

Chapter 2

Theoretical Modelling Methods

Density functional theory methods allow for the calculation of the total energy of a system of atoms and the forces acting on the individual atoms. Finding these forces allows the relaxation of structures to their lowest energy structure by driving the atomic forces towards zero. Calculation of the forces on a system also allows further quantities to be studied. The nudged elastic band (NEB) method can be used to find the minimum energy pathway across the potential energy surface between two minima by calculating the relevant forces along the pathway. This allows the saddle point and the corresponding energy barrier between two minima to be found, which can be used to determine the kinetics of various processes. Forces can also be used to determine the lattice dynamics of a system which can be used to study phonons and calculate the vibrational free energy. In molecular dynamics simulations the forces on each atom are evaluated at each sequential time step in order to evaluate the atomic motion.

A variety of these calculations are used in this thesis to study different properties involved in epitaxial graphene growth. In this chapter the methodology of density functional theory calculations as well as the DFT-based methods will be discussed in detail.

2.1 Density Functional Theory

2.1.1 Formalism

In density functional theory (DFT) the many-body Schrödinger equation for a system of electrons and nuclei interacting with each other is solved self-consistently. Using the Born-Oppenheimer approximation the nuclei are treated as being effectively fixed in position while the electrons move in the effective potential generated by them [1].

The Hohenberg-Kohn theorem states that the energy of a system of electrons in the potential of the nuclei can be written as a functional of the electronic density $\rho(\mathbf{r})$ [2]:

$$E[\rho(\mathbf{r})] = F[\rho(\mathbf{r})] + \int d\mathbf{r} V_{ext}(\mathbf{r})\rho(\mathbf{r}) \quad (2.1)$$

where V_{ext} is the effective external potential of the nuclei and $F[\rho(\mathbf{r})]$ is an unknown universal functional of the electronic density that represents all the electron effects, which does not depend on the system in question. This will include their kinetic energy and the electron–electron interaction, $F[\rho(\mathbf{r})] = T[\rho(\mathbf{r})] + V_{ee}[\rho(\mathbf{r})]$, including all exchange-correlation effects. When $E[\rho(\mathbf{r})]$ is minimised with respect to the electronic density it corresponds to the ground state energy of the system E_0 . Furthermore the exact electronic density which minimises $E[\rho(\mathbf{r})]$ is the ground state density $\rho_0(\mathbf{r})$. The ground state energy is given by

$$E_0 = E[\rho_0(\mathbf{r})] \leq E[\rho(\mathbf{r})] \quad (2.2)$$

In order to find the ground state energy the Kohn–Sham method is used [3]. To perform the minimisation the energy term $E[\rho(\mathbf{r})]$ is separated into its constituents which each have specific functional dependence on the electronic density $\rho(\mathbf{r})$. This maps the system to that of a system of non-interacting electrons within an effective potential. The electron density is described in terms of the effective one-particle wavefunctions $\psi_i(\mathbf{r})$ for a system containing N_e electrons:

$$\rho(\mathbf{r}) = \sum_{i=1}^{N_e} |\psi_i(\mathbf{r})|^2 \quad (2.3)$$

For the many-particle system the total energy is formed of the kinetic energy of the non-interacting electrons $T_{KS}[\rho(\mathbf{r})]$ and the potential energy of interactions between electrons $V_{KS}^{ee}[\rho]$ (the Hartree energy), as well as the external potential $\int d\mathbf{r} V_{ext}(\mathbf{r})\rho(\mathbf{r})$ due to the atomic cores:

$$E[\rho(\mathbf{r})] = T_{KS}[\rho(\mathbf{r})] + V_{KS}^{ee}[\rho(\mathbf{r})] + \int d\mathbf{r} V_{ext}(\mathbf{r})\rho(\mathbf{r}) + E_{xc}[\rho(\mathbf{r})]. \quad (2.4)$$

