumps is found to follow an Arrhenius dependence on temperature, and the activation barriers for single and double jumps are determined to be $E_{d1} = 0.81$ eV and $E_{d2} = 0.89$ eV, respectively.

New theoretical results by Jacobsen et al. [21] confirm that such a thermally activated form for the double jump rate is to be expected, and show that the energy difference between the two activation barriers can be interpreted as the extra energy fluctuation that has to be present in the system for a long jump to occur.

References

REFERENCES


REFERENCES


Chapter 6

Pt/Pt(110)-(1\times2): Dimer dissociation

In the previous chapter, a detailed analysis of adatom diffusion in the Pt/Pt(110)-(1\times2) system was presented. The analysis was based on STM movies which directly reveal the migration of adatoms in the troughs of the missing row reconstructed surface. This type of data also provides a detailed insight into nucleation and growth phenomena in this directly at the atomic level. Thus, in the acquired STM movies, adatoms are observed to meet in the missing row troughs, stay bound as a dimer for a while and then break apart again. In this chapter we will focus on a quantitative analysis of the kinetics of these dimer dissociation/formation events.
6.1 Introduction

Elucidating the force-laws that determine the stability and dynamic behaviour of small clusters adsorbed on surfaces is crucial for a detailed understanding of nucleation and cluster diffusion during epitaxial growth. In this respect, atomic-scale information on the behaviour of interacting adatoms is invaluable.

Previously, a number of investigations relying on the FIM to image individual adatoms have been carried out [1,2]. Thus, so-called equilibrium experiments have provided valuable and detailed information on the adatom-adatom interaction potential for adatom pairs in adsorption sites of different separations. The information is derived through a Boltzmann factor from the observed probability of finding adatoms at given separations [1–6].

The dynamic behaviour of interacting adatoms, however, including a process such as dimer diffusion, is determined not only by the adatom-adatom interaction at the adsorption sites, but also by the way in which the adatom-adatom interaction modifies the activation barriers passed by the adatoms as they move between sites in the vicinity of each other. Kinetic experiments that focus on investigating this by determining the rates for such adatom transitions have been performed much less extensively [1,2,7,8].

In contrast to direct studies of the type described above, STM has hitherto mainly contributed information on the cohesion in dimers and other small clusters adsorbed on surfaces through indirect nucleation and growth experiments. In such studies information on cluster stability is inferred through the concept of a critical island size for nucleation [9–12]. With its capability of resolving individual adatoms, however, STM also has great potential for revealing directly the dynamic behaviour of interacting adatoms. Such data, obtained in the form of time-lapse STM movies, are inherently kinetic in nature and allow information on the rates for dynamic processes to be derived.

The FIM experiments on adatom-adatom interactions have focused mainly on a range of transition metal adatoms adsorbed on tungsten surfaces [1–8]. With the growing interest in elucidating the atomistic details of metal-on-metal growth, however, there is evidently a need to extend the database on adatom-adatom interactions to include a wider range of adatom-substrate combinations, especially homo-systems which are more easily handled theoretically.

In the following, we present results, derived from time-lapse STM
movies, on the interaction among Pt adatoms adsorbed in the one-dimen-
sional missing row troughs of the Pt(110)-(1×2) reconstructed surface.
The self-diffusion on this surface is extremely well-characterized as re-
ported in the previous chapter [13].

The kinetics of not only dissociation but also association (formation)
of dimers has been quantified from the acquired STM data. The dissociation
rate for Pt dimers situated in the missing row troughs is found to be
only a factor of 2-3 lower than the hopping rate for an isolated Pt adatom,
implying a weak dimer binding energy. We find that the activation barrier
for the dimer formation process where an adatom jumps to a site next to
another adatom is reduced compared to the activation barrier passed in
diffusion of an isolated adatom. The results are interpreted in terms of
the potential energy surface that controls the rates by which such attach-
ment/detachment processes occur. From this it is found that the saddle
point passed by an adatom during dimer formation is reduced compared
to the activation barrier for ordinary adatom diffusion, and a value for
the binding energy in the Pt dimer of $E_b = 0.07$ eV is determined. The
observations on dimer association kinetics have implications with respect
to dimer diffusion and this is discussed. Finally, we find an increase in sta-
bility between dimers and longer one-dimensional adatom chains, trimers
and above, which are considerably more stable. This evidence of interac-
tion beyond nearest-neighbour pair-potentials is discussed in the context
of nucleation and growth experiments.

6.2 Experimental procedures

The experimental procedures in this study are identical to those described
in the previous chapter, where adatom diffusion was discussed. The sam-
ple is sputter cleaned and annealed, a submonolayer amount of Pt is de-
posited on the reconstructed surface and the sample is transferred to the
STM for imaging at a given temperature. Dimer dissociation and forma-
tion have been quantitatively analyzed from STM movies obtained in the
temperature interval from 303 to 353 K. The time that elapses between
the moments when the tip is at the same position in consecutive images, $t$,
(the image acquisition time plus a possible waiting time between images)
is constant for a given movie and lies between 6 and 19 seconds for the
data discussed here.
CHAPTER 6 — DIMER DISSOCIATION

6.3 Observations

The general impression of dimer formation/dissociation from the STM movies is that when adatoms diffusing one-dimensionally in the missing row troughs meet, they form an adatom dimer that is stable for a while, after which it dissociates. The dimers are often observed to break apart and reform a couple of times before the adatoms that formed the dimer eventually diffuse away from each other. The dimers are also sometimes observed to shift their position in the missing-row trough by a single lattice spacing from one image to the next. The excerpt from an STM movie depicted in fig. 6.1 shows examples of such events. Longer adatom chains that have formed in the missing row troughs, trimers and above, are considerably more stable than the adatom dimers towards dissociation. In the temperature interval considered here, events where such islands decay by loss of an adatom are practically not observed in the acquired movies.

In order to quantify the information on dimer dissociation kinetics as described above it is, for each image where a dimer is observed, noted how it has evolved in the subsequent image, that is, whether it has moved, dissociated or remains unchanged. In a similar fashion, dimer association kinetics is quantified from the image-to-image evolution of the configuration where two adatoms are separated by an empty lattice site. In this case, the possibilities are that the two adatoms either remain unchanged, form a dimer or move further apart. The described events for dimer dissociation and association are shown schematically in fig. 6.2.

To illustrate typical results we will here describe the observations acquired at one temperature (344 K). In this case, a total of 237 observations of dimers has been attained. The dominant observation is that the dimer is left unchanged in the next image. This is observed 190 times. In 24 cases, the dimer has dissociated and the adatoms that constituted the dimer are observed to be separated by one, or occasionally more, empty lattice sites. About equally often (23 times), the dimer is found to have moved (left or right) by one lattice spacing.

The configuration with two adatoms separated by a single empty lattice site is observed much less frequently than a dimer. Consequently, the statistics for the dimer association events is inferior compared to that obtained for the dissociations. In the example discussed here, 27 such adatom pairs are observed. In the majority of the cases (18), a dimer is formed in the next image. In 6 cases no change is found, and the adatoms are in only 3 cases observed to have moved further away from each other.
Figure 6.1: Excerpt from STM movie showing the dynamic behaviour of Pt adatoms situated in the missing-row troughs of the Pt(110)-(1×2) surface; images progress from (a) to (d). In image (a) an adatom dimer (1) as well as a pair of adatoms separated by a single empty lattice site (2) are identified. From (a) to (b) the dimer (1) dissociates and from (b) to (c) it reforms at the same position. The adatom pair (2) forms a dinner from (b) to (c) and this dinner is observed to move from (c) to (d). Aside from single adatoms and dimers, two larger islands can be identified in the troughs - a trimer in the lower right corner and a four-adatom long chain above the dimer marked by (1).
Figure 6.2: Schematic model depicting the observations of dimer dissociation (a) and association (b). In (a) the left column illustrates a dimer observed in image \( n \) and the right column shows the evolution of this dimer as observed in image \( n + 1 \). The centre column indicates intermediate states not seen due to the finite image acquisition time, especially the dashed line indicates dimer movement by a concerted motion that does not involve separation of the adatoms. In (b) the evolution of a pair of adatoms separated by a single empty lattice site is similarly illustrated. The numbers refer to observations at a single temperature as discussed in the text.

6.4 Analysis

As also emphasized in the previous chapter, one has to be careful when analysing data obtained from the STM movies, such as the described observations of dimer dissociation and mobility, not to uncritically equal the observed events with processes actually occurring. It is necessary also to consider possible intermediate states that are not seen due to the finite image acquisition time. With respect to the particular example described above, the mean residence time in a lattice site for an isolated adatom has from our previous analysis of adatom diffusion been determined to be 14.7 seconds [13] and the image-to-image time is \( t = 13.7 \) seconds. The images of the movie are thus sampled fairly frequently compared to the rate by which the dynamic processes occur. The chance that an isolated adatom performs several jumps between images is thus reasonably small, but non-negligible.
6.4. ANALYSIS

Dimer dissociation

The mean lifetime of a dimer before dissociation, \( \tau \), is related to the activation barrier for dissociation, \( E_{\text{diss}} \), by \( 1/\tau = \nu \exp(-E_{\text{diss}}/k_BT) \), where \( \nu \) is the prefactor, \( T \) is the temperature and \( k_B \) is the Boltzmann constant. The probability \( P(t) \) that a dimer observed in one image has not dissociated in the following image after time \( t \) is given by \( P(t) = \exp(-t/\tau) \). The observed image-to-image evolution of dimers included that they remained unchanged, dissociated or moved by a single lattice spacing. Below we will discuss how to derive the dimer lifetime from these data.

In principle, the observed dimer displacements could be caused by a concerted motion where the whole dimer moves in unison. However, since a considerable number of dimer dissociations are observed, the dimer displacements may also be due to a dissociation-reformation process as illustrated in the centre column of fig. 6.2(a). This route to dimer displacement involves a reformation step following the dissociation. The number of observations of dimer displacements is therefore expected to be somewhat lower than the number of observations of dimer dissociations, which is not observed. However, the acquired statistics are probably not sufficient enough for one to expect such a difference to be revealed, especially since the dimer reformation process may be comparatively fast as suggested by the preference of the separated adatom pair to form a dimer compared to moving further apart. The observed dimer displacements can thus reasonably be ascribed to dissociation-reformation events. The possibility that a concerted motion may also be effective cannot be ruled out, but it is not necessary to invoke it in order to account for the observed dimer movements between images.

The intermediate state with an adatom pair separated by an empty lattice site is symmetric with respect to which of the two adatoms that hop towards the other to reform the dimer. In one case a dimer movement results, while in the other case the dimer reforms at its original position. Thus part of the observations of stable dimers must in fact be dimer dissociation-reformation events that are not resolved due to the limited time-resolution. From the symmetry of the intermediate state, it is reasonable to assume that the number of such unobserved dissociation-reformation events equals the observed number of dimer movements.

Motivated by the discussion above, we take both the actually observed number of dimer dissociations (d) as well as the dimer moves (m) to represent dimer dissociations. The probability, \( P(t) \), that a dimer has not dissociated after the image-to-image time \( t \) is then obtained as
Figure 6.3: Arrhenius plot of the derived dimer dissociation rates. The dotted line shows for reference the hopping rate for isolated Pt adatoms in the missing row troughs ($\nu = 10^{10.7}\text{sec}^{-1}$, $E_d = 0.81\text{ eV}$). The solid line is the best fit to the dimer dissociation rates assuming the same prefactor as for adatom hopping and yields $E_{diss} = 0.84\text{ eV}$.

