Theoretical Studies of Epitaxial Graphene Formation on Metal Surfaces

by

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Statement of Originality

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Abstract

In this thesis we develop a set of pheneomenological models that we apply to the problem of epitaxial growth of graphene on metal substrates. The high temperature and typically low flux conditions under which graphene growth occurs are such that state of the art techniques such as kinetic Monte Carlo (kMC) are extremely difficult to apply to study the growth processes. Rather we utilise simpler theories based on rate equations and also develop a technique based on the phase-field method of island front tracking. The latter method may be considered to be an addition to the class of techniques known as "island dynamics" models [1].

We use rate equations to study the nucleation and growth of graphene [2] and to explore the dehydrogenation sequence of ethylene CH$_2$CH$_2$ on iridium [3]. In the former study we develop a method for parameterising the parameters appearing in rate theories and apply the method to correct a previously reported rate theory to account for the exponential dependence of island density on temperature. In the former we find that kinetic models parameteried with ab-initio calculations are able to account for much of the dehydrogenation sequence observed experimentally. Reasons for discrepancies for the species observed at 300 K are discussed.

We then present a detailed explanation of the phase-field simulations of epitaxial growth in the submonolayer regime. We demonstrate how the method is able to obtain agreement with KMC simulations of reversible and irreversible aggregation by reporting on the island size distributions and the scaling of island density with $D/J$ in both regimes. Here $D$ is the diffusion constant of adatoms on the substrate and $J$ is the deposition rate. Discrepancies for the scaling of island density with $D/J$ when temperature is varied is traced back to the dependence of phase field parameters on temperature. This conclusion is strengthed by the quality of the results obtained for phase-field simulations obtained for fixed temperature and varying flux, $J$. We also show how a simple variation of the algorithm allows us to obtain agreement with results obtained from KMC simulations in which nucleation rules for critical nuclei are explicitly incorporated and where detachment of adatoms from island boundaries are forbidden. Finally, we describe how such a pheneomeological method may be used to
describe qualitatively the growth of graphene on polycrystalline copper substrates.
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Submitted / Published Articles


Chapter 1

Introduction

Graphene is the name given to a planar monolayer of carbon atoms arranged in a hexagonal lattice with a C-C bond length of 0.142 nm. It is the building block for a number of other well known carbon allotropes which have, historically, been the focus of much research. These include carbon nanotubes, fullerenes and of course graphite (Fig. 1.0.1). The interest that surrounds this “super-material” [5] is such that it has not even escaped the notice of policy makers, with the British government earmarking funds specifically for research into graphene technologies [5] and the European Commission providing as much as one billion euros to aid graphene research [6].

There are many reasons for the interest in graphene. These include the unusual linear dispersion of $\pi$ bonds [7], extremely high electrical and thermal conductivity, [8] tensile strength, 130 GPa [9], spring constant, $K \sim 50 \text{ eV }^{-2}$ and elastic modulus, $Y \sim 1 \text{ TPa}$ [9]. The latter four attributes are due to the relatively strong in-plane bonding while the high conductivity of graphene is due to the hybridisation of atomic $p_z$ orbitals over the whole graphene flake which allow electrons to move with ease through the crystal lattice. Graphene has in fact been studied by theoreticians since the 1940’s [7] where a tight-binding study by Wallace demonstrated the well known linear dispersion relation for a layer of graphite at $K$ points in the
Brillouin zone. This is one property that is described by a Hamiltonian which has exactly the same form as that of photons described by the Dirac equation and it is for this reason that electrons in graphene can be referred to as Dirac fermions. However, the enormous acceleration in graphene research can be traced back to 2003-2004 when Nobel prize winning work by the Manchester group led by Andrei Geim isolated graphene using the so-called “scotch tape” method [10].

With the large number of technological possibilities that graphene provides it is important to be able to find a way to consistently produce defect free graphene. The exfoliation methods used by Geim are able to produce graphene samples with areas of up to 1 mm$^2$ and extremely good electrical properties [11]. However, they are difficult to scale up to an industrial level. Epitaxial growth is one way in which graphene can be produced on an industrial scale. It has the benefit of already being a standard fabrication method in transistor and semiconductor production [12] and so could possibly be a route into realising a number of the electronic applications of graphene.

Despite the vast amount of theoretical interest in graphene, research into nucleation and growth has in some manners lagged behind explorations of properties and applications of graphene. Particularly, studies that look into kinetics of growth [13] or the very earliest stages of growth (nucleation) are somewhat in the minority. Much work has focused on the most stable carbon cluster configurations on transition metal surfaces [14, 15], the macroscopic structure of graphene [16, 17, 18] or the attachment of carbon atoms at the growth front [19, 20].

In the following, we will give a brief introduction to the epitaxial growth process (Sec. 1.1) and review a selection of the most important theoretical methods for studying them (Sec. 1.4). We will then review some of the experimental works relating to the nucleation and growth of graphene, concentrating on those most pertinent to this thesis (Sec. 1.3). A more detailed review of the theoretical and experimental works on graphene nucleation and growth can be
1.1 Epitaxial growth

Epitaxial growth is the process of forming a crystalline structure by deposition onto a substrate of a material which has either different chemical or geometrical properties to the deposited material [21, 12]. In this way it differs from crystal growth in two possible ways. In the first, the lattice parameter of the substrate and the equilibrium structure formed by the deposited material differ so that there exists a lattice mismatch (and therefore an associated strain energy) between the two structures [21]. Secondly, it is possible for epitaxial growth to occur when there is no lattice mismatch (because both structures have the same lattice parameter) but instead there is a difference in the strength and/or nature of the chemical bonds in the two materials [21].

In principle a complete theoretical description of epitaxial growth involves taking into
account all of the processes responsible for the nucleation and growth, beginning from the de-
position of molecules or atoms onto the substrate and ending when the final stable structure is
formed. The geometry and the composition of the final structure is governed by the balance of
thermodynamics and kinetics; the extent to which the structure can reach the most favourable
equilibrium structure is limited by the kinetics of the growth processes.

These growth processes, depicted diagrammatically in Fig. 1.1.1, begin with the deposition
of either the atom of which the material we wish to grow comprises or a molecule containing
said atom. In the case of graphene this is usually a hydrocarbon, most commonly ethylene.
This is accomplished by an experimental technique such as molecular beam epitaxy (MBE) or
chemical vapour deposition (CVD) [12]. The growth occurs under controllable conditions (i.e.
temperature, pressure, flux rate) and the final structure formed is usually strongly dependent
on what these conditions are.

Following deposition a complex sequence of events must be considered. These include, but
are not limited to, the energetics of absorption at different surface sites, the possibility that a
molecule may desorb from the surface and the need for larger deposited molecules to break up.
CHAPTER 1. INTRODUCTION

We must then consider ways in which an adatom or possibly a dimer can hop between different energetically favourable sites on the substrate. This process is activated such that an energy barrier must be overcome for the atom to move to a different surface site. Additionally, such processes can be even more complicated than this, involving substitution reactions between substrate atoms [23].

At some critical concentration of carbon adatoms (or some other relevant carbon cluster) there exists the possibility that islands can nucleate on the substrate. There are two possible ways that this can happen. Firstly, nucleation can occur homogeneously. In this case there are no preferential sites on the surface for nucleation to occur. We can then imagine a situation whereby reactions occur between adatoms to form larger species. These larger clusters may be unstable and decompose quickly, or may grow until a critical size (which may possibly be determined by thermodynamics) has been reached and an island nucleates. Heterogenous nucleation occurs when there are preferential sites on the substrate, such as step edges, point defects or extended defects, that lower the free energy required for nucleation to occur.

Finally, once an island has nucleated it is then necessary to describe the possible ways that an island can grow. Classically, we imagine this is through the capture of adatoms by islands [12]. However, the situation is complicated by the presence of the substrate which may result in the energy barrier for adatom attachment to be very high [24, 25]. Thus, it is necessary to consider larger species in the growth process, or novel substitution reaction involving substrate atoms [26, 19].

It is clear that understanding the nucleation and growth processes occurring during epitaxial growth is an inherently multiscale problem, both in time and space. For example, while a typical nucleation event can occur on very short time scales, growth can occur over minutes or hours [4]. It is therefore, not surprising that a wide variety of modelling techniques can be applied to the problem. The length and time scales that these techniques look at is similarly disparate. Thus, sophisticated ab-initio techniques are widely used to look at lowest energy
structures of different clusters forming on a metal surface, but rate equations that look at time scales on the order of hours have also been successfully employed to understand growth mechanisms. It is to a review of such theoretical technique that we now proceed.

\section*{1.2 Review of theoretical techniques}

\subsection*{1.2.1 \textit{Ab-initio} techniques}

The properties of epitaxial systems are ultimately governed by quantum mechanics. However, the solution of the many-body Schrodinger equation, for all but the smallest systems, represents an intractable computational challenge and even approximate methods suffer from the same, albeit alleviated limitation. Thus, it is typical to consider reduced models for which the approximate methods of solving the many-body problem may be applied and, hopefully, the physics of the system illuminated.

By far the most commonly utilised \textit{ab-initio} technique in the study of graphene and other epitaxial systems is the Density Functional Theory (DFT) which is a ground-state theory valid only for quantum systems at zero temperature. As well as ground-state energies of systems of nuclei and electrons it is able to give accurate results for the forces on atoms via the Feynman-Hellman theorem \cite{27}, that may be used to find the optimal geometries of clusters on a substrate \cite{27} or in molecular dynamics (MD) simulations.

So far we have mentioned only static properties of a quantum system, however, DFT can also provide valuable insights into the dynamics of a system. For instance, the mobility of adatom species on a crystalline substrate is largely determined by the minimum free energy path connecting two absorption sites on the surface which at its highest point is known as the transition state. In practice this path may often be obtained by making an educated guess of an initial geometry and then using DFT to calculate the forces on atoms which are then used to propagate the molecule across the transition state to a lower energy geometry. Special care
must be taken to ensure that a global minimum of the free energy has been found. To this end it may be possible to use local minimisers (e.g. Newtonian or conjugate gradient optimisers) but perform many calculations for different geometries. As an alternative method it may be possible to implement global minimisers such as Langevin optimisers or simulate annealing techniques. Applications of DFT to the study of graphene growth will be discussed in Sec. 1.4.

### 1.2.2 Other methods: empirical potentials and tight-binding

Although DFT is not an exact theory since it relies on approximate forms of the exchange-correlation functional, it often provides the most complete knowledge we may have of a quantum system. However, it is computationally very expensive and it may often be advantageous or indeed necessary to utilise less exact but cheaper methods to obtain forces on atoms. This allows energy minimisations and MD simulation to be performed over longer time periods and for larger system sizes.

One possibility is to make use of an empirical potential (EP) which neglects entirely the electronic degrees of freedom and instead makes use of analytical expressions for the many-body potential including one body, two body, ... *ad infinitum* interactions which are parameterised using experimental data (e.g. lattice parameters, elastic constants) or *ab-initio* calculations. In general, the number of terms that are included in the potential is highly dependent on the problem at hand and, indeed, much effort has been spent on developing force-fields which are capable of describing specific systems more accurately by the inclusion of additional terms which better describe the bonding present. Some examples of the simplest two-body potentials include the well known Lennard-Jones model which describes interactions between neutral molecules or the Morse potential. Multi-body potentials which are well suited to describing covalently bonded atoms such as diamond or graphene include the Stillinger–Weber [28], Tersoff [29, 30], and Brenner [31] potentials. In metals, where bonding is characterised by the
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delocalisation of the electron density about positively charged ions embedded-atom or the
Finnis-Sinclair models [32] are often employed.

1.2.3 Molecular dynamics

If the forces on all the atoms in a system are known then their motion can be determined by
integrating Newton’s equations,

\[ m_i \ddot{v}_i = F_i, \quad \dot{r}_i = v_i, \quad (1.2.1) \]

where \( v_i \) and \( r_i \) are the velocity and position of the \( i \)-th atom of mass \( m_i \), respectively. Here
the overdot refers to differentiation with respect to time, \( t \). In practice, time is discretised and
Eq. (1.2.1) solved using a method of numerical integration such as the Verlet algorithm [33]
with appropriate conditions applied at the boundaries of the system (e.g. periodic boundary
conditions).

Statistical ensembles are characterised by how particles in an open system are able to
interact with the (infinite) outside world (the bath). For instance, consider the canonical or
NVT ensemble, which is the name given to a system of constant particle number and volume
in contact with a heat bath which maintains a constant temperature. In this case, particles in
the system are able to interchange with particles in the heat bath in such a way that the total
temperature and number of particles remains constant. In an MD simulation, clearly only a
system is realised, but a particular ensemble may readily be simulated by altering the way in
which the velocities or positions of the particles are updated in such a way as to include the
effects of interactions with the outside world. Practically, this is accomplished using a number
of algorithms designed to model specific ensembles (e.g. in the case of the canonical ensemble
one could implement an Andersen [34] or Nose-Hoover thermostat [35]).

Since the trajectory of each of the particles is deterministic and determined by initial
positions and momenta, a molecular dynamics simulation represents an extremely detailed
description of a systems dynamics. However, this approach to modelling can be extremely inefficient if we are interested in systems whose motion may be partitioned into fast and slow processes. An approach that lends itself to the description of such systems are the so-called Monte Carlo methods, a review to which we now turn.

1.2.4 Monte Carlo and other stochastic methods

Monte Carlo methods encompass any algorithm which evolves the system based on random numbers [36]. The equivalence between such a stochastic description and molecular dynamics may be obtained informally by imagining that it is possible to “coarse-grain” the original deterministic description, whose evolution is obtained by integrating Newton’s equations, so that we are left only with an approximate description of the slow-processes that have been obtained by “integrating out” the fast processes which we do not wish to reproduce exactly. We are left with a probabilistic knowledge of the configuration of a system whose evolution is determined by stochastic transitions which occur at a given rate. The rate of a transition may be calculated using the transition state theory (TST) which incorporates the effect of fast processes phenomenologically. The central quantity is the probability that the system is in configuration $\sigma$ at time $t$ denoted by $P(\sigma, t)$. The process governed by transitions between configurations $\sigma$ and $\sigma'$ is assumed to be Markovian, with the transition rate $W_{\sigma,\sigma'}$. The equation of motion for $P(\sigma, t)$ when the process is Markovian is the master equation:

$$\frac{dP(\sigma, t)}{dt} = \sum_{\sigma'} \left\{ -W_{\sigma,\sigma'} P(\sigma, t) + W_{\sigma',\sigma} P(\sigma', t) \right\}. \quad (1.2.2)$$

Often the master equation is mapped on to a lattice (although it is also possible to perform Monte Carlo simulations without a lattice). This is especially appropriate in the case of modelling epitaxial growth since the lattice may be considered to be an approximate realisation of the substrate. Furthermore, in epitaxial growth the configuration $\sigma$ unambiguously refers to
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the different ways in which the constituent particles (e.g. adatoms, clusters) may be distributed on the substrate. The transitions refer to the various different physical processes that an adatom or cluster may undergo (e.g. an adatom diffusing from site to site, an atom detaching from a cluster, an adatom desorbing from the surface, etc.).

The master equation is a formidable equation to solve. Kinetic Monte Carlo (KMC) methods are a set of algorithms that solve Eq. (1.2.2). The basic idea behind the method is as follows. Starting from an initial configuration, $\sigma$, a list is formed of all the possible states, $\sigma'$, which are able to be reached from $\sigma$ by one of the predetermined local processes. The total rate out of the initial configuration, $R_{\sigma}$, is:

$$R_{\sigma} = \sum_{\sigma'} W_{\sigma,\sigma'},$$

where the transition rates are assumed to be of Arrhenius form,

$$W_{\sigma,\sigma'} = \nu_{\sigma} \exp \left[ -\beta E_{\sigma,\sigma'} \right],$$

and $\nu$ and $E$ are the attempt frequency and energy barrier of the process that moves the system from $\sigma \rightarrow \sigma'$. If the probability of leaving state $\sigma$ is exponentially distributed in time, then the mean waiting time for a successful transition from $\sigma$ will be:

$$\Delta t_{\sigma} = \frac{1}{R_{\sigma}} \ln Y_1,$$

where $Y_1$ is a uniform random deviate between 0 and 1. A second random number is drawn to determine the state to which the system is moved to from $\sigma$. This is accomplished by selecting a uniform random variate, $Y_2 \in (0, 1]$. If it satisfies the condition

$$R_{i-1} < Y_2 < R_i,$$
where $R_i = \sum_{j=1}^{i} W_{\sigma,j}$ is the cumulative rate out of the initial configuration $\sigma$, then the process $i$ is chosen as the result of the transition over time $\Delta t_\sigma$. The system is then propagated forward in time by repetition of this algorithm.

### 1.2.5 Transition state theory

In the above description of Monte Carlo methods the rates of processes were said to be of Arrhenius form, but we did not discuss the foundations of such an assumption. In the following we will do just this by reviewing a formalism known as transition state theory (TST) [37, 38].

Recall that we wish to calculate within a statistical mechanical framework the rate of crossings of particles traversing a saddle point connecting two minima of a potential energy surface. For simplicity we shall perform the calculation in one dimension. The transition rate, $\nu$ is given by the number of particles per unit time (the flux) crossing the saddle point divided by the total number of particles in the first minimum, which in the canonical ensemble is given by,

$$\nu = \frac{\int_0^\infty dp \int_{q_{\text{saddle}}} dq e^{-\beta H(p,q)}}{\int_{-\infty}^{\infty} dp \int_{q_{\text{well}}} dq e^{-\beta H(p,q)}}$$

(1.2.7)

where $p$ and $q$ are generalised momenta and position respectively, the overdot denotes differentiation with respect to time and the Hamiltonian $H = \frac{p^2}{2m} + V(q)$ which is simply the kinetic energy of a particle with momentum $p$ moving in a potential $V(q)$. Note that in the above integral the numerator contains one less dimension than the denominator because it is evaluated at a saddle point. The numerator is trivial to evaluate since the constraint that the trajectory passes through the sample is enforced with a delta function and Laplace's method may be applied to the integral over the generalised coordinate $q$ in the denominator. The result of such calculations is:
This is of the Arrhenius form given by Eq. (1.2.4) where we associate the multiplicative factor in Eq. (1.2.8) with the frequency, $\nu$. To generalise to the multidimensional problem is straightforward and in this case the frequency factor is given by

$$\nu = \frac{1}{2\pi} \sqrt{\frac{V''(q_{\text{well}})}{m}} e^{-\beta(V(q_{\text{saddle}})-V(q_{\text{well}}))}.$$  

(1.2.8)


\[ \nu = \frac{1}{2\pi} \sqrt{\frac{V''(q_{\text{well}})}{m}} e^{-\beta(V(q_{\text{saddle}})-V(q_{\text{well}}))}. \]

where $\omega_i^{w,s}$ denotes the square root of the $i$-th eigenvalue of the dynamical matrix evaluated at the well and saddle point, respectively, and $N$ is the number of particles. Note that the eigenvalue corresponding to the direction normal to the dividing surface (the hypersurface separating the initial and final states) will be negative (the frequency imaginary) but it is not included in the product in the denominator. The reason for its absence can be understood by recognising that the multidimensional integral is evaluated within a harmonic approximation where normal mode coordinates are defined within the dividing surface. As such, the direction normal to this dividing surface (the direction of the diffusing particle) are not included in the normal mode expansion. A derivation of Eq. (1.2.9) may be found in the original paper by Vineyard [37].

**1.2.6 Continuum equations**

It is also possible to formulate continuum equations represented by either stochastic or deterministic partial differential equations for the average mass density of species present on the surface. There are a great number of such equations, for example, the Kardar-Parisi-Zhang (KPZ) equation [39] which describes a wide range of phenomena, for instance the motion of an interface driven far from equilibrium. Another example would be the diffusion equation which has a number of applications, such as modelling the distribution of temperature in some
region over time [40] or the evolution of a stock option written on some underlying prior to expiration [41].

As an illustrative example of the possible benefits of a continuum description, consider the diffusion equation which describes the average density of a large number of non-interacting particles performing a brownian motion on a surface. In a discrete theory, for example a KMC simulation of adatoms hopping from site to site on a surface, the location of each particle would be known and the system would be propagated forward in time by an amount proportional to the rate of hopping. Since this timescale is on the order of nanoseconds it represents a rigid constraint on the capabilities of KMC simulations where the rate of hopping is particularly high. However, the ensemble average of the positions of particles (i.e. the density appearing in the diffusion equation) varies on timescales and lengths much larger than that needed to resolve each of the individual hops and so in principle the system may be larger (often macroscopic) and can be propagated in time much further than in the discrete description.

Continuum equation are often derived using a combination of conservation laws, for example of energy or mass, symmetry constraints present in the system and constitutive relations whose basis may be phenomenological or derived from first principles. It may also be possible to derive continuum equations directly from a discrete formulation such as the master equation [42]. The diffusion equation discussed earlier may be derived in more than one way, for instance, by utilising the law of conservation of mass coupled with Fick’s first law of diffusion or by coarse graining a master equation description of particles on a lattice which have equal probabilities of hopping to nearest neighbour lattice sites at a constant rate [43].

Finally, for practitioners, the benefits of transforming to a continuum description may be the availability of a wide range of numerical and analytical tools for the solution or analysis of stochastic and partial differential equations.
1.2.7 Rate equations

Rate equations for epitaxial kinetics [44, 45] are first-order (in time) differential equations for the evolution of spatially-averaged densities of the surface species deemed to be important for a particular experimental scenario. The general form of such rate equations for the densities $x_i$ ($i = 1, 2, \ldots, n$) are

$$\frac{dx_1}{dt} = R_0 + \sum_i R_i^{(1)} x_i + \sum_{i \leq j} R_{ij}^{(1)} x_i x_j + \sum_{i \leq j \leq k} R_{ijk}^{(1)} x_i x_j x_k + \cdots, \quad (1.2.10)$$

$$\frac{dx_2}{dt} = \sum_i R_i^{(2)} x_i + \sum_{i \leq j} R_{ij}^{(2)} x_i x_j + \sum_{i \leq j \leq k} R_{ijk}^{(2)} x_i x_j x_k + \cdots, \quad (1.2.11)$$

$$\vdots$$

$$\frac{dx_n}{dt} = \sum_i R_i^{(n)} x_i + \sum_{i \leq j} R_{ij}^{(n)} x_i x_j + \sum_{i \leq j \leq k} R_{ijk}^{(n)} x_i x_j x_k + \cdots. \quad (1.2.12)$$

The rate $R_0$ is the deposition rate of surface species, which is determined by the experimental conditions and, therefore, is a known quantity, while the remaining rates are associated with the indicated processes. Depending on the nature of the species being deposited, there may be corresponding source terms in other equations. This is necessary, for example, if there are complex reaction sequences with intermediate species that can influence the evolution of the system. As the $x_i$ are spatially averaged, the interpretation of collision terms such as $x_i x_j$ is as the probability of species $i$ and $j$ occupying the same site on the substrate, whereupon the reaction proceeds at the indicated rate. Thus, the rate equations include no correlations and are, accordingly, referred to as mean-field rate equations.

Equations (1.2.10)–(1.2.12) are used to study epitaxial systems in several contexts. In one, there is an equation for adatoms and islands of every size which, of course, means that there could be a large number of equations, depending on the growth conditions. The goal in such studies is rarely a quantitative analysis of a particular system, but as a starting point for more general results, such as the scaling theory of island-size distributions [46, 47].
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A more common use of rate equations is in a contracted form, where the islands are grouped into a single entity, leading to fare fewer equations, and more a manageable basis for a quantitative analysis of experimental data.

Finally, we note that rate equations also appear in model reduction strategies [48], where beginning with a full atomistic description, as provided by KMC simulations, a systematic reduction is used to reduce the number of variables in a high-dimensional dynamical model, while still providing an accurate description of quantities of interest. There is an optimisation step in this methodology, which compares experimental measurements with the predictions of a reduced-order model.

Due to the spatial averaging, rate equations assume that adatom and island densities are spatially homogenous. Furthermore, they do not include a diffusion term even though adatoms are assumed to be mobile. This means that in general the rate equations are likely to be more accurate on flat surfaces and at low coverages. However, it is often important to include spatial affects within the rate equation description to describe correctly the evolution of adatom and island density as a function of time or the scaling of their densities appearing in a the governing equations [49, 50].

This concludes our brief review of a selection of theoretical methods used to explore different aspects of epitaxial growth processes. We now turn to a review of a number of experimental works which we view as being particularly important or have motivated some of the theoretical work contained in this thesis.

1.3 Review of experimental work

We consider here the fabrication of graphene on a transition metal substrate by two processes, Chemical Vapour Deposition (CVD) and Temperature Programmed Growth (TPG). For a treatment of different growth techniques there exists a number of reviews which summarise the large number of experimental works on graphene growth [51]. These methods include
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CVD and Molecular Beam Epitaxy (MBE) growth of graphene on a hexagonal face of metal substrates Cu(111) [52], Rh(111) [53], Ir(111) [25, 54, 55]; on polycrystalline substrate, in particular copper [57, 58, 59]; on thin metal films deposited on a larger non metal bulk [60, 61]. We also do not describe growth by sublimation of carbon atoms [62, 63], from SiC or by any other methods. Furthermore, we only consider monolayer graphene, not, for example, studies exploring bilayer graphene growth [64]. Elements of this section and much more can be found in the extensive review of graphene growth compiled by members of our group, and myself [4].

1.3.1 Observations during CVD

Growth of graphene by CVD is the major technique for graphene grown epitaxially on metal substrates. A typical experimental procedure is as follows. Typical carbon precursors are ethylene or methane [25, 55] but it is also possible to grow graphene using a variety of different larger carbon based molecules [65]. Prior to the deposition of hydrocarbons the surface of the transition metal is cleaned. The sample is placed in an ultra high vacuum (UHV) chamber, with a base pressure of approximately 10−11 mbar and then sputtered with energetic (⇠1 keV) ions (e.g. Ar+) and flash annealing at around 1200-1500K. Then the sample is kept at some specific temperature, usually greater than 700K [55, 58]. Gaseous molecules are then introduced onto the hot surface. The pressures and flow rates of vapours in the dosing tube are varied to produce different fluxes of molecules onto the transition metal surface.

Nucleation

A central issue that concerns both researchers and industry is the quality of the graphene produced. We are usually able to quantify “quality” by referring to the reduction in one of graphenes advantageous physical characteristics, such as a reduction in the mobility of charge carriers leading to a drop in conductance due to the presence of defects in a graphene sheet [66]. It is very likely that the nature of the nucleation of graphene will directly affect the quality
of graphene. Homogenous nucleation means there are no preferential nucleation sites on the substrate. There is, therefore, a higher likelihood of multiple graphene islands coalescing and perhaps forming grain boundaries and edge dislocations in the process. On the other hand this scenario is less likely if nucleation occurs heterogeneously at a small number of preferential nucleation sites such as defect sites or steps separating terraces simply because there is less chance of coalescence.

Scanning Tunnelling Microscopy (STM) observation of graphene growth on Ir(111) at an ethene partial pressure of $5 \times 10^{-10}$ mbar show graphene nucleating almost entirely at step edges in temperatures ranging between 790-1320K [55]. For high temperatures, ($> 1120$K) a small fraction of islands were found to nucleate at terrace sites. The situation is qualitatively similar on Ru(0001) where nucleation was observed to occur at step sites at low carbon adatom coverage but also on terrace for higher coverages [24]. These observations have the obvious interpretation that step edges are in someway responsible for lowering the graphene nucleation barrier [67, 24, 68]. Heterogenous nucleation of graphene has also been observed on Cu(111) and polycrystalline copper substrates [59, 69, 70]. In the latter case it is probable that the treatment of the surface prior to growth impacts the nucleation mechanisms. This is discussed in detail in [71] where they compare the differences in the nucleation density of graphene islands due to electropolishing of the copper surface. Surprisingly, they found a higher density of nuclei present on the smoother surfaces which they attributed to the higher mobility of carbon adatom mobility compared to that on the rougher surfaces. The heterogenous nucleation of graphene is not universal to all metal substrates. Graphene has been seen to nucleate homogeneously on the terraces of Rh(111) and Pt(111) [53, 72].

Graphene morphology

Just as we see difference in the observed nucleation mechanisms on different substrates we also see differences in the morphologies observed during growth of graphene. This is expected
as the strength (and perhaps nature) of the carbon-metal bond differs on these substrates. On Ru(0001) a number of groups have observed that graphene only grows in the step down direction \[62, 73, 74, 24, 25\]. The mechanisms by which the growth front moves from upper to lower terraces was explored in detail by Gunther et al. \[74\], who observed that the growth front did move coherently down steps. Rather, a mechanism was observed whereby growth continued at a single point of the front whereby, presumably due to some fluctuation, part of it was able to attach to a lower terrace. This produced a number of “finger-like” protrusions shown in Fig. 1.3.1. In contrast graphene on Ir(111) is able to transverse both up and down steps \[55\]. In the same work \[55\] STM images of growth (taken at 300K) which occurred at 1120K at \(5 \times 10^{-10}\) mbar initially show a number of islands of uniform size and shape followed by a drop in the island density later in the growth. This observation was attributed to a ripening mechanism, most likely Smoluchowski ripening \[55\]. There are also apparent similarities in the processes by which growth proceeds on Ir(111) and Ru(0001). Longinova et al. \[24, 25\] observed the same non-linear growth velocity of the graphene growth front on both substrates, indicating that the cluster attachment mechanism for growth \[26\] is common to both metals.

\section*{1.3.2 Observations during TPG}

Temperature programmed growth (TPG) differs from the aforementioned CVD growth in that the atoms are deposited onto a surface held at room temperature \[55\]. Growth is then accomplished by annealing for shorter times at a much higher temperature. TPG occurs under ultra high vacuum.

The method is interesting for theorists as it is capable of distinguishing between different stages of growth. For example, using TPG, Coraux et al. \[55\] were able to determine that growth of graphene begins between 870-970K. They were also able to monitor the island density as well as the morphology of growing islands. Here they again see a drop in island
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Figure 1.3.1: A series of in situ STM images at 665°C showing the growth of graphene (blue) across the steps of the Ru(0001) surface (orange). (a-f) Details from panels b and c, the dashed lines mark the changed step position between the consecutive panels c and f. [Reproduced with permission from [74].]
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density as they do in CVD growth. They also observe how, while at 970K islands are small and compact, at temperatures > 1120K islands are not only larger but also more irregular [55]. Small initial carbon clusters were also observed on Ir(111) using high resolution photo-electron spectroscopy [54].

On Rh(111) a TPG study found that the presence of clusters of seven hexagonal carbon units were found to coincide with the nucleation of graphene [65]. Their conclusions were based on carefully tracking the cluster size distribution and isolating a species of diameter 1nm present just prior to the appearance of graphene islands. This is yet more compelling evidence that larger carbon precursors are required for nucleation graphene on some substrates. Further observations of carbon precursors have been observed on Ru(0001) [75].

1.3.3 Choice of precursor molecules

The most common choice of precursor molecule for CVD and TPG are ethylene and methylene molecules [4]. However, it is also possible to use larger molecules to initiate graphene growth [76]. The choice of precursor can be especially important in TPG. This is because molecules are absorbed onto a surface maintained at relatively low temperatures and thus, any fragmentation occurs solely due to the increase of temperature during the growth process. This in contrast to CVD growth whereby fragmentation can depend on the kinetic energies of molecules absorbed onto the surface [77].

In general, X-ray photon spectroscopy (XPS) is used to measure the 1s core level of carbon atoms. Since the spectra obtained are sensitive to the molecules present on the surface they may be used to identify temperature windows for which particular species are likely to be the most populous. Studies investigating the evolution of species present on transition metal surfaces as a function of temperature have a long history. The identification of the decomposition of ethylene to ethylidene (CCH$_3$) at $\sim 300$ K on Pt(111) was made almost thirty year ago in a series of experimental papers [78, 79, 80]. More recently Baraldi et al. studied the evolution
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of ethylene on Ir(111) for much higher temperature ranges and identified the complete dehydrogenation of carbon species at \( \sim 500 \ \text{K} \) [81]. However, the interpretation of XPS spectra is difficult, with analysis complicated by the presence of vibrational replicas. In fact, a recent collaboration between experimentalists and theorists has lead to a different interpretation of such experiments and a better understanding of the dehydrogenation sequence of ethylene on iridium compared to that reported in [81]. Aspects of this work will be discussed in Chapter 3.

\section*{1.4 Review of theoretical works}

Explorations into graphene growth using DFT can be divided into two groups. Firstly, DFT is used to calculate the equilibrium structure of graphene sheets or small carbon clusters on a specific transition metal surface. In this case DFT yields the forces of carbon atoms and usually a specified number of layers of metal atoms. A minimisation routine (e.g. conjugate gradient) is then used to obtain a structure for which the forces on all atoms of which the structure is comprised are zero within some tolerance. Secondly, it is also possible to obtain kinetic information through DFT calculations by obtaining the energy barriers associated for different atomistic processes. In this section we will begin with describing calculations of the structure graphene sheets on metals.

\subsection*{1.4.1 Graphene Structure}

A number of works have observed that graphene on metal substrates forms a periodic moiré structure [16, 82, 17, 18]. This arises due to the lattice mismatch between the graphene layer and the substrate. The different possible graphene on metal super-structures that can be formed are usually denoted by labelling a supercell by the number of hexagonal units of the metal (denoted \( N \times N \)), on which \( M \times M \) hexagonal graphene units lie. The supercell is then often referred to as an \( N \times M \) moiré structure. Obviously, the size of the lattice
mismatch depends on the choice of substrate, ranging from a $23 \times 25$ moiré formed on Ru(0001) [83, 17, 18], to no lattice mismatch between graphene and the nickel substrate [84].

The graphene within the moiré structure on a number of metals is corrugated [16, 82, 17, 18], the corrugation being induced by strain fields created by the lattice mismatch. This is clearly due to the relative strengths of bonding between graphene and metal in different regions of the moiré structure [83]. Specifically, the regions of corrugation can be identified by the positions of carbon atoms within graphene relative to substrate atoms. For example, in Ru(0001) atoms located on top of substrate atoms are bonded more strongly that those located in surface sites between substrate atoms [83]. Thus, troughs in the corrugated graphene are located at regions where graphene atoms lie above substrate atoms.

Finally, graphene can form with more than one orientation on a particular substrate [56, 85]. This tends to mean that they form different moiré structures and so the details of the bonding can vary between orientations. This can have implications for growth. It was shown by Loginova et al. [24, 25] and in simulations [13] that particular rotational domains have growth fronts which move quicker than others. A collection of data found in the literature for graphene grown on a selection of substrates can be found in Tab. 1.1. Note that in the literature a naming convention arises whereby a graphene lattice whose zig-zag rows align with the most densely packed rows of the metal is referred to as the R0 phase. Graphene which forms with a different orientation is then defined by how much it is rotated compared to the R0 phase.

**1.4.2 Absorption Sites**

It is widely assumed that once a carbon based molecule is deposited onto a surface it decomposes completely to form carbon monomers that diffuse on the surface. The first question that can be asked is: where do monomers (and possibly dimers) like to sit on the metal substrate? Thus, a number of studies have explored the possible sites on the transition metal surface
### Table 1.1: The details of the structure of graphene on various surfaces. The surfaces are listed in the order from the strongest graphene-surface interaction (Ru(0001)) to the weakest (Pt(111)). The corrugation is described in terms of the peak-to-peak height with the data in brackets being from available DFT calculations. Reproduced with kind permission from Tetlow et al. [4]

<table>
<thead>
<tr>
<th>Surface</th>
<th>Lattice constant, Å</th>
<th>Angle of graphene to surface</th>
<th>Graphene moiré superstructure</th>
<th>Corrugation, Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru(0001)</td>
<td>2.71</td>
<td>0°</td>
<td>(25 × 25) [18, 83]</td>
<td>0.82 [18], 1.53 [83], 0.15 [87] (1.5 [17])</td>
</tr>
<tr>
<td>Rh(111)</td>
<td>2.69</td>
<td>0°</td>
<td>(13 × 13) [83] (12 × 12) [86]</td>
<td>(1.59 [83]) (1.5 [86])</td>
</tr>
<tr>
<td>Ir(111)</td>
<td>2.72</td>
<td>0° [56, 89]</td>
<td>incommensurate [90], (10 × 10) [89] (4 × 4) [89] (3 × 3) [89] (19 × 19) [89] (37 × 37) [89]</td>
<td>~0.3 [91, 56] (0.423 [89]) (0.101 [89]) (0.051 [89]) (0.022 [89]) (0.015 [89])</td>
</tr>
<tr>
<td>Pt(111)</td>
<td>2.77</td>
<td>30° [56, 89] 19° [72] 14° 6° 3° 2°</td>
<td>(2 × 2) (3 × 3) (4 × 4) (37 × 37) [16, 72] (61 × 61) (67 × 67)</td>
<td>&lt;0.3 0.04 [56] (0.014 [89])</td>
</tr>
<tr>
<td>Ni(111)</td>
<td>2.49</td>
<td>0° 17±7</td>
<td>(1 × 1)</td>
<td>0.5 - 0.8</td>
</tr>
<tr>
<td>Cu(111)</td>
<td>2.56</td>
<td>0° 7°</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
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Figure 1.4.1: Various adsorption sites on the Cu(111) surface: (a) top and (b) side views. [Reproduced with permission from [93].]

that carbon atoms can be absorbed and determined which of these is the most energetically favourable [67, 93]. These studies are of further importance in determining the diffusion paths, attachment/detachment barriers of monomers and dimers as it is essential when calculating (e.g. using NEB) the energy barriers to know the initial and final states (which are assumed to be the equilibrium sites). The results that different groups obtained were found to be strongly dependent on the size of the simulation cell. In particular it was noted by Riikonen et al. [93] that carbon adatom migration barriers could differ by as much as 0.5eV for smaller cell sizes. When referring to the possible absorption sites on hexagonal surfaces we adopt the naming convention of [93]. Thus, we label bulk interstitial sites by A and A’ and surfaces sites by FCC, HCP and BRI, Fig. 1.4.1.

The most stable position found in [93] for a carbon monomer on Cu is the bulk interstitial sites, referred to as A and A’ in Fig. 1.4.1. The surface sites labelled BRI, FCC and HCP are found to be metastable with respect to adsorption of a single C atom as it would quickly diffuse (with the barrier of the order of 0.1 eV) from these into either A or A’ site. The diffusion deeper into the Cu bulk (A’ →B’) was found to require overcoming an energy barrier of at least 1.5 eV. The formation of dimers from two carbon atoms lying on several nearby surface sites was found to require no activation energy, i.e. dimerisation is spontaneous. Further, the diffusion barrier they calculated for a dimer was found to be very small (0.27eV). Thus, the
energy required to disassociate a dimer is found to be larger than the diffusion barrier between different adsorption sites. This suggests that dimers are a persistent species and could possibly dominate the nucleation of larger carbon structures that eventually form graphene.

In a similar manner to the above study Chen et al. [67] investigated the stability of monomers at different sites on the surfaces of Ru(0001), Ir(111) and Cu(111). The most stable sites on Ru and Ir were both found to be the HCP sites, with absorption energies of -7.66 and -7.44 eV, respectively. In agreement with the results of Riikonen et al. [93], the most stable absorption site on Cu(111) was found to be the subsurface octahedral (A and A' in the notation of Riikonen et al.). On both Ir and Ru similar values were obtained for the absorption energy at step edges and it was also found that while the barrier for dimer formation is relatively high, 1.37 and 1.49 eV respectively, on Cu(111) the barrier for dimerisation is much lower, 0.32 eV. The authors also find that the energy required to form a dimer is greatly reduced on Ru and Ir when dimerisation occurs at a step edge. They further suggest that these results could possibly explain the observations of heterogeneous nucleation at step edges on Ir and Ru. Since the formation energy of dimers on the Cu(111) surface is so low, it was also suggested that nucleation on weakly interacting metals (like Cu) should occur homogeneously. On metals with a stronger C-metal bond the above results for dimer formation at step edges would mean that nucleation is more likely to occur at steps, i.e. heterogeneously. However, while these results predict that nucleation on Rh(111) would occur predominantly at steps, nucleation on Rh(111) was observed to occur homogeneously [65]. Furthermore, islands with different morphologies growing on Cu(111) have been found to exist predominantly at step edges and other defect sites [69].

A study by Wu et al. [23] used both DFT and MD to investigate steps in the reaction sequence describing dimer formation not previously considered. Their work is based on the following observation: while it is indeed true that spontaneous dimerisation occurs when two atoms are placed on nearest neighbour sites, there are intermediate states that must occur
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Figure 1.4.2: Calculated dimerisation process path (a)-(e) showing formation of a dimer (e) on the Cu(111) surface from two monomers sharing the same Cu atom (a). Several intermediate states were found along the minimum energy path. [Reproduced with permission from [23].]

before monomers occupy these sites that must be considered. These states are derived by considering the beginning of the dimerisation process to begin with two monomers occupying next nearest neighbour sites, which share a common Cu atom. Relaxation of this state leads to the formation of novel structures shown in Fig. 1.4.2(b)-(d) which manifest themselves on the potential energy curve as metastable minima. The change in the activation barrier that occurs by considering these intermediate states in dimerisation and other reaction sequences could be important in calculating the rates of processes occurring on the surface. We again repeat the point made in Sec. 1 that the diffusion of adatoms can be in some instances much more complicated that one first imagines. It also highlights the power of ab-initio methods in uncovering processes that have previously not been considered.

1.4.3 Carbon Clusters

The rate equation model derived by Zangwill and Vvedenksy [26] and refined by Posthuma de Boer et al. [2], using data from the growth of graphene on Ir(111) and Ru(0001) [24, 25]
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suggested that nucleation of graphene on these surfaces (for the temperature ranges 790-
1020K) could proceed by the collision of a number smaller intermediary species. Thus, we
now consider a number of theoretical and experimental works that looked at small carbon
clusters on transition metal surfaces and to highlight the agreement with the observation of
[24].

The transformation of carbidic species to free-standing graphene has been explored by
Lacovig et al. [54]. They compared the temperature dependence of surface core level shifts
(SCLS) between $10^{-6}$ and $10^{-9}$ mbar at 300 K and subsequent annealing to 820, 970 and 1270
K, see Fig. 1.4.3. These spectra allowed the authors to deduce that three different carbon
species, referred to as $C_A$, $C_B$ and $C_C$, each interacting differently with the Ir surface, are
present during growth. Further, the change in spectra with increasing temperature indicates
that the number of these C species is dependent on temperature. To explain these observations
the authors performed a number of DFT calculations, relaxing carbon clusters of different sizes
on an iridium surface after a simulated annealing procedure (this is a way to approach a global
energy minimum in a system, i.e. the most energetically favourable structure: MD simulations
are run starting at rather high $T$ with subsequent slow cooling down to zero). The structures
they obtained were distinctly “dome-like.” The interactions between substrate and cluster
were limited to carbon atoms found at the cluster edge, and a relatively large distance between
central atoms of clusters and the surface was found. This distance was seen to increase with the
size of carbon clusters. Comparison of the SCLS obtained from simulations to those obtained
experimentally allowed the authors to identify the three carbon species as belonging to cluster
dges ($C_A$ and $C_C$) and to the central carbon atom ($C_B$). The temperature dependence of the
SCLS was then explained as follows: high temperature ripening processes occurring on Ir [55]
cause the average size of carbon cluster to increase. Increasing cluster size causes the relative
number of edge $C_A$ and $C_C$ to decrease while the amplitude of the peak in the C 1s spectrum
associated with the central $C_B$ species increases to that found in graphene.
Figure 1.4.3: C 1s (left) and Ir 4f$_{7/2}$ (right) spectra after annealing at different temperatures of the Ir(111) surface saturated with $C_2H_4$ at 300 K. The spectra were measured at 300 K. The different components represent inequivalent C and Ir atoms. [Reproduced with permission from [54].]
Similar carbon clusters have been identified by experimentalists on Rh(111) [65], Ru(0001) [75], and Ir(111) [55]. A number of other groups have used DFT to examine the stability of different sized clusters. For instance, Yuan et al. [15] examined the formation energy of clusters containing 16-26 atoms on the hexagonal faces of Rh(111), Ru(0001), Ni(111) and Cu(111). The results, summarised in Fig. 1.4.4 show that the persistent species on these surfaces must be the cluster containing 21 atoms (C\textsubscript{21}). Using an NEB like technique combined with transition state theory allowed them to estimate the lifetime of the C\textsubscript{21} cluster (before coalescence with another C\textsubscript{21}) as a function of temperature. They find that in the range of temperature between 930-985K, the lifetime is approximately 100-1000s on Ir(111) which agrees with experimental observations of coalescence of clusters into graphene islands at 970K on Ir(111) [55].

Further similar work on smaller clusters were performed by Wu et al. [13] on Ir(111), Gao
et al. [20] on Ni(111) and Wesep et al. [14] on Cu(111). Both Gau and Wesep find that for clusters containing \( N < 13 \) atoms on Cu and \( N \leq 12 \) atoms on Ni the most stable structures are linear chains. For clusters greater than this \( sp^2 \) networks become more favourable. This effect is solely due to the stabilising effect of the transition metal substrate which passivates dangling bonds in linear chains. Using NEB calculations Wesep also found that the energy required to break a six member ring was as low as 0.6 eV, a barrier easily surmountable at typical growth temperatures. However, break up of rings greater than \( N > 10 \) require more than one bond the energy required to break the cluster should be considerably higher. Therefore, they conclude that under typical growth conditions the surface will be dominated by islands containing 10-13 atoms.

An important question that was considered by Gau but not Wesep is the role of steps in stabilising cluster formation. It was found that the formation energy, \( E_N \) of \( N \) atom clusters decreased by as much 2eV when they repeated their DFT calculations but allowed carbon atoms to bond to a (110) Ni step edge. These results have interesting consequences concerning whether nucleation occurs homogeneously or heterogeneously on metallic substrates. For example, nucleation of graphene on Cu(111) has recently been shown to mostly occur at step edges or defect site [69].

1.4.4 Attachment

The works described in Sec. 1.4.3 go some way into determining the most common carbon species present on a substrate during the early stages of growth. These species are perhaps responsible for the nucleation of graphene as suggested by Zangwill and Vvedensky [26] and Posthuma de Boer et al. [2], or they could be involved in the growth of graphene that has already nucleated on the surface. We consider now works which explore the latter case. How growth proceeds depends strongly on the structure of the graphene edge. The most stable edge structure clearly depends on the choice of substrate. For example, DFT investigations by
[94] have found that the zig-zag terminated edge is most stable while on Cu(111) using similar methods the armchair terminated edge passivated by Cu bulk atoms were found to be the most likely. These theoretical works offer an explanation to the widely reported experimental observation of the zig-zag termination of Cu [95, 96, 97]. Also, DFT calculations which demonstrate that a particular edge structure is favoured in vacuum are found to be the least likely structure when the stabilising effect of the substrate is included [98]. DFT studies were also conducted into attachment of different species onto the edge of graphene flake on Cu(111) [19], Ir(111) [13] and Ni(111) [98].

Interestingly, in the work of Wu et al. [13], they find that while the energy required for a monomer to attach and occupy an hollow hcp site is energetically favourable (-0.86eV), the energy required to detach from certain sites is also extremely low. Thus, detachment of monomers from the graphene edge is likely to occur at a faster rate than attachment [13]. They also find that the energies required for the attachment of larger clusters are relatively low and, furthermore, the chances of them detaching are much smaller. This suggest a mechanism by which the growth front can propagate based on cluster attachment. They further find, by investigating the attachment barriers of carbon species to the R30 phase of graphene, that the energy required for monomer attachment is highly dependent on the orientation of graphene on the substrate. In the case of the R30 graphene phase, a number of inequivalent edge sites exist. The barriers of monomer attachment vary at different edge sites, such that attachment can be favourable or not. In the latter case, they find that the barrier for cluster attachment is much smaller and so growth proceeds by the attachment of larger carbon clusters.

1.4.5 Kinetics

There have been only a handful of studies that have used kinetic models to look examine the growth process as a whole. Wu et al. [13] used a kinetic Monte Carlo like technique to examine the dependence of the growth rate of the graphene front on the carbon monomer.
population. The technique, referred to by the authors as the standing-on-the front KMC (SOF-KMC), considers only the graphene growth front which propagates by the attachment and detachment of different sized carbon clusters. The diffusion and attachment barriers are all calculated using DFT as discussed in the final paragraph of the preceding section. To account for the disparity in the concentrations of different species and the detrimental effect this has on the efficiency of a traditional KMC scheme, the authors implement an ad-hoc procedure whereby they consider only events which occur on a “slow” timescale whenever the growth front gets stuck. In other words, when the growth front gets stuck the update scheme is altered so as to ignore fast detachment/attachment events of smaller species which presumably have reached a steady state and consider only the attachment of larger species e.g. five atom clusters. They found that the growth rate obtained from such KMC simulations depended on the monomer concentration raised to the power 5.25. This result agrees well with the LEEM studies of Loginova et al. [24, 25] who observed a quintic dependence on the monomer concentration. Although no detailed analysis was made as to the origins of such a dependence on the availability of larger clusters it seems likely that the availability of larger clusters and the relatively large barriers for monomer attachment play a key role in obtaining such a non-linear growth rate. A more recent study [99] considered a minimal model KMC model in which only monomer attachment and 5 atoms clusters were able to attach to the different sites on the growth front. In this case it was found that the rate limiting step in the growth process was the attachment of 5 atom clusters and a similar value of the exponent discussed above was obtained.

The only other substrate which has received some attention from researchers using kinetic models is copper. Zhang et al. [100] used DFT calculations, rate equations and KMC simulations to examine the dependence of graphene growth on carbon dimers. They conclude that dimers are the dominant species for growth on copper. Largely this conclusion is made on the basis of energy barriers calculated for the diffusion and attachment of monomers and dimers.
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Specifically, dimers diffuse as easily as adatoms and the formation of dimers is found to be energetically favourable. The barrier for the attachment of monomers to zig-zag and armchair sites is found to be relatively high whereas dimers attach fairly easily (e.g. a barrier of 0.63 eV for dimer attachment to armchair sites). Recently, Gaillard et al. [101] used DFT calculations and KMC to examine the effects of deposition rate on the shape of graphene island on Cu(111). They found a tendency for graphene islands to be more hexagonal as the deposition rate for a given simulation was decreased. In these simulations a key role was played by detachment from graphene islands.

■ 1.5 Outline of thesis

In the previous sections we have explored both experimental and theoretical studies of graphene growth on different transition metals. We will now briefly reviews some of the key findings before discussing the contents of this thesis.

We have seen that on iridium we have seen that there is compelling evidence for nucleation occurring at step edges. The strongest evidence being the study of Coraux et al. [55] in which graphene was observed to nucleate predominantly at steps between 790-1320 K. There are also a number of studies in which the role of intermediary species have been highlighted [25, 24, 26, 65]. In particular it seems that smaller clusters of carbon molecules have some role to play in at least the growth of graphene on iridium and ruthenium. Evidence for this have comes from experiment [24, 25] but also from theoretical studies that utilise ab-initio calculations [13]. Furthermore, good agreement was found with experiment in a phenomenological study by Zangwill et al. [26] in which nucleation begins with the coalescence of 5 atom clusters. In Chapter 2 we will return to this model and refine a set of rate equations investigating the nucleation of graphene on Ru(0001) and Ir(111) to account for the experimental observations of the temperature dependence of the steady state island density.

We have seen that hydrocarbons, in particular ethylene is a common choice of precursor
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in many experiments. Since it is of importance to understand what are the most abundant species as a function of temperature we have reviewed studies in which the dehydrogenation sequence has been investigated experimentally and theoretically. However, it seems that while platinum has received a lot of attention [77, 102] iridium less so. As such, in chapter 3 we formulate a set of rate equation describing the dehydrogenation sequence of hydrocarbons on the Ir(111) and Pt(111) surface. These equation supplement a more complete study involving experimental input and \textit{ab-initio} calculations of reaction rates on iridium.

The second strand of the thesis is concerned with introducing spatial effects into models for submonolayer growth. In Chapter 4 we describe our efforts to describe submonolayer growth in both the reversible and irreversible regime utilising the phase field method of front tracking. Finally, in Chapter 5 we discuss an application of the methods developed in the preceding chapter to the growth of graphene on copper during growth conditions known as “flash deposition”. 

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Chapter 2

Rate equations for graphene growth on \textit{Ir}(111) and \textit{Ru}(0001)

\textit{Old Fashioned Whiskey Cocktail}

“Dissolve a small lump of sugar with a little water in a whiskey-glass; add two dashes Angostura bitters, a small piece of ice, a piece of lemon-peel, one jigger whiskey. Mix with small bar-spoon and serve, leaving spoon in glass.” - George Kappeler

In this chapter we describe an algorithm that searches the parameter space of rate theories to optimise the associated rate coefficients based on a fit to experimental (or any other) data. We demonstrate the applicability of the method by modifying a previously proposed rate theory for the nucleation and growth of graphene on \textit{Ru}(0001) and \textit{Ir}(111) to account for the temperature dependence of the graphene island density. We find that the agreement with experimental findings is greatly improved in the new model. In particular, we find that this quantity shows an exponential decrease as the temperature is raised, in contrast to the power law decrease predicted by conventional nucleation theory. Elements of this chapter have been published in [2].
CHAPTER 2. RATE EQUATIONS FOR GRAPHENE GROWTH ON IR(111) AND RU(0001)

The formation of thin films on well-oriented substrates is vital to many technologies, including those based on the optical, magnetic, and transport properties of such systems. Accompanying the many experimental advances in the production and analysis of epitaxial films are developments in the theoretical description of the growth process. We recall that the most informative methods for providing insight into the morphological evolution of thin films during the growth process are kinetic Monte Carlo simulations [103] and rate equations [44]. Molecular dynamics can provide a more highly resolved description of the evolution of the system, but suffers from the small time step required to sample atomic vibrations. The effectiveness of KMC simulations is derived from the fact that the molecular dynamics calculation is replaced by transitions between neighbouring minima, whose rates are determined in the spirit of transition-state theory [38, 37]. KMC simulations have been used to provide real-time information for many types of epitaxial system and have revealed many general aspects of the nucleation and aggregation process [45, 104, 105].

However, there are systems and experimental conditions for which even the most efficient KMC algorithms fall short, that is, where high adatom mobility is combined with a low deposition rate of adatoms onto the substrate. In such cases, rate equations provide the only alternative. Rate equations are formulated by first identifying the important surface species that determine the growth of the thin film, such as adatoms, islands, and any intermediate species. If the delivery of the material to the substrate is in the form of a polyatomic molecule, then the fragments in the decomposition sequence may also need to be included if they influence the growth process, for example, by inhibiting attachment processes at the edges of islands. The processes that cause the surface species to change are then identified and, together with their rate constants, are written as a set of coupled first-order (in time) differential equations. These quantities are spatially averaged, so these equations are often referred to as homogeneous rate equations. They provide no spatial resolution as compared to the KMC method, but they are also less computationally demanding to solve, the property of stiffness being the only
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problematic issue. Thus, rate equations can be used to model experimental scenarios that are inaccessible to KMC simulations.