$P(t) = (N - d - 2m)/N$, where $N$ is the total number of observations and the factor of 2 accounts for the dimers reformed in their original position. From this expression, the dimer lifetimes are derived. In the specific example considered, we obtain $\tau = 39$ seconds.

Dimer dissociation rates ($1/\tau$) obtained by similar analysis of data acquired at a range of temperatures are plotted in Arrhenius form in fig. 6.3. It is relevant to compare the determined dimer dissociation rates to the hopping rates for isolated adatoms on the same surface. The diffusion of single Pt adatoms was analysed thoroughly in the previous chapter, where it was found that the adatom hopping rate, $h = \nu \exp(-E_d/k_BT)$, is described by a prefactor of $\nu = 10^{10.7}\text{sec}^{-1}$ and an activation barrier of $E_d = 0.81\text{ eV}$ [13]. The dotted line on fig. 6.3 indicates these adatom hopping rates.$^1$ As may be seen from the figure, the determined dimer

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$^1$ In the present context, the fact that double jumps where found to participate in the diffusion can be neglected. In the previous chapter, the adatom hopping rate was defined so that $1/h$ equaled the mean residence time of an adatom in an adsorption site.
dissociation rates are lower than the hopping rates for isolated adatoms by only a factor of 2.3. If the prefactor for dimer dissociation is taken to be identical to the one determined for the adatom hopping, then a value of $E_{\text{diss}} = 0.84 \pm 0.01 \text{eV}$ is determined from the dimer dissociation rates\(^2\).

### Dimer association

We will now turn to the kinetics of dimer association. The data obtained on dimer formation of the type shown in fig. 6.2(b) suggest that an adatom placed at a next-nearest neighbour distance from another adatom has a higher rate for jumping towards ($r_+$) this other adatom than to jump away ($r_-$) from it. If the two processes are assumed to have equal prefactors, and the preference of an adatom for jumping towards another adatom rather than away from it is thus assumed to be attributed to a difference, $\Delta E$, in the magnitude of the corresponding activation barriers, then $r_+ / r_- = \exp(\Delta E / k_B T)$.

Again, possible intermediate processes that are not resolved due to the finite time resolution must be considered before the ratio $r_+ / r_-$ can be derived from the attained data. Consider the configuration with two adatoms separated by a single empty lattice site. An adatom that starts by jumping away from the other adatom may in principle perform two more jumps in the reverse direction and form a dimer before the consequent image is acquired. If instead a dimer is formed in the first step, it will most likely be stable until the next image due to the lower dissociation rate for the dimers. As a result, a slight preference for observing dimer formation with respect to further separation of the adatoms is to be expected even if the rates $r_+$ and $r_-$ are not different. However, since the image-to-image time $t$, depending on the acquisition temperature, is considerably lower than or equal to the mean residence time of an isolated adatom, $1/\nu$,

\(^2\)Clearly, an independent determination of the prefactor for dimer dissociation would have been preferable. With the acquired statistics this does not seem feasible, however. The best fit to the dimer dissociation rates corresponds to $\nu = 10^9 \text{sec}^{-1}$ and $E_{\text{diss}} = 0.77 \text{eV}$, in principle suggesting that the barrier for dimer dissociation is lower than that for adatom hopping. The difference between this best fit and the curve shown in fig. 6.3 is only marginal over the temperature interval where data have been acquired, however, and nothing in the data suggests this otherwise interesting result has any significance whatsoever. We therefore follow the common practice \cite{1,2} of attributing the lower rate for dimer dissociation as compared to adatom hopping solely to a difference in the activation barriers for these two processes.
the described effect is small and can not at all account for the observed preference for dimer formation. The ratio \( r_+ / r_- \) is therefore taken to equal directly the ratio between the number of observations of dimer formation and that of further separation of the adatoms.

Over the temperature interval from 303 to 353 K, dimer association kinetics has been quantified at a number of temperatures, in the individual cases with fairly limited statistics. The total numbers of observations of dimer formation and further separation in this temperature interval are 69 and 18, respectively. If the difference in activation barriers \( \Delta E \) is small (as it turns out to be), the ratio \( r_+ / r_- \) does only vary slightly over the investigated temperature interval. From the integral numbers of observations, a value of \( \Delta E = 0.038 \pm 0.013 \) eV is determined. The stated error bar reflects both the statistical uncertainty and the variation in temperature.

It may be remarked that since the statistics obtained for the dimer association events are limited, it is not possible to reliably determine the absolute values for the rates \( r_+ \) and \( r_- \), which could have been compared to the hopping rate for isolated adatoms. We have therefore focused on the relative rate \( r_+ / r_- \) as described above since this quantity is quite accessible as also shown.

6.5 Discussion

Dimer binding energy

The binding energy of an adatom dimer, \( E_b \), may be defined as the energy gained when two isolated adatoms, adsorbed on the surface but sufficiently separated for their mutual interaction to be negligible, are brought together to form the dimer [1,2]. Consider the schematic diagram shown in fig. 6.4 of the potential energy surface experienced by an adatom as it moves in the vicinity of another adatom with which it interacts. The thin black line indicates the potential energy surface if the adatom-adatom interaction is turned off and defines the activation barrier for diffusion of an isolated adatom, \( E_d \). We now relate the results from the analysis above to the modified potential energy surface.

From the dimer dissociation rate, the difference, \( E_{diss} \), between the minimum of the potential energy surface in position 1 and the value at the saddle point passed when the adatom moves from position 1 to position 2 during dimer dissociation has been determined. From the observations of dimer association kinetics, it was found that the activation barrier passed
6.5. DISCUSSION

Figure 6.4: Schematic diagram of the modified potential energy surface (grey line) felt by an adatom as it moves between the sites marked 1-3 in the presence of another adatom as shown in black. The black line is the corresponding potential energy surface if the adatom-adatom interactions are turned off (or the black adatom is placed so far away on the surface that the adatom-adatom interactions become negligible). See text for details as well as definition of the symbols.

when moving from position 2 to 1 during dimer formation was smaller than the barrier passed when moving from position 2 to 3, and the difference in barriers, $\Delta E$, was obtained.

From fig. 6.4 we now determine the binding energy of the dimer to be $E_b = E_{diss} - E_d + \Delta E = 0.07 \pm 0.02$ eV. The figure also shows that the magnitude of the saddle point on the potential energy surface passed when moving from position 1 to 2 or vice versa is reduced compared to the potential energy surface for the isolated adatom.

Some comments regarding these results are warranted. First, determining $E_b$, relative to the reference level of noninteracting adatoms in principle requires that the rates for transitions between positions 1 and 2, 2 and 3, 3 and 4, etc. are measured out to a distance where the adatom-adatom interaction has died away [14]. Here only a part of these rates have been determined, and consequently the potential energy surfaces shown in fig. 6.4 are taken to coincide from position 2 and outwards. Although some studies of adatom-adatom pair-potentials have been able to discern an interaction out to a distance of several lattice spacings [3-6], by far the dominant contribution is found at the nearest neighbour site, and the approximation made is not expected to have much influence on the derived value for $E_b$. 
The analysis presented is in any case an improvement over the interpretation of several previous experiments on dimer dissociation by FIM [1,2,7], where the simpler approximation \( E_{\text{diss}} = E_d + E_h \), which ignores a possible modification at the saddle point passed during dimer dissociation, has typically been used. Secondly, assigning the difference in activation barriers, \( \Delta E \), to a reduction in the saddle point passed during dimer dissociation is not unambiguous. In principle the barrier passed when moving from position 2 to position 3 could be increased while the barrier passed when moving from position 2 to position 1 is unmodified. The first interpretation seems more reasonable, however. Finally, the analysis assumes the prefactors for dimer dissociation and adatom hopping to be equal. Within this assumption, the determination of the difference \( E_{\text{diss}} - E_d \) from fig. 6.3 has a very small uncertainty as is clear from the figure. Although assumptions of this type are common [1,2], more work could be invested in elucidating how justified they are.

The determined binding energy in the Pt dimer is extremely small compared to 1/6 of the cohesive energy in Pt (\( E_{\text{coh}} = 5.84 \text{ eV/atom} \) [15]) which could otherwise be a simple estimate for the energy required to break a “bond” between two Pt atoms. This finding is in line with previous observations from FIM experiments on transition-metal dimers adsorbed on surfaces on tungsten [1–8], where typically very low values at or below a few tenths of an eV are found for the energy required to separate a dimer into two isolated adatoms adsorbed on the surface. Thus e.g. the binding energy of a W dimer on W(110) is found to be only 0.285 eV despite the fact that W has a cohesive energy of 8.7 eV/atom [8,16]. This phenomenon of very weak cohesion in adatom pairs has been addressed by Feibelman in total-energy first-principles calculations for Al adatom pairs on Al(100) [16]. This work ascribes the effect to adatom-surface interactions and a corresponding bond-order bond-strength correlation. The calculations show that as the Al-dimer dissociates the adatoms bind stronger to the surface. The energy gained in this way to a large extent compensates for the energy lost in breaking the adatom-adatom bond, resulting in an overall low dimer binding energy.

**Nucleation**

The nucleation of diffusing adatoms to form stable structures is a fundamental step in crystal and thin film growth. The STM data presented in the present chapter provide a direct atomic-scale view of such nucleation processes. While the average lifetime of an adatom dimer is found to be
only slightly increased by a factor of 2-3 over the mean residence time of an isolated adatom in an adsorption site, longer adatom chains situated in the missing row troughs, trimers and upwards are considerably more stable. At the temperatures considered here, such structures are practically not observed to decay by detachment of adatoms\(^3\). From this observation, an upper bound on the island decay-rate can be estimated. It has to lie at least 1-2 orders of magnitude below the dimer dissociation rate, suggesting that an adatom at the end of such a chain is bound by at least an extra \(\sim 0.10\) eV compared to the binding energy in a dimer.

In the context of nucleation and growth experiments, the phenomenon of nucleation is typically discussed in terms of the critical island size, \(i\), where clusters of size \(i+1\) are the smallest islands that are not liable to decay during the course of deposition due to thermally activated detachment of adatoms [9–12].

Although the observed difference in stability between dimers and longer adatom chains is suggestive of \(i = 2\) behaviour, the concept of a critical island size is strictly only meaningful in the context of a deposition experiment with an associated time-scale defined by the deposition rate. In spite of this, whether the observed stability difference is due to longer-range attractive interactions or is a true many-body effect in cohesion, it underscores the limitation of simple bond-counting arguments that take into account only nearest-neighbour interactions. From such arguments, one would naively expect, in a one-dimensional system as the present, that either a dimer is stable \((i = 1)\), or that no structures are stable at all.

### Dimer diffusion

The observation of dimer association kinetics and the inferred reduced magnitude of the potential energy surface at the saddle point passed during dimer dissociation/association is interesting not only because it improves the determination of the dimer binding energy but also because of its implications with respect to dimer diffusion in this one-dimensional system.

The dynamic behaviour of the adatom pair in a dimer is strongly influenced by the magnitude of the activation barrier passed during the dissociation/association process. If this barrier is small, the adatom pair can readily dissociate and reform which, as discussed above, in half of the cases will lead to a shift of the centre of mass of the dimer, i.e. dimer diffusion. The extent to which such diffusion processes occur before the dimer “genuinely” dissociates and the two adatoms move away from each other

\(^3\)This is treated in depth in the following chapter 7.
depends on the details of the potential energy surface for the two interacting adatoms, notably the strength of the binding in the first and, possibly, second nearest neighbour site as well as the magnitude of the reduction in the saddle point.

In the Pt$_2$/Pt(110)-(1×2), system the saddle point is only slightly reduced and no indication of binding in the next-nearest neighbour position has been obtained. Thus, the general impression from the acquired movies is that dimer dissociation/reformation typically occurs a few times after which the adatoms move further apart from each other. The attained observations on dimer dynamics have therefore been discussed in the context of “dimer dissociation” rather than “dimer diffusion”, but the two concepts are closely related as it is clear from the discussion above.

It may be remarked that in-channel Re dimers on the channelled W(211) surface have previously been observed to be mobile [17]. The diffusion was attributed to a dissociation/reformation mechanism similar to the one described above, but in that case the intermediate dissociated state was not observed and consequently the dimer association kinetics was not quantified.

6.6 Conclusion

Atomically resolved time-lapse STM movies can reveal the dynamic behaviour of interacting metal adatoms. If the frequency of image-acquisition is comparable to the rate by which the involved atomic processes occur, the data acquired by this approach are kinetic in nature. From the derived rates for adatom transitions between different sites the corresponding activation energies can be inferred. This is interesting with respect to the direct assessment of the stability and binding energy for dimers and small clusters, but also from the point of view of elucidating the factors underlying the dynamic behaviour of these structures, such as dimer diffusion.

In the present study we have quantified the dissociation and association kinetics for Pt dimers situated in the missing row troughs of the Pt(110)-(1×2) reconstructed surface and have also reported on the stability of longer adatom chains. The Pt dimer is found to be very weakly bound with a determined binding energy of $E_b = 0.07$ eV. A separated adatom pair is found to have a preference for dimer formation, signifying a reduced activation barrier for dimer formation compared to adatom diffusion. Finally, trimers and longer adatom chains are considerably more stable than dimers, demonstrating interactions beyond those encompassed
in nearest neighbour pair-potentials.

The obtained results have been discussed in relation to previous determinations of dimer binding energies, as well as in the contexts of adatom nucleation and dimer diffusion.

References

Chapter 7

Pt/Pt(110)-(1×2): Island mobility and coarsening

The present chapter describes an investigation of coarsening and island mobility with respect to the islands situated in the missing row troughs. Dynamic observations of island dynamics are obtained from the STM movies discussed in the two previous chapters. The information obtained in this way is combined with that derived from annealing experiments of the quench-and-look type.
7.1 Introduction

The structures created in metal-on-metal growth are typically non-equilibrium in nature and determined by kinetic factors of the growth process. Given enough time, or if the temperature is raised thereby increasing the speed of microscopic processes, such structures will approach thermodynamic equilibrium. This involves coarsening, an increase in the length-scale of the typical growth structures [1,2].

In traditional Ostwald ripening, larger islands grow at the expense of smaller ones. Thermodynamically, this process is driven by the Gibbs-Thomson effect, which implies that the vapour pressure outside a curved gas-surface interphase depends on the radius of the interphase curvature, being larger for smaller curvature [1,2]. Microscopically, ripening involves that atoms detach from smaller islands and meander about on the surface and attach to larger ones, but a microscopic understanding of such phenomena is only beginning to emerge [2–6].

Kern and co-workers have studied the ripening of Ag clusters on Pt(111) using experiments of the quench-and-look type [4–6]. They find that the scaled size-distributions of the ripened structures are considerably more narrow than those obtained from traditional nucleation and growth. In recent measurements on coarsening in the Ag/Ag(100) system, Thiel and co-workers have used dynamic observations of a surface covered with large islands to show that coalescence of diffusing islands can play an important role in coarsening and dominate over the traditional Ostwald ripening scheme [7]. Two possible mechanisms have been invoked to explain island diffusion in such a two-dimensional case—evaporation-recondensation and perimeter-diffusion [8]. In these mechanisms, the centre of mass movement of an island is due to adatoms detaching from the island and re-attaching elsewhere on the same island and adatoms moving around the island edge (perimeter), respectively.

As has been discussed in the two previous chapters, self-diffusion on the Pt(110)-(1×2) surface is one-dimensional (1-D) since the adatoms are confined to the missing-row troughs. Furthermore, deposition of Pt on this surface results in the formation of 1-D islands situated in the troughs. The Pt/Pt(110)-(1×2) system may therefore constitute a 1-D model system in which to study ripening phenomena of the type described above, and investigations in this regard are described and discussed in the present chapter.

In general the work can be motivated by some interesting fundamental differences with respect to ripening and island diffusion between this 1-D
7.1. **INTRODUCTION**

An atom placed at the end of a "reasonably long" 1-D island will not know how big an island it is part of and must detach from the end-position at a rate that is independent of the island size. Given this, and the fact that the islands furthermore are 1-D and thus have no curvature, it is not clear whether a "Gibbs-Thomson like" principle still applies. Also, the lattice gas between the islands will be strongly interacting due to simple site-exclusion – in one dimension, adatoms will not be able to pass each other. These considerations suggest that there may be interesting differences between Ostwald ripening in one- and two-dimensional systems.

The 1-D case also differs from that of 2-D in that the detachment of adatoms from islands requires only the breaking of a single bond. In 2-D systems the "core" of the islands can only decay if adatoms incorporated in step-edges or corners can detach, which requires the breaking of two or more bonds.

With respect to island diffusion, it seems to be less likely that the adatom chains situated in the missing-row troughs should be mobile. The evaporation-recondensation mechanism can not lead to a shift in the centre of mass of these islands since a detached atom is forced to attach at the same position again. Similarly, the edge-diffusion mechanism is ruled out since the edges of the adatom chains are blocked by the surrounding close-packed rows.

Results from two different types of experiments will be presented. First, experiments of the quench-and-look type, where the surface morphology is imaged after cooling to temperatures where the dynamic processes are stopped and, secondly, dynamic observations of the type described in the two previous chapters utilizing STM movies.

The experiments of the quench-and-look type investigate the changes that follow when a surface configuration with Pt islands situated in the missing row troughs is annealed to temperatures in the interval from 369 to 395 K. Two interesting phenomena are observed. First, coarsening is found to occur, that is, the average island size increases. Secondly, a restructuring of the islands is found, involving mass transport from the the missing row troughs and into the second layer (on top of the islands), eventually leading to the islands being covered with adatoms (see fig. 7.1).

Both phenomena that are observed to follow upon annealing can be viewed as an approach towards thermodynamic equilibrium. The coarsening since the increase in island size reduces the number of unsaturated bonds at the ends of the islands, and the restructuring, somewhat more tentatively, based on the following reasoning. When an islands is formed
in the missing row troughs, a small patch of unreconstructed \((1 \times 1)\) surface is created. The equilibrium structure of the Pt(110) surface is the \((1 \times 2)\) missing row reconstruction, however. It is thus likely that a repulsive interaction exists between the island atoms and the atoms in the surrounding close-packed rows with a corresponding free energy gain associated with moving half of the atoms in the island from their position in the trough and up on top of the remainder of the island, thereby reducing the extent of the \((1 \times 1)\) patch. This may act as a thermodynamic driving force for the island restructuring.

The experiments providing dynamic observations are to a large extent identical to those analysed in the two previous chapters with respect to adatom diffusion and dimer dissociation. Here we focus on the information concerning the dynamic behaviour of adatom islands that can be extracted from these acquired movies. The central observation is that the 1-D islands situated in the missing row troughs are in fact mobile and are occasionally observed to shift their position in the troughs by a single lattice spacing. This phenomenon is interesting in its own right, but is clearly also relevant in relation to the observed coarsening in the annealing experiments.

The perspective in the present study is to combine the information on dynamic processes obtained from the STM movies with the observations
from the quench-and-look experiments in order to reach an understanding of the mechanism by which the system relaxes towards equilibrium in terms of the involved microscopic processes. Both types of experiments have advantages. The dynamic observations allow processes to be quantified directly and provide important ideas as to what is occurring during the evolution of the system. Experiments of the quench-and-look type, on the other hand, make possible that a large statistical ensemble is probed resulting in a characterization of the average properties of the system. This is advantageous as the dynamic evolution becomes more complex in which case one may risk to focus on the evolution of singular structures with the dynamic experiments.

A suitable tool to establish a quantitative connection between the two types of experiments is Kinetic Monte Carlo (KMC) simulations. These types of simulations are often used in an attempt to extract key parameters from nucleation and growth experiments, but are never better than the initial assumptions regarding which processes are of relevance. Often the complexity of the problem precludes unambiguous disentanglement of the rates for the different processes included. In the present case, the extensive dynamic observations provide the perspective of using KMC simulations to understand the observed relaxation towards equilibrium in terms of the associated microscopic mechanisms using rates for many of the associated processes that are known from direct experiments.

In this introduction, some interesting questions and perspectives have been outlined. The remainder of the chapter is structured in the following way. Experimental details regarding the two types of experiments are described in the next section. This is followed by a description of the results obtained from analysis of the annealing and dynamic experiments, respectively. Subsequently, a discussion section is provided where the results of the two types of experiments are treated and related to each other. The first two subsections of this discussion section treat island mobility and coarsening in qualitative terms, while the latter subsection provides the results of KMC simulations.

While very interesting results have been attained, it should be emphasized from the outset that the experimentation and modelling with respect to island mobility and coarsening in the Pt/Pt(110)-(1×2) system has not reached a fully conclusive state at the present moment. The central result arrived at in the present chapter is that the data from the annealing experiments cannot be reconciled with the dynamic observations within a fully 1-D model. Certain suggestions as to why this disagreement occurs are provided from the dynamic observations, however. The chapter is con-
cluded by an outlook in which possible directions for future related studies are suggested.

7.2 Experimental procedures

For both the dynamic as well as the quench-and-look experiments, the procedures for crystal preparation are identical to those described in chapter 5. In brief, the Pt(110) crystal was sputtered by 1.5 kV Ne ions for \( \sim 15 \) minutes followed by annealing to \( 970 \) K. This produced a clean, \((1\times2)\) missing-row reconstructed surface. Deposition was performed from a resistively heated Pt filament. The sample temperature during deposition was controlled by electron bombardment of the sample-holder from the rear side, and the temperature during deposition was measured with a thermocouple mounted directly to the back of the sample.

Quench-and-look experiments

These experiments investigate changes to the island morphology that follow when the surface is annealed.

The starting configuration for the annealing experiments was prepared as follows. Pt was deposited at the surface for 5 minutes at a sample temperature of \( 344 \pm 2 \) K. After the deposition flux was turned off, the sample was kept at this temperature for a further 10 minutes. This waiting stage after deposition was introduced to allow the deposited adatoms to incorporate into islands. Characterization by STM of the island morphology resulting from this procedure reveals that it consists of relatively small islands (mean size \( \sim 6 - 7 \) atoms) situated in the missing row troughs. The deposited amount corresponds to \( 27 \pm 4 \% \) of the sites available in the missing-row troughs as determined from the STM images.