The formulation of rate equations for particular systems are based typically on phenomenological considerations, though with input from experiment and first-principles calculations for complex systems. Although direct connections between rate equations and KMC simulations can be made [49, 50, 106], and derivations of rate equations are available [107], the rates of processes which are not directly accessible from experiment are typically assigned Arrhenius rates whose parameters, the frequency prefactor and the energy barrier, are regarded as fitting parameters. This effectively assumes the validity of transition-state theory (Sec. 1.2.5). Depending on the system and the available data, this fitting can either be done by hand, or a more systematic procedure must be developed.

In this chapter, we describe a method for optimising solutions to rate equations by fitting the parameters of the theory to various types of experimental data. The chapter will be ordered as follows. In Sec. 2.1 we describe this method and present a simple illustrative example. We then present the central result of this chapter in Sec. 2.2 which is an application of our approach to correcting a previously proposed rate theory for the nucleation and growth of graphene on Ru(0001) and Ir(111) to account for the temperature-dependence of the graphene island density, which shows an exponential decrease as the temperature is raised, in contrast to the power law decrease predicted by conventional nucleation theory. We summarise our results and discuss additional applications in Sec. 4.5.

2.1 Rate equations and optimisation strategy

We consider a set of rate equations as described in Sec. 1.2.7. These equations are completely specified by their initial conditions and indeed the choice of rates themselves. A typical choice is the Vineyard form [37] where the rate of a process \( R_i \) is given by

\[ \text{rate} \]
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\[ R_i = \nu e^{-E_i/k_B T} \]  \hspace{1cm} (2.1.1)

where \( k_B \) is Boltzmann’s constant, and \( T \) is the absolute temperature of the substrate, which is known from the experimental growth conditions, \( \beta = 1/(k_B T) \) and \( E_i \) is an energy barrier. The prefactor \( \nu \), emerges directly from the equipartition theorem applied to estimate the vibrational frequencies in Vineyard’s [37] formula, but its weak temperature dependence has also been explained [108] as the compensating effects of the stiffening and softening vibrational modes of the diffusing adatom. If extensive first-principles calculations are available, key processes and their rates can be determined directly [109], but otherwise the rates must be treated as fitting parameters.

2.1.1 Optimization of parameters occurring in rate theories

The derivation of our search algorithm proceeds by defining the state vector \( \mathbf{X} \), whose components are the densities of the surface species:

\[ \mathbf{X} = (x_1, x_2, \ldots, x_n), \]  \hspace{1cm} (2.1.2)

in terms of which the most general set of rate equations (1.2.10)–(1.2.12), defined in the previous chapter (Sec. 1.2.7) can be written symbolically as

\[ \frac{d\mathbf{X}}{dt} = \mathbf{F}(\mathbf{X}, \mathbf{E}), \]  \hspace{1cm} (2.1.3)

where the components of \( \mathbf{F} = (F_1, F_2, \ldots, F_n) \) are the right-hand sides of the rate equations for the corresponding surface species \( x_i \), and

\[ \mathbf{E} = (E_1^{(1)}, E_2^{(1)}, \ldots, E_{123}^{(n)}, \ldots) \]  \hspace{1cm} (2.1.4)
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is the vector of rate parameters which, in our case, are energy barriers. By differentiating (2.1.3) with respect to each component \( E_q \) of \( \mathbf{E} \) and interchanging the order of this derivative and the time derivative, we obtain

\[
\frac{\partial}{\partial E_q} \frac{d\mathbf{X}}{dt} = \frac{d}{dt} \frac{\partial \mathbf{X}}{\partial E_q} = \frac{\partial \mathbf{F}}{\partial E_q} + \sum_r \frac{\partial \mathbf{F}}{\partial X_r} \frac{\partial X_r}{\partial E_q}.
\] (2.1.5)

The \( p \)th component of this equation can be written in a compact form by introducing the abbreviation \( X_{pq} \equiv \frac{\partial X_p}{\partial E_q} \):

\[
\frac{dX_{pq}}{dt} = \frac{\partial F_p}{\partial E_q} + \sum_r \frac{\partial F_p}{\partial X_r} X_{rq}.
\] (2.1.6)

If there are \( n \) rate equations in (1.2.10)–(1.2.12) with \( r \) energy parameters in (2.1.1), then (2.1.6) yields \( nr \) differential equations which must be solved numerically.

To determine the matrix of derivatives on the right-hand side of (2.1.6) at some values \( \mathbf{E} \) of the parameters, we solve the rate equations to obtain \( \mathbf{X}(t) \). These functions provide the time-dependent coefficients appearing in the differential equations for the \( X_{pq} \) (the sensitivity in a population computed at a given time to the value of a model parameter), which are then solved. In practice, (2.1.3) and (2.1.6) are advanced through time simultaneously. The resulting derivatives \( X_{pq} \) enable us to perform a guided search through parameter space to minimise the error with respect to the test data. In the following this is performed manually. For a given set of initial energy barriers we solve the set of rate equations. The solutions to the rate equations allows us to evaluate the Jacobian which provides a set of search directions. These determine the directions in which each of the energy barriers is to be varied. The magnitude of the change in energy barrier is chosen by trial and error so as to ensure that the change produces a smaller value of the cost function. In the following chapter we will describe one way in which this process may be automated by applying a multidimensional optimisation algorithm which uses the gradient information provided by the Jacobian obtained from the
above equations.

The latter is calculated as follows. Suppose that there are experimental data points \( y_i^{\text{exp}} \), for \( i = 1, 2, \ldots d \). If \( \{ y_i^{\text{calc}} \} \) represent the corresponding quantities calculated from the rate equations, then the error is defined as

\[
\sum_i \left( \frac{y_i^{\text{exp}} - y_i^{\text{calc}}}{y_i^{\text{exp}}} \right)^2. \tag{2.1.7}
\]

This choice of cost function is somewhat arbitrary and others are possible. We note that the above choice may add greater weight to experimental points that are very small. As such it is often necessary to decide whether this produces sets of parameters which explain only a subset of the observed trends.

An example of an automated search for parameters in rate equations

As a simple illustration of the optimization method described in Sec. (2.1.1) we shall consider irreversible aggregation. The rate equations describing the process are,

\[
\frac{d n}{d t} = J - 2Dn^2 - DnN, \tag{2.1.8}
\]

\[
\frac{d N}{d t} = Dn^2, \tag{2.1.9}
\]

where \( J \) is the flux onto the surface, \( D \) is the diffusion constant and \( n \) and \( N \) are the density of adatoms and islands respectively. If we assume that the diffusion constant is of Arrhenius form, then

\[
D = a^2 \nu \exp(-\beta E_D),
\]

where we take \( \nu = 10^{13} \text{ s}^{-1} \) and \( a \) is the lattice constant which in the following we set equal to one. Thus, there is one parameter that enters into the rate equations describing irreversible
aggregation. We test the optimization algorithm by generating a set of data by solving the rate equations with a known value, i.e. $E_D = 2$ eV at a temperature of 800 K, and check that we obtain the same values when we minimise the cost function starting from a random value of $E_D$. In this case the cost function, $S$, has the following form,

$$S(E_D) = \sum_{t_i=1}^{N} \left\{ (n^*(t_i) - n(t_i; E_D))^2 + (N^*(t_i) - N(t_i; E_D))^2 \right\}, \quad (2.1.10)$$

where $n^*$ and $N^*$ are the values of the adatom and island density obtained from the solution of the rate equations for $E_D = 2$ eV evaluated at a set of times $\{t_1, t_2, \ldots, t_N\}$. $S(E_D)$ is plotted for a range of values (Figure. 2.1.1).

The equations for the derivatives of $n$ and $N$ with respect to $E_D$ are,
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Figure 2.1.2: The derivative of the cost function with respect to the energy barrier $E_D$ evaluated at $E_D = 1.5$ eV at 800 K as a function of time.

\[
\frac{d}{dt} \left( \frac{\partial n}{\partial E_D} \right) = 2\beta D n^2 - 4D' \frac{\partial n}{\partial E_D} n + \beta D n N - D \left( \frac{\partial n}{\partial E_D} N + \frac{\partial N}{\partial E_D} n \right),
\]
(2.1.11)

\[
\frac{d}{dt} \left( \frac{\partial N}{\partial E_D} \right) = -\beta n^2 + 2D \frac{\partial n}{\partial E_D} n,
\]
(2.1.12)

and the expression for the $\frac{dS}{dE_D}$ is given by:

\[
\frac{dS}{dE_D} = - \sum_{t_i=1}^{N} \left( 2(n^*(t_i) - n(t_i; E_D)) \frac{\partial n(t_i; E_D)}{\partial E_D} \right) \frac{\partial n(t_i; E_D)}{\partial E_D} - 2(N^*(t_i) - N(t_i; E_D)) \frac{\partial N(t_i; E_D)}{\partial E_D} \right)
\]
(2.1.13)

In Figure 2.1.2 we also plot the derivative of the cost function with respect to the energy
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Barrier \( E_D \) evaluated at 1.5 eV as a function of time. From this figure we understand that at this value of \( E_D \) and temperature for all points in time an increase in the energy barrier produces a lower value of the cost function. While it is also possible to take one more derivative and obtain the components of the Hessian matrix we note that the equations become unwieldy for rate equations with many parameters.

The cost function and its first and second derivatives are calculated using the above formula and the one similar to it, and the results are shown in Fig. (2.1.1). We begin from some value of the energy barrier, \( E^0_D \), and update using the following Newton-Raphson expression,

\[
E^{i+1}_D = E^i_D - S \left( E^i_D \right) \left( \frac{dS(E^i_D)}{dE_D} \right)^{-1}
\]

We find that \( E_D \) converges to the correct value in approximately 10 iterations.

For more complicated sets of rate equations with more parameters we can use exactly the same method for finding the gradients of the cost function, \( \frac{dS(E)}{dE} \), but it would be necessary to implement a multidimensional optimization algorithm that is designed to make use of the gradient information, for example the conjugate gradient method. This of course constitutes a difficult problem, especially as the cost function may contain many local minima. In that case one could use global minimisers such as stochastic gradient methods or simulated annealing algorithms, although, the computational cost of such methods is expected to be high.

### 2.2 A case study: LEEM measurements of graphene on Ru(0001)

As discussed in the introductory chapter graphene has many intriguing properties that have already triggered proposals for a number of revolutionary technological applications. But a major problem standing in the way of harnessing this material for the commercial sector is the ability of produce large defect-free sheets of graphene in significant quantities. One possibility
being pursued by many groups is the epitaxial growth of graphene on a hexagonal substrate. Considerable progress has been achieved in this direction in the laboratory, though, little is known about the atomistic formation kinetics of epitaxial graphene on any substrate.

Several years ago, the Sandia group reported the results of low-energy electron microscopy (LEEM) measurements [24, 25] that provided unprecedented information on the epitaxial growth kinetics of graphene in Ru(0001), including the direct measurement of the carbon adatom density from the electron reflectivity of the substrate (Fig. 2.2.1). The edges of graphene islands were found to advance with a velocity that varied as the fifth power of the adatom density, which led the authors to conclude that islands grow by the attachment of five-atom clusters, rather than by the usual mechanism of attachment by single atoms. Later work by the same authors extended this conclusion to the growth of graphene on Ir(111).

The data in Fig. 2.2.1 show an initial linear increase while the carbon concentration builds up on the surface to the point $n_{\text{nuc}}$ where nucleation occurs. The concentration reaches a steady state (the first horizontal plateau) and, when the incident carbon source is removed, evolves toward its equilibrium value $n_{\text{eq}}$. The values of $n_{\text{nuc}}$ and $n_{\text{eq}}$ over an extended temperature
CHAPTER 2. RATE EQUATIONS FOR GRAPHENE GROWTH ON IR(111) AND RU(0001)

range were also published [25]. The graphene island density was also measured (Fig. 2.3.1) but not published. A rate theory [26] was able to account for all of the published data, but not the temperature density of the data, which shows an exponential decrease as the temperature is raised, in contrast to the power law decrease predicted by conventional nucleation theory.

2.3 Rate equations for graphene nucleation and growth

The rate equations for the growth of graphene on metal surfaces are expressed in terms of the densities of adatoms \( n \), five-atom clusters \( c \), and islands \( n \) as

\[
\frac{dn}{dt} = J - iDn^i + iKc - DnN + K'N, \tag{2.3.1}
\]

\[
\frac{dc}{dt} = Dn^i - Kc - D'cN - jD''c^j, \tag{2.3.2}
\]

\[
\frac{dN}{dT} = D''c^j. \tag{2.3.3}
\]

In these equations, \( D \) and \( D' \) are constants originating from the diffusion of carbon adatoms and five-atom \((i = 5)\) clusters, \( K \) is the cluster dissociation rate and \( K' \) is the detachment rate of adatoms from islands. The quantity \( D'' \) is a new constant describing the rate of graphene island formation from \( j \) clusters each containing five atoms. In the original model [26], \( D'' \) and \( D' \) were equal, but in our reformulation these rate constants are allowed to assume different values. We will discuss this further below. Finally, \( J \) is the flux of adatoms onto the surface and \( i \) and \( j \) denote the order of the reactions producing clusters (from \( i \) atoms) and islands (from \( j \) clusters), corresponding to the critical size for these activated processes. Let us briefly consider the physical origin of each of the terms in the above equations.

Initially, the surface is populated by adatoms provided by a flux onto the metal surface. We consider the first stage in the nucleation and growth process to be the formation of clusters containing \( i \) atoms (as discussed \( i = 5 \) is inferred from experiment) which occurs at a rate
CHAPTER 2. RATE EQUATIONS FOR GRAPHENE GROWTH ON IR(111) AND RU(0001)

Figure 2.3.1: LEEM images[110] showing the temperature dependence of graphene nucleation density on Ru(0001). The field of view is 46µm.

given by the second term in Eq. (2.3.1). This expression is related to the probability that \( i \) monomers performing a random walk on the surface characterised by diffusion constant \( D \) meet at the same point on the surface and react to form an \( i \)-atom cluster. The \( i \)-atom cluster is itself assumed to be able to move on the surface with diffusion constant \( D' \). The third term in Eq. (2.3.1) describes the rate that an \( i \)-atom cluster decomposes into \( i \) monomers which are then free to move on the surface while the final two terms in Eq. (2.3.1) describe the rate of attachment/detachment of monomers to the edges of a graphene island respectively. Graphene islands are assumed are nucleated when \( j \) (\( j \) is a free parameter which is to be optimised with respect to experimental data) clusters meet to form an island containing \( i \times j \) carbon atoms.

Finally, the third term in Eq. (2.3.2) describes the rate of attachment of carbon clusters to the edge of graphene islands.

Each of the rate constants in the rate equations (2.3.1)–(2.3.3), apart from the flux, have the Arrhenius form (2.1.1). Hence, the vectors \( \mathbf{X} \) and \( \mathbf{E} \) in (2.1.2) and (2.1.4) are

\[
\mathbf{X} = (n, c, N), \quad \mathbf{E} = (E_D, E_K, E_K', E_{D'}, E_{D''}), \quad (2.3.4)
\]

so there are 15 equations (2.1.6). The experimental data used to calculate the quality of the fit according to (2.1.7) has been chosen as eight points of the adatom coverage, four each
CHAPTER 2. RATE EQUATIONS FOR GRAPHENE GROWTH ON IR(111) AND RU(0001)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>$j = 5$</th>
<th>$j = 6$</th>
<th>$j = 7$</th>
<th>Original</th>
</tr>
</thead>
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<tr>
<td>$E_D$</td>
<td>1.30</td>
<td>1.29</td>
<td>1.29</td>
<td>0.92</td>
</tr>
<tr>
<td>$E_D'$</td>
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<td>2.21</td>
<td>1.60</td>
<td>0.87</td>
</tr>
<tr>
<td>$E_K$</td>
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<td>2.08</td>
<td>2.14</td>
<td>1.72</td>
</tr>
<tr>
<td>$E_K'$</td>
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<td>1.64</td>
<td>1.64</td>
<td>1.27</td>
</tr>
<tr>
<td>$E_D''$</td>
<td>0.10</td>
<td>0.46</td>
<td>0.28</td>
<td>0.87</td>
</tr>
<tr>
<td>Error</td>
<td>2.68</td>
<td>2.59</td>
<td>2.63</td>
<td>2.69</td>
</tr>
</tbody>
</table>

Table 2.1: Optimized parameters in the rate equations (2.3.1)–(2.3.3). Energy barriers are in eV. The minimum error for each fit and the parameters in the original rate theory [26] are also shown.

with the flux on and the flux off, and the adatom coverage at nucleation and at equilibrium (Fig. 2.2.1) and density of graphene islands (Fig. 2.3.1). Island densities were obtained by counting directly from the images, so are limited by the resolution of the microscope. Thus, the first eight experimental data points correspond to a single temperature of 1020 K, while the remaining data points are related to the measured temperature dependence of $n_{\text{nuc}}, n_{\text{eq}}$ and $N$.

### 2.4 Results and discussion

Starting points in the parameter phase space were chosen randomly and then guided by the calculated derivatives $X_{pq}$ to find the point corresponding to the minimum error. Several values of $j$ (the number of five-atom clusters required to form a graphene island) were used and the corresponding optimised values and their minimum errors are compiled in Table 2.1, along with the original set of parameters [26]. The minimum errors show a shallow minimum for $j = 6$. Extending the range of $j$ to four (minimum error 2.97) and to eight (minimum error 4.74) excludes these possibilities and indicates that nucleation begins with the agglomeration of either five, six or seven five-atom clusters. Note that in the original parameterisation [26] $E_{D'}$ and $E_{D''}$ were taken to be the same, while in our optimisation, $E_{D''}$ was found to be much
CHAPTER 2. RATE EQUATIONS FOR GRAPHENE GROWTH ON IR(111) AND RU(0001)

smaller than $E_D^r$. This makes island formation a much faster processes and produces a better account of the measured temperature dependence of the island density. Moreover, the value of $E_D^r$ increased as a result of the optimisation, resulting in a decreased attachment rate of five-atom clusters to islands.

Figure 2.4.1 compares the measured time dependence of the carbon adatom density at $T = 1020$ K (Fig. 2.2.1) with the corresponding curves obtained by integrating the rate equations (2.3.1)–2.3.3) with the optimised parameters for $j = 5, 6, 7$ in Table 2.1. All theoretical curves are in broad agreement with the measured data and with the original parameter set used in [26], though there are differences in detail. Of the four theoretical curves in Fig. 2.4.1, the parameter set corresponding to $j = 5$ provides the best fit in terms of the height and position of $n_{nuc}$, as well as the concentration in the steady state, and the profile of the concentration as the system tends toward equilibrium after the cessation of the incident flux.

The temperature dependences of $n_{nuc}$ and $n_{eq}$ are shown in Fig. 2.4.2. The same values of $n_{eq}$ are produced by all sets of parameters because, as noted previously [26]

$$n_{eq} \sim \frac{K'}{D} = e^{\beta (E_{K'} - E_D)}, \quad (2.4.1)$$

and each optimised fit yields $E_{K'} - E_D = 0.35$ eV (Table 2.1). There are, however, differences for $n_{nuc}$. While the original parameter set and that for $j = 7$ provide comparable fits to the experimental data, those for $j = 5$ and $j = 6$ show a systematic decrease in the slope. As $j$ is decreased even further, the slope eventually changes sign, that is, $n_{nuc}$ becomes a decreasing function of temperature. The positive slope of $n_{nuc}$ is due to the fact that, as the temperature increases, the rate of break-up of five-atom clusters increases more strongly than their rate of formation [26]. These rates are proportional to $D$ and $K$, respectively. This has the effect of increasing the effective nucleation barrier, or decreasing the nucleation rate of five-atom clusters at a given adatom density. Thus the peak adatom density $n_{nuc}$ needed to generate
Figure 2.4.1: Carbon adatom density on Ru(0001) at $T = 1020$ K obtained from the rate equations (2.3.1)–(2.3.3) using the parameter sets in Table 2.1 (black curves), and labelled by the cluster size parameter $j$. The corresponding measured values obtained from electron reflectivity during ethene deposition at $P = 3 \times 10^{-9}$ Torr are indicated by the red points [25]. The black dots indicate the points along this profile used for the fitting procedure described in Sec. 4.2
CHAPTER 2. RATE EQUATIONS FOR GRAPHENE GROWTH ON IR(111) AND RU(0001)

Figure 2.4.2: The experimental temperature dependence of the carbon adatom density required to nucleate graphene ($n_{\text{nuc}}$) (red symbols) and at equilibrium ($n_{\text{eq}}$) (blue symbols), with results for the ethene source indicated by filled symbols and those for a carbon-rod source by open symbols. The corresponding calculated quantities for each of the parameter sets in Table 2.1 are indicated by red ($n_{\text{nuc}}$) and blue ($n_{\text{eq}}$) curves.

clusters at a significant rate will increase with temperature.

The temperature dependence of the island density, obtained directly from LEEM images such as those in Fig. 2.2.1, is shown in Fig. 2.4.3. It is immediately apparent from this figure that the original set of parameters (used in [26]) completely fails to account for the experimental data. The original parameterisation considered the process of nucleation to occur whenever six five-atom clusters collided, with the clusters and islands regarded as “point” particles with no spatial extent. Spatial corrections to rate theories have been determined for the diffusion and attachment of single adatoms [44, 49, 50, 106], but the scenario for graphene where predominantly clusters are attached instead requires a separate discussion.

There have been some studies that have identified carbon nanoislands as being important precursors to graphene growth. For example, on Rh(111) clusters containing 24 atoms were...
identified as being present on the surface in the early stages of growth [65]. In [15] DFT was used to examine the stability of clusters containing 19-26 atoms on the Rh(111) surface. They found that although all of these nanoislands were stable those containing 21 and 24 appear to be preferred configurations. Unfortunately, nanoislands containing more than 26 atoms were not considered, however it is clear that ab-initio calculations are needed to determine whether a particular nanoisland is likely or not.

As was noted above (Table 2.1), our optimised barrier $E_D^0$ for the nucleation of graphene islands was found to be much small than the barrier $E_D$ which originates in the surface diffusion of five-atom carbon clusters for all values of $j$. This larger barrier in the original model strongly suppresses the formation of islands over the temperature range considered and as such we see very little dependence on the concentration of island with temperature compared
CHAPTER 2. RATE EQUATIONS FOR GRAPHENE GROWTH ON IR(111) AND RU(0001)

to the new model. There are at least two ways to account for the substantially smaller barrier to nucleation in our fit. The first is based on the atomic configurations of migrating five-atom clusters, which need not be, and most likely are not, [111, 112] compact. This increases the spatial extent of these species, which enhances their cross-section for collisions, and increases the island nucleation rate by reducing the effective barrier $E_{D'}$ in comparison with $E_D$ (Table 2.1). But a more likely reason is that the nucleation is heterogeneous, with the step edges of the substrate providing preferential nucleation sites with much lower energy barriers [67, 113]. While a more atomistic approach would be required to confirm this hypothesis, the results of our phenomenological analysis are compelling.

2.5 Summary and Conclusions

We have described a procedure for parameterising rate theories which we have applied to a modified theory for graphene growth on Ru(0001) based on the experiments of the Sandia group [24, 25], as well as their unpublished data on the temperature dependence of the island densities. We found that fitting solutions of our rate equations to experimental data produces a shallow minimum in the fitting error corresponding to the agglomeration of six five-atom carbon clusters to initiate the formation of a graphene island. However, the statistics available for the number of islands at different temperatures may not be of high enough quality to distinguish this fit from cases where nucleation involves the agglomeration of five and seven five-atom clusters. Specifically, because there is a large error in the number of islands for lower temperatures it is not possible to disregard either set of parameters. Thus, with a more detailed data set for the evolution of island concentration, we could use the same method to obtain a more definite set of parameters. Nevertheless, the model strongly suggests that the nucleation of graphene islands proceeds through a sequence of two activated processes each requiring the formation of a critical cluster composed of several copies of a relevant monomer. Such a conclusion provides valuable insight into the fundamental stages in the formation of
CHAPTER 2. RATE EQUATIONS FOR GRAPHENE GROWTH ON IR(111) AND RU(0001)

Epitaxial graphene sheets on Ir(111) and Ru(0001).

Other experiments could also benefit from our methodology. The temperature-programmed growth of graphene from ethylene \((\text{C}_2\text{H}_4)\) on Rh(111) [65] and Ir(111) [81] provides the opportunity to investigate the details of the decomposition reaction sequence prior to the formation of graphene. An altogether different type of experiment is a recent study [58, 71] of graphene growth on polycrystalline copper surfaces with chemical vapour deposition using methane \((\text{CH}_4)\). In each of the foregoing studies there is a plausible mechanism for the formation of graphene, together with estimates of rates of individual processes. There is also sufficient high-quality data to enable the algorithm described in this chapter to be implemented. Such an analysis would yield the most accurate estimates of the reaction rates for a given reaction sequence.
In this chapter we show how a set of rate equations can be used alongside DFT calculations and experimental observations to isolate the most probable route through the complex reaction pathways that ethene may undergo during the temperature programmed growth of graphene on transition metals. We apply the set of rate equations to the TPG growth of graphene on different transition metal surfaces and examine the difference in intermediate species formed. The results of our analysis indicate that carbon adatoms are likely to be the most populous species at temperatures where graphene nucleation is expected. Furthermore, when ethylene is the feedstock for graphene growth, the splitting of the carbon bond to form monomers is a prerequisite to the formation of clusters containing an odd number of atoms. Thus, this conclusion is in agreement with experimental observations [24, 25] and theoretical work [26, 2, 13] which suggest that the growth of graphene proceeds by the attachment of clusters of 5 atoms.
In Sec. 1.3 we have seen that graphene is grown on a variety of different transition metal surfaces using many different precursors [4]. Once a precursor molecule is absorbed onto the surface it may undergo a sequence of reactions that are dependent on the composition of the molecule and substrate as well as the temperature and pressure at the surface. Obtaining some idea about the distribution of reaction products for a given experimental procedure is the first step to building or validating phenomenological theories of graphene nucleation and growth. For example, in the previous chapter we presented a rate theory for nucleation of graphene on Ir(111) and Ru(0001) in which one step of the growth process involved the formation of five atom clusters from carbon monomers [26, 2]. In some of these experiments ethylene was deposited onto the iridium surface [25] and so, for the rate theory to be a valid description of the growth process, ethylene must decompose to form carbon monomers.

In principle, an approach that would be ideally suited to studying this problem would be KMC simulations. One could construct an events list that was based on the possible reactions that molecules can undergo, beginning from the deposition of the precursor molecule. The rates for these processes could be calculated using the methods described in Sec. 1.4 and a given experimental scenario could be readily simulated. If the computational overhead of a KMC simulation is too great it is possible to construct mean field rate equations based on the above reactions with rates calculated in the same manner. The solution of these rate equations would give the evolution in time of the concentration of species present on the surface. Comparison with experimental observations would then serve to confirm the reaction pathway and that the correct local processes have been identified.

An experimental method that allows in-situ observations of the types of molecules present on the surface during growth are the XPS methods discussed in Sec. 1.3. Particularly relevant are the TPG of graphene on transition metal surfaces. Here, ethylene is deposited onto a surface kept at room temperature or lower and then heated at a constant rate while measurements are made of the C 1s core level [81]. This allows the composition of the most abundant
molecules to be measured as a function of temperature/coverage. From the experimentalist’s perspective, one of the difficulties involved in such a study is the correct identification of the molecule from the spectra. This turns out to be a non-trivial task. DFT calculations supplemented by kinetic models such as those described below are extremely useful in the correct identification of the molecules present at a given temperature.