In the annealing experiments, the sample temperature was increased to the final annealing temperature following the 10 minute waiting stage. This change of temperature was performed within less than 2 minutes and care was taken that the temperature did not increase above its final value. The final annealing period lasted another 10 minutes after which the sample was cooled to temperatures where adatom mobility and other dynamic processes are completely frozen out. Quenching to less than room temperature lasted less than 1 minute. The imaging was subsequently performed at low temperatures in the interval from 230 to 270 K. This type of experiment was carried out for 5 annealing temperatures in the interval between 369 and 395 K. During the final annealing period, the temperature
was maintained constant to within ±1 K. The sample was not imaged prior to the final annealing in order to avoid unnecessary temperature transients. From the acquired STM images, between 100 and 300 adatom islands were analysed for each annealing temperature as well as for the initial configuration.

**Dynamic experiments**

The dynamic experiments are largely the same as those yielding the STM movies analysed in the previous two chapters with respect to adatom diffusion and dimer stability. Island mobility and dynamics have been analysed from such movies acquired in the temperature interval from 334 to 382 K and with image-to-image times between 6 and 14 seconds.

It should be remarked that these data were acquired with parameters that make them optimum with respect to analysis of adatom diffusion. Thus, the coverage was kept at a very low level in order to minimize interactions between diffusing adatoms. Consequently, the number of adatom islands appearing in a given movie is low, typically only one or a few islands are visible. As a result, the observations on island dynamics reported here are based on a fairly small dataset.

### 7.3 Observations

#### 7.3.1 Annealing experiments

STM images that depict results from the annealing experiments are shown in fig. 7.2. In the images, the missing row troughs are shown in black. An island situated in the troughs is grey, as are the surrounding close-packed rows. The structures depicted in white are covered islands. In a covered island, an adatom chain fills some or all of the adsorption sites formed by the part of the island that remains in the missing-row trough and one of the two surrounding close-packed rows (see fig. 7.1).

The images (a)-(d) are obtained after progressively higher annealing temperatures from 373 to 395 K. Two trends that follow with increasing annealing temperature are very apparent from the series of images shown. First, an increasing number of islands become covered, and, secondly, the sizes of the islands increase, this latter fact being especially clear remembering that a covered island contains twice as many atoms per length as an island that is not covered.
Figure 7.2: STM-images showing the changes to the island morphology on the Pt(110)-(1×2) surface that occur upon annealing. With reference to image (a), the missing row troughs are black, separated by close-packed rows represented in grey. The troughs have been partly filled by islands situated in the troughs (grey) and some of the islands are restructured and as a result are imaged in white. The images (a)-(d) are obtained after annealing to 373, 379, 384, and 395 K respectively. Note that the area imaged in (a) (153 × 163 Å²) is smaller than that in (b)-(d) (230 × 244 Å²). The starting configuration for the annealing experiments is quite similar to (a), except that no islands are restructured and the islands are somewhat shorter.
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At the temperatures at which not all islands are covered, it is characteristic that islands are either covered completely or not covered at all. The fraction of islands that are partially covered is very small. Despite the fact that there is room for two adatom chains on top of each island in the troughs, islands which are covered in this way are not observed.

The obtained STM images have been quantitatively analysed with respect to the sizes and degree of coverage of the islands. Typically, the images do not have atomic resolution. The island sizes in atoms are therefore derived from the measured lengths of the islands and the known lattice spacing along the troughs. For covered islands, the stated sizes include both the atoms in the troughs as well as those in the second layer.

In fig. 7.3 quantitative results for the evolution of the island distribution are shown. Panel (a) shows the fraction of the number the of islands that are covered fully and partially, respectively. As also commented on above, the fraction of islands that are partially covered is very low at all annealing temperatures while the fraction of completely covered islands increases with increasing temperature. In panel (b) of fig. 7.3 the average island sizes are depicted. The average sizes have been evaluated separately for islands that are covered completely and those that are not covered in the second layer, respectively. A marked difference between the two types of islands can be seen. While the average size of the covered islands increases with increasing annealing temperature, the islands that are not covered roughly remain to have the same size. With reference to image (d) of fig. 7.2, the general picture at the highest temperature probed is thus that nearly all the adatoms are found in islands that are completely covered. A number of small not covered islands can still be found, however. As a result, the fraction of the number of islands being covered, which is depicted in fig. 7.3(a), have not quite reached unity.

The described trends become especially clear if the island size-distributions derived from the annealing experiments are considered. In fig. 7.4 we show the distribution for the starting configuration as well as those obtained after annealing to 379 and 395 K, respectively. In the distributions, the contribution from not covered and covered islands has been separated and are shown in black and grey, respectively. As it is apparent, an increasing fraction of the islands become covered with increasing annealing temperature, and the islands that are not covered are the smaller ones. The annealing also introduces a shape-change in the distributions, which become bi-modal at the highest annealing temperature.
Figure 7.3: Quantitative results from analysis of STM-images as shown in fig. 7.2. Panel (a) shows the fraction of the number of islands that are completely and partially covered, respectively versus the annealing temperature (the fraction of not covered islands is left out for clarity, but can be inferred since the three fractions have to sum to unity). Panel (b) shows the mean size of the islands that are completely covered and those that are not covered, respectively. In both panels the datapoints at 344 K represent the starting configuration for the annealing experiments.
Figure 7.4: Island size distributions derived from the annealing experiments. The contribution from covered islands is shown in grey, whereas the contribution from islands that are not covered is shown in black. Panel (a) shows the start-configuration whereas (b) and (c) depict the distributions obtained after annealing to 379 and 395 K, respectively. In evaluating the distributions, binsizes of 1,2, and 3 atoms have been used for the distributions (a)-(c), respectively. The island sizes have been scaled by the average island size $s_{av}$ (averaging over both covered and not covered islands), and the distributions are normalized to unit area. This scaling is equivalent to that proposed by Bartelt and Evans [9] and used for the size-distributions discussed in chapter 4. Note that the distributions (a) and (c) are shown un-scaled in fig. 7.11.
7.3.2 Dynamic observations

We now turn to a description of observations with respect to island dynamics derived from STM movies. The central observation is that the 1-D islands situated in the missing row troughs are mobile and occasionally shift their position by a single lattice spacing along the troughs. This fact is very apparent from the movies which have a drift between images that is considerably less than the length of one lattice spacing and where, furthermore, a number of other features typically exist within the field of view to which positions can be related — a step-edge, another island or single adatoms, some of which happen to be immobile while the island moves. The islands observed in the movies have lengths between 3 and 6 adatoms. Typically ~15 island movements are observed during 200-500 image-to-image observations of islands at a given temperature.

Compared to the analysis of adatom diffusion and dimer dissociation in the previous two chapters, deriving the rates for the island movement events is straightforward since they occur so rarely that many images are acquired between events. Thus if n island movements occur during N image-to-image observations of an island obtained with time-separation t, the average time between moves is \( \tau = Nt/n \) and the rate for island displacement is \( 1/\tau \). The derived island displacement rates are shown in fig. 7.5, where the rates for adatom hopping and dimer dissociation determined in the previous chapters are also shown for comparison.

In addition to mobility, possible island dynamics also involves detachment of adatoms. In the movies, this is observed very rarely. At a given temperature, typically 1-2 events are observed where an atom at the end of an island has detached to a next-nearest neighbour site in the trough. These events nearly all lead to re-incorporation of the detached atom in one of the following images. Events where the island size decays through loss of an adatom that migrates away in the trough are thus practically not observed.

The detachment of an end-atom to a next-nearest neighbour site may not be resolved in the movies because it is followed by a fast re-attachment as discussed further below. The process where an island atom detaches and moves further away from the island, however, involves that the adatom moves over the unperturbed adatom diffusion barrier and it is therefore so slow that it should be observed in the movies, even if the detached atom eventually returns to the island.

The observations of adatom detachments are attained from the same statistical material that yielded the typically ~15 observations of island
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Figure 7.5: Arrhenius plot of the derived rates for island displacement. The previously determined rates for adatom hopping (dotted) and dimer dissociation (dashed) are shown for reference. The Arrhenius fit to the island displacement rates, $1/\tau = \nu \exp(-E/\kappa T)$, is described by a prefactor of $\nu = 10^{5.6 \pm 1.2} \text{sec}^{-1}$ and an energy of $E = 0.80 \pm 0.08 \text{eV}$.

movements described above. The described data therefore shows that the rate by which islands decay by loss of adatoms lies considerably below the island displacement rates depicted in fig. 7.5.

From the acquired STM movies, certain further observations are attained which may provide a tentative clue to the mechanism behind the observed island mobility. These observations will be described in a later section in which such possible mechanisms are discussed.

Pt/Pt(110)

An adatom placed on top of one of the islands situated in the missing row troughs will have a local environment almost identical to that of an adatom on the unreconstructed Pt(110) surface. The evidence from the annealing experiments that atoms can move up on top of such islands makes information on the diffusional properties of Pt on the unreconstructed Pt(110) surface relevant for a discussion of the observed ripening and island mobility. The Pt/Pt(110) system has been studied by several authors using
Figure 7.6: Arrhenius plot of adatom hopping rates on the unreconstructed Pt(110) surface obtained from ref. [11]. Shown for reference are the rates for adatom hopping, dimer dissociation, and island displacement on the reconstructed surface derived in the present study. The line-segments representing these rates cover the temperature intervals over which they have been measured. The gray-shaded area designate the temperature interval covered in the annealing experiments.

FIM [10,11], and below we refer some important observations from these studies.

First, self-diffusion on the unreconstructed Pt(110) surface is 2-D, occurring with equal rates along the close-packed direction as perpendicular to it. This surprising result was first reported by Basset and Webber [10], who were also the first to propose the now accepted idea that the diffusion across the close-packed direction occurs through an exchange-mechanism [12].

Second, self-diffusion on the unreconstructed surface occurs with a considerably higher rate than that found in the present work for Pt diffusion in the missing row troughs (see chapter 5). Detailed diffusion measurements have been performed by Kellogg [11] in the temperature interval from 253-282 K. If we convert the reported diffusivities from this study to adatom hopping rates, we obtain the values shown on fig. 7.6.
trapolate these adatom hopping rates to the temperature regime where the island mobility is observed, it is approximately two orders of magnitude higher than the adatom hopping rate found in the missing row troughs and roughly four orders of magnitude higher than the displacement rate determined for the islands.

The question of dimer stability on the unreconstructed surface is also addressed in the paper by Kellogg. It was found that dimers did not dissociate even if the temperature was raised to 335 K. The duration of the heating periods is not provided, which makes it difficult to place a lower bound on the dimer lifetime from the reported observation, but the result suggests that the lifetime of a Pt dimer on the unreconstructed surface is at least as long as that determined in the present study for a dimer situated in the missing-row troughs.

Finally, it should be mentioned that a transformation of the (1×1) surface somewhat similar to the island restructuring reported here was observed at the temperature of 335 K in the FIM study by Kellogg.

7.4 Discussion

In the previous section, several interesting observations were presented. The described island mobility is of considerable interest in its own right and also because it may play an important role in the coarsening that follows upon annealing. The island restructuring is a surprising result since it involves mass transport from the troughs to a position on top of the islands. While descending motion of adatoms over a step-edge is quite common, it is typically assumed that adatoms that incorporate into a step-edge from the lower terrace side are stable, and ascending motion as observed here is not considered. As will be discussed, the fact that adatoms are able to move up on top of the islands may be of importance with respect to the island mobility.

In this section, the described observations are discussed and related to each other. The first two subsections present a qualitative and somewhat speculative discussion of the island mobility and the results of the annealing experiments, respectively. In the final subsection, results from initial KMC simulations aimed at establishing a connection between the dynamic observations and the results of the annealing experiments are briefly presented.
7.4.1 Island mobility

The mechanisms typically invoked to explain the diffusion of islands on surfaces are (i) perimeter-diffusion and (ii) evaporation-recondensation[8]. In the present case, neither of these can explain the observed island mobility since (i) the edges of the adatom chains are blocked by the surrounding close-packed rows, and (ii) a detached atom is forced in the 1-D troughs to attach at the same position as where it left the island.

In fig. 7.7 two possible mechanisms that could be responsible for the observed island mobility are suggested.

In the first, the island motion is initiated by the detachment of an end-atom from the island. If the detached atom jumps back, the island is left unchanged and at the same position. Alternatively, however, another atom may detach from the island and move next to the first atom that detached. Effectively, this process can be viewed as motion of the vacancy generated by the initiating detachment event. By repetition of such a process, the generated vacancy can diffuse through the island and emerge at the other end resulting in a net displacement of the whole island by a single lattice spacing. We will refer to such a scenario as the vacancy diffusion mechanism.

The second mechanism is inspired by the evidence from the annealing experiments that ascending motion is possible. If an atom at one end of an island is somehow displaced from its position in the missing row trough and up on top of the island, it may diffuse over the island and become incorporated at the other end, leading to a net displacement of the island. This proposed mechanism we call on-top diffusion. In a sense, the on-top
mechanism is reminiscent of the perimeter-diffusion mechanism invoked to explain diffusion of clusters in two dimensions.

It should be remarked that it is not a priori clear that the island motion can be explained by a mechanism that consists of simple elementary steps as suggested above. The island mobility may also in principle be due to some complex concerted motion involving simultaneous displacement of two or more atoms. While there does not appear to be examples where the detailed mechanism for the mobility of small clusters larger than dimers has been determined, the evidence from several investigations suggest, however, that the mobility of small clusters is due to displacements of individual atoms of the clusters [12].

Clearly, the direct way to discriminate between the proposed mechanisms for the observed island mobility is to carefully peruse the acquired movies and look for islands that are in an intermediate state with either a vacancy in the island or an atom on top, respectively. Below we discuss the two mechanisms in more detail and present some relevant observations from the movies.

Vacancy diffusion

The vacancy diffusion mechanism for the island mobility is a direct extension of the dimer diffusion by dissociation-reformation discussed in the previous chapter. Recall the observations presented there of dimer dissociation and association and the interpretation in terms of a potential energy surface with a reduction at the saddle point passed during dimer formation/dissociation (see fig. 6.4). If the potential energy surface for an adatom moving at the end of an island has qualitatively the same shape and perhaps involves binding also at the site next-nearest neighbour to the end of the island, this could lead to island mobility through vacancy diffusion. In that case, the initiating event where an end-atom detaches from the island to a “semi-bound” state at the next-nearest neighbour site could occur often compared to the rate by which atoms leave the island completely. Once the initiating event has occurred, it is likely that the diffusion of the vacancy through the island occurs with a high rate since simultaneously as an atom breaks away and moves to fill in the vacancy during the vacancy diffusion process, it also forms a new bond to the atom at the other side of the vacancy and the barrier for this process can therefore be expected to be low.

As described earlier, detachment of island end-atoms by a single lattice spacing followed by reattachment in a subsequent image is in fact observed
in the movies, but less frequently than the island displacement events. This does not necessarily imply that the rate for the detachment process is lower than the rate for island displacement (which would clearly rule out the vacancy mechanism), since if the re-attachment process occurs with a high rate, the end-atom will not spend much time in the detached state, and this is consequently not observed due to the finite time resolution in the movies. The few observations of end-atom detachment demonstrate that the step believed to initiate the vacancy diffusion mechanism does in fact occur.

In a few instances a trimer is in the movies observed to move by first detaching one end-atom by a single lattice spacing followed in the subsequent image by the two remaining atoms catching up with the first one, see fig. 7.8(d-f). Aside from this, no direct observation of an adatom-chain with a diffusing vacancy has been attained. As suggested above, however, the vacancy diffusion may be fast and the finite imaging time may well be the reason that the vacancy diffusion mechanism has not been directly observed.

On-top diffusion

The on-top mechanism is unusual in that it involves the ascending motion of an island atom to be initiated. The annealing experiments establish that this process is possible, but do not provide any clue as to how it occurs. The promotion into the upper level may occur through a concerted motion where the atom next to the end-atom moves upwards while the end-atom moves to fill its place. The re-incorporation could occur through the reverse steps. This route would probably be energetically favourable compared to a simple roll-over process where the end-atom itself ascends or descends the end of the island.

As remarked earlier, an adatom positioned on top of an island has a different environment than an atom situated in the missing row troughs, and it is likely that the diffusional properties for such an atom are quite close to those on the unreconstructed surface. The results described for self-diffusion on the unreconstructed Pt(110) surface therefore indicate that the adatom diffusion rate on top of the islands will be very fast.

Some direct observations in support of the on-top diffusion mechanism have been attained. Consider the sequence of images in fig.7.8(a-c). In the first image an island of length 4 is situated in the trough. In the subsequent image the island is of length 3 but something is on top of the island. In the last image the island is again of length 4, but shifted by one lattice spacing
with respect to the initial image. These observations strongly suggest that at least this island movement is due to the on-top mechanism. In a few other instances the movement of an island is accompanied by a “glitch” on top of the island which may be interpreted as a fast diffusing atom. The dominant part of the observed island movements show no evidence of an atom on top of the island. Again, this could be due to the finite time resolution and a fast diffusion rate on top of the islands, however.

Figure 7.8: Excerpt from STM-movies showing island displacement events that are believed to be due to the on-top (a-c) and the vacancy diffusion (d-f) mechanism, respectively. In the inserted ball-models black circles represent island atoms and empty circles unfilled sites in the troughs. Sequence (a-c), shows a four-atom long island that moves by one lattice spacing from (a) to (c), and in the intermediate frame (b), the island has a length of 3 atoms while something is resolved on top of the island. Sequence (d-f) shows the displacement of a three-atom long island, where (e) depicts an intermediate state with an end-atom detached. The white line is inserted to clarify the movement of the island. Both series are cut-outs from larger images.
General Considerations

As described above, some suggestive evidence of both proposed mechanisms for island mobility has been obtained from the movies. It is clearly not impossible that both mechanisms are effective and play a role in the observed island mobility. It should be emphasized, however, that the observations shown in fig. 7.8 are more or less singular events and accordingly should be interpreted with caution.

It is common to both proposed mechanisms that they involve an initiation event followed by a 1-D random walk of some disturbance through or over the adatom chain. Only for the fraction of the initiating events where the disturbance manages to move through to the opposite end of the chain without being re-emitted at the end where it was initiated does a net displacement of the island result. If the process by which the disturbance moves through the chain is fast compared to the rate of the initiating event, there is only little likelihood that a new initiating event occurs before the previous one has led to either success or failure with respect to displacing the chain. In that case, as a guideline, the situation may be compared to that of a 1-D random walk started at one end of an $n$ spacing long string. The probability that the walker succeeds in getting to the opposite end without hitting the starting point is in this case $P(n) = 1/n^1$.

The simple argument above suggests that for islands of size 3-6 adatoms, as observed in the movies, the rate for the initiating event (adatom movement on top or end-atom “semi”-detachment) is roughly a factor of $\sim 4$ higher than the observed island displacement rate. A slight length dependence on the mobility rate is also suggested, e.g. roughly a factor of 3 from an island of length 3 to one of length 10.

The argument is quite simplistic, though, and the situation may be more complicated. For instance, with respect to the on-top mechanism, there could be an additional (Schwoebel) barrier for descending from the island which could confine an adatom on top of the island long enough for it to bounce back and forth between the ends several times. In that case, one would expect the island displacement rate to be independent of the island length, and every second initiating event would lead to island displacement.

In general, the observed island mobility may be viewed as a model-case of a composite process consisting of several elementary steps. Such complex processes are not well understood [13]. Fundamental questions include how the rate for the overall process depends on the rates for the elementary

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1 This result is easily verified from a small computer program.
steps, and whether it for instance follows an Arrhenius behaviour. From this perspective, it would be interesting to obtain an improved quantitative characterization of the processes involved in the island displacement and relate this information to the overall island displacement rate. The rates depicted in fig. 7.5 apparently show a tendency to level off for higher temperatures, and it is not clear whether they in fact follow an Arrhenius dependence. Initial attempts to model the island displacement rates within the on-top model using KMC simulations have been performed as discussed in a later section (see fig. 7.11), but this work is still very premature.

### 7.4.2 Coarsening and island restructuring

We now turn to a more detailed discussion concerning the observations of coarsening and island restructuring obtained from the annealing experiments. As commented on in the introduction, both these phenomena may be viewed as approaches of the system towards a thermodynamic equilibrium structure. With respect to the island restructuring, this observation was based on the assumption of a repulsive interaction between the atoms of an island situated in the troughs and the surrounding close-packed rows. We remark that the existence of such a repulsive interaction is supported by the fact that two adjacent adatom chains are never observed on top of the restructured islands.

The interesting perspective is to relate the dynamic observations obtained from the STM movies to the data from the annealing experiments and elucidate the mechanism by which the relaxation towards equilibrium occurs. Some differences in parameters between the two experiments should be recalled in this respect. The annealing experiments span the temperature range from 369 to 395 K. Dynamic observations are available up to a temperature of 382 K, and thus a considerable overlap exists between the temperatures where the two types of experiments have been performed (see fig. 7.6). The main difference between the experiments is in the different coverages used. While in the start-configuration for the annealing experiments, \( \sim 25\% \) of the sites in the missing-row troughs are filled out, the coverage in the dynamic experiments is much lower, and thus only one or two islands, each containing 3-6 atoms, are within the field of view of typically \( \sim 160 \times 160 \ \text{Å}^2 \) in a given STM movie. Thus, although the movies acquired at present provide some very valuable input with respect to interpreting the annealing experiments, they do not directly reveal the island restructuring and coarsening observed in these
experiments.

It is tempting to attribute the island mobility and the island restructuring to be the results of very similar mechanisms initiated by island atoms being promoted to a position on top of the islands. While the island mobility results from atoms diffusing over the islands, the island restructuring would follow from such atoms nucleating and growing into the adatom chains found on top of the islands. Presumably, the observation that islands are typically covered either completely or not at all, could result from such a mechanism. Nucleation would require the more or less likely event that two atoms were promoted to a position on top of the island at the same time and met there. Once such a dimer was formed, the adatom chain would quickly grow to cover the island. The details of such a model would depend on the rates by which atoms ascend and descend the island and also on the stability of the structures formed on top of the islands - is the dimer stable for a sufficient amount of time to allow for more atoms being promoted to the upper level before it dissociates, and are the adatom chains formed on top of the islands stable at the temperatures considered? Within this model, the island mobility and the restructuring are linked, and parameters should be able to account for both phenomena. Whether or not realistic values can be found for the parameters controlling these rates which reproduce the experimental observations is best investigated with KMC-simulations. We return briefly to this in the following section.

In traditional Ostwald ripening, the redistribution of mass between the islands is mediated by adatoms that detach, migrate over the surface and attach to other islands. While such a process may occur to some extent in the present case, the fact that islands are observed to undergo displacement considerably more often than adatoms detach from them and diffuse out on the surface strongly suggests that island diffusivity and coalescence of migrating islands must play an important role in the coarsening that is observed to follow upon annealing.