This fundamental task is the motivation for the work presented in the following sections. Specifically, we investigate the sequence of reactions and determine what species we expect to be present on the surface at temperatures where graphene is expected to be nucleated. It represents a cumulative effort between experimentalists utilising XPS on transition metal surfaces and theorists implementing DFT calculations and simple kinetic models. Primarily, we will focus on the construction of kinetic models which could be applied to TPG of graphene on transition metal surfaces. All DFT calculations were performed by Holly Tetlow.

The chapter will be structured as follows. In Sec. 3.1 we will briefly review the experimental procedure. Primarily, we are interested in the iridium surface, however, the set of rate equations are in principle applicable to reactions on any surface, and their use is limited only by the availability of experimental data or \textit{ab-initio} simulations to obtain parameters. There turns out to be a wealth of both sets of data for the dehydrogenation of ethene on the Pt(111) surface. Thus, the rate equation approach will be validated by comparison with experimental observations on Pt(111) and the KMC simulations performed by [102]. In Sec. 3.2 we present the possible reaction pathways that can be taken by ethene on which the rate equations are based. Sec. 3.4 will give a brief account of the DFT calculations that fix the parameters appearing in the rate equations that will be described in detail in Sec. 3.3. Finally, we will discuss the results of our calculations and our conclusions in Sec. 3.5 - 3.7.
CHAPTER 3. KINETICS OF ETHYLENE DECOMPOSITION ON IR(111)

3.1 Experimental procedure

We are interested in the following experimental procedure. Ethene is deposited onto a transition metal surface which is at room temperature or cooled to temperatures of \( \sim 90 \, \text{K} \). The surface is then heated at a constant rate of \( 1.5 \, \text{Ks}^{-1} \) and measurements are made of the C 1s core level spectra. Determination of the species present and their coverage can then be made based on analysis of the spectra. As well as XPS measurements, insights can also be gleaned from measurements of the molecules desorbed from the metal surface. Such TPD studies are useful in verifying that the correct processes have been isolated.

3.2 Dehydrogenation scheme

In order to formulate the equations describing the evolution of the concentrations of different molecular species it is necessary to tabulate all of the reactions that can occur between them beginning from the deposition of ethene. The exercise is straightforward and has been completed by a number of authors \[114\]. We first specify the types of reactions that a hydrocarbon may undergo. These are (i) hydrogenation, (ii) dehydrogenation, (iii) isomerisation, (iv) desorption and (v) carbon splitting. With these possibilities in mind we can map the possible pathways beginning from ethene and in our case ending with carbon monomers. The final reaction scheme for the Ir(111) surface is shown in Fig. 3.2.1. Not explicitly shown in the reaction scheme is the transformation of hydrogen atoms. Clearly, the availability of hydrogen atoms on the surface must be taken into account. Adsorbed hydrogen can reattach to any of the molecular species and can also be lost through the formation of molecular hydrogen followed by its desorption from the surface.
Figure 3.2.1: Reaction scheme for the dehydrogenation of ethene CH\textsubscript{2}CH\textsubscript{2}. Energy barriers for the reactions 1-18, indicating (de)hydrogenation and isomerisation and reactions CB1-CB8, indicating carbon breaking (forming) can be found in Table 3.2. Arrows indicate forward and backwards reactions and the species index label (Tab. 3.1) is indicated in brackets.
### 3.3 Rate equation model for dehydrogenation

In order to correctly account for the species present on the iridium surface it is necessary to construct a model describing the dynamics of the system. This must include all of the possible reaction processes shown in Fig. 3.2.1. Even the simplest mean-field expressions for the rate of a given reaction will depend in some way on the concentration of the species present on the surface. This means that it is not possible to predict correctly the reaction pathway taken by ethene by considering Arrhenius rates parameterised by the calculated energy barriers alone.

We have found that rate equations, which are the most simple way of describing a systems dynamics, are capable of reproducing the experimental observations.

We consider a system of 15 ordinary differential equations for the concentration of all the carbon containing species, $N_i$, where $i \in [1,14]$ for each species in Table 3.2, and the concentration of hydrogen, $N_H$. The reactions that are considered are hydrogenation, dehydrogenation, isomerisation, C-C splitting reactions and the desorption of hydrogen from the surface via the reaction $H+H \rightarrow H_2$ (gas). We do not consider the desorption of hydrocarbons and carbon monomers or dimers.

Each of the reactions in Fig. 3.2.1 contributes a term to the rate equation of the species whose concentration is changed as a result of that reaction. The sign of the term depends on whether the reaction increases (+) or decreases (-) the concentration of the species described by that rate equation. In the language of chemical kinetics we can describe all of the reactions considered as being either unimolecular or bimolecular depending on whether one or two species are involved in the reaction. Unimolecular reactions, which take $N_i \rightarrow N_j$ contribute terms of the form $\pm R_{i,j} N_i$, where $R_{i,j}$ is the rate associated with transforming species $N_i$ to $N_j$. The expression for a bimolecular reaction, describing the formation of $N_j$ due to the collision of $N_i$ with $N_k$, have the form $\pm R_{i,j} N_i N_k$.

We assume that any $H_2$ formed immediately evaporates from the surface and so the loss of
hydrogen is due only to the reaction, $\text{H} + \text{H} \rightarrow \text{H}_2\text{(gas)}$. This contributes a loss term in the rate equation for $N_H$ of the form $-2R_{\text{H}_2}\text{H}_2N_H^2$. For carbon-carbon bond splitting/forming reactions where the carbon-carbon bond holding the two atoms within a hydrocarbon molecule is broken to form two molecules which may or may not be the same we adopt the following notation. Let the hydrocarbon molecule $N_i$ be made up of two smaller molecules $N_j$ and $N_k$ connected by a carbon-carbon bond. Then the rate of the carbon-carbon bond splitting/forming reactions that takes $N_i \rightarrow N_j + N_k$ will be written $R_{i,j(k)}$. For example, the reaction $\text{CH}_3\text{CH}_2 \rightarrow \text{CH}_3 + \text{CH}_2$ occurs at the rate $R_{2,11(12)}$.

The full set of rate equations is then constructed by considering each reaction shown in Fig. 1 in turn, forming the correct expression based on the reaction type and inserting it with the correct sign into the right hand side of the equations for which the reaction effects a change in that species concentration. For example, consider reaction 2 in the forwards direction. This

---

### Table 3.1: The labels corresponding to all species used in the rate equations corresponding to Fig. 3.2.1.

<table>
<thead>
<tr>
<th>Index</th>
<th>Species</th>
</tr>
</thead>
<tbody>
<tr>
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</tr>
<tr>
<td>14</td>
<td>C</td>
</tr>
</tbody>
</table>
Chapter 3. Kinetics of Ethylene Decomposition on Ir(111)

corresponds to the bimolecular reaction $\text{CH}_2\text{CH}_2+\text{H} \rightarrow \text{CH}_2\text{CH}_3$ which has a rate $R_{12}$ and contributes the term $R_{12}N_1N_H$ to the three rate equations for $N_1$, $N_2$ and $N_H$,

\[
\frac{dN_1}{dt} = \ldots - R_{12}N_1N_H + \ldots \\
\frac{dN_2}{dt} = \ldots + R_{12}N_1N_H + \ldots \\
\frac{dN_H}{dt} = \ldots - R_{12}N_1N_H + \ldots
\]  

(3.3.1)  

(3.3.2)  

(3.3.3)

For carbon-carbon splitting/forming reactions between two of the same molecules, for example, as in the reaction $\text{CH}_2\text{CH}_2 \rightarrow \text{CH}_2 + \text{CH}_2$ then we must also include the correct stoichiometric coefficients in the rate equations to reflect the number of single carbon species released from a molecule or needed to form a molecule containing two carbon atoms. The full set of rate equations for Ir(111) are given below with the numeric labels corresponding to all possible species as provided in Table 3.1:

\[
\frac{dN_1}{dt} = -R_{1,2}N_1N_H + R_{2,1}N_2 + R_{3,1}N_3N_H - R_{1,3}N_1 - R_{1,5}N_1 + R_{5,1}N_5 + R_{12(12)}N_{12} - R_{1,12(12)}N_1, \\
\frac{dN_2}{dt} = R_{1,2}N_1N_H - R_{2,1}N_2 - R_{2,4}N_2N_H - R_{2,5}N_2 + R_{5,2}N_5N_H + R_{12(11)}N_{12}N_{11} - R_{2,12(11)}N_2, \\
\frac{dN_3}{dt} = R_{1,3}N_1 - R_{3,1}N_3N_H - R_{3,5}N_3N_H + R_{5,3}N_5 - R_{3,6}N_3 + R_{6,3}N_6N_H - R_{3,7}N_3 + R_{7,3}N_7 + R_{9,3}N_9N_H - R_{3,9}N_3 - R_{3,12(13)}N_3 + R_{12(13),3}N_{12}N_{13}, \\
\frac{dN_4}{dt} = R_{2,4}N_2N_H, \\
\frac{dN_5}{dt} = R_{1,5}N_1 - R_{5,1}N_5 + R_{2,5}N_2 - R_{3,5}N_5N_H + R_{3,5}N_3N_H - R_{5,3}N_5 - R_{5,7}N_5 + R_{11(13),5}N_{11}N_{13} - R_{5,11(13)}N_5 + R_{7,5}N_7N_H.
\]
\[
\frac{dN_6}{dt} = R_{3,6}N_3 - R_{6,3}N_6N_H - R_{6,7}N_6N_H + R_{7,6}N_7 \\
- R_{6,9}N_6 + R_{9,6}N_9 - R_{6,8}N_6 + R_{8,6}N_8N_H + R_{14(12),6}N_{12}N_{14} - R_{6,14(12)}N_6,
\]
\[
\frac{dN_7}{dt} = R_{3,7}N_3 - R_{7,3}N_7 + R_{5,7}N_5 - R_{7,5}N_7N_H - R_{7,6}N_7 + R_{6,7}N_6N_H,
\]
\[
\frac{dN_8}{dt} = R_{6,8}N_6 - R_{8,6}N_8N_H - R_{8,9}N_9N_8 + R_{9,8}N_9 + R_{14(13),8}N_{14}N_{13} - R_{8,14(13)}N_8 \\
- R_{8,10}N_8 + R_{10,8}N_{10}N_H,
\]
\[
\frac{dN_9}{dt} = R_{3,9}N_3 - R_{9,3}N_HN_9 + R_{6,9}N_6 - R_{9,6}N_9 + R_{8,9}N_8N_H - R_{9,8}N_9 \\
+ R_{13(13),9}N_{12}^2 - R_{9,13(13)}N_9,
\]
\[
\frac{dN_{10}}{dt} = R_{8,10}N_8 - R_{10,8}N_{10}N_H + R_{14(14),10}N_{14}^2 - R_{10,14(14)}N_{10},
\]
\[
\frac{dN_{11}}{dt} = -R_{11(12),2}N_{11}N_{12} + R_{2,11(12)}N_2 + R_{5,11(13)}N_5 - R_{11(13),5}N_{11}N_{13} \\
+ R_{12,11}N_{12}N_H - R_{11,12}N_{11},
\]
\[
\frac{dN_{12}}{dt} = -R_{12(13),3}N_{12}N_{13} + R_{3,12(13)}N_3 - R_{12(11),2}N_{11}N_{12} \\
+ R_{2,12(11)}N_2 - R_{12(14),6}N_{12}N_{14} + R_{6,12(14)}N_6 \\
- R_{12,11}N_{12}N_H + R_{11,12}N_{11} + R_{13,12}N_{13}N_H - R_{12,13}N_{13},
\]
\[
\frac{dN_{13}}{dt} = -R_{13(12),3}N_{13}N_{12} + R_{3,13(12)}N_3 - R_{13(11),5}N_{11}N_{13} + R_{5,13(11)}N_5 \\
- R_{13(14),9}N_{13}N_{14} + R_{8,13(14)}N_8 - 2R_{13(13),9}N_{13}^2 \\
+ 2R_{13(13),9}N_9 - R_{13,12}N_{13}N_H + R_{12,13}N_{12} \\
+ R_{14,13}N_{14}N_H - R_{13,14}N_{13},
\]
\[
\frac{dN_{14}}{dt} = -R_{14(12),6}N_{14}N_{12} + R_{6,14(12)}N_6 - R_{14(13),8}N_{13}N_{14} \\
- R_{14,13}N_{14}N_H + R_{13,14}N_{13} + R_{8,14(13)}N_8 - 2R_{14(14),10}N_{14}^2 + 2R_{10,14(14)}N_{10},
\]
\[
\frac{dN_H}{dt} = -R_{1,2}N_1N_H + R_{2,1}N_2 - R_{3,1}N_3N_H + R_{1,3}N_1 - R_{2,4}N_2N_H - R_{2,5}N_2 \\
+ R_{5,2}N_5N_H - R_{3,5}N_3N_H + R_{5,3}N_5 + R_{3,6}N_3 - R_{6,3}N_6N_H + R_{5,7}N_5 \\
- R_{7,5}N_7N_H - R_{6,7}N_6N_H + R_{7,6}N_7 + R_{6,8}N_6 - R_{8,6}N_8N_H \\
+ R_{8,9}N_9 - R_{9,3}N_9N_H - R_{8,9}N_9N_8 + R_{9,8}N_9 + R_{8,10}N_8 - R_{10,8}N_{10}N_H
\]
The rate equations are solved subject to the initial condition $N_1(0) = N_1^0$, where $N_1^0$ is the concentration of ethene in ML present at the beginning of the experiment when temperature is low. All other species including hydrogen initially have zero concentrations. Over time the temperature is increased subject to $T = kt + T_0$, where $k$ is the rate at which the temperature is increased and $T_0$ is the initial temperature of the surface.

3.4 Parameterising rate equations: rates obtained from *ab-initio* calculations

As we have seen, the method described in Sec. 2.1 allows us to parameterise rate equations given a set of experimental data. However, fitting to the above set of equations represents a formidable challenge due to the large number of parameters ($\sim 46$) and relatively small data set. Thus, in this case, *ab-initio* calculations are invaluable in parameterising the rate equations and, ultimately, to obtain solutions which agree well with the experimental observations. In Section 1.2 we said that DFT is often the best description we have of reality. However, because the description of exchange-correlation functional is approximate, in turn so are the results obtained. For iridium, the reported energy barriers (Tab. 3.2) are calculated using two iridium layers. It could be possible that these reported energy barriers differ by as much as 0.2 eV.

In general, the rate is a product of an attempt frequency, $\nu$ for changing from one state to another, in this case from the products to the reactants, and a Boltzmann factor containing the energy barrier determined within the framework of transition state theory (TST). Thus, the rate of a reaction whose free energy barrier was calculated to be $E_{ij}$ is given by,
Table 3.2: Energy barriers for the forwards and backwards reactions 1-18 and CB1-CB8 described by the reaction scheme Fig. 3.2.1. Energy barriers provided with kind permission from Holly Tetlow.
where $k_B$ is the Boltzmann constant, $T$ is the temperature and $\nu$ is typically of the order of $10^9 - 10^{14}$ s$^{-1}$ [115]. However, clearly the rates $R_{ij}$ have different units depending on whether the reaction is bimolecular ($[L]^2[T]^{-1}$) or unimolecular ($[T]^{-1}$). What is missing? Apparently, we must recognise that for bimolecular reactions we have to account for the diffusion of molecules prior to and just after a reaction. In particular, we assume that while hydrocarbon species remain fixed, hydrogen atoms can diffuse freely at all temperatures. It is then necessary to determine the rate at which hydrogen atoms reach the hydrocarbon species to react known as the diffusion controlled reaction rate. The latter quantity is in general difficult to determine but an approximate framework that is often utilised is that of Smoluchowski [116]. Here one takes into account explicitly the diffusion of one of the reacting species about the second stationary reactant. One normally defines a reaction region (e.g. in 3D a sphere with a certain radius) which is assumed to be a perfectly absorbing boundary surrounding the reactant. The rate of reaction is given by the flux of particles diffusing through the reaction boundary which is obtained from the diffusion equation for the non-stationary molecule.

The overall bimolecular rate of formation including both attachment and diffusion kinetics is obtained by altering the basic form of the rate, Eq. (3.4.1) [117]. In this case the functional form of the rate of a bimolecular reaction is derived by dividing it into two separate processes. These are the rate at which two reactant molecules diffuse onto adjacent sites, the resulting configuration referred to as a “complex”, and the rate at which this intermediary complex react to form the product. If we let the concentrations of the two reacting species be $A$ and $B$, the concentration the reaction complex be $[AB]$ and the of the reactant be $C$ this is represented by the following reaction,
where \( k_D \) is the diffusion limited reaction rate and \( k'_D \) and \( k_i \) are unimolecular reaction rates. The rate equation describing the evolution in time of concentration of the complex is,

\[
\frac{d[AB]}{dt} = k_D AB - k'_D [AB] - k_i [AB].
\]

By applying steady state conditions to the concentration of the complex allows us to obtain the following,

\[
[AB] = \frac{k_D}{k'_D + k_i} AB,
\]

so that the rate of formation of the product \( C \) is,

\[
R = \frac{k_i k_D}{k_i + k'_D}.
\]

It is highlighted in [117] that there are two regimes in which Eq. (3.4.3) may be simplified. The first is termed a diffusion-limited reaction rate which occurs when \( k_i \gg k'_D \), in which case \( R \approx k_D \). The second is referred to as an attachment-limited reaction rate which occurs when \( k_i \ll k'_D \) such that \( R \approx \frac{k_D}{k'_D} k_i = K_{eq} k_i \), where \( K_{eq} \) is called the equilibrium constant.

The geometry optimisation and nudged elastic band (NEB) calculations were performed by Holly Tetlow using the CP2K [118] density functional theory code. Initially, calculations were performed to find the lowest energy absorption sites for all of the molecules listed in Table 3.1. In practice this was accomplished by optimising the geometry of many different structures and selecting the one with the lowest energy. These structures are shown in Figure 3.4.1.
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Figure 3.4.1: The lowest energy geometries of the hydrocarbon species adsorbed onto the Ir(111) surface. The binding energies of each species is also included. Ir atoms are shown in blue, while C and H are dark and light grey, respectively. Note that the CH$_3$CH$_3$ molecule is found not to bind to the surface and therefore its binding energy is not given. Figure reproduced with kind permission from Holly Tetlow.
Figure 3.4.2: Reaction scheme for the dehydrogenation of ethene CH₂CH₂. Energy barriers for the reactions 1-8, indicating (de)hydrogenation and isomerisation can be found in Table 3.2. Arrows indicate forward and backwards reactions and the species index (Tab. 3.1) is indicated in brackets.

3.5 Validating the rate equation model: dehydrogenation on Pt(111)

To investigate whether the simple rate equations described previously can accurately predict the concentration of species as a function of temperature/coverage we look at the dehydrogenation of ethene on Pt(111). This system has been investigated experimentally using XPS by [77] and theoretically using DFT/KMC by [102]. The latter study provides the energy barriers, Table 3.3, for the reaction rates and also allows us to compare the results of the rate equations to a more complete description of the systems kinetics. In this case, we will assume that for all bimolecular reactions \( R_{i,j} \) are all of Arrhenius form but based on the discussion in the previous section recognise that this is an approximation.

Experiments on Pt(111) are carried out over a much smaller temperature range which leads to significant simplifications of the dehydrogenation scheme (Fig. 3.4.2) and likewise a smaller set of rate equations is needed. These are given below:
CHAPTER 3. KINETICS OF ETHYLENE DECOMPOSITION ON IR(111)

\[
\begin{align*}
\frac{dN_1}{dt} &= -R_{1,2}N_1N_H + R_{2,1}N_2 + R_{3,1}N_3N_H - R_{1,3}N_1, \\
\frac{dN_2}{dt} &= R_{1,2}N_1N_H - R_{2,1}N_2 - R_{2,5}N_2 + R_{5,2}N_5N_H, \\
\frac{dN_3}{dt} &= R_{1,3}N_1 - R_{3,1}N_3N_H - R_{3,5}N_3N_H + R_{5,3}N_5 - R_{3,6}N_3 + R_{6,3}N_6N_H, \\
\frac{dN_5}{dt} &= R_{2,5}N_2 - R_{5,2}N_5N_H + R_{3,5}N_3N_H - R_{5,3}N_5 - R_{5,7}N_5 + R_{7,5}N_7N_H, \\
\frac{dN_6}{dt} &= R_{3,6}N_3 - R_{6,3}N_6N_H + R_{6,7}N_6N_H - R_{7,6}N_7 - R_{6,9}N_6 + R_{9,6}N_9 \\
&\quad - R_{6,8}N_6 + R_{8,6}N_8N_H, \\
\frac{dN_7}{dt} &= R_{5,7}N_5 - R_{7,5}N_7N_H + R_{7,6}N_7 - R_{6,7}N_6N_H, \\
\frac{dN_H}{dt} &= -R_{1,2}N_1N_H + R_{2,1}N_2 - R_{3,1}N_3N_H + R_{1,3}N_1 \\
&\quad + R_{2,5}N_2 - R_{5,2}N_5N_H - R_{3,5}N_3N_H + R_{5,3}N_5 \\
&\quad + R_{3,6}N_3 - R_{6,3}N_6N_H + R_{5,7}N_5 - R_{7,5}N_7N_H \\
&\quad - R_{6,7}N_6N_H + R_{7,6}N_7 - R_HN_H^2.
\end{align*}
\]

We performed two sets of calculations. In the first set, we used the calculated free-energy barriers with the prefactors, \( \nu = 10^{13} \text{ s}^{-1} \) for all reactions, as was done in [102]. In the second, we optimised the free-energy barriers subject to the experimental data [77] using the calculated barriers as initial points in the parameter space. The optimisation is carried out using the gradients calculated according to Sec. 2.1 and the BFGS/Conjugate Gradient algorithm [119] with inexact line searches [120] for the descent directions. The various systems of ODEs are solved using the implicit Rosenbrock method implemented in BOOST C++ [121]. The summary of the results of these calculations are as follows.

Firstly, it is apparent Fig. 3.5.1 that the agreement between the KMC results [102] and rate equation model is, on the whole good. Both predict the correct order of species, i.e. \( \text{CH}_2\text{CH}_2 \rightarrow \text{CCH}_2 \rightarrow \text{CCH}_3 \) and a peak in the hydrogen concentration for the temperature at which \( \text{CCH}_2 \) is formed. The increase in \( \text{CCH}_3 \) at 260 K is observed in both the rate equations and KMC. However, the appearance of \( \text{CCH}_2 \) occurs approximately 40 K later in the rate equation.
solution compared to the KMC. Furthermore, CH$_2$CH$_2$ is observed to a persistent species in the KMC simulations while a decrease to zero concentration is observed at approximately 280 K by the rate equations. The agreement for the evolution of hydrogen production between both methods is similarly acceptable. The change in the barriers after optimisation is in general small and in fact leaves many of the energy barrier unchanged. However, clearly the agreement with experiment is very good and specifically we see a crossover from CH$_2$CH$_2$ to CCH$_3$ which is observed at approximately 280 K. We note, that the optimisation (resulting in a reduction in the cost function from 0.031 to 0.007) most likely corrects the use of constant prefactors for all reactions or could possibly be a result of the rate equations not taking into account spatial effects that are taken into account by the more accurate KMC results.

The results are encouraging. On platinum, if we are interested only in the concentration of species as a function of coverage/temperature and the order at which species are observed, we lose very little by replacing KMC simulations with rate equations. Of course, if we are interested in more complicated quantities (e.g. island-size distributions) then we must resort to KMC. Furthermore, the effects of the diffusion of hydrogen/carbon species is likely to become important as temperature increases and species become more mobile. Indeed this turns out to be the case on iridium where we are interested in a much higher temperature range.
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<table>
<thead>
<tr>
<th>Reaction</th>
<th>$E_f$ [eV]</th>
<th>$E_b$ [eV]</th>
<th>Optimised $E_f$ [eV]</th>
<th>Optimised $E_b$ [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 $\text{CH}_2\text{CH}_2 \rightarrow \text{CH}_2\text{CH} + \text{H}$</td>
<td>0.78</td>
<td>0.63</td>
<td>0.81</td>
<td>0.87</td>
</tr>
<tr>
<td>2 $\text{CH}_2\text{CH}_2 + \text{H} \rightarrow \text{CH}_3\text{CH}_2$</td>
<td>0.91</td>
<td>0.67</td>
<td>0.91</td>
<td>0.67</td>
</tr>
<tr>
<td>3 $\text{CH}_2\text{CH} \rightarrow \text{CH}_2\text{C} + \text{H}$</td>
<td>0.55</td>
<td>0.72</td>
<td>0.47</td>
<td>0.8</td>
</tr>
<tr>
<td>4 $\text{CH}_2\text{CH} + \text{H} \rightarrow \text{CH}_3\text{CH}$</td>
<td>0.82</td>
<td>0.63</td>
<td>0.82</td>
<td>0.63</td>
</tr>
<tr>
<td>5 $\text{CH}_3\text{CH}_2 \rightarrow \text{CH}_3\text{CH} + \text{H}$</td>
<td>0.69</td>
<td>0.77</td>
<td>0.68</td>
<td>0.77</td>
</tr>
<tr>
<td>6 $\text{CH}_3\text{CH}_2 + \text{H} \rightarrow \text{CH}_3\text{CH}_3$</td>
<td>0.8</td>
<td>0.66</td>
<td>0.8</td>
<td>0.66</td>
</tr>
<tr>
<td>7 $\text{CH}_2\text{C} + \text{H} \rightarrow \text{CH}_3\text{C}$</td>
<td>0.83</td>
<td>1.20</td>
<td>0.82</td>
<td>1.2</td>
</tr>
<tr>
<td>8 $\text{CH}_3\text{CH} \rightarrow \text{CH}_3\text{C} + \text{H}$</td>
<td>0.83</td>
<td>0.20</td>
<td>0.82</td>
<td>1.04</td>
</tr>
</tbody>
</table>

| $\text{H} + \text{H} \rightarrow \text{H}_2$ | 1.17 | 0.00 | 1.17 | 0.00 |

Table 3.3: Energy barriers for the forwards and backwards reactions 1-8 and the desorption of hydrogen described in the reaction scheme Fig. 3.4.2. Note, that in the absence of an energy barrier for the formation of $\text{H}_2$ from two hydrogen atoms we use the barrier for the equivalent reaction calculated on an iridium surface.
Figure 3.5.1: The densities of a selection of surface species obtained from (a) rate equations with free energy barriers obtained from DFT calculations [102] and constant prefactors; (b) experimental data from [77] obtained from XPS observation on platinum showing the concentrations of the most abundant species. These were observed to be \( \text{CH}_2\text{CH}_2 \) (empty squares) and \( \text{CCH}_3 \) (open circles) with a the black and red solid lines being fits to these experimental values. The dotted lines are solutions to rate equations with optimised energy barriers and represent concentration of \( \text{CH}_2\text{CH}_2 \) (black) and \( \text{CCH}_3 \) (red); (c) KMC results parameterised with energy barriers from DFT from [102] (c).
CHAPTER 3. KINETICS OF ETHYLENE DECOMPOSITION ON IR(111)

<table>
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<td>0.77</td>
</tr>
<tr>
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<td>0.66</td>
</tr>
<tr>
<td>7 $\text{CH}_2\text{C} + \text{H} \rightarrow \text{CH}_3\text{C}$</td>
<td>0.83</td>
<td>1.2</td>
</tr>
<tr>
<td>8 $\text{CH}_3\text{CH} \rightarrow \text{CH}_3\text{C} + \text{H}$</td>
<td>0.83</td>
<td>0.2</td>
</tr>
</tbody>
</table>

\[ \text{H} + \text{H} \rightarrow \text{H}_2 \]

Table 3.4: Energy barriers for the forwards and backwards reactions 1-8 and the desorption of hydrogen described in the reaction scheme Fig. 3.4.2. Note, that in the absence of an energy barrier for the formation of $\text{H}_2$ from two hydrogen atoms we use the barrier for the equivalent reaction calculated on an iridium surface.