Again, KMC simulations can be used to quantify these ideas and relate the dynamic observations to the coarsening data. Some results in this regard will be discussed further below. The central and interesting conclusion reached from these simulations is that they apparently reveal an incompatibility between the results of the annealing experiments and the rates derived from the dynamic observations, the rates being much too low to account for the degree of coarsening that is in fact observed to follow upon annealing. The apparent disagreement large enough that it is in fact quite readily revealed, even without resorting to simulations, as will be discussed now.
7.4. DISCUSSION

The starting configuration for the annealing experiments consists of islands of mean size \( \sim 7 \) atoms with \( \sim 25\% \) of the sites in the missing-row troughs being covered by adatoms. The mean island-island distance along the troughs is thus \( \sim 21 \) sites. Following annealing for 10 minutes to 379 K, the mean island size has increased to \( \sim 14 \) atoms as may be verified from figs. 7.3(a) and (b). This temperature is close to the highest temperatures covered in the dynamic experiments, and here the determined island displacement rate is \( \sim 0.01 \text{sec}^{-1} \). Thus, during the annealing period, an island is expected to make on average \( \sim 6 \) displacements, and the number of times an atom leaves such an island is expected to be even smaller. It does not seem reasonable that this should result in a doubling of the average island size by either Ostwald ripening or diffusion of islands along the troughs.

We can attempt to estimate the island displacement rate necessary for this latter island diffusion mechanism to result in the observed coarsening. Roughly, the requirement is that the islands are able to meet two and two. For a diffusing island to have an RMS displacement of 21 lattice spacings during the 10 minutes annealing period would require \( \sim 21^2 \) moves, or equivalently a displacement rate of \( \sim 0.7 \text{sec}^{-1} \). Thus, the observed displacement rates seem to be 1-2 orders of magnitude too low with respect to accounting for the coarsening within this 1-D model.

Clearly, the presented argument is very crude and does not take into account fluctuations in neither the island-island separation nor in the distances covered by the individual islands in their random walk during the annealing time. The disagreement is so large, however, that these details are not crucial for the argument. In any case the result is similar to that found from more elaborate simulations.

The intriguing question is evidently how to reconcile the apparent discrepancy between the observations from the two types of experiments. An interesting suggestion is provided from the STM movies and is illustrated by the image sequence shown in fig. 7.9(a-f). This sequence depicts an observation obtained in one of the rare cases where two neighbouring islands are found in the movies despite the low coverages used when acquiring the dynamic data. As is very apparent from the size-fluctuations of the islands in the images shown, the two islands situated in adjacent troughs are able to exchange atoms. This observation is in fact perfectly reasonable within the framework of island mobility and restructuring presented earlier. The two adjacent islands form a small patch of \((1 \times 1)\) surface. From the described FIM observations of diffusion on unreconstructed Pt(110), it is to be expected that an atom promoted up on top of one of the islands is able
Figure 7.9: Excerpt from STM-movie showing two adatom islands in adjacent rows. During the sequence there is a total of 8 atoms in the two islands, but the islands exchange atoms as shown in the inserted ball-models. The images shown are cut-outs from larger images, and it can be ruled out that the observations are due to atoms detaching and attaching to the two islands separately in their respective troughs.

to diffuse across the close-packed row separating them and descend in the adjacent channel, resulting in the observed size-fluctuations.

Although the described observation of interacting islands is again quite singular and not well-established, it strongly questions the assumption that the system can be treated as purely 1-D at the higher coverages used in the annealing experiments. With this new piece of information, let us review the previous simple estimate for the amount of coarsening to be expected. To obtain a guideline as to the effect of interaction between islands in adjacent troughs, we may consider the mean distance (along the troughs) from the end of a given island to the beginning of the next island in either the same or one of the two adjacent troughs. If, in the starting configuration with mean size $\sim 7$ atoms and $\sim 25\%$ coverage,
7.4. DISCUSSION

we imagined the islands from such three troughs to be placed together in a single trough, \( \sim 25\% \) empty sites would be left over. There would thus be \( \sim 7 \) empty sites to share between three islands, or on average \( \sim 2 \) lattice spacings island-island distance. Taking into consideration the inevitable fluctuations in the island positions, the argument shows that, in the starting configuration, islands will often have a neighbour very close in either the same or in one of the two adjacent rows (as is also found from the actual STM images not shown here). Given this, and the fact that neighbouring islands may interchange atoms, it now seems considerably more conceivable that the observed coarsening may in fact be reconcilable with the observations from the dynamic experiments.

With respect to the described model for island-island interaction, it is worth remarking that events where an isolated island decays by loss of an atom to one of the adjacent troughs, which could be envisioned to occur if an adatom on top of the island descended over the sides rather than at the ends of the island, are not observed from the movies. Thus, if during the size-fluctuations experienced by two interacting islands, one of them was reduced to a dimer (as in fig. 7.9(d)) and this dimer dissociated, then the channel for mass-transport between the troughs would be blocked and the atoms would remain in the larger island. This could provide an intuitive explanation as to why the described island-island interactions can lead to coarsening.

To end this section, we briefly comment on the size-distributions\(^2\). With increasing annealing temperature, the shapes of the scaled size-distributions change, and at the highest annealing temperature, the distribution becomes bi-modal. It may be speculated that the presence of small not covered islands and the corresponding bi-modal size-distribution could result from detached atoms nucleating in the troughs which is far more likely to occur in 1-D than in 2-D systems. It should also be remarked that island mobility in 2-D systems was shown in KMC simulations by Kuipers et al. to lead to a bi-modal size-distribution with an increase for small island sizes [14].

Kern and co-workers have reported size-distributions obtained for post-

\(^2\)A remark in relation to the elaborate discussion of size-distributions in chapter 4 is warranted. The distributions shown in fig. 7.4 have been scaled in essentially the same way as the distributions shown in that chapter. Comparison should be exercised with caution, however. The shapes of the scaled distributions depend on the ratio between the rates for adatom hopping (h) and deposition (R), and the shape only converges for large values of \( h/R \) [9]. Here we are in a fundamentally different regime, where the adatom hopping rate is very low. Furthermore, the distributions obtained here are not the result of pure nucleation and growth, but involve post-growth and coarsening.
growth in the Cu/Ni(100) system (ie deposition at sufficiently low temperatures that nucleation and growth persist after the deposition flux has been turned off) [15]. These are monotonously decaying for increasing island size (similarly to the distribution shown in fig. ??(b)). It is interesting that the starting configuration for the annealing experiments does not show such a behaviour since the deposition experiment by which this start-configuration is created could be expected to belong to this post-growth category given the fairly low island mobility at 344 K. It should be remarked, however, that the regime for \( s/s_{\text{eq}} < 0.5 \) for the distribution (a) corresponds to trimers and below. For such small features, broadening due to tip-curvature becomes increasingly important. This has not been corrected for in the analysis, and the size of such features may therefore have been over-estimated.

Ripening in the 2-D Ag/Pt(111) system has been extensively studied by Kern and co-workers [4–6]. In this case, it was found that the scaled size-distributions became considerably more narrow upon coarsening. As may be seen from fig. 7.4, the scaled distributions do not show any such tendency in the present case and in fact appear to become broader with increasing annealing temperature. The reasons for this difference are not understood, but it is probably related to the quite subtle coarsening mechanism believed to be effective in the present system.

### 7.4.3 KMC-simulations

As alluded to several times above, modelling by KMC simulations aimed at illuminating various aspects of the described experimental observations has been performed. These efforts are still premature. Consequently, we will not discuss them in detail, but only provide a brief survey of what has been done and refer the most important results.

The central processes included in the simulations are illustrated in fig. 7.10. They are the ascending and descending motion towards and from the position on top of the island, adatom diffusion on the islands as well as in the troughs, and end-atom detachment from islands (or dimers) in the troughs or adatom chains (or dimers) on top of the islands.

The simulations carried out consider only the on-top mechanism for island mobility and make no attempt to reproduce the vacancy diffusion mechanism. The interesting suggestion that interactions between adjacent channels may play an important role in the coarsening has not yet been included in the simulations, which are performed in a completely 1-D model (except for the promotion into the upper layer).
7.4. DISCUSSION

Figure 7.10: Illustration of the processes included in the simulations. The rectangle represents an island situated in the missing row trough. The processes are the ascending and descending motion towards and from the position on top of the island (marked (a) and (b), respectively), adatom diffusion on top of the islands (c) as well as in the troughs (d), end-atom detachment from islands (e) or dimers (f) in the troughs and finally detachment from adatom chains (or dimers) (g) on top of the islands.

Island restructuring

Initially, simulations were performed in a simplified model aimed at testing quantitatively the scenario for island restructuring by nucleation and growth in the upper layer as proposed in the previous section. Ripening or other interactions between islands were not considered. Thus only a single island (not covered) was placed in each trough in the starting configuration for the simulations. Simulations were performed for the same annealing temperatures as used in the experiments. For each case, the sizes of the islands were taken to match the size-distribution obtained experimentally after annealing. The processes included were diffusion up and down from the islands, adatom diffusion on top of the islands, and detachment from dimers on top of the islands (detachment from longer adatom chains was not allowed). The main question to be answered was whether the rates for these processes could be adjusted to produce the behaviour depicted in fig. 7.3(a), i.e., islands being covered either completely or not at all, and an increasing fraction of the islands being covered with increasing annealing temperature.

In short, the simulations revealed that this was in fact quite possible, thus lending some faith to the described nucleation and growth scenario. Importantly, however, it was concluded that the parameter space was so large (and the model so crude) that the simulations could not be used to quantitatively assess the magnitude of any of the relevant kinetic parameters by comparison to the data depicted in fig. 7.3(a) alone.
Coarsening

Subsequently, simulations aimed at investigating the annealing experiments in a more realistic model were carried out. Both island mobility as well as traditional Ostwald ripening were considered as origins of the coarsening. The processes included were those shown in fig. 7.10\textsuperscript{3}.

The annealing experiments provide an extensive dataset to model, consisting of both the island size-distributions and the information on island restructuring. Given this, one could in principle attempt to adjust the rates for the processes included in the simulation model to see if they could be made to reproduce these observations. Even for a comparatively simple problem as discussed here, however, the parameter space to be probed in this procedure is very large. Thus, even if one was to succeed, there would not be any certainty that the model assumed in the simulations was correct. In the present case, however, the alternative possibility exists of using the information from the dynamic experiments to determine or estimate the rates for the various processes included and thereby, in reality, test whether the assumed model is in fact correct.

To keep the number of parameters to a minimum, the prefactors for all processes were taken to equal the value determined for adatom diffusion in the troughs ($\nu = 2.5 \times 10^{10} \text{ sec}^{-1}$), and the rates are thus characterized uniquely by their respective activation barriers. In this way, the rates for adatom diffusion (0.81 eV) and dimer dissociation (0.84 eV) in the troughs are known from the results presented in the two previous chapters. The rate for adatom diffusion on top of the islands was taken to equal that observed by FIM on self-diffusion on unreconstructed Pt(110) as discussed earlier [11], providing a value for the barrier for this process of 0.65 eV. The detachment rate from islands in the troughs was estimated from the observation that adatoms detach more rarely than islands move, yielding a barrier of 0.97 eV. With respect to detachment from adatom chains and dimers on top of the islands, the rates for these processes were assumed to be equal and the corresponding barrier was estimated to be 0.88 eV from the dimer lifetimes reported by Kellogg [11]. Finally, to obtain the barriers for ascending and descending motion, the observations of island mobility were considered. Values of 0.87 and 0.66 eV for the two barriers, respectively, reproduce the island mobility rates derived from the dynamic observations (see inset in fig. 7.11), and were used in the simulations.

\textsuperscript{3}In addition, the barriers for adatom attachment to dimers and islands were reduced slightly compared to those for diffusion, in agreement with the results from the previous chapter.
The start-configuration for the simulations was islands (not covered) with sizes complying to the size-distribution obtained from the start-configuration for the annealing experiments. Realizing that island-island correlations are likely to be important for coarsening phenomena, the islands were placed in a correlated fashion incorporating random fluctuations and reproducing the coverage used in the experiments.

The central conclusion arrived at from the simulations was already reported in the previous section, namely that with the rates derived from the dynamic experiments as explained above, the simulations are not at all able to account for the observed coarsening.

To illustrate the disagreement, we show in fig. 7.11 a comparison between size-distributions derived from the annealing experiments and two examples of distributions obtained from the simulations. The experimental distributions are those of the start-configuration (which, as explained, is also the start-configuration for the simulations) and that obtained after annealing for 10 minutes at the highest temperature probed in the experiments of 395 K. The resulting increase in island size is very apparent. For comparison, distributions derived from two different simulations are shown. Both simulations were performed using the parameters described above and correspond to annealing at the same temperature of 395 K, but for a much longer time of 400 minutes. The two simulations differ in that in one (solid line) the ascending motion of adatoms was not allowed, thereby preventing island mobility from occurring, while in the other (dashed line) the detachment from islands was blocked, making island mobility the only channel for coarsening in the island sizes. As could be expected, given the higher rate for island displacement than for adatom detachment, the simulation incorporating island mobility produces the most pronounced change in the size distribution. However, as is very clear from the figure, none of the simulations are able to reproduce the coarsening found in the experiments, not even with the extended annealing period employed.

The most important factor with respect to island coarsening in the 1-D model employed is island mobility. As mentioned, the rates for atoms to ascend and descend the islands were adjusted to reproduce the observed island displacement rates. This procedure clearly presupposes the validity of the on-top model for island mobility. With respect to coarsening, however, the important point is that the resulting island displacement rates in the annealing simulations match those found in the dynamic experiments as can be verified from the inset in fig. 7.11.

In general, the disagreement with the experimental results for the size-distribution is so pronounced that fine-adjustment of the parameters em-
Figure 7.11: Comparison between island size-distributions derived from the annealing experiments and the simulations. The light gray and dark gray experimental distributions are those of the start-configuration and that obtained after annealing to 395 K for 10 minutes, respectively. The distributions derived from simulations correspond to annealing at the same temperature, but for 400 minutes, using processes and parameters as discussed in the text. The solid line shows a distribution resulting from a simulation where island mobility has been blocked, whereas the dashed line correspond to a simulation where adatom detachment from islands is not allowed. The inset shows a comparison between the island mobility rates obtained with the parameters used in these simulations and the experimental data of fig. 7.5.

ployed in the simulation model (while still being consistent with the dynamic observations) can not be expected to improve the agreement significantly.

From the simulations, it is therefore concluded that the 1-D model is insufficient to describe the system at the higher coverages used in the annealing experiments. Whether the incorporation of inter-row interactions as described in the previous section can lead to quantitative agreement with the experimental results, not only with respect to coarsening of the island sizes, but also concerning the island restructuring as well as the more subtle shape changes in the island size-distribution, remains to be investigated.
7.5 Conclusion

In summary, the present chapter has provided an account of work performed to investigate coarsening and island mobility in the Pt/Pt(110)-(1×2) system.

From annealing experiments of the quench-and-look type, coarsening in the sizes of the 1-D islands situated in the missing row troughs was revealed and furthermore a restructuring of the islands was found to occur. These observations were quantified in terms of island size-distributions and a characterization of the island restructuring.

In addition, information was obtained from dynamic experiments (STM movies). These experiments revealed that the islands situated in the missing row troughs are mobile and provided some suggestive evidence with respect to the mechanism of this mobility. From the STM movies, quantitative information was derived on the rates for island displacement and adatom detachment from the islands.

The observations attained from these two different types of experiments were subsequently discussed and compared quantitatively using KMC simulations and simple dimensional arguments. A model was put forth in which both the mobility and the restructuring of the islands arise from the promotion of island atoms into the upper layer on top of the part of the islands that remains in the troughs. Within this model, it proved possible to determine, or estimate fairly precisely, the rates for all the included microscopic process. This was done from the dynamic observations presented in this and the previous two chapters as well as FIM data for the unreconstructed surface. When KMC simulations were used to evolve the start-configuration for the annealing experiments using these derived rates, it was found, however, that there was a very large disagreement between the coarsening observed in the experiments and that obtained in the purely 1-D simulation model.

However, suggestive evidence from the STM movies indicates that interactions between islands in adjacent troughs may contribute strongly to the observed coarsening. It therefore appears to be too simplistic to treat the system in a purely 1-D model at the higher coverages used in the annealing experiments, and it is possible that the information provided by the two types of experiments may be reconciled by including inter-row interactions. As discussed, such interactions are, in fact, quite reasonable within the on-top model proposed for the island restructuring and mobility.

The work described in this chapter illustrates the unique potential of STM to provide, on one hand, detailed dynamic observations including
atomic-scale processes, and on the other hand, a large statistical material on growth phenomena occurring on extended substrates. It is worth stressing the importance of dynamic observations in relation to elucidating the microscopic mechanism of growth and coarsening processes. Thus, in the present case we started from the (fairly) correct rates for a range of processes derived from such dynamic observations and found that with these rates we could not account for the observations from the quench-and-look experiments within the proposed (1-D) model. For this reason the model was revised on the basis of observations from the dynamic experiments. Had we started out with only the (1-D) model and the results of the annealing experiments, it is not impossible that the rates could have been adjusted to fit the data, but the results would clearly not have been correct.

Outlook

While the methodology used in the present study is promising as explained above, it is evident that many questions are still left unanswered. To conclude this chapter we briefly mention some such questions and suggest possible directions for future related studies.

While more extensive modelling could be performed, it is likely that it would be more rewarding to first extend the dynamic experiments to the higher coverages used in the annealing experiments. In this way it would probably prove possible to directly reveal the mechanism of the coarsening and island restructuring. The surface dynamics observed by this type of measurements is likely to be quite complicated and experiments of the quench-and-look type may still provide important input since they, as discussed in the introduction, allow a large statistical ensemble to be characterized.

The proposed change to the 1-D model involving inter-row interactions is likely to be correct, but there are still open questions. With reference to fig. 7.2(d), it appears that after annealing at the highest temperature, nearly all islands are completely covered, and neighbouring islands in adjacent troughs are practically not found. It is interesting what evolution such a configuration will undergo if it is annealed for longer time-periods — does the coarsening belong to a transient regime that stops when neighbouring islands have merged together and all islands are covered?

At the high coverages used in the annealing experiments, the Pt/Pt(110)-(1×2) system can apparently not be treated as a 1-D. Consequently, some of the questions outlined in the introduction for ripening in the 1-D case
have not been extensively addressed. At lower coverages, it may still be possible to treat the system as 1-D, however, and annealing experiments could be performed at such lower coverages to investigate, for instance, the development of the scaled island size-distribution.

As outlined earlier, elucidating and quantifying the detailed mechanism by which the observed island mobility occurs would also be highly interesting. The main problem in this respect is that the elementary processes involved are likely to be very fast. In this regard, an interesting perspective would be to use the STM to obtain line-scans along the length of the island instead of acquiring full STM images. In this way, the dynamic resolution could be considerably improved allowing vacancies diffusing through the islands or adatoms diffusing over them to be resolved.

In conclusion, a large number of interesting phenomena have been found to occur in the Pt/Pt(110)-(1×2) system. While not complete, the work presented in the present chapter has posed some intriguing questions and provides a thorough foundation for future investigations.

References

REFERENCES


Chapter 8

Summary and outlook

This chapter provides a summary of the investigations presented in the previous four chapters, emphasizing the most important results that have been reached. At the end of the chapter there is a brief outlook where interesting directions for future related studies are mentioned.
CHAPTER 8 — SUMMARY AND OUTLOOK

8.1 Summary

In the previous four chapters we have presented a number of STM-based investigations concerning fundamental aspects of metal-on-metal growth in the sub-monolayer coverage regime, ranging from the diffusion of individual adatoms over nucleation and growth of adatom islands to coarsening of the resulting growth structures. In general, the investigations have been quantitative, relying on the analysis of large numbers of STM images.

8.1.1 Pt/Pt(100)-hex

The investigation with respect to the Pt/Pt(100)-hex system belongs to a class of quantitative nucleation and growth experiments based on the “evaporate-quench-and-look” approach. Such investigations have been performed quite extensively in recent years using the STM to monitor the monoatomically high growth islands that result from the nucleation and growth process. The work presented in chapter 4 exemplifies how this field has benefited tremendously from the interplay between experiment and theory, allowing much information on the involved microscopic processes to be inferred from statistical analysis of the observed growth morphology.

In the present case special emphasis was placed on anisotropic effects, something which has only been addressed to a very limited extent in previous investigations. Especially, we showed how the usual analysis in the form of a scaling law for the variation of island density with rate and temperature can be supplemented in the anisotropic case by information derived from an autocorrelation analysis of the spatial distribution of the islands, allowing the degree of anisotropy in the adatom diffusion to be quantified.

Also much information was extracted from the scaled island size-distributions. Thus, an early onset of island coalescence due to anisotropic effects was revealed, dimers were found to have negligible mobility and a critical island size of $i = 1$ was inferred, the latter result in agreement with the one obtained from the scaling law analysis.

Finally, Kinetic Monte Carlo simulations investigating the effects of anisotropic surface diffusion in combination with finite island sizes yielded new insight into the way in which these two factors affect the island size distribution and the scaling behaviour of the island density with deposition rate and temperature.
8.1. SUMMARY

8.1.2 Pt/Pt(110)-(1×2)

In the investigation into the Pt/Pt(110)-(1×2) system a fundamentally different approach from the “archeology-like” quench-and-look method was used. By imaging the surface for extended periods of time with atomic resolution we obtained time-resolved STM movies directly revealing the elementary processes of diffusion, nucleation and growth as they occur. This work demonstrates how variable-temperature STM can be used quantitatively to obtain a very extensive statistical material on single adatom diffusion and other atomic-scale processes involved in nucleation and growth.

With respect to adatom diffusion, as discussed in chapter 5, the key result that has been reached from this investigation is the demonstration that direct “long jump” transitions between non-nearest neighbour sites can occur in a metal self-diffusion system at temperatures not much above the onset of diffusion. In particular, it is shown for the first time that the rate for such long jump transitions follows an Arrhenius dependence on temperature with an activation barrier \(E_{d2} = 0.89\) eV) slightly larger than that for ordinary “single jumps” \(E_{d1} = 0.81\) eV).

In addition to adatom diffusion, aspects of nucleation and growth have been investigated at the atomic level from the acquired STM movies. For instance, as discussed in chapter 6, we have quantified the kinetics of dimer dissociation and association and determined a value for the binding energy of the Pt dimer in the missing row troughs \(E_b = 0.07\) eV). Also the issue of cluster mobility on surfaces has been addressed based on the observation that the 1-D adatom-chains in the missing row troughs are mobile. Certain suggestions to the mechanism behind this process were provided from the dynamic STM observations.