3.6 Results for dehydrogenation on Ir(111)

3.6.1 Experimental observations: interpretation of the XPS experiments

We now briefly review what molecules were identified in which temperature range on Ir(111) during the TPG experiments described in Sec. 3.1. These observations are made on the basis of experimental observations supplemented by \textit{ab-initio} calculations. Note that a more detailed discussion may be found in [3] but we will briefly review the process that lead to the identification of each molecule.

Let us consider the interpretation of the spectra (Fig. 3.6.1) obtained from an XPS measurement of the Ir(111) surface at 90 K. The peaks appearing in the XPS configuration are determined by the core electrons configurations of the carbon atoms contained in each mo-
leucle. Thus, in general a peak will be generated by each atom contained in a molecule, but additional peaks may also be generated by an atom’s vibrational satellites. To aid in the identification of such molecules DFT can be used to calculate relative binding energies (BEs) of the C 1s levels for all of the hydrocarbon species considered in Table 3.1. Although the absolute values are not expected to bear much relation to the experimental values, the energy differences between the core level shifts in different molecules are likely to be reasonably accurate. By aligning a DFT core-level shift with an experimentally measured value, obtained by fitting the low temperature high-resolution spectrum [122], one can make use of the energy differences between C 1s levels obtained from DFT calculations to aid in the interpretation of the spectra. The molecule chosen for the alignment of energies is CCH$_2$ at approximately 200 K which was chosen on the basis of kinetic factors such as rates of reactions from CH$_2$CH$_2$ and the solution of rate equations to be discussed later. Specifically, the solutions of the rate equations by parameters obtained using DFT strongly suggest that CCH$_2$ is the first species to appear after CH$_2$CH$_2$. We note that the identification of CHCH for which vibrational splitting is observed is aided by DFT calculated C*-H vibrational energy of 380 meV for CHCH with core-hole excited C atom (denoted C*).

3.6.2 Results and discussion

We perform two sets of calculations for Ir(111). Firstly, we solve the set of rate equations in which some of the vibrational prefactors are obtained from *ab-initio* calculations utilising the harmonic transition state theory. All other prefactors are set equal to $10^{13}$ s$^{-1}$. The results of such a calculation is shown in Figure. 3.6.3 c. We see that agreement is obtained for the majority of molecules observed experimentally, Figure 3.6.3(a). Particularly, the decrease of CCH$_2$ is seen, although at a slightly higher temperature, $\sim$ 290 K, i.e. higher than observed experimentally, $\sim$250 K. We also see an increase in CH at $\sim$ 350 K which is in good agreement with the experimental observations (Fig. 3.6.3 a). The appearance of $C_N$ species is observed
Figure 3.6.1: High-resolution and high-statistics XPS spectra acquired after annealing the ethylene covered substrate to selected temperatures. In (a) the intensity spectra for experiments undertaken after exposure at 90 K, and after annealing to different temperatures are shown. Here the intensity spectrum obtained from experiments undertaken at a given temperature are shown displaced by the temperature to which the surface was annealed. This is indicated on the left vertical axis and labelled on the rightmost tails of each spectrum. The DFT calculated BEs for different species (shown on the left with different colours) found to be present on the surface have been marked with the same colour ticks. In (b), one of these spectra, that of CHCH acquired after annealing to ~ 350 K and marked in red in (a) is shown in detail. This spectrum shows the main peak with vibrational replicas, and the vibrational splitting has been found to be 405 meV. A small amount of the CH species is already present at this temperature as can be seen by the presence of the small blue peak. [3]
experimentally at ~ 450 K while the rate equations predict the appearance of C monomers but at a higher temperature ~500 K. Thus, broad agreement with the experimental observations is found for four out of the five species present on the Ir(111) surface for temperatures ranging from 100 - 500 K. However, there is a discrepancy between the species observed experimentally at temperatures ranging from 250 to 400 K. As discussed in Sub. 3.6.1, at these temperatures the XPS and core-level shift results suggest that the molecule present on the surface is CHCH, but, the rate equations predict CCH₃ as was the case for the decomposition of ethylene on Pt(111). We see from the plot of absorption energies and barriers (Fig. 3.6.2) that the formation of CCH₂ is favourable and also that CH and carbon monomer are clearly very stable. This is in agreement with the experimental observations. However, between CCH₂ and the formation of CH it is not at all clear based on energetics alone what the actual reaction path is. This is due mainly to the similar magnitudes in energy barriers for reactions beginning with CCH₂. For instance, the barrier to form CCH₃ form CCH₂ is 0.76 eV which is very similar to forming CHCH₂ (0.79 eV) from CCH₂. From CHCH₂ the barrier to form CHCH and then to form two CH molecules by breaking the carbon-carbon bond is relatively small and so it seems likely, in agreement with the rate equation results that both CH and C molecules are observed on the surface.

Clearly, errors in the DFT calculations for these reactions will then be of great importance in determining the lifetimes of CCH₂, CCH₃ and CHCH. However, the neglect of diffusion for bimolecular reactions maybe of even greater importance. Since it is extremely difficult to quantitively attribute the error in the rate of a reactions as arising from either the neglect of spatial effects (the prefactor) or the energy barrier we elect to fit the former in an attempt to obtain agreement with the XPS observations. We note that it is necessary to perform more exact KMC simulations to determine what effect the neglect of spatial effects has on the rates of particular reactions.

The second set of calculations we performed aimed at addressing this discrepancy and
Figure 3.6.2: Absorption energies and barriers for two possible dehydrogenation routes. The top figure represents the most probable dehydrogenation route from \( \text{CH}_2\text{CH}_2 \) to C based on experimental observations. On the bottom we show the most likely route from \( \text{CH}_2\text{CH}_2 \) to \( \text{CCH}_3 \) which is one of the species predicted to be observed based on the solution to the rate equations with constant prefactor \( \nu = 10^{13}\text{s}^{-1} \) but ruled out by XPS measurements.
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<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\nu_{AF}$ [s$^{-1}$]</th>
<th>$\nu_{FF}$ [s$^{-1}$]</th>
<th>$\nu_{AB}$ [s$^{-1}$]</th>
<th>$\nu_{FB}$ [s$^{-1}$]</th>
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</thead>
<tbody>
<tr>
<td>3</td>
<td>$1.7 \times 10^{12}$</td>
<td>$10^{11}$</td>
<td>$5.3 \times 10^{12}$</td>
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<tr>
<td>7</td>
<td>$1.2 \times 10^{12}$</td>
<td>$10^{11}$</td>
<td>$1.7 \times 10^{13}$</td>
<td>$10^{14}$</td>
</tr>
<tr>
<td>14</td>
<td>$7.8 \times 10^{12}$</td>
<td>$10^{12}$</td>
<td>$2.6 \times 10^{13}$</td>
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<tr>
<td>CB6</td>
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<td>$10^{9}$</td>
<td>$5.9 \times 10^{11}$</td>
<td>$10^{12}$</td>
</tr>
</tbody>
</table>

Table 3.5: The prefactors for reaction 3, 7, 14, CB6 as determined by *ab-initio* calculations and fitting to experimental data. Here $\nu_{AF}$ and $\nu_{AB}$ denote the prefactor obtained from *ab-initio* calculations for the forwards and backwards reactions, respectively; $\nu_{FF}$ and $\nu_{FB}$ are correspondingly the prefactors obtained from fitting to experimental results.

To determine a route through the reaction scheme to ensure agreement with experimental observations, we elect to fit the prefactors for reactions 3, 7, 14 and CB6 to obtain agreement for the species observed on the surface at 250 K. We note that we have fit these prefactors only to an order of magnitude with the goal of reproducing the order of the species observed as a function of temperature in the XPS experiments. These reactions are determined on the basis of an examination of the possible reactions from CCH$_2$. Specifically, the energy barriers associated with the scission of the carbon-carbon bond, isomerisation to CHCH (2.52 eV) and for the dehydrogenation to CCH (1.17 eV) are all high and because of this we elect to discount these routes. Only those reactions were left that serve as possible routes to the formation of CHCH and CCH$_3$. After altering these relevant prefactors, the results found in Table 3.5, we obtained results analogous to those discussed but with CHCH observed instead of CCH$_3$, albeit over a slightly smaller temperature range than observed experimentally (Fig. 3.6.3b).

Finally, based on the experimental and theoretical findings reported above the dehydrogenation sequence of ethylene on iridium is as follows. Soon after starting at 100 K the concentration of ethylene (CH$_2$CH$_2$) is seen to decrease as that of vinylidene (CH$_2$C) increases. We note that in the initial study [81] the dehydrogenation of ethylene was reported as being at higher temperatures $\sim$ 200 K. However, experiments performed at these lower temperatures along with support from the rate equation results demonstrate that dehydrogenation of
CHAPTER 3. KINETICS OF ETHYLENE DECOMPOSITION ON IR(111)

ethylene occurs at ~100 K. Since there are two dehydrogenation reactions needed to reach vinylidene it is clear that the reactions 2 (CH₂CH₂→CH₂CH+H) and 3 (CH₂CH→CH₂C+H) occur so quickly that vinyl (CH₂CH) is not stable for long enough to be observed. The CH2C concentration begins to decrease at ~300 K due to the hydrogenation reaction (reverse reaction 3) leading back to CH₂CH followed immediately by the dehydrogenation reaction to acetylene (CHCH) (reaction 14). For this molecule the rate of reaction for C-C breaking is sufficiently high so that methyldyne (CH) can be produced at ~350 K. This is the only species present until ~500 K when dehydrogenation of CH results in the formation of C monomers. The reverse reaction is then limited by the amount of hydrogen present on the surface (Figure. 3.6.4). In summary, the reaction pathway is given by the following set of equations:

\[
\begin{align*}
CH₂CH₂ & \rightarrow CH₂CH + H, \\
CH₂CH & \rightarrow CH₂C + H, \\
CH₂C & \rightarrow CHCH + H, \\
CHCH & \rightarrow CH + CH, \\
CH & \rightarrow C + H.
\end{align*}
\]

3.7 Summary and Conclusions

Let us begin this concluding section by reminding the reader that prior to this study while much work had been done on dehydrogenation sequences of hydrocarbons on platinum surfaces, there had been very few theoretical efforts on iridium. The inferences from XPS studies of iridium [81, 123] were partially based on conclusions made on the basis of the identifications of hydrocarbon species as a function of temperature on the platinum surface [77]. Such studies identified CCH₃ as the most probable hydrocarbon present at 300 K. However, XPS spectra interpreted with the aid of DFT calculations of the C 1s core level shifts indicate that this species is actually CHCH. We note, that within the context of understanding graphene formation the presence of this molecule is largely unimportant since graphene formation occurs at
Figure 3.6.3: The densities of the most populous species present on the Ir(111) substrate obtained from (a) experimental observations of the species present on the Ir(111) substrate; (b) rate equations with the prefactors of reactions 3, 7, 14 and CB6 optimised and (c) with the prefactors of the same reactions obtained using harmonic transition state theory (HTST).
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Figure 3.6.4: The rate of hydrogen desorption obtained from the rate equations with the prefactors of reactions 3, 7, 14 and CB6 optimised. The second peak corresponds to the temperature region where the remaining atomic hydrogens forms H₂ and desorbs from the surface.

higher temperatures at which no hydrogen is present on the surface. Briefly, we have also seen due to a small energy barrier for the breaking of the CHCH carbon bond that it is likely that carbon monomers are present on the surface at temperatures for which graphene nucleation is observed (> 600 K).

At higher temperatures we have found that there is much importance associated with the prefactors for (de)-hydrogenation and dissociation reactions in determining the correct reaction scheme. When calculated barriers are similar in magnitude the assumption that $\nu \sim 10^{13}$ s⁻¹ in kinetic studies of dissociation may not be adequate. Furthermore, the necessity of fitting the prefactors may also indicate the inadequacy of the harmonic transition state theory (HTST) for reactions at elevated temperatures or more likely that coverage effects may influence the electronic environment that determines the curvature of the potential energy surface (PES) and hence magnitude of the prefactor. In fact, differences between prefactors found
experimentally and calculated using DFT within the framework of HTST were reported for the dehydrogenation of a number of hydrocarbons on the platinum substrate [124]. Surprisingly, the difference between the calculated and observed prefactors could be as large as three orders of magnitude for some reactions. For example, the prefactor for the dehydrogenation of CHCH$_2$ on Pt(111) was observed to be $10^{9.5\pm2}$ s$^{-1}$ while the calculated value was $10^{12}$ s$^{-1}$ which is beyond that which can be explained away by experimental uncertainty. There is no general rule of thumb that could be applied to these few reported prefactors since some experimental values also exceed the calculated values.

The limitations of the rate equations have been discussed in Sec. 1.4. We recall, that we can describe only what we build into the rate equations a priori i.e. only the reactions listed in Table 3.2, although this same limitation occurs in KMC simulations of surface processes. In fact many more reaction may be possible if we include the diffusion of larger carbon species. This is indeed likely at high temperatures where the probability of forming larger carbon clusters is perhaps not negligibly low. As discussed, within a rate equation framework one disregards the spatial dependence of species present on the surface and characterises the state of the system at a given time by their average concentrations. Spatial information may only be included implicitly by choosing the form of the reaction rates appropriately. It would be interesting to study the effect of diffusion of certain hydrocarbon species, for instance CH and C, on the rates of formation of species present on the surface. Most likely, this would be within the framework of KMC and as such it remains to be seen whether such a study is feasible. Comparison of the rate equations results with experimental observations indicates that particular attention must be paid to the evolution of the system away from CCH$_2$ at approximately 300 K since this is the point at which agreement is poorest.

In conclusion, we have used a simple rate equation approach to describe the evolutionary kinetics of decomposition of hydrocarbons on iridium and confirmed that such a description is adequate by comparing our results to a KMC study of a similar reaction scheme on Pt(111).
We have seen that such a scheme adequately describes much of the reaction sequence of ethylene on iridium and platinum. Experimental observations coupled with *ab-initio* calculations indicate that CHCH is the dominant species present on the iridium surface between 250 K and 350 K as opposed to CCH$_3$ seen on Pt(111) at similar temperatures. Such a result may only be obtained from a rate equation analysis if the pre-exponential factors calculated within the framework of harmonic transition rate theory (HTST) are substantially different from those obtained theoretically assuming unimolecular rates so that coverage and diffusion effects are not taken into account adequately by the simple rate theory. To preclude, the latter of these possibilities would require a KMC study with additional barriers calculated for the diffusion of all hydrocarbon species which constitutes significant additional work to that already accomplished.
Phase field model of submonolayer growth

Whiskey Cocktail

“3 or 4 dashes of gum syrup; 2 do. bitters(Bogart’s); 1 wine glass whiskey, and a piece of lemon peel.

Fill one-third of whiskey; a shake and strain in a fancy red wine-glass.” - Jerry Thomas

We introduce a procedure for simulating epitaxial growth based on the phase-field method. We consider a basic model in which a flux of atoms impinges on a heated surface. The subsequent diffusion of these atoms produces collisions which lead to the formation of islands, which grow by the capture of migrating atoms at their boundaries. Our implementation of the phase-field method for this model includes stochastic nucleation (in both space and time), which creates islands whose boundaries evolve as the surface atoms "condense" into and "evaporate" from the islands. Computations of this model are carried out for the submonolayer regime, where there is an abundance of analytic, simulational, and experimental work with which to compare. Broad agreement is demonstrated with kinetic Monte Carlo (KMC) and level-set simulations for island-size distributions for both reversible and irreversible growth. Reasons for discrepancies between our results (which are the same as those obtained with the level-set method) and KMC simulations are traced to the way nucleation is carried out. We also obtain agreement with the scaling of the island densities obtained from KMC simulations, which has eluded previous implementations of the phase-field method for this model.
One of the main challenges facing the study of epitaxial growth is the disparate length and time scales in the system. This is typified by the epitaxial growth of graphene on metal substrates. Here, it is necessary to understand a number of fast atomistic processes: adsorption and decay of precursor molecules, the desorption of their fragments, the nucleation of clusters of carbon atoms, and the growth of these clusters by the attachment of carbon atoms. However, graphene growth can occur on time scales extending to hours, producing graphene sheets up to micrometers in length.

An approach that goes some way to overcoming this problem is the “island-dynamics” model [1]. In these simulations the Burton-Cabrera-Frank (BCF) equations [125], which describe the growth and shrinkage of epitaxial islands due to the attachment and detachment of adatoms, are solved using the level-set method of front-tracking [126]. A simple rate equation for the density of islands that depends only on the average adatom density determines when a nucleation event takes place and the position of a nucleated island is determined using a stochastic algorithm. Excellent agreement is found with experiment and KMC simulations for irreversible aggregation, where adatoms cannot detach from island edges, in the submonolayer regime. Further modifications have extended the method to take into account detachment of adatoms from island edges (reversible aggregation) [127] and Ostwald ripening [128] as well as the effects of strain due to lattice mismatch [129].

Here, we apply an alternative front-tracking strategy based on the phase-field method to model the submonolayer growth of a monatomic crystal. The phase-field method is based on the Ginzburg–Landau theory of phase transitions and provides a mathematical description for moving boundary problems during phase transformations, such as solidification, in which the interface has a finite, but small, thickness. The central quantity in this method is an auxiliary function, called the “phase field”, whose value identifies the phase at every point in space and time. The phase-field model of the solid-liquid phase transformation was first proposed by Langer [130], and has developed into a widely-used method of computing realistic
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morphologies in a variety of settings [131]. For our purposes, the phase-field method offers several advantages over the level-set method, including the ability to treat irreversible and reversible aggregation within a single framework, that is, without resorting to \textit{ad hoc}, albeit sophisticated, schemes [127]. Moreover, because no change in method is needed to simulate both reversible and irreversible aggregation there is only a small extra computational cost associated with simulations of reversible growth. This in contrast to KMC simulations where the computational cost of a simulation increases dramatically with increasing detachment rate [127]. We will also describe a method that utilises the so-called “critical cluster”. In this approach one neglects the treatment of sub-critical nuclei and instead solves an irreversible problem in which clusters of size greater than a dimer are nucleated and then grow by the attachment of monomers.

The organisation of this chapter is as follows. In Sec. 4.1 we review how the growth of islands can be described by the BCF equations. The phase-field equations that solve these equations in the “thin interface limit” are introduced in Sec. 4.2, where we review some aspects of their derivation. The nucleation of islands, which is an addendum to the phase-field equations, is described in Sec. 4.3, where we describe when and where on the surface dimers are to be placed and how they are incorporated into the phase field. Our results are presented in Sec. 4.5, and includes surface morphologies, island-size distributions, and island densities as a function of temperature. Our conclusions are summarised in Sec. 4.6.

4.1 The Model

We consider the idealised scenario in which adatoms are the only mobile species. For some materials under typical growth conditions other species, such as clusters of atoms, can diffuse on the surface and, hence, contribute to the nucleation and growth of islands [2]. However, in our model, all other species (i.e. dimers, trimers, etc.) are assumed to be immobile and are referred to as “islands” which can grow/decay by the gain/loss of adatoms at their edges.
The limit where no detachment of adatoms from islands occurs is known as irreversible aggregation [22]. This is the regime of lower temperatures and/or high fluxes in relation to the bond strength of adjacent atoms. This means that when e.g. two adatoms collide on the surface they combine irreversibly to form an immobile dimer which can then only grow by capturing diffusing adatoms since, for instance, the temperature is not high enough to overcome the interaction between two atoms. The growth is termed “reversible” if adatoms can detach from the edges of islands. In the language of classical nucleation theory [44] reversible growth corresponds to the critical nucleus size greater than two, in contrast to unity for irreversible growth. The assumption of irreversibility reduces the number of atomistic processes that must be considered and, although somewhat idealised, many materials exhibit a growth regime which on average follows irreversible aggregation [132].

4.1.1 The BCF equations

The aim of coarse-grained models for epitaxial growth, such as the phase-field method described here, is to replace some of the discrete atomistic processes by a continuum description which is valid over large length and time scales. This is accomplished in part by introducing a continuous field $c(r,t)$ for the mobile adatom density as a function of a position $r$ on the surface at time $t$. Away from island boundaries the evolution of $c(r,t)$ is determined by the diffusion equation,

$$\frac{\partial c}{\partial t} = D \nabla^2 c,$$

where $D$ is the diffusion coefficient for adatoms, assumed to be spatially invariant. Island boundaries act as sources or sinks for adatom density and hence provide a natural (and moving) boundary conditions for the diffusion equation. The motion of boundaries is determined by the flux of adatoms to and from the boundary and is associated with a velocity with magnitude

$$v = AD\hat{n} \cdot (\nabla c|_+ - \nabla c|_-)$$
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for an interface with outward normal \( \hat{n} \). Here, the index \( +(-) \) refers to the lower (upper) terrace of an island (Fig. 4.1.1) and \( A \) is an atomic area. Finally, the effect of the interfacial curvature is accounted for by an approximate form of the Gibbs–Thomson equation, whereby the density of adatoms at the interface is given by,

\[
c_i \approx c^s_{eq} (1 + \Gamma \kappa),
\]

where \( \Gamma = A\gamma/(k_B T) \) is the capillary length, \( c^s_{eq} \) is the equilibrium adatom density at a straight island boundary, \( \gamma \) is the step stiffness, \( \kappa \) is the curvature of the interface, \( k_B \) is the Boltzmann constant and \( T \) is the absolute temperature of the substrate. Equation (4.1.3) serves as the boundary condition for Eq. (4.1.1) at the interface. We note that in the case of irreversible growth this boundary condition is replaced by:

\[
c_i = 0,
\]

which simply states that during irreversible aggregation island boundaries act as perfect sinks to adatoms diffusing on the surface. The set of equations (4.1.1)–(4.1.3) is referred to as the BCF equations [125]. When Eq. (4.1.3) is replaced by Eq. (4.1.4) we obtain a classical Stefan problem.

4.1.2 Reversible growth

In general, different approaches to modelling reversible submonolayer growth can be grouped into two categories. In the first, one builds into the theory the rate of detachment for clusters of all sizes. In this case it is necessary to describe clusters of all sizes at every point in time. This approach is typical in KMC simulations where the detachment rate may be determined by simple bond counting arguments. However, despite the accuracy and success of such approaches it clearly adds much complexity to the description of a system. This problem is
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Figure 4.1.1: Schematic diagram for the system described by the BCF equations with two terraces ("+" and "+") separated by a sharp interface. The arrow to the surface depicts deposition of adatoms with flux $J$ and their subsequent diffusion with diffusion constant $D$. Arrows to and from the interface show the flux into the interface from the upper and lower terraces, which is encapsulated mathematically in Eq. (4.1.2).

alleviated in the second category by introducing the critical cluster [44], which is a widely used approximation that greatly simplifies models for submonolayer growth in the reversible regime. It is motivated by the observation that there exist clusters below a critical size which are only short lived and therefore less important to the description of the system. The rate of nucleation will then be determined by the probability of an diffusing adatom colliding with a critical cluster to attach to it before it disintegrates.

■ 4.2 The Phase-Field Method

■ 4.2.1 Solution of BCF equations

The phase-field method enables us to solve the BCF equations without explicitly keeping track of the motion of interfacial boundaries.

In phase-field models of epitaxial growth an auxiliary field (the phase field) is introduced to describe the position and extent of immobile islands on the substrate surface. The phase field, $\phi(r, t)$, varies continuously between $\phi = 1$, indicating the presence of an island, and
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\( \phi = 0 \) (otherwise), and represents the density of atoms per site on the surface in the island.

The equation of motion for the phase field is derived by first postulating a (dimensionless) free energy-like quantity \( \mathcal{F}[\phi] \) which is a functional of the phase field. The choice of the free energy functional depends on the problem at hand and is almost always based on phenomenological considerations. A typical choice is based on the sum of two terms: one representing a “bulk free energy”, which in a two-phase system is a double well potential, and the second being a gradient term representing the free energy cost of introducing heterogeneity such as interfaces in the system. If \( \phi \) is not conserved locally, the evolution in time can be obtained by assuming that the dynamics is dissipative, such that,

\[
\frac{\tau}{\partial t} \left( \frac{\partial \phi}{\partial t}(\mathbf{r},t) \right) = \frac{\delta \mathcal{F}}{\delta \phi},
\]

where \( \tau \) is a time scale that determines the relaxation of the phase field to equilibrium and \( \delta / \delta \phi \) denotes the functional derivative with respect to \( \phi \).

The free energy functional used in this work was first postulated by Liu and Metiu [133] and has since been used to model the spiral growth of steps [134] and epitaxial growth [135, 136]:

\[
\mathcal{F}[\phi] = \int d^2 \mathbf{r} \left\{ \frac{W^2}{2} |\nabla \phi|^2 - \frac{1}{\pi} \cos (2\pi \phi) \right. \\
\left. + \lambda (u - u_{\text{eq}}) \left( \frac{1}{\pi} \sin (2\pi \phi) - 2\phi \right) \right\},
\]

where \( u = a^2 c \) is the dimensionless adatom density and \( a \) is the typical spacing between absorption sites, \( u_{\text{eq}} \) is the dimensionless equilibrium adatom concentration at a straight step, which we take as \( u_{\text{eq}} = \exp(-\beta E_s) \), where \( E_s \) is the energy difference between a free adatom and an atom found in a step, \( W \) is the width of the interface separating regions where \( \phi = 1 \) and \( \phi = 0 \), \( \lambda \) is a dimensionless coupling constant, and \( \beta = 1/(k_B T) \). The first and second terms on the right-hand side of Eq. (4.2.2) are the squared gradient and “bulk free energy”
contributions to the free energy mentioned above. The final term is an additional contribution that accounts for the presence of adatoms diffusing on the substrate. This term introduces a coupling between the phase field and the adatom density \( u(r, t) \), whose evolution in time is determined by a diffusion equation similar to Eq. (4.1.1) but with additional terms that take into account adatom attachment/detachment at island boundaries and the flux of adatoms onto the surface:

\[
\frac{\partial u(r, t)}{\partial t} = D \nabla^2 u(r, t) - \frac{\partial \phi(r, t)}{\partial t} + J,
\]

where \( J \) is the flux of adatoms per site onto the surface. The diffusion coefficient has the Arrhenius form, \( D = a^2 \nu \exp(-\beta E_D) \), where \( \nu \) is an attempt frequency \((\sim 10^{11} - 10^{13} \text{ s}^{-1})\), and \( E_D \) is the free energy barrier for hopping between nearest neighbour lattice sites. The dimensionless adatom density \( u \) is defined per site and we measure length in terms of \( a \). The equation of motion for the phase field is obtained from Eqs. (4.2.1) and (4.2.2):

\[
\tau \frac{\partial \phi(r, t)}{\partial t} = W^2 \nabla^2 \phi(r, t) - 2\sin(2\pi \phi) - 2\lambda (u(r, t) - u_{eq}^s) (\cos(2\pi \phi) - 1).
\]

The evolution of an island boundary, which might be regarded as the contour \( \phi = 0.5 \), is then determined by the solution of the two coupled partial differential equations (4.2.3) and (4.2.4). This system of phase-field equations corresponds to the “isothermal variational formulation” [137] in which the two phase-field equations are not derived from a single free energy functional. Rather, the second term in the right hand side of Eq. (4.2.3), which describes the loss/gain of adatoms by islands, is entirely phenomenological and justified by the thin interface analysis which we now briefly review.
4.2.2 Thin Interface Limit

The connection between the parameters appearing in the phase-field formulation and the BCF equations is provided by the thin interface analysis [137]. The full analysis will be presented in Appendix B, but, here we will give a brief summary of the method. Firstly, one defines $\phi^{in}$, $u^{in}$, $\phi^{out}$ and $u^{out}$ to be solutions to Eqs. (4.2.3) and (4.2.4) valid in an “inner region” in the vicinity of the interface, and an “outer region” far away from the interface. In the outer region $\phi^{out}$ is a constant whose value is determined by the minimum of the free energy functional and $u^{out}$ satisfies the ordinary diffusion equation with source, $J$, because the source/sink term, $-\partial \phi / \partial t$, in Eq. (4.2.3) is equal to zero. The equations that satisfy $\phi^{in}$ and $u^{in}$ are obtained by first transforming into a coordinate system local to the interface and making a Galilean transformation into a reference frame that moves with the velocity of the interface. Both $\phi^{in}$ and $u^{in}$ are then expressed as asymptotic expansions of the form

$$\phi^{in} = \phi^{in}_{0} + \varepsilon \phi^{in}_{1} + \varepsilon^2 \phi^{in}_{2} + O(\varepsilon^3),$$

where $\varepsilon = W/l$ is a small parameter that represents a scaled interface thickness and $l$ is a characteristic macroscopic length scale in the problem. Here this will be the average distance between islands but it will differ depending on the problem. For instance, in phase field formulations of step flow growth this quantity is the average distance between steps [133] on the substrate. These equations are solved order by order subject to matching conditions for the inner and outer solutions at the interface. In this way one recovers Eq. (4.1.2) to $O(\varepsilon)$ in the thin interface analysis. At $O(\varepsilon^2)$ an expression is obtained for the adatom density at the interface which, when compared with Eq. (4.1.3), provides relationships between the phase-field parameters and those appearing in the BCF equations. In the limit of instantaneous
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attachment of adatoms to island edges these are:

$$\tau = \frac{a_1 a_2 W}{w_{eq} \Gamma D},$$  \hspace{1cm} (4.2.6)

$$\lambda = \frac{a_1 W}{w_{eq} \Gamma},$$  \hspace{1cm} (4.2.7)

where $a_1$ and $a_2$ are numerical constants which depend on the form of the free energy functional. For $F$ given by Eq. (4.2.2), these have been calculated $[135]$ as $a_1 = 0.36$ and $a_2 = 0.56$.

4.2.3 Numerical solution of the phase field equations

The phase-field equations are solved on a square numerical grid. The main computational challenge is the large value of $D$ (in range $10^4 - 10^7 a^2 s^{-1}$) which makes explicit finite differences expensive. This is due to the well known stability criterion for explicit differencing of the diffusion equation $[119]$,

$$\frac{2D \Delta t}{\Delta x^2} \leq 1$$

where $\Delta x$ is the grid spacing and $\Delta t$ is the computational time step. This physically means that the maximum time step is proportional to the time it takes to diffuse across a length $\Delta x$.

As we are interested in length scales much greater than the grid spacing the number of time steps needed in a simulation is prohibitively large.

However, there are many ways to reduce the computing time for these types of calculations. Firstly, one can try to solve Eqs. (4.2.3) and (4.2.4) using semi-implicit methods, which are usually some combination of implicit methods combined with an operator splitting strategy to take into account any non-linear terms. Secondly, one can retain finite differences but try to formulate the problem in such a way as to make it parallelisable, for example, as is done in domain decomposition approaches $[136]$. We choose the former approach and implement the exponential time differencing method described in $[138]$. 

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This method is related to semi-implicit Fourier methods that have been widely used in finding numerical solutions to partial differential equations. These two methods describe a process in which the equations governing the time evolution of the quantity of interest are solved exactly after which the integrals of the non-linear terms are treated approximately [138]. The idea behind the exponential time differencing scheme is as follows.

Suppose we wish to solve the following partial differential equation subject to periodic boundary conditions,

$$\frac{\partial \phi}{\partial t} = B \nabla^2 \phi + g(\phi),$$  \hspace{1cm} (4.2.8)

where \( g(\phi) \) is a non-linear function of \( \phi \) and \( B \) is a constant. We proceed by Fourier transforming Eq. (4.2.8) and multiplying through by an integrating factor to obtain,

$$\frac{\partial}{\partial t} \left\{ \mathcal{F} \{ \phi \} e^{+Bk^2t} \right\} = e^{+Bk^2t} \mathcal{F} \{ g \},$$  \hspace{1cm} (4.2.9)

where \( k^2 = |k|^2 \) and \( \mathcal{F} \) denotes the Fourier transform. The formal solution of the problem is the integration of Eq. (4.2.9) subject to initial conditions. Numerical time-stepping schemes may be obtained by approximating the integral,

$$\int_0^t e^{Bk^2t'} \mathcal{F} \{ g \} \, dt'.$$

The results in the following sections were almost entirely obtained using a first order approximation which gives the following time stepping scheme:

$$\mathcal{F} \{ \phi(t + \Delta t) \} = e^{-Bk^2\Delta t} \mathcal{F} \{ \phi(t) \} + \frac{1}{k^2B} \left( 1 - e^{-Bk^2\Delta t} \right) \mathcal{F} \{ g \} \quad k \neq 0, $$

$$\mathcal{F} \{ \phi(t + \Delta t) \} = \mathcal{F} \{ \phi \} + \Delta t \mathcal{F} \{ g \} \quad k = 0.$$
CHAPTER 4. PHASE FIELD MODEL OF SUBMONOLAYER GROWTH

which retains a reasonably simple form and allows the solutions of the phase field equation to be propagated forward in time using a larger value of $\Delta t$ than would be possible with explicit integrators. In practice, Fourier transforms are performed using the fast Fourier transform (FFT) algorithm implemented using the FFTW library [139].

There are a number of different algorithms that could be utilised. Some belong to the class of spectral methods which include Fourier-Galerkin, collocation and pseudospectral methods [140]. Finally, one could also use implicit finite-difference methods such as the Crank-Nicholson scheme [119]. In this case any non-linear terms must be linearised about the solution at the current time step.

4.3 Nucleation

4.3.1 Nucleation rate

Dimers

Since the phase field equations do not take into account the nucleation of epitaxial islands, it is necessary to introduce this process into the framework separately. It is assumed here that nucleation events occurs when two atoms meet.

There are two ways to choose when a nucleation event occurs and in each case the spatial location of the seed will be determined randomly. Firstly, nucleation can be considered to be deterministic in time and based upon solving a rate equation:

$$\frac{dN}{dt} = \sigma_1 D \langle u(r,t) \rangle^2,$$

for the density of islands $N$ during irreversible aggregation, as was done in [1]. This rate equation is integrated at each time step and a nucleation event is said to occur whenever the quantity $NL^2$, where $L$ is the physical length of one of the sides of the square domain,
increases past the next integer value.

In Eq. (4.3.1), $\sigma_1$ is the adatom capture number which describes the sink strength of islands. We use the following analytical form [49, 141] for the capture number,

$$\sigma_1 = \frac{4\pi}{\ln[\alpha(u)(D/a^4J)]},$$

(4.3.2)

where the constant $\alpha$ is related to the radius $R_s$ of non-circular islands via the empirical power-law relation,

$$R_s \approx \alpha s^{1/d_f},$$

(4.3.3)

where $d_f$ is the fractal dimension of the island. For circular islands $d_f = 2$ and $\alpha = 1/\sqrt{\pi}$.

Alternatively, nucleation events can be treated as being stochastic in time. In this case at each time step we form the quantity $\sigma_1 D \langle u(r,t) \rangle^2 L^2$, which is the average rate of dimer production in the system. Assuming that nucleation events are Poisson-distributed means that the probability that a nucleation event occurs in a time $\Delta t$ is given by,

$$1 - \exp \left( -\sigma_1 D \langle u(r,t) \rangle^2 L^2 \Delta t \right),$$

(4.3.4)

which can be sampled from by comparing this value to a random variable uniformly distributed between 0 and 1. This is the same as demanding nucleation event occurs whenever $\Delta t^* < dt$, where $dt$ is the time step and $\Delta t^*$ is given by,

$$\Delta t^* = \frac{1}{\sigma_1 D \langle u(r,t) \rangle^2 L^2 \ln[Y]},$$

(4.3.5)

In this case we must check for a nucleation event at each integration step. The advantage of this is that the rate of nucleation itself is a function of time and as such varies as we step forward in time during the simulation. In the following we always consider nucleation to be
stochastic in time with $\alpha = 1$ in Eq. (4.3.2). The introduction of temporal fluctuations into the nucleation rate is not expected to have a large effect on our results [142]. For simplicity, we choose the time step $dt$ to be equal to the integration time-step.

**Critical cluster, $i^*$**

In models that explicitly include a critical cluster we assume that there exist clusters containing $i^* + 1$ atoms for which the probability of decaying (i.e. an adatom being able to detach from an edge site) is negligibly low [22]. Any clusters containing $i^*$ atoms or less are able to decay and their average density, $\langle u_i \rangle$, is usually assumed to follow from the Walton relation [143],

$$
\langle u_i \rangle \propto \langle u_1 \rangle^i e^{E_i/k_BT} \quad i < i^*,
$$

(4.3.6)

where $E_i$ is the binding energy of a cluster containing $i$ atoms [141]. We note that this equation embodies the assumption that small clusters are in equilibrium with adatom density. Since a nucleation events occur when a subcritical nucleus captures a diffusing adatom, the nucleation rate may be approximated by multiplying the density of subcritical nuclei by the rate of attachment of monomers to these nuclei, the latter term been given by $\sigma_{i^*+1}D\langle u_1 \rangle$. Putting this together we obtain the rate of nucleation of critical clusters,

$$
\sigma_{i^*}De^{E_{i^*}} \langle u_1 \rangle^{i^*+1}. \quad (4.3.7)
$$

An analysis of the functional form of the capture number of critical clusters has been undertaken by Evans et al. [144] within the framework of random walks on two-dimensional lattices. The expression obtained in [144] is the same as Eq. (4.3.2) but with $\alpha$ replaced with a different constant. We choose to keep this constant equal to unity since it will make only a small difference to the nucleation rate.
4.3.2 Location of the nucleating cluster

Methods for choosing the position of the nucleated dimer have been explored [142] using the level-set method. It was shown that the best agreement with the distribution of island sizes obtained from KMC simulations of irreversible aggregation in the precoalescence regime was found when the position of the nucleated dimer was chosen randomly and weighted by the local value of $u^2(r,t)$. This ensures that islands are more likely to nucleate in regions of high adatom density. In practice this is accomplished by treating the probability distribution as being proportional to $u^2(r,t)$. For critical clusters we modify this distribution by simply raising the adatom density to the appropriate power $i^* + 1$. In both cases the position of a nucleating cluster is then determined at random, specifically by implementing a simple rejection sampling method [119].

Once the position of the nucleated dimer, $r_{\text{nuc}}$, has been selected, it is necessary to increase the value of $\phi$ around the nucleation point, $r_{\text{nuc}}$. We do this by adding to the phase an isotropic distribution, $\tilde{\phi}$, that is centred about $r_{\text{nuc}}$. The function $\tilde{\phi}$ represents a new island composed of $i^* + 1$ atoms. We choose the following:

$$\tilde{\phi}(r; z) = \frac{1}{2} \left[ 1 - \tanh \left( \frac{r - z}{W} \right) \right], \quad (4.3.8)$$

where $r$ is the radial distance from $r_{\text{nuc}}$ and $z$ is the solution to the normalisation condition stating that exactly $i^* + 1$ atoms correspond to the distribution $\tilde{\phi}$:

$$2\pi \int_0^{\infty} r\tilde{\phi}(r; z) \, dr = \frac{1}{2} \pi \int_0^{-\exp(2z/W)} \frac{\ln(1-s)}{s} \, ds = i^* + 1. \quad (4.3.9)$$

The second integral in Eq. (4.3.9) is a representation of the dilogarithm function [145]. For $W = 1$ and $i^* = 1$ Eq. (4.3.9) is satisfied by $z = 0.27a$. Note that in the limit of $W \to 0$ the area of the surface taken up by a dimer would simply be $2a^2$ or a circular shaped island with
radius \( r = a\sqrt{2/\pi} \).

### 4.3.3 Removal of adatom density

To ensure that mass is conserved, we must simultaneously remove an amount of adatom density equal to that of the nucleated cluster. This may be accomplished in two ways, either locally about the nucleation centre or uniformly from the entire domain. In the first method, we add up the adatom density as we move from grid point to grid point beginning from the nucleation centre until we reach a value that is equal to the mass added to the system due to the nucleation event. We then set to zero the adatom density at all the grid points that we visit. In practice this means we end up cutting out approximately a square from the adatom density centred about \( r_{nuc} \).

In the second method we simply add up all the grid points for which islands are not present. These may be identified as those points for which the value of \( \phi \) less than some threshold value. We then divide the amount of mass that must be removed uniformly between the remaining grid points and take the appropriate amount from the adatom density. We note that this threshold value of \( \phi \) is somewhat arbitrary. When fixing this value we must take into account the value of the adatom density at these points. This is because at no point should the adatom density be allowed to become negative.

### 4.4 Outline of the algorithm

In the preceding sections we have provided details on each of the separate aspects of the method. Before moving on to discuss the results we shall give a brief summary of the implementation. The code is written in Fortran 90. Fourier transforms and linear algebra calculations are performed using the FFTW and LAPACK libraries, respectively.

Initially the user is required to input all of the parameters required for the simulation of a given regime. These include the following:
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- Grid spacing
- Numerical lengths of the square grid
- Total time of a simulation
- Temperature
- Diffusion barrier for monomers
- Step stiffness
- Energy required to incorporate an adatom into a straight step
- Flux
- Size of the critical nucleus,

as well as a number of other parameters which determine specifics of the codes functionality (e.g. whether nucleation is determined stochastically or deterministically). At this point all of the required parameters have been determined and the necessary matrices allocated. Finally, before the time loop begins the seed radius is calculated using Eq. (4.3.9) and the initial time for a nucleation event is determined.

Within the time loop four routines are utilised. Firstly, the nucleation rate is calculated. For this we need the average adatom density on the substrate which is simply an average sum over grid points for which the values of $\phi$ are less than some threshold value which we generally choose to be $\phi = 0.5$. We then check for a nucleation event in the current time step and if so call another routine which uses a simple rejection algorithm to determine a seed location and place an island on the surface, removing an amount of adatom density locally about the seed centre. Note, that when choosing where to nucleate an island a check is made to see if another island is present and if so choose another seed location. The final two routines solve the phase field equation using one of the algorithms described above and deposit an amount
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Figure 4.5.1: The morphologies of islands generated in two simulations representative of irreversible (left) \((E_s = 1.2 \text{ eV and } \gamma = 10^3 \text{ eV} \cdot \text{a}^{-1})\) and reversible growth (right) \((E_s = 0.7 \text{ eV and } \gamma = 0.5 \text{ eV} \cdot \text{a}^{-1})\). \(D/J \sim 10^5\) and the system size for both simulations was \(L_N = 512\). Both figures show contour plots obtained from the solution for \(\phi\) at a coverage \(\Theta = Jt = 0.1 \text{ ML}\). For reversible growth we observe a much lower density of islands compared to the irreversible case at the same coverage.

of adatoms uniformly on the surface. The latter mean-field like assumption has been shown to work well for submonolayer growth [142].

### 4.5 Results

Unless explicitly stated, Eqs. (4.2.3) and (4.2.4) are solved on a grid of numerical size \(L_N \times L_N = 512 \times 512\) and lengths are given in units of \(a\). We choose a grid spacing of \(\Delta x = 0.5a\), such that the physical length of one side of the square domain is \(L = \Delta x \times L_N = 256a\) and averages are obtained over 20-30 independent runs. We set \(J = 1 \text{ ML s}^{-1}\) and vary the diffusion constant. The width of the interface is chosen to be \(W = a\) and we have performed occasional spot checks in which we run a simulation with the same physical parameters but with a smaller interfacial widths to ensure the same results are obtained (confirming the thin interface limit has been reached).
4.5.1 Reversible and irreversible aggregation

In KMC simulations of submonolayer growth the degree of reversibility is often controlled by a microscopic energy barrier associated with the strength of the lateral bond between adatoms [22]. Such a parameter does not appear in the phase field formulation. However, we will demonstrate that by varying $\Gamma$ and $u_{eq}^s$ we obtain results that agree qualitatively with the crossover between irreversible and reversible growth. Since, during irreversible growth, adatoms are not able to detach from epitaxial islands, we will use this terminology if an island, once nucleated, cannot become smaller in size for the given set of phase field parameters. If the choice of phase field parameters allows islands to decay or evaporate entirely then the growth is termed reversible.

Initially, we simulate irreversible growth by choosing $u_{eq}^s \Gamma \sim 10^{-6} - 10^{-8}a$ such that $\tau \sim 1$. This choice is motivated by the simulations [134] in which convergence to the thin interface limit has been demonstrated. For this choice we obtain results that are consistent with irreversible growth, details of which are to be discussed below. In general by keeping $u_{eq}^s$ small, and choosing $\Gamma$ such that $u_{eq}^s \Gamma < 10^{-6}a$, no islands are able to evaporate, and we find results that are consistent with irreversible growth.

Choosing larger values of $u_{eq}^s \Gamma$ introduces the possibility that nucleated dimers are unstable and decay, depending on the density of adatoms at the interface. In this case we find that during the late stages of nucleation almost all nucleated dimers evaporate and are absorbed by existing islands, which leads to there being lower numbers of larger more regularly sized islands (Fig. 4.5.1). This observation is fully consistent with morphologies obtained from KMC and stochastic geometry simulation of reversible growth [144]. The effect of dimer break-up also manifests itself in the island density as a function of coverage $\Theta = Jt$, shown in Fig. 4.5.2. Here we notice that for the simulations which correspond to smaller values of $E_s$ and $\gamma$ the density of islands is much lower for all coverages than for the irreversible case.
Figure 4.5.2: The density of islands as a function of coverage obtained from phase-field simulations for reversible aggregation (red line), $E_s = 1.5$ eV and $\gamma = 10^4$ eV·a$^{-1}$ and for irreversible aggregation (black line) with $E_s = 2.5$ eV and $\gamma = 10^5$ eV·a$^{-1}$. In both cases $D/J \approx 6 \times 10^5$.

### 4.5.2 Island-size distributions

An important measure of the ability of our method to accurately describe the spatial arrangement of epitaxial islands is the distribution of island sizes. Islands grow by accreting mass from the ambient adatom population. The availability of adatoms is determined by neighbouring islands. Hence, any inaccuracy in the spatial arrangement of islands is reflected in the island-size distribution (ISD). The standard for such comparisons is based on KMC simulations, which capture all of the spatial correlations between islands and have been shown to quantitatively account for experimental measurements of island-size distributions. Data is plotted by using dimensionless scaled variables, which produce a data collapse for different growth conditions where the same mechanisms are operative [146, 46, 47].

Figure 4.5.3 shows typical island size distributions produced for different values of $u_{eq}^s \Gamma$ corresponding to reversible and irreversible growth. The symbols represent the results of our phase-field simulations, while the red lines are optimised analytic fits to KMC simulations [147]. We consider the irreversible case first. Although the simulations closely follow the optimised curve for $s/s_{av} \gtrsim 0.6$, there are appreciable and systematic deviations for smaller
Figure 4.5.3: Island size distributions for (a) irreversible and (b) reversible aggregation at 950 K (circles), 1000 K (squares) and for the simulations in which flux was varied corresponding to $J = 0.4$ ML and $T = 975K$ (triangles). Here, $N_s$ is the number of islands containing $s$ atoms and $s_{av}$ is the average number of atoms in an island. Squares represent the initial simulation of irreversible aggregation for $u_{eq} \Gamma \sim 10^{-6} - 10^{-8}$ such that $\tau \sim 1$ (see text). All symbols represent an average over 20-30 runs and are sampled at a coverage $\theta = 0.1$ ML. The values of the parameters for reversible aggregation are $E_s = 0.7$ eV and $\gamma = 0.5$ eV $a^{-1}$ (circles and squares) and $E_s = 0.8$ eV and $\gamma = 0.3$ eV $a^{-1}$ (triangles) and for irreversible aggregation $E_s = 1.2$ eV and $\gamma = 10^3$ eV $a^{-1}$. Red curves are fits [147] to KMC simulations for critical island sizes of one and two adatoms in (a) and (b), respectively.
values of $s/s_{av}$ which are manifested as a shoulder. Similar observations have been made for level-set calculations [142] of irreversible aggregation. In fact, the same behaviour is seen in rate equations and KMC simulations of “point” islands, that is, islands with no spatial extent, but which can still accumulate migrating adatoms in proportion to their size [46]. This suggests that the shoulder seen here and in level-set simulations is due to the breakdown of our mean-field-like nucleation rule for the positions of new islands. An examination of the left panel in Fig. 4.5.1 does indeed reveal many small closely-spaced islands. The growth rate of each island is diminished by the proximity of neighbouring islands, resulting in an over-estimate of the numbers of small islands.

The main effect of reversibility is to narrow the ISD. Notice also that the shoulder for small island sizes for irreversible growth has disappeared. Both effects are due to the fact that the system can “correct” inefficient nucleation sites by eliminating them by accretion to a neighbouring larger island. Thus, there are fewer islands than in the irreversible case for the same coverage and more uniform distribution of size and spatial arrangement. The surface morphology in the right panel in Fig. 4.5.1 confirms these observations. We note that there is no change in the phase-field simulation in obtaining these ISDs, rather, they are determined solely by the initial values of $\gamma$ and $E_s$. This is to be contrasted with KMC simulations, where the increased number of diffusional hops per unit time leads to substantially greater computational overhead, while in the level-set simulations a somewhat ad-hoc procedure must be adopted [127]. In the case of nucleation with a critical nucleus we also find good agreement for the case of $i^* = 2$ and we recognise the characteristic narrowing of the ISD discussed above (Fig. 4.5.5).
Figure 4.5.4: Log-log plot of the island density as a function of $D/J$ for three sets of parameters representing irreversible aggregation (black squares), reversible aggregation varying temperature (red open circles) and reversible aggregation varying flux (blue open circles). The dashed lines are lines of best fit and the magnitude of the gradients give values for the exponent $\chi$ in Eq. (4.5.1): $\chi = 0.32$ (black line), $\chi = 0.79$ (red line) and $\chi = 0.54$ (blue line). The values of the parameters for reversible aggregation are $E_s = 0.8$ eV and $\gamma = 0.3$ eV $a^{-1}$ and for irreversible aggregation $E_s = 2.6$ eV and $\gamma = 10^6$ eV $a^{-1}$. The error bars are of the order of the symbol size or smaller.
4.5.3 Scaling of the Island Density

In the precoalescence regime the island density, $N$, is known \cite{44} to scale as a power law with $D/J$ (Appendix C),

$$N \propto \theta^{1/3} \left( \frac{D}{J} \right)^{-\chi} e^{-\beta E_{i^*}/(i^*+2)},$$  \hspace{1cm} (4.5.1)

where the value of $\chi$ depends on the degree of reversibility. For irreversible aggregation a simple rate equation analysis results in $\chi = \frac{1}{3}$ where $i^*$ is effectively zero and $E_{i^*=0}$ is defined to be zero while for reversible aggregation $\chi = i^*/(i^*+2)$ and $E_{i^*>1}$ is non-zero. KMC simulations without a critical nucleus produce results that are in good agreement with Eq. (4.5.1) \cite{22}. The phase field simulations give results which describe such observations reasonably well. For irreversible aggregation we obtain $\chi = 0.32$, which is in very good agreement with the rate-equation result. For simulations consistent with reversible aggregation we see that the value of $\chi$ increases, in agreement with observations made using KMC simulations (Fig. 4.5.3). However, we note that the value of $\chi$ for the simulation of reversible growth shown in Figure 4.5.3 seems somewhat high. This seems to be characteristic of the phase field simulations of reversible growth. To some extent this can be rationalised by the presence of $E_{i^*}$ in Eq. (4.5.1). This is because if we vary $D$ by changing the temperature of the substrate then the effect of increasing $E_{i^*}$ is to increase the value of $\chi$. This can be seen by taking logarithms of Eq. (4.5.1) to obtain,

$$\ln (N) \sim \frac{-i^*}{i^*+2} \ln \frac{D}{J} + \frac{\beta E_{i^*}}{(i^*+2)},$$  \hspace{1cm} (4.5.2)

and using $D/J = \nu e^{-\beta E_D}/J$ to rewrite $\beta^{-1}$ as $E_D/\ln (\nu/D)$. Substitution of this expression into Eq. (4.5.2) gives,

$$\ln (N) \sim \frac{-i^*}{i^*+2} \ln \frac{D}{J} - \frac{1}{i^*+2} E_D \ln \left( \frac{D}{J} \right) - \frac{1}{(i^*+2)} E_D \ln \left( \frac{J}{\nu} \right),$$  

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from which we may obtain,

\[ \chi = \frac{i^*}{i^* + 2} + \frac{1}{i^* + 2} \frac{E_{i^*}}{E_D}. \]

Thus, the phase field simulations are in reasonable qualitative agreement with conventional simulation methods of reversible aggregation for large values of \( E_{i^*} \). To isolate the effect of temperature on the island scaling we perform a set of simulations for the phase field parameters corresponding to reversible growth reported in Fig. (4.5.3) at constant temperature but varying the flux over an order of magnitude. This results in a value \( \chi \sim 0.54 \) which smaller than that reported for the simulations in which temperature was varied and in line with typical values obtained from KMC simulations [148], which ranged between \( \sim 0.5 \) and 0.65.

Summarising, for irreversible aggregation the results agree quantitatively with rate equations as well as KMC and level-set simulations. Furthermore, the results for the irreversible case are much improved over a previous phase-field study [136], where \( \chi \) was overestimated by a factor of two. Interestingly, we obtain very good agreement for the simulations of reversible aggregation with a critical nucleus (Fig. 4.5.6). In this case if we choose \( i^* = 2 \) and set \( E_2 = 0 \) we obtain a value of \( \chi = 0.56 \) which agrees reasonably well with the rate equation results \( \chi = \frac{1}{2} \). We note due that it will be a subject of further work to increase the range of value of \( D/J \) for which \( \chi \) is calculated. We expect this to be a lengthy exercise in increasing the efficiency of solving the phase field equations. This could be by performing simulations on a variable grid or by exploring integrators that are higher order in time. It may also be possible to parallelise the simulations by utilising methods such as domain decomposition.

4.5.4 Capillary Length and Reversibility

We now propose the following qualitative explanation for the effects of varying \( \Gamma \). The capillary length controls the extent to which curvature effects play a role in the growth and decay of nucleated islands. For values of \( \Gamma \) which are very small compared to the radius of curvature
of islands, capillary effects have very little influence and islands grow at a rate proportional to the supersaturation of the adatom density. However, for larger values of $\Gamma$ capillary effects become important and islands below a certain critical radius will decay unless the surrounding adatom density is sufficiently high (so that detachment from island boundaries is balanced by attachment).