In the final investigation on coarsening and island restructuring we reverted to some extent to the “quench-and-look” approach. The interesting perspective in this study was to combine the information from the two different types of investigation — on one hand the quench-and-look approach which allows for a large statistical ensemble to be probed resulting in a characterization of the average properties of the system, and on the other hand the dynamic observations which provide not only quantitative input on the rates for different processes involved but also, not least importantly, provide a direct picture of how the system develops.

While the coarsening and island restructuring that follow upon annealing of the surface have been characterized in detail, there are still many open questions from this investigation. Especially it is puzzling that the observations on coarsening can not be reconciled with the dynamic obser-
vations within a simple 1-D model using KMC simulations that incorporate the known rates for the microscopic processes believed to be important. However, the suggestive evidence attained from the STM movies of interaction between islands in adjacent troughs, signifying a breakdown of the simple 1-D model at higher coverages, seems promising with respect to resolving this issue.

In general, the work presented in chapter 7 illustrates the unique ability of STM to provide information on both growth phenomena at extended terraces as well as on the dynamics of atomic-scale processes.

8.2 Outlook

While the understanding of nucleation and growth phenomena has reached a very detailed level at present, much less is known about the subsequent evolution of the resulting growth structures. Consequently the study of ripening and related phenomena is a field that is receiving increasing attention. This is not least motivated by its importance in relation to the issue of nano-structuring where the question of the stability of created structures evidently is relevant. Dynamic observations by variable temperature STM, also on larger length scales, will be very rewarding in this respect as it has already been demonstrated in several experimental investigations [1,2]. In this regard the work presented in chapter 7 on island mobility and coarsening points very much forward. Detailed suggestions for future investigations in the interesting Pt/Pt(110)-(1×2) system were provided at the end of chapter 7.

The time-resolved STM observations presented in this thesis provide important new insight into the way in which diffusion occurs. From the perspective of extending the data-base on metal-on-metal adatom diffusion it is clearly valuable that the STM can also be used for this type of atomic-scale investigations. It is evident, however, that much work has already been done in this field in the form of the very detailed investigations using the Field Ion Microscope.

A very interesting related issue, however, that is currently receiving much attention is the question of the influence of adsorbed gases on metal adatom diffusion. For instance it has been speculated that a “sky-hook” effect could exist where the adsorbate binds to the adatom, thereby weakening the adatom-surface bond resulting in an increased metal adatom diffusivity [3,4]. A detailed understanding of such phenomena is desirable, not least from the perspective of catalysis [5].
Time-resolved STM observations can be used to investigate such adatom-adsorbate interactions in a very detailed way. For instance it is likely that it could be possible to identify which adatoms are affected by the mentioned “sky-hook” effect, since the attached atom could cause changes to the local density of states allowing for such species to be distinguished from ordinary metal adatoms in the STM images. This would constitute an important difference to FIM, where the imaging field causes the adsorbates to desorb. Efforts in this direction are currently being pursued extensively in the STM group here at University of Aarhus.

References


Dansk resumé


Arbejdet beskrevet i denne afhandling har drejet sig om detaljeret at afdække hvorledes dette scenarie udspiller sig når Platin (Pt) atomer pådampes to forskellige rekonstruerede krystalfacetter af Pt ekrystaller.

De beskrevne eksperimenter er alle udført under meget idealiserede forhold på overfladen af perfekte metal ekrystaller under ultra højt vacuum (UHV) betingelser for at sikre renheden af de undersøgte overflader. Den altoverejende eksperimentelle teknik der har været anvendt er Skanning Tunnelerings Mikroskopi (STM). Denne teknik tillader at man, ved at føre en uhyre spids nål henover overfladen der undersøges, kan aftaste dennes konturer på længdeskalaler der strækker sig fra det atomare niveau og op til afstande af størrelsesorden 1/1000 mm. Denne yderst store spændvidde er den unikke egenskab ved STM og er det som tillader at man med dette instrument kan opnå information om både de detaljerede vækstprocesser på atomart niveau og om de resulterende vækststrukturer på større længdeskalaler.

Den umiddelbart fascinerende egenskab ved STM er instrumentets evne til direkte at afbilde strukturerne af overflader og dermed give "STM billeder"
der viser hvorledes sådanne overflader ser ud\textsuperscript{1} helt ned til positionerne af de enkelte atomer. Denne kvalitative visualisering er således hvad instrumentet er bedst kendt for. Det er imidlertid en hovedpunkt i de her beskrevne studier, at man ved statistisk analyse af information uddraget fra store mængder af sådanne STM billeder, kan opnå en detaljeret kvantitativ beskrivelse af de processer der foregår på overfladen. I den henseende illustrerer afhandlingen en generel tendens indenfor STM baserede studier i disse år.

STM billeder der viser de to undersøgte Platin overflader, benævnt Pt(100)-hex og Pt(110)-(1×2), er afbildet i kapitel 1 i henholdsvis figur 1.1 og 1.2. Med reference til disse to figurer vil vi i det følgende skitsere principperne i de udførte studier og fremhæve nogle vigtige resultater. Begge STM billeder er med atomar oplossen, og er gengivet i en gråtone skala således at mørkt svarer til lave områder og lyst svarer til atomer der rager langt frem i overfladen.

Det øverste atomare lag på Pt(100)-hex overfladen udviser, som det kan ses på figur 1.1, en højdevariation der mindsker overfladens symmetri og giver anledning til 6-atomer brede "kanaler" på overfladen. De udførte eksperimenter bestod i at pådampe Pt på denne overflade ved temperaturer hvor mobiliteten af adatomerne er høj, og dernæst, efter vækstprocessen var afsluttet, at nedkøle krystallen til temperaturer hvor alle processer stopper og afbilde den resulterende struktur. Resultatet var aflange vækst過程中 som vist i det indsatte billede i figur 1.1. Ideen i denne type eksperiment er at man ved at karakterisere den resulterende struktur med hensyn til antalstæthed, størrelse og fordeling på overfladen af de dannede vækstører, efterfulgt af sammenligning med resultater fra teori for kondensation og vækst, kan slutte sig tilbage til de mikroskopiske processer der førte til den observerede struktur. Denne type undersøgelse har været gennemført tidligere i adskillige systemer hvor overfladen er simpel og isotrop. Studiet af Pt/Pt(100) systemet havde som sit vigtigste mål at udforske hvilken effekt den anisotrope højdevariation har for diffusionen af de enkelte adatomer og for den resulterende krystalvækst.

Resultaterne fra dette studie, som er beskrevet i kapitel 4, skyldes et udbrydeligt sammenspil mellem eksperiment og teori, hvor teoretikere på Danmarks Tekniske Universitet bidrog med modellering af vækstprocesserne. Som eksempel på dette samarbejde kan nævnes en ny undersøgelsesmetode der består i at karakterisere hvorledes vækstørerne rumlighelt er

\textsuperscript{1}Dette udsagn er en tilnærmelse, men ikke ukorrekt da vi ikke nærmere har specificeret hvad der meneres med "ser ud". I realiteten er det tætheden af elektronflyen fra de yderste atomer i overfladen der afbilledes.
fordelt på overfladen. Denne fordeling indeholder information om hastigheden hvorned de diffunderende adatomer bevæger sig. Fra de eksperimentelle data kunne det afgøres at afstanden mellem ørner i retningen langs de omtalte kanaler var langt større end i retningen vinkelret herpå, og ud fra denne information kunne det sluttes at overfladens anisotrope højdevariation har stor betydning for diffusionen af de enkelte adatomer, og forårsager at de foretrukket bevæger sig langs disse kanaler.

Den beskrevne undersøgelsesmetode i Pt/Pt(100) tilfældet er undertiden blevet kaldt ”overflade-arkæologi” på grund af den indirekte måde hvorpå man slutter sig tilbage til de elementære processer ud fra den endelige vækststruktur. I kontrast hertil baserer studiet af Pt/Pt(110) systemet sig på en direkte visualisering af de elementære dynamiske processer på atomar skalde der ligger til grund for krystalvækst.

Strukturen af Pt(110)-(1×2) overfladen er afbildet i figur 1.2. Denne overflade består af tætpakke rækker af atomer adskilt af eet atomart lag dybe græffer der ses som sorte streger på STM bildeled. Det viste bildeled er optaget efter at en lille ændrefe Pt atomer er pådampet overfladen, og disse atomer kan ses i græfferne både som enkelte atomer og som korte kæder skabt ved at diffunderende adatomer, der er mødtes i græfferne, har bundet sig til hinanden og dannet disse ør.

Eksperimenterne med henblik på at undersøge dette system har primært bestået i at anvende STM til at optage mange (hundredevis) af på hinanden fulde billeder med atomar oplosning. Når sådanne ”STM film” afspilles, giver de et levende indtryk af de atomare processer der udspiller sig på overfladen2. Således kan det direkte ses hvorledes de enkelte adatomer diffunderer i græfferne, mødes, binder sig til hinanden og dannet en adatompar der siden brydes op igen eller, alternativt, danner en mere stabil ø idet det gror ved indfangning af yderligere adatomer. STM filmene tillader på denne måde at man følger de elementære processer involveret i diffusion, inddannelse og krystalvækst direkte som de forløber.

Ved at optage denne type tidspænteste STM data ved en række temperaturer af overfladen, efterfulgt af grundig statistisk analyse, kan man opnå meget detaljeret information om de observerede processer. Således er undersøgelsen af enkelt-adatom diffusion beskrevet i kapitel 5. Hovedresultatet fra denne undersøgelse er en påvisning af at diffusionsprocessen i dette tilfælde ikke alene består af simple hop mellem nærmeste nabo positioner, som detellers typisk antages, men også består af ”lange hop” hvor adatomer laver en direkte overgang mellem pladser to gitter-afstande

2Eksempler på sådanne film kan ses på STM gruppens hjemmeside: 
http://www.dnl.aau.dk/condensm/surface/stmlab/ptmovies/ptmovies.htm
fra hinanden. Det er ydermere blevet påvist at raten for sådanne "lange hop" overgange følger en Arrhenius afhængighed af temperaturen, noget som ikke var klart fra tidligere studier.

Også de fundamentelle processer involveret i kimdannelsen og vækst er blevet kvantitativt undersøgt fra de optagne STM-film i Pt/Pt(110) systemet. Specielt analyseres dissociationsraten for par af adatomer i kapitel 7. Endeligt beskrives i kapitel 8 en undersøgelse af hvorledes vækststrukturen, i form af de en-dimensionale kæder af adatomer, udvikler sig når krystallen opvarmes og et større omfang af mikroskopiske processer derved bliver mulige.

De udførte studier er som nævnt udført under specielle betingelser i idealiserede modelsystemer. De fundamentelle processer der er observeret er imidlertid ikke forskellige fra dem der forløber i mere "virkelige" situationer hvor tynde metalfilm pålægges enner i praktisk øjemed, for eksempel i forbindelse med korrosionsbeskyttelse, ændring af linsers optiske egenskaber eller overfladebehandling med henblik på at øge værktøjs slidstyrke. Håbet er således at man på længere sigt, ved at opnå en detaljeret forståelse af hvorledes sampillet mellem de involverede mikroskopiske mekanismer kontrollerer udfaldet af den endelige vækststruktur, kan blive i stand til at styre teknologisk vigtige processer på et langt finere niveau end man er i stand til i dag.