The effect of $u_{eq}$ can be explained by looking at the issue of reversibility in relation to the boundary conditions applied to the BCF equations solved by (4.2.3) and (4.2.4). These points are discussed in more detail by Petersen et al. [127] in their study of the reversibility in level-set simulations, but we repeat the main elements of this argument here. The crucial observation is that, if growth is irreversible, island boundaries act as perfect sinks and the diffusion equation is solved subject to the boundary condition,

$$u_i = 0,$$  \hspace{1cm} (4.5.3)

where $u_i$ is the value of the adatom density at the interface. If adatoms can detach from island boundaries, this condition is changed to,

$$u_i = u_{eq}(R),$$  \hspace{1cm} (4.5.4)

where $u_{eq}(R)$ is the equilibrium adatom density for an island of radius $R$. For large circular islands this will be given by the Gibbs–Thomson relation (4.1.3), which is satisfied by the phase-field equations in the thin interface limit where the width of an island interface remains smaller than other characteristic macroscopic length scales in a problem [149], in this case the average separation between islands growing on the surface. This highlights two features of our model. Firstly, the assumption that the linearised Gibbs–Thomson equation holds for islands containing as few as 2-3 atoms. This approximation clearly captures some of the curvature effect necessary to produce the crossover between irreversible and reversible growth.
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Figure 4.5.5: Island size distribution obtained from the phase field simulations for nucleation with a critical nucleus of two atoms.

demonstrated above. However, the obtained large values of $\chi$ could be in part due to the breakdown of this assumption for smaller islands. Secondly, for irreversible aggregation the phase-field equations do not reproduce exactly the boundary condition (4.5.3). However, for $u_{eq}^{\delta} \Gamma \ll 10^{-6} a$, we have demonstrated agreement with previous models of irreversible aggregation and so conclude that errors resulting from the perfect sink boundary condition represented by Eq. (4.5.3) are negligible.

4.6 Summary and Conclusions

We have described a method of simulating submonolayer epitaxial growth by utilising the phase field as a front tracking tool to solve the modified BCF equations in the presence of island
Figure 4.5.6: Log-log plot of the island density with $D/J$ for nucleation with a critical nucleus of two atoms. The exponent obtained is $\chi = 0.56$.

nucleation. Our results are an improvement on previous phase-field studies [136, 135] and we have verified and extended some of their observations. In particular, we find that variation of both the capillary length, $\Gamma$, and the equilibrium concentration of adatoms, $u_{eq}^s$, provides a unified framework for producing results that are consistent with both irreversible and reversible aggregations. The main advantage of the method over level-set simulations is that there is no change in algorithm needed to simulate these cases. Furthermore, compared with KMC simulations there is no appreciable increase in the computational overhead required to account for reversible growth. However, the discrepancy we found in the scaling of the island density with $D/J$ especially for the case of varying temperature in comparison with that reported in KMC simulations of reversible growth necessitates further investigations into the connection between microscopic parameters such as the lateral bond strength between adatoms and the macroscopic parameters $u_{eq}^s$ and $\gamma$.

The model we have used is the most basic for describing epitaxial growth, where a single monatomic species is deposited onto a surface, which then diffuses isotropically on that surface until incorporation into a freshly nucleated island or capture by an existing island. While this
model has been used to great effect in understanding a wide range of epitaxial phenomena, there are many scenarios that require additional processes to be considered, including evaporation, mobile dimers or small clusters, and mobile islands. Each of these processes can be readily incorporated into the phase-field formulation presented in Sec. 4.2.

An altogether different approach is required for modelling strain effects during epitaxy, which necessitates substantial modification [150] to the basic formulation of Sec. 4.2. There are many experiments that exploit elastic effects for the formation of epitaxial nanostructures [151] and the advantages afforded by the phase-field method should enable the simulation of such nanostructures under realistic experimental conditions over extended time scales.
Chapter 5

A phase field model of epitaxial graphene on Cu

Rob Roy

“2 oz scotch; 1 oz sweet vermouth; 2 dashes Bitters. Stir with ice and strain into chilled coupé. Express lemon oil over drink and garnish with lemon peel twist.” - Albert S Crockett

Experimental observations of the Arrhenius plot of graphene island density during CVD growth on copper indicate two different growth processes being operational between 1000 – 1300 K. In this chapter we employ a phase field model of submonolayer epitaxial growth to explore the growth of graphene flakes on polycrystalline copper under conditions representative of those in [71] to investigate whether a model of submonolayer growth including desorption can reproduce the Arrhenius plot, cumulative island size distribution and Arrhenius plots of the graphene growth rate reported in [71]. We find that while including desorption does predict an Arrhenius plot of island density in broad agreement with the experimental observations, the same agreement cannot be found for the growth rate. By introducing detachment, included phenomenologically in the phase field simulations, we find qualitative agreement with the island density and growth rate. The agreement with a basic model for growth by monomer attachment/detachment provides further evidence for such growth processes being dominant on polycrystalline copper surface under experimental conditions described in [71].
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The substrates that we have considered so far have all been comprised of a single crystal face. However, as was discussed in Sec. (1.3), much experimental progress has been made on polycrystalline copper surfaces [4]. Samples of graphene flakes are regularly reported as being of the orders of millimetres in size [152] with some groups managing to grow samples as large as one metre [153]. These constitute the largest samples grown using epitaxial techniques and this, as well as the low-costs associated with the method, have lead to CVD growth of graphene on polycrystalline copper being the most widely used technique for the synthesis of monolayer graphene [152].

What influence does the polycrystalline nature of the substrate have on graphene growth compared to that on substrates comprised of a single crystal face? Firstly, if nucleation is heterogenous grain boundaries in the copper foil must be considered as possible locations of nucleation sites [59]. Secondly, we must consider how the graphene growth front moves over substrate grain boundaries. The affinity between carbon on the copper substrate is apparently very weak [59] and as such graphene grains have been observed readily growing over grain boundaries in the substrate. However, it would not be correct to entirely neglect the polycrystallanity of the copper substrate. The concentration and distribution of substrate grains have been shown to influence the growth and in turn the quality of the graphene [154, 7].

The conditions of growth also have a great impact on the sizes and shapes of graphene flakes. Indeed, much effort has also been directed into understanding the effect of growth parameters and of the tuning of these to produce samples of graphene with optimal properties [155, 152].

The role of intermediary species during graphene growth on Ir(111) and Ru(0001) was discussed in Chapter 2. Recall, that the experiments [24, 25] demonstrate the importance of clusters containing more than one or two carbon atoms in the growth process. Such species complicate theoretical analysis since they necessarily add complexity to the description of the system, for instance by increasing the number of rate equations or the length of an events list.
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in a KMC simulation. However, such nucleation and growth processes are not universal to all transition metal surfaces and growth conditions. In fact, on polycrystalline Cu surfaces there is increasing experimental evidence that elementary theories of nucleation and growth (i.e. where only diffusion of monomer species is considered) are detailed enough to describe much of the initial stages of growth.

In the following, we consider a work in which such a conclusion was reached based on experimental observations rationalised using a number of theoretical techniques including rate equations and the Johnson-Mehl-Avrami-Kolmogorov (JMAK) model [156] of coarsening. Though the conclusions made in that work were compelling, it is clearly advantageous to model such a system within a single theoretical framework. Agreement with the observations made in [71] would constitute another strand of evidence for monomer nucleation and growth processes to be active on polycrystalline copper under the experimental conditions described in [71]. The phase field method described in the previous chapter is well suited for modeling this system as it is based on the assumption that nucleation and growth proceeds via processes mediated by monomers.

The following chapter will be ordered as follows. In Sec. 5.1 we will give a brief description of the experimental procedure. We will then briefly describe how we include desorption in the phase field method described in Chap. 4 since this is expected to be an important process at the temperatures at which growth takes place (>1000 K). Finally, we will discuss the results and provide our conclusions in Sec. 5.3.

■ 5.1 Review of experimental procedure

We are primarily interested in the subset of experiments in [71] referred to by the authors as “flash deposition”. In a typical experiment, after the surface has undergone a number of preparatory procedures, it is heated to a high temperature (>1000 K) and a high concentration of gaseous methane molecules is then introduced into the vessel. The flow is maintained
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Figure 5.1.1: Morphologies obtained using STM from the flash deposition experiments reported in [71]. The temperatures of the surface are 993 K, 1073 K, 1173 K and 1273 K (increasing from left to right). Reproduced with kind permission from [71].

for a short period of time (~1 s) before being shut off. Once growth has finished the final morphologies are observed using a combination of SEM, STM and AFM. No in-situ measurements were made. However, the island density, island size distributions and growth rates, as well as other quantities were obtained for a number of different temperatures while all other experimental conditions were maintained.

5.2 A phase field model for submonolayer growth

In the phase field simulations described in Chap. 4 desorption was not included. As discussed, this approximation is justified at low temperatures (or high energy barriers for desorption) when the probability of an adatom desorbing from the surface is negligibly low. However, at higher temperatures such as in the experiments on copper [157] and if the barriers for desorption are relatively low it must be included.

We recall that deposition in the phase field model is treated as being uniform in both space and time. This allows for us to account for desorption using a mean-field ansatz by replacing the flux, $J$ with an effective flux,

$$ J' = J - \frac{\langle u(x,t) \rangle}{\tau_{De}} $$

(5.2.1)

where $\tau_{De}$ is the inverse of the adatom desorption rate appearing in Eq. (5.3.1) and $\langle \rangle$ denotes
the spatial average. We assume that $\tau_{De}$ is of Arrhenius form,

$$\tau_{De}^{-1} = \nu \exp (-\beta E_{De})$$

where $E_{De}$ is the free-energy barrier associated with desorption of an adatom from the surface and we have disregarded any coverage dependence. The experimental verification of this form of the desorption rate is well documented [141].

In Chap. 4 we discussed some of the complications associated with the temperature dependence of parameters in the phase field model and their relation to the microscopic processes responsible for particularly the dimer dissociation rate. We argued there that the phase field model is able to obtain the qualitative effect of reversibility while in the limit of irreversible aggregation we found quantitative agreement. Thus, in interpreting results obtained using the method in the former regime we must keep in mind that the trends obtained can only be interpreted qualitatively. However, for our purposes this is enough.

The choice of desorption rate is motivated by the rate equation modeling of [158] in which good qualitative agreement is found with experiments using the desorption rate of the form shown in Eq. (5.2.1). It should be noted that it may be possible to improve on this spatially independent desorption rate described above by allowing the rate to become dependent on the local adatom density. This of course must be a more accurate description of the desorption process. However, for different atomic processes, for example deposition, we have seen that good agreement is found for the evolution of adatom density and island density in level-set and phase field simulation when such a mean-field ansatz is used [142]. Furthermore, because we are describing experiments occurring at high temperatures (> 1000 K) where the rate of hopping is high it is likely that the density of atoms is relatively uniform and as such the form of the desorption rate used above may possibly be justified. However, the use of the spatially average desorption rate is clearly in need of further investigation which is to be left to further work.
5.3 Results

We model flash deposition by choosing a large value of $J$ and depositing for a short amount of time. Specifically, we deposit 1 ML onto the surface over a period of 10 $\mu$s. The adatoms on copper surfaces are expected to be very mobile, with energy barriers for hopping being quoted as low as $E_D = 0.05 - 0.1$ eV [71]. At the temperatures at which the experiments take place this corresponds to a diffusion constant, $D \sim 10^{11} a^2 s^{-1}$ which means that it would be simply too computationally expensive for our phase field method. Thus, we use an artificially high barrier, $E_D \sim 1.5$ eV, with the aim of reproducing qualitatively the trends observed experimentally.

We perform two sets of simulations. The first one will correspond to growth in the irreversible aggregation and as such we choose the phase field parameters $G$ and $u_{eq}$ such that their product is small so as to effectively eliminate the effects of curvature in the Gibbs-Thomson boundary condition Eq. (4.1.3). In the second set we increase the values of these phase field parameters so as to allow the dissolution of smaller islands and alter the boundary conditions at island interfaces to those corresponding to irreversible aggregation (Sec. 4.1.1).

5.3.1 Island density

Review of rate equation analysis

In [71] the authors noted that the Arrhenius plot of island density may be explained using rate equations with desorption included. It is quite simple to write down such a set of rate equations. An analysis of this type was first performed by Robinson et al. [158] who wrote down a set of equations that in our notations read:

$$\frac{dn}{dt} = F - 2Dn^2 - DnN - \tau_D n,$$

(5.3.1)
Figure 5.3.1: Log plot of the island density as a function of inverse temperature obtained from rate equations of the form given in [158].

\[
\frac{dN}{dt} = Dn^2, \tag{5.3.2}
\]

which we recognise as describing the simplest case of irreversible aggregation but where the last term takes into the account the possibility of an adatom desorbing from the surface. Here \(\tau_D\) is the inverse of the adatom desorption rate and we recall that \(N = \sum_{s>1} n_s\), i.e. \(N\) is the density of stable islands with \(n_s\) denoting the density of clusters of \(s\) atoms.

For completeness, we solve Eq. (5.3.1) - (5.3.2) numerically choosing conditions that are representative of the flash-deposition experiments over a temperature range 1100-1300K. Figure 5.3.1 reproduces correctly the experimentally observed Arrhenius plot of island density [71]. We recognise the two distinct regions which is indicative of two different processes being dominant in regions identified by the temperature of the substrate. In this case, the rate of desorption at lower temperatures is initially negligible but, as temperature is increased its effect becomes observable in the reduction in the island density compared to its value if there were no desorption.
Phase field observations

We can see in the set of phase-field simulations representing reversible growth (Fig. 5.3.2 (a)) that the observed Arrhenius diagram is qualitatively very similar to the rate equation results (Fig. 5.3.1) and that observed in experiments (Fig. 5.3.2 (b)). However, as expected, these features of the experimental observations are not dependent on whether the growth occurs in the irreversible or reversible regime: the same features are seen for both sets of simulations. This is simply because in both regimes the desorption of adatoms from the surface of the substrate increases with temperature which reduces the nucleation rate and in turn the island density.

5.3.2 Growth rate

Although, the qualitative features of the Arrhenius plots of the island density for reversible and irreversible growth regimes are both in agreement with those obtained experimentally, the same cannot be said of the growth rate. To explore the growth rate as a function of temperature we measure the average area of islands in phase field simulations as a function of time for different temperatures. For reversible simulations we find an Arrhenius relationship, the same as was observed experimentally. However, no such trend is obtained for the fully irreversible growth. This is likely because during irreversible growth at each temperature after the initial burst of nucleation the adatom density left available for growth of islands is small. However, in reversible growth increasing temperature in turn increases the rate of dissolution of smaller islands and provides a source of adatoms to be incorporated into larger more stable islands.

5.3.3 Morphology and cumulative island size distributions

The cumulative size distributions (CDFs) obtained experimentally can be seen to narrow with decreasing temperature and as can be seen from Figure 5.3.5 this behaviour is reproduced
Figure 5.3.2: Log plot of the density of islands as a function of inverse temperature as obtained from (a) the phase field simulations in the temperature range 1050-1300 K compared to the same quantities obtained experimentally [71] (b). Here we use $E_D = 1.5$ eV, $E_{De} = 1.8$ eV, $E_N = 1.0$ eV and $\gamma = 1$ eV $a^{-1}$. 
Figure 5.3.3: Log plot of the growth rate of islands as a function of inverse temperature as obtained (a) the experiments of [71] and (b) from the phase field simulations in the temperature range 1050K-1300K. Here we use $E_D = 1.5$ eV, $E_{De} = 1.8$ eV, $E_N = 1.0$ eV and $\gamma = 1$ eV $a^{-1}$. 
Figure 5.3.4: Some examples of morphologies of epitaxial islands obtained from the phase field simulations for different temperatures: 1300 K (top), 1250 K (middle), 1150K (bottom). Here we use $E_D = 1.5 \text{ eV}$, $E_{De} = 1.8 \text{ eV}$, $E_N = 1.0 \text{ eV}$ and $\gamma = 1 \text{ eV } a^{-1}$. 
reasonably well by the phase field simulations. What inferences can be drawn from this? As temperature is increased in the phase field simulations we have seen that the rate of detachment from islands is increased. This increased rate of detachment from islands leads to a larger concentration of adatoms available for the growth of islands and, given the high temperatures, adatoms are able to easily diffuse across the surface and attach to islands. This can be seen in Figure 5.3.4 by the visibly lower concentration of larger islands. Smaller islands are still present at all temperatures but these are in the latter stages of evaporating and at later times will almost certainly have been fully incorporated into larger islands. We recall that the phase field simulations have a tendency to exaggerate this increase in the detachment rate. In this monomer picture of nucleation and growth lower temperatures cause the island density to decrease for two reasons. Firstly, the lower mobility of adatoms reduces the likelihood of them attaching to existing islands and secondly the rate of dissolution of existing smaller islands decreases.

5.4 Summary and Conclusions

In this chapter we have described a set of phase field simulations to examine qualitatively growth of graphene grown using the flash deposition method described in [71]. The phase field model is valid for nucleation and growth mediated by adatom processes, e.g. nucleation by the collision of two adatoms, the attachment of an adatom to an island, etc. The most severe approximation in such a model is most likely the use of the mean field diffusion equation in the flash deposition regime where the concentration on the substrate surface becomes relatively high. However, it is likely that the depletion of the monomer density due to the small transient nucleation regime sufficiently decreases the adatom population to small enough concentrations to make the assumption justifiable.

We have observed that such a model for submonolayer epitaxial growth in the reversible regime including the desorption of carbon monomers from the substrate surface is sufficient to
Figure 5.3.5: Cumulative distribution functions obtained from the phase field simulations at three different temperatures: 1050K (dashed line), 1100K (dotted line) and 1150K (dot-dashed line). Here we use $E_D = 1.5$ eV, $E_{De} = 1.8$ eV, $E_N = 1.0$ eV and $\gamma = 1$ eV $a^{-1}$. 


reproduce many of the experimental observations reported in [71]. These include the Arrhenius plots of graphene island density and the rate of island growth as well as a characteristic narrowing of the CDF with decreasing temperature. It was found that agreement with the Arrhenius plot of the growth rate may only be obtained in a model that included reversible attachment of monomers at island edges. This is in agreement with the conclusions of [71] where it was reported that a rate-limiting step is the attachment of carbon atoms to the graphene edge. In our model such a process must be interpreted with the framework of a continuum theory and therefore represents the average rate of attachment taking into account possible detachment events from the growth front at the same time. At such high temperature it is hardly surprising that one must consider a reversible model.

Recently it has been suggested that dimer diffusion plays an important role in the nucleation and growth of graphene on copper (111) and (100) surfaces [100]. These finding are based on DFT as well kinetic studies of dimer formation and attachment to graphene islands. Furthermore, the nucleation of graphene on copper has been reported to begin heterogeneously at defect sites on the polycrystalline substrate. However, despite this it remains interesting that such a simple model is capable of reproducing a number of the experimental observations.

We now discuss briefly ways in which we can reconcile the qualitative agreement of these results based on a simple model with the observations of more complex growth processes reported in [100]. Firstly, we note the importance of the KMC rate prefactors for dimer formation and dissociation as discussed in Chapter 3. This is of some importance because in [100] the prefactors for the rates of the dimer formation and dissociation are both chosen to be constants of the order of $10^{13}$ s$^{-1}$. Since neither of the energy barriers for these processes were large enough to be rate limiting it is of some importance to obtain an accurate calculation of the prefactor and in turn rates of the process to be input into kinetic models.

It is also possible that the presence of dimer diffusion can also account for the experimental observations reported in [71] either with/without simultaneous adatom processes. The inclu-
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sion of dimers in a model of growth processes becomes relevant when their diffusion coefficient becomes of a similar size or larger to that of adatoms and when the rate of dimer dissociation is such that the dimer is likely to diffuse and meet an atom or cluster before falling apart [159]. On graphene DFT calculations of dimer hopping has shown that this is indeed possible [100]. The effect of introducing island mobility in simulations of epitaxial growth have been investigated by [160, 161, 162, 159]. Here it is found that the introduction qualitatively changes scaling relations that are found in the case of immobile islands. For instance, though qualitatively the scaling of the island density, \( N \) with \( D/J \) is found to remain the same the growth exponent \( \chi \) (Eq. 4.5.1) is found to decrease from approximately \( \frac{1}{3} \) to \( \frac{2}{5} \). A demonstration of the crossover between growth dominated by monomer diffusion to that modified by dimer diffusion may be found in the KMC simulations of [159] and [163]. While the former concentrates on the scaling of island density with temperature in systems where dimer diffusion is active the latter contains an examination of changes to the island size distribution as well as a derivation of relations which parameterise the crossover.

We note also that conflicting reports exist for the energetic favourability of the attachment of monomer and dimer species to the growth front and as such further studies are required to settle the issue.
Conclusions

In this final chapter we will take some time to recall and summarise the results that we have obtained in this thesis as well as discussing our contributions we also discuss some of the outstanding questions that demand further investigation.

Throughout this thesis we have highlighted how the high temperature and low flux conditions for which graphene growth occurs create difficulties for those wishing to study the kinetics of growth processes. We recall that this is largely due to the computational challenges of applying the most suitable tool to study these systems, namely KMC, under such growth conditions. Such difficulties in using more detailed techniques of describing kinetic processes necessitates the use of much more basic tools, such as rate equations and phase field theory, which describe only approximately the state of the system in time. Despite their simplicity we have demonstrated the ability of rate equation models to shed much light on the growth processes. To this end we have discussed two applications of rate equations used to study firstly the early stages of graphene nucleation from multi-atomic clusters and secondly the dehydrogenation sequence of ethylene on the Ir(111) surface. We will begin this concluding chapter by summarising each of the studies in turn. We will then move on to summarise the phase-field simulations of submonolayer growth developed in Chapter 4. As discussed the
method is to be considered an addition to the “island-dynamics” methods introduced in [1] but includes the effect of reversibility differently to that discussed in [127]. Finally, we will finish this conclusion with a short summary of the current state of research into the epitaxial growth of graphene.

The work [24, 25] as well as the unpublished LEEM images found in [2] provided a surfeit of information ripe for theoretical analysis. The results of Zangwill and Vvedensky were compelling but ultimately incomplete given the poor predictions for the island density as a function of temperature. In Chapter 2 we completed the theoretical analysis of the experiments on Ir(111) and Ru(0001) by modifying the rate theory such that it accounted for the exponential decrease of graphene islands with temperature. To this end we developed a simple method for the calculation of the gradients required to optimise the parameters appearing in rate theories which found applications elsewhere in this thesis.

Interestingly, we were able to find better agreement with experiment not by altering the form of the rate equations proposed in [26], but by allowing the rate of graphene nucleation to become independent of the rate of attachment of five atom clusters to islands, the latter assumed to be diffusion limited. Given that it is likely that nucleation of graphene on iridium is heterogenous [13] it is not at all surprising that the two rates would differ.

To date, by far the most extensive ab-initio study of the kinetics of graphene growth is the study conducted by Wu et al. [13] which provided evidence of the importance of 5-atom clusters in the attachment to the graphene edge and of the iridium step edges in the nucleation of graphene. However, still no consensus for the exact nucleation pathway has been reached and further microscopic studies will be necessary to fully understand the role of clusters, if any, in the nucleation of graphene.

Until recently the role of the precursor in the initial stages of graphene growth, especially on Ir(111), had received little attention. Furthermore, relatively few of those studies considered the kinetic aspects of the growth, nor the role of the prefactor in determining the route
through various dehydrogenation pathways. On the other hand the solitary study that did consider kinetics [102] seemed to have success in obtaining a sequence of reaction products which agreed with experimental observations of the dehydrogenation sequence of ethylene on Pt(111). In Chapter 3 we performed a study similar in spirit to [102] but instead considered the relatively less well studied substrate Ir(111), over a larger temperature range and for a much larger set of possible reactions. Due to the higher temperatures considered in this study we implemented simple rate equations to examine the change in concentration of species as a function of coverage/temperature rather than KMC simulations. We also compared the solutions to such sets of rate equations to KMC results to investigate whether the use of the less accurate method adversely affected our results. In the case of ethylene decomposition on Pt(111) we found that this was not the case which motivated the use for the more complicated reaction pathway on iridium.

The main results of the various analyses discussed in Chapter 3 are a reinterpretation of the dehydrogenation sequences reported in [81]. Specifically, CCH$_2$, CHCH and CH were identified for the first time as being the most abundant species in the temperature range 100 - 600 K during TPG growth on Ir(111) with an ethylene precursor. An important step in this sequence was the splitting of the carbon bond which turns out to be energetically favourable for the CHCH molecule. This makes it likely that carbon monomers are present on the surface at temperatures at which graphene is observed to nucleate, although the change in XPS spectra at temperatures approaching 550 - 700 K (Fig. 3.6.1) indicate the presence of large carbon species that are active on the surface.

The species obtained by the solving a system of rate equations agreed with many of the experimental observations except for the species present at approximately 300 K. While experimental observations strongly suggested the presence of CHCH, rate equations parameterised by \textit{ab-initio} rates with a subset of prefactors calculated within the framework of HTST predict CCH$_3$ as being the most populous species. Possible reasons for the discrepancy could be the
CHAPTER 6. CONCLUSIONS

effect that diffusion of hydrogen or carbon species have on the rates of bimolecular reactions. Other possibilities include coverage effects that are not captured in the theoretical calculation of the prefactor or indeed the failure of the HTST for this system at these temperatures. This latter possibility is discussed in [115, 124] where deviations between prefactors obtained using ab-initio methods similar to those used in our study and those obtained experimentally exist for similar substrates and reactions. To entirely eliminate the first of these possibilities would require a KMC study using the rates already calculated as well as additional processes that may have to be taken into account (e.g. the diffusion of hydrocarbon species).

We have discussed already the ways in which a rate equation description of submonolayer growth can fail, and furthermore, there is a wealth of literature in which these issues are examined [22, 148, 44]. The phase field methods presented in Chapter 4 are an addition to the class of methods referred to as “island dynamics” models developed primarily using level-set implementation by Ratsch and coworkers [1, 142]. These methods offer a significant speed up of simulations of submonolayer growth, particularly in the reversible regime where KMC simulations become significantly more computationally expensive.

The benefits of the phase-field of front tracking in this context are primarily their ability to capture the change in boundary conditions applied at island edges in the irreversible and reversible regime by the variation of two free parameters, namely $\Gamma$, the effective interface boundary width, which depends on the stiffness of an interface and $u_{eq}$, the adatom equilibrium concentration outside an infinitely long interface. The drawback of such a description is that these boundary conditions are designed and typically applied to much larger islands and as such may be inaccurate when applied to much smaller islands. These issues have been discussed at length in [164] where deviations from the Gibbs-Thomson equation when applied to small islands in lattice gas models were reported.

We note that the method proved successful in obtaining island size distributions for both reversible aggregation and irreversible aggregation in agreement with a previous phase field
model [136]. Furthermore, the scaling of island density with $D/J$ was found to agree well with known results in the irreversible regime in contrast to a previous implementation [136]. However, in the reversible regime, although the phase simulations reproduced the expected Arrhenius behaviour, they predicted systematically larger values of the scaling exponent than those obtained from KMC simulations when $D$ was varied with changing the temperature. The slight alleviation of this by simulating a range of values of $D/J$ at constant temperature but varying flux suggests that we are not correctly accounting for the temperature dependence of $u_{eq}$ and $\Gamma$. However, it is also possible that the Gibbs-Thomson boundary condition is not capable of reproducing the correct detachment rate. We note that simulation which nucleate critical nuclei directly reproduced not only the correct ISD but also the scaling of islands density with $D/J$.

To summarise, the method almost certainly obtains the qualitative features of the crossover from irreversible to reversible growth in the submonolayer regime. Further microscopic analyses of the detachment rate and its relation to the Gibbs-Thomson condition for small islands is required to make a direct connection between KMC simulations and the phase field simulations.

In the final chapter of this thesis we use the phase-field method to examine the growth of submonolayer epitaxial islands under flash deposition conditions with the inclusion of desorption. The motivation for this study was the rationalisation of experimental observations of the growth of graphene on polycrystalline copper reported in [71]. The main aim was to reproduce the qualitative features of the growth on copper using a single simulation method to demonstrate that a model based on a simple monomer picture is sufficient to capture many of the experimental observations. We found that this indeed proved to be the case. In particular, we found that the Arrhenius form of the growth rate could only be reproduced by including detachment from the surface which is in line with the attachment-limited growth reported in [71].
CHAPTER 6. CONCLUSIONS

Finally, let us take a more general look at the current state of theoretical research into graphene growth particularly concentrating on kinetics. It seems that there has been some effort spent on understanding the growth of graphene flakes [100, 13, 101, 99]. However, still little is known about the earliest stages of nucleation. In particular, while DFT has been used extensively to try and understand the stability of different types of carbon clusters both on terraces and on steps, there have been no studies utilising KMC to examine the earliest stages of growth. An understanding of nucleation is key to understanding the formation of grain boundaries in graphene sheets grown using epitaxial methods and in turn the production of better quality graphene. Furthermore, there is still much work to be done in understanding how different size clusters diffuse on the surface which would hopefully help to elucidate their role, if any in the earliest stages of graphene growth.

We believe that in this thesis we have demonstrated the continuing applicability of simple phenomenological methods in examining epitaxial systems. However, these types of studies often raise questions that perhaps only more detailed microscopic methods can answer. This and the relative lack of kinetic studies of graphene demonstrate the limitations of current computational methods. Clearly, there is still a need for further research into cheaper methods which retain enough precision for researchers to have confidence in the accuracy of their conclusions.
Appendix A

Curvilinear coordinates

We wish to find a transformation from curvilinear coordinates to a set of coordinates local to the interface Figure A.0.1.

Firstly, let’s define a point $P$ which has cartesian coordinates $(x, y)$ and we wish to find the transformation such that we can express the coordinates of $P$ in terms of the new coordinates $(\xi_1, \xi_2)$. $\xi_1$ is the length connecting the points $Q$ and $P$ which is $\parallel$ to the vector normal to the interface, $\hat{n} (\xi_2)$. $\xi_2$ is the arc length from an arbitrary reference point $T$. A vector $\mathbf{r}(x, y)$ from the point $P$ to the origin can be expressed as,

$$\mathbf{r} = \mathbf{R}(\xi_2) + \xi_1 \hat{n}(\xi_2),$$

where the vector normal to the interface is given by,

$$\hat{n} = \sin(\theta) \hat{e}_x - \cos(\theta) \hat{e}_y.$$

We first calculate the quantities $\frac{\partial \mathbf{r}}{\partial \xi_1}$ and $\frac{\partial \mathbf{r}}{\partial \xi_2}$.

$$\frac{\partial \mathbf{r}}{\partial \xi_2} = \frac{d \mathbf{R}}{d \xi_2} + \xi_1 \frac{d \hat{n}}{d \xi_2} = \mathbf{r} (1 + \xi_1 \kappa),$$  \hspace{1cm} (A.0.1)
Figure A.0.1: Schematic representation of the curvilinear coordinate system.
\[
\frac{\partial \mathbf{r}}{\partial \xi_1} = \hat{n}.
\]  
(A.0.2)

where we used. Next we write,

\[
d\mathbf{r} = \frac{\partial \mathbf{r}}{\partial \xi_1} d\xi_1 + \frac{\partial \mathbf{r}}{\partial \xi_2} d\xi_2 = \hat{n} d\xi_1 + \hat{\mathbf{r}} (1 + \xi_1 \kappa) d\xi_2,
\]

and after some algebra obtain,

\[
d\mathbf{r}^2 = d\xi_1^2 + (1 + \xi_1 \kappa)^2 d\xi_2.
\]

Finally, using the general expression for the arc length, \(d\mathbf{r}^2\) in a curvilinear coordinate system we can identify the scale factors, \(h_1\) and \(h_2\) for the coordinate transformation,

\[
h_1 = 1,
\]

\[
h_2 = 1 + \xi_1 \kappa.
\]

We are then free to use the general expression for differential operators expressed in a curvilinear coordinate system. For example, the laplacian as,

\[
\nabla^2 = \frac{\partial^2}{\partial \xi_1^2} + \frac{\kappa}{1 + \xi_1 \kappa} \frac{\partial}{\partial \xi_1} + \frac{1}{(1 + \xi_1 \kappa)^2} \frac{\partial^2}{\partial \xi_2^2} - \frac{\xi_1}{(1 + \xi_1 \kappa)^3} \frac{\partial \kappa}{\partial \xi_2} \frac{\partial}{\partial \xi_2}.
\]
Appendix B

The thin interface analysis

In the following we perform the thin interface analysis of the phase field equations, transformed into a frame of reference co-moving with the interface. This analysis, first performed by Karma and Plapp [137, 134] shows that both boundary conditions that must be applied when solving the BCF equations arise naturally at different orders of the expansion of the generic phase field equations,

\[ \frac{\partial u(r, t)}{\partial t} = \nabla^2 u(r, t) + F - \frac{\partial \phi(r, t)}{\partial t} - \frac{u(r, t)}{\tau_D}, \]  
\[ \tau \frac{\partial \phi}{\partial t} = W^2 \nabla^2 \phi - \frac{\partial f}{\partial \phi} - \lambda u \frac{\partial g}{\partial \phi}. \]

The analysis consists of two stages. Firstly, the equations are written in terms of rescaled length and time scales to obtain two sets of equations valid in an inner region local to the interface and an outer region far away from the interface. We then define a small parameter, \( \epsilon \),

\[ \epsilon = \frac{W}{L}. \]
APPENDIX B. THE THIN INTERFACE ANALYSIS

where \( L \) is a characteristic macro-length scale of the system under consideration and substitute the expansions

\[
\phi = \phi_0 + \epsilon \phi_1 + \epsilon^2 \phi_2 + \ldots, \\
u = u_0 + \epsilon u_1 + \epsilon^2 u_2 + \ldots,
\]

into the resulting equations. The first stage of the calculation is completed by writing down \( n \) differential equations of the phase field and concentration field at different \( \mathcal{O}(\epsilon^n) \) where \( n = 0, 1, 2 \ldots \) in the inner and outer region. It is only necessary to retain terms up to \( \mathcal{O}(\epsilon) \).

The second and final stage of the calculation is to match the two solutions in the overlap region.

In the following we first show how we obtain the equations for the concentration and phase field in the inner and outer regions.

\section*{B.1 Inner expansion}

Following Protovas [165] we first transform to a set of curvilinear coordinates which are local to the interface. The coordinate system that is generally used in the literature is described in detail in the previous Appendix. In this coordinate system a point in space, \( P \) denoted in cartesian coordinates by the variables \((x, y)\) is now described by the points \((\xi_1, \xi_2)\) where \( \xi_1 \) is the length of a line perpendicular to the interface that joins the points \( Q \) on the interface to the point \( P \) and \( \xi_2 \) is the arc length along the interface from an arbitrary reference point to the point \( Q \). In this coordinate system Eq. (B.0.1) and (B.0.2) are transformed to,

\[
\tau \frac{\partial \phi}{\partial t} = \tau \left( v_n \frac{\partial \phi}{\partial \xi_1} + \xi_2 \frac{\partial \phi}{\partial \xi_2} \right) + W^2 \left( \phi_{\xi_1}^2 + \frac{1}{(1 + \kappa \xi_1)^2} \phi_{\xi_2}^2 \right) \quad (B.1.1)
\]
and a similar equations for $u$. Note, that for notational convenience we have dropped the superscript "in" for this subsection only.

In the inner region the following re-scalings are made,

$$z_1 = \frac{\xi_1}{W},$$

$$z_2 = \frac{\xi_2 v_s}{D},$$

$$\bar{t} = t \left( \frac{v_s}{D} \right).$$

Substituting these equations into Eq. (B.1.1) results in the following expression for $\phi$,

$$D \epsilon^2 \frac{\partial \phi}{\partial \bar{t}} - \epsilon \tilde{v}_n D \frac{\partial \phi}{\partial z_1} - D \epsilon^2 \frac{d z_2}{d \bar{t}} \frac{\partial \phi}{\partial z_2} = \frac{\partial^2 \phi}{\partial z_1^2} + \left( \epsilon^2 - \epsilon^3 \tilde{z}_1 \right) \frac{\partial^2 \phi}{\partial z_2^2} + \left( \epsilon^2 - 3 \epsilon \tilde{z}_1 \right) \frac{\partial \phi}{\partial z_1} + \frac{\partial f}{\partial \phi} - \lambda u \frac{\partial g}{\partial \phi},$$

and for $u$,

$$\epsilon^2 \frac{\partial u}{\partial \bar{t}} - \epsilon \tilde{v}_n \frac{\partial u}{\partial z_1} - \epsilon^2 \frac{d z_2}{d \bar{t}} \frac{\partial u}{\partial z_2} = \frac{\partial^2 u}{\partial z_1^2} + \left( \epsilon^2 - \epsilon^3 \tilde{z}_1 \right) \frac{\partial^2 u}{\partial z_2^2} + \left( \epsilon^2 - 3 \epsilon \tilde{z}_1 \right) \frac{\partial u}{\partial z_1} - \frac{\partial h}{\partial \phi}.$$
B.1.1 The phase field

\[ \mathcal{O}(1) : \quad \frac{\partial^2 \phi_0}{\partial z_1^2} - \frac{\partial f}{\partial \phi} \bigg|_{\phi=\phi_0} - \lambda u_0 \frac{\partial g}{\partial \phi} \bigg|_{\phi=\phi_0} = 0, \tag{B.1.4} \]

\[ \mathcal{O}(\epsilon) : \quad \bar{v}_n D \frac{\partial \phi_0}{\partial z_1} + \frac{\partial^2 \phi_1}{\partial z_1^2} + \bar{k} \frac{\partial \phi_0}{\partial z_1} - \frac{\partial f}{\partial \phi} \bigg|_{\phi=\phi_0} - \lambda u_1 \frac{\partial g}{\partial \phi} \bigg|_{\phi=\phi_0} - \lambda u_0 \frac{\partial g}{\partial \phi} \bigg|_{\phi=\phi_1} = 0. \tag{B.1.5} \]

B.1.2 The concentration field

\[ \mathcal{O}(1) : \quad \frac{\partial^2 u_0}{\partial z_1^2} = 0, \tag{B.1.6} \]

\[ \mathcal{O}(\epsilon) : \quad \bar{v}_n \frac{\partial u_0}{\partial z_1} + \frac{\partial^2 u_1}{\partial z_1^2} + \bar{k} \frac{\partial u_0}{\partial z_1} - \frac{\bar{v}_n}{2} \frac{\partial h^0}{\partial z_1} = 0 \tag{B.1.7} \]

B.2 Outer expansion

In the outer expansion the equation for the concentration field reduces to the diffusion equation,

\[ \frac{\partial u}{\partial t} = D \nabla^2 u, \]

and the phase field at all orders is equal to the values of the order parameter at equilibrium. We will use \( x_1 \) for the scaled outer expansion coordinates.

B.3 Matching of the inner and outer expansions

The solutions to the equations in the inner and outer region must now be matched at the interface position. This is accomplished by taking the limits \( z_1 \to \pm \infty \) and \( x_1 \to 0^\pm \) in the inner and outer regions respectively and demanding that the solutions and their gradients
agree in this matching region. It transpires that the matching condition for the gradients of the concentration field yields the flux boundary condition and the Gibbs-Thomson condition is obtained from a closure condition of the $O(\epsilon)$ solution of the phase field equation. We will consider each in turn.

**B.3.1 Kinetic boundary condition**

The matching condition that yields the kinetic boundary condition are,

$$\lim_{z_1 \to \pm \infty} \frac{\partial u^{in}_{1}}{\partial z_1} = \lim_{x_1 \to 0^\pm} \frac{\partial u^{out}_{0}}{\partial x_1}, \quad (B.3.1)$$

where $\frac{\partial u^{in}_{1}}{\partial z_1}$ can be obtained by integrating Eq. B.1.7 and noting that $u^{in}_{0} = 0$,

$$\frac{\partial c^{in}_{1}}{\partial z_1} = a_1 + \frac{\bar{v}_n}{2} h^0. \quad (B.3.2)$$

Subtracting the two equations, Eq. B.3.1 we obtain the kinetic boundary conditions,

$$\frac{v_n}{2} \left( \lim_{z_1 \to \infty} h^0 - \lim_{z_1 \to -\infty} h^0 \right) = \frac{\partial u^{out}_{0}}{\partial x_1} \bigg|_{0^+} - \frac{\partial u^{out}_{0}}{\partial x_1} \bigg|_{0^-} = -v_n, \quad (B.3.3)$$

where we used that $\lim_{z_1 \to \pm \infty} h^0 = \mp 1$.

**B.3.2 Gibbs-Thomson relation**

Obtaining the Gibbs-Thomson relation is more involved. The derivation is simplified by noting that $\frac{\partial \phi_0}{\partial z_1}$ is a solution to the equation $\mathcal{L} \frac{\partial \phi_0}{\partial z_1 \infty} = 0$, where $\mathcal{L}$ is the self-adjoint operator,

$$\mathcal{L} = \frac{\partial^2}{\partial z_1^2} - \frac{\partial f}{\partial \phi_1} \bigg|_{\phi = \phi_1}.$$

Since Eq. (B.1.5) can be written as,
APPENDIX B. THE THIN INTERFACE ANALYSIS

\[ \mathcal{L} \phi_1 = -\bar{v}_n \tilde{D} \frac{\partial \phi_0}{\partial z_1} - \bar{\kappa} \frac{\partial \phi_0}{\partial z_1} + \lambda u_1 \frac{\partial g}{\partial \phi_0} + \lambda u_0 \frac{\partial g}{\partial \phi_1} = 0, \quad (B.3.4) \]

the solvability condition (guaranteeing that \( \phi_1 \) exists) is determined by requiring that \( \frac{\partial \phi_0}{\partial z_1} \) is orthogonal to the r.h.s. of Eq. B.3.4,

\[ \int_{-\infty}^{\infty} dz_1 \frac{\partial \phi_0}{\partial z_1} \mathcal{L} \phi_1 = 0. \quad (B.3.5) \]

The matching condition for the inner and outer solutions of the concentration field at \( O(\epsilon) \) is,

\[ \lim_{z_1 \to \pm \infty} u_1^{in} = \lim_{z_1 \to 0^\pm} \left\{ u_1^{out} + z_1 \frac{\partial u_0^{out}}{\partial x_1} \bigg|_{x_1 = z_1} \right\}, \]

\[ = u^\pm \pm z_1 \frac{\partial u_0^{out}}{\partial z_1}, \quad (B.3.6) \]

where we defined \( u^\pm = \lim_{x_1 \to 0^\pm} u_1^{out} \). An expression for \( \lim_{z_1 \to \infty} u_1^{in} \) can be found by integrating Eq. (B.3.2) to obtain,

\[ \lim_{z_1 \to \pm \infty} \left\{ A_1 + A_2 z_1 + \frac{v_n}{2} \int_0^{z_1} d z'_1 h^0(z'_1) \right\} = A_1 + \left( A_2 + \frac{v_n}{2} \right) \int_0^{\pm \infty} d z'_1 (1 + h_0(z'_1)), \]

\[ = A_1 \pm z_1 \frac{\partial u_0^{out}}{\partial z_1} + F^\pm, \]

where following Karma et al. [137] we used Eq. (B.3.2) and (B.3.3) to eliminate \( A_1 \) and introduced the function \( F^\pm = \int_0^{\pm \infty} d z'_1 (1 + h_0(z'_1)) \). Using Eq. (B.3.6) we are now able to obtain an expression for \( u^\pm \):

\[ u^\pm = A_1 + \frac{v_n}{2} F^\pm, \quad (B.3.7) \]
and all that is left is to obtain an expression for $A_1$ using the closure condition Eq. (B.3.4).

Writing out Eq. (B.3.5) in full:

$$
\int_{-\infty}^{\infty} dz_1 \frac{\partial \phi_0}{\partial z_1} \left\{ -\left( \vec{v}_n \vec{D} + \vec{K} \right) \frac{\partial \phi_0}{\partial z_1} + \lambda \frac{\partial g}{\partial \phi_0} \left( A_1 + A_2 z_1 + \frac{\tau^2}{2} \int_0^{z_1} dz'_1 h^0 \right) \right\} = 0. 
$$

(B.3.8)

In order to eliminate any dependence of the value concentration field at the interface on its normal derivative at the boundary it is necessary to eliminate terms proportional to $A_2$ which may be accomplished by choosing $f$ and $g$ to be even and odd functions of $\phi$ respectively. These two symmetry constraints eliminate the term proportional to $A_2$ in Eq. (B.3.8). A further symmetry constraint must be imposed on $h$, namely that it be an odd function of $\phi$, ensures that $F^+ = F^- = F$ and eliminates the discontinuity in the concentration at the interface. We are finally left with an equation that can be solved for $A_1$ to obtain,

$$
A_1 = -\frac{I}{\lambda J} \left( \vec{v}_n \vec{D} + \vec{K} \right) + \frac{K}{2J} \vec{v}_n, 
$$

(B.3.9)

where $I$, $J$ and $K$ are defined by the following integrals:

$$
I = \int_{-\infty}^{\infty} dz_1 \left( \frac{\partial \phi_0}{\partial z_1} \right)^2, 
$$

(B.3.10)

$$
J = \int_{-\infty}^{\infty} dz_1 \frac{\partial \phi_0}{\partial z_1} \frac{\partial g}{\partial \phi_0}, 
$$

(B.3.11)

$$
K = \int_{-\infty}^{\infty} dz_1 \frac{\partial \phi_0}{\partial z_1} \frac{\partial g}{\partial \phi_0} \int_0^{z_1} dz'_1 h^0 (z'_1). 
$$

(B.3.12)

Finally, upon substitution of Eq. (B.3.9) into Eq. (B.3.7) and rescaling of the various physical constants we obtain an equation which has the form of the Gibbs-Thomson condition,
APPENDIX B. THE THIN INTERFACE ANALYSIS

\[ u = u^+ = u^- = -\frac{a_1 W \kappa}{\lambda} - a_1 D \left(1 - a_2 \frac{\lambda}{D}\right) \frac{W v_n}{\lambda}, \]  

(B.3.13)

where \( a_1 = I/J \) and \( a_2 = (K + JF)/2I \). If the moving interface is in local equilibrium then the second term in Eq. (B.3.13) may be set to zero and allows relations to be obtained between \( W, \lambda \) and \( \tau \).
Appendix C

Review of scaling relations for irreversible and reversible growth

In the following we will review the derivation of certain scaling relations obtained from rate equations for reversible and irreversible aggregation. We recall that while it is not possible to obtain the correct scaling of island size distribution using rate equations the scaling of island density with $D/J$ has been shown to agree well with experimental and simulative results. To derive such relations we seek to obtain solutions to the rate equations for $N = \sum_{s>1} N_s$ in the long time limit (complete condensation) when nucleation of critical clusters has become negligibly small. Let us consider the cases of irreversible and reversible aggregation in turn.

C.1 Irreversible aggregation

Let us begin by once again recalling the equations that describe irreversible aggregation,

$$\frac{dn_1}{dt} = J - 2D\sigma_1 n_1^2 - Dn_1 \sum_{s>1} \sigma_s n_s,$$
APPENDIX C. REVIEW OF SCALING RELATIONS FOR IRREVERSIBLE AND REVERSIBLE GROWTH

\[
\frac{dn_2}{dt} = D \sigma_1 n_1^2 - Dn_1 \sigma_2 n_2, \\
\vdots \\
\frac{dn_s}{dt} = D \sigma_{s-1} n_{s-1} n_1 - D \sigma_s n_1 n_s, 
\]

which may be contracted into the much simpler set of equation,

\[
\begin{align*}
\frac{dn_1}{dt} &= J - 2D \sigma_1 n_1^2 - Dn_1 N, \\
\frac{dN}{dt} &= D \sigma_1 n_1^2, 
\end{align*}
\]

where \( N \) is defined as above and we have set \( \sigma_s = 1 \) which results in the much simpler last term in Eq. (C.1.1). In the long time limit we expect \( \frac{dn_1}{dt} \approx 0 \) and because in this regime \( n \ll N \) we are able to neglect the second term in Eq. (C.1.1). This approximation enables us to obtain an expression for \( n_1 \) which may be substituted into Eq. (C.1.2) to provide a simple differential equation for the island density, \( N \),

\[
\frac{dN}{dt} = D \sigma_1 \left( \frac{J}{DN} \right)^2,
\]

which may be integrated to obtain the desired scaling relation,

\[
N = (3 \sigma_1 \theta)^{\frac{1}{3}} \left( \frac{J}{D} \right)^{\frac{1}{3}},
\]

where \( \theta = Jt \) is the coverage.
C.2 Reversible aggregation

In the following we consider the case of reversible aggregation with a critical nucleus of size $i^*$. In this case the contracted rate equations are,

\[
\frac{dn_1}{dt} = J - (i^* + 1) \sigma_{i^*+1} e^{\beta E_{i^*}} Dn_{1_{i^*+1}} - Dn_1 \sum_{s>i^*} \sigma_s n_s \\
= J - (i^* + 1) e^{\beta E_{i^*}} \sigma_{i^*+1} Dn_{i^*+1} - DN \langle \sigma \rangle ,
\]

\[
\frac{dN}{dt} = \sigma_{i^*+1} e^{\beta E_{i^*}} Dn_{1_{i^*+1}} ,
\]

where we introduced the average capture number \( \langle \sigma \rangle = (\sum_{s>i^*} \sigma_s n_s) / (\sum_{s>i^*} n_s) \) and \( E_{i^*} \) is the energy required to disassemble a cluster containing \( i^* \) atoms into adatoms [141]. Clearly, this set of equations has been cast into exactly the same form as that of the equations for irreversible aggregation. Since the same assumptions that we used in the previous section apply to the case of reversible aggregation we can follow the same steps to obtain the differential equation,

\[
\frac{dN}{dt} = \sigma_{i^*+1} e^{\beta E_{i^*}} D \left( \frac{F}{DN \langle \sigma \rangle} \right)^{i^*+1} ,
\]

which is integrated to obtain the following scaling relation,

\[
N = \eta (\theta, i^*) e^{\beta E_{i^*}/(i^*+2)} \left( \frac{F}{D} \right)^{i^*+2} , \quad \eta (\theta, i^*) \left( \frac{(i^* + 1) \sigma_{i^*+1} \theta}{\langle \sigma \rangle^{i^*+1}} \right) .
\]
Appendix D

Derivation of the capture number, $\sigma_1$

In what follows we briefly review the derivation of the capture number,

$$\sigma_1 = \frac{4\pi}{\ln(1/\alpha) \langle u \rangle \langle D/\Omega^2 J \rangle},$$  \hspace{1cm} (D.0.1)

where found in the original work of [49]. Their main insight was to consider a single island of radius $R_s$, surrounded by an ensemble averaged density of adatoms, $n_1(r,t)$. This density is the ensemble average of the entire system containing both monomers and adatoms which far away from the island can be found by solving the spatially independent rate equation,

$$\frac{d}{dt} \langle n_1 \rangle = J - 2D\sigma_1 \langle n_1 \rangle^2 - D \langle n_1 \rangle \sum_{s=2}^{\infty} \sigma_s \langle n_s \rangle - \kappa_1 \langle n_1 \rangle - \sum_{s=1}^{\infty} \kappa_s \langle n_s \rangle,$$ \hspace{1cm} (D.0.2)

where $\sigma_s$ is the capture number and $\kappa_s$ is the rate of detachment of monomers from islands containing $s$ atoms. Derivations of this and similar sets of rate equations from master equations [107, 166] show that to obtain Eq. (D.0.2) a mean-field approximation is needed to reduce an infinite hierarchy of equations (including correlation functions and higher moments) to obtain a finite set of equations. The capture numbers $\sigma_s$ were originally introduced to account for correlations between $n_1$ and the other species $n_s$ that would otherwise be entirely neglected.
APPENDIX D. DERIVATION OF THE CAPTURE NUMBER, $\sigma_1$

[49]. They essentially describe the sink strength of islands and can be found self-consistently from the expression,

$$\sigma_s = \frac{2\pi R_s \partial n_1}{\langle n_1 \rangle} \bigg|_{r=R_s}. \quad (D.0.3)$$

The evolution of the adatom density obeys a diffusion equation with sink and source terms,

$$\frac{\partial n_1}{\partial t} = D \nabla^2 n_1 + J - D \xi^{-2} n_1, \quad (D.0.4)$$

where we note that islands are assumed to be circular so that we perform the calculation in a cylindrical coordinate system. It is easy to see that in the case of irreversible aggregation the boundary condition at the island boundary will be $n(R, t) = 0$. The constants $J$ and $\xi$ are determined as follows. Firstly, we recall that the far-field boundary condition for the ensemble average adatom density is $n_1 (r = \infty, t) = \langle n_1 \rangle$. Thus, comparing Eq. (D.0.2) with Eq. (D.0.4) in this limit gives the following expressions,

$$J = 1 - \sum_{s=1}^{\infty} \kappa_s \langle n_s \rangle,$$

$$\xi^{-2} = 2 \sigma_1 \langle n_1 \rangle + \sum_{s=2}^{\infty} \sigma_s \langle n_s \rangle + J \kappa_1.$$

The solution of this set of equations must be determined self-consistently. The equation actually solved to find $n_1$ in [49] is a Helmholtz equation obtained by subtracting Eq. (D.0.2) from Eq. (D.0.4) and assuming that $\frac{\partial n_1}{\partial t} \approx \frac{d\langle n_1 \rangle}{dt}$. It admits the following solution:

$$n_1 (r, t) = \langle n_1 \rangle \left( 1 - \frac{K_0 \left( \frac{r}{\xi} \right)}{K_0 \left( \frac{R}{\xi} \right)} \right),$$

where $K_j$ are modified Bessel functions of order $j$. The capture number is then found using
APPENDIX D. DERIVATION OF THE CAPTURE NUMBER, \( \sigma_1 \)

Eq. (D.0.3),

\[
\sigma_s = 2\pi \frac{R_s K_1 \left( \frac{R_S}{\xi} \right)}{\xi K_0 \left( \frac{R_s}{\xi} \right)}.
\]

Finally, in the limit of larger coverages for which we expect \( N \gg \langle n_1 \rangle \) and \( \frac{d\langle n_1 \rangle}{dt} \approx 0 \), we may replace the modified Bessel functions with their small angle approximations [145] to obtain,

\[
\sigma_1 = \frac{4\pi}{\ln \left( \frac{1}{\alpha} \left( \frac{D}{\Omega J} \right) \langle n_1 \rangle \right)}
\]

where \( \Omega \) is the area of an absorption and as mentioned in Chap. 4, the constant \( \alpha \) is related to the radius \( R_s \) of non-circular islands via the empirical power-law relation,

\[
R_s \approx \alpha s^{1/d_f},
\]

where \( d_f \) is the fractal dimension of the island. For circular islands \( d_f = 2 \) and \( \alpha = 1/\sqrt{\pi} \).
Appendix E

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