The form of the Hartree energy is $V_{KS}^{ee}[\rho] = \frac{e}{2} \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r} d\mathbf{r}'$. Errors in the kinetic energy due to interactions are incorporated into the exchange-correlation term $E_{xc}[\rho(\mathbf{r})]$, as well as the corrections to the electron–electron interaction. The full form of $E_{xc}[\rho(\mathbf{r})]$ is therefore

$$\begin{aligned} E_{xc}[\rho(\mathbf{r})] &= F[\rho(\mathbf{r})] - V_{KS}^{ee}[\rho(\mathbf{r})] - T_{KS}[\rho(\mathbf{r})] \\ &= (V^{ee}[\rho(\mathbf{r})] - V_{KS}^{ee}[\rho(\mathbf{r})]) + (T[\rho(\mathbf{r})] - T_{KS}[\rho(\mathbf{r})]) \end{aligned} \quad (2.5)$$

Developing the correct form of $E_{xc}[\rho(\mathbf{r})]$ is crucial for generating a more accurate functional. This will be discussed in Sect. 2.1.2.

Minimisation of the energy functional (2.4) allows the formulation of an effective potential. The ground state density of this many particle system is then equivalent to that of a system of non-interacting electrons moving in this effective external potential field given by

$$V_{eff}(\mathbf{r}) = V_{ext}(\mathbf{r}) + \int d\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \frac{\delta E_{xc}}{\delta \rho(\mathbf{r})}. \quad (2.6)$$

The Kohn–Sham Hamiltonian is formed of $V_{eff}(\mathbf{r})$ and the kinetic energy of the “fictitious” non-interacting electron gas [3],

$$H_{KS} = -\frac{1}{2}\nabla^2 + V_{eff}(\mathbf{r}). \quad (2.7)$$

This Hamiltonian has no direct interactions between electrons, but includes the effect of each electron moving in a potential field dependent on the distribution of electrons $\rho(\mathbf{r})$. This solves the Schrödinger equation,

$$\left[-\frac{1}{2}\nabla^2 + V_{eff}(\mathbf{r}) \right] \psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r}). \quad (2.8)$$

Solving the Kohn–Sham equations [3] to find the ground state density is achieved self-consistently by an iterative process. First a starting density $\rho(\mathbf{r})$ is used to calculate the effective potential and solve the Schrödinger equation. From this a new density is constructed which is used to generate new one-electron wavefunctions and restart the iteration. This process ends when the density has converged to within a certain error. This value will correspond to the ground state.

2.1.2 The Exchange-Correlation Functional

The main cause for inaccuracy in this Kohn–Sham method is in the approximation needed for the exchange and correlation effects. Choosing the correct form of $E_{xc}[\rho]$ is important in order to reduce the error. Popular choices for this are the local-density approximation (LDA) and the generalised gradient approximation (GGA).

In the LDA the exchange-correlation functional is expressed only in terms of the electron density,

$$E_{xc} = \int \rho(\mathbf{r}) \epsilon_{xc}(\rho) d\mathbf{r} \quad (2.9)$$

where ϵ_{xc} is the exchange-correlation energy per particle [4]. In Eq. (2.9) it is assumed that the electron density changes smoothly throughout space. In the GGA E_{xc} is expressed in terms of the electron density and the electron density gradient $\nabla\rho(\mathbf{r})$,

$$E_{xc} = \int \rho(\mathbf{r}) \epsilon_{xc}(\rho, \nabla \rho) d\mathbf{r}. \quad (2.10)$$

This improves the exchange-correlation energy in situations when the density varies rapidly [5, 6]. Both the LDA and GGA functionals do not take into account any non-local interactions, such as the dispersion interaction. To include van der Waals (dispersion) forces, additional functionals are needed. These are discussed in Sect. 2.1.3.

2.1.3 Van der Waals Forces in DFT

An important consideration in density functional theory calculations is the ability to incorporate van der Waals (vdWs) forces. These forces play a major role in many systems (such as molecules and proteins) and affect their structure and stability. They arise from the dispersion interaction. Charge fluctuations in different parts of an atomic system become correlated over long ranges which results in the attractive vdWs force. However DFT based on standard functionals such as LDA and GGA fails to correctly model vdWs forces.

In order to model dispersion forces many DFT based techniques have been developed with varying accuracy. Some methods (semi-empirical) rely on input parameters to formulate a description of the dispersion energy whereas others calculate it directly from the electron density. Some of these various techniques are described below.

2.1.3.1 DFT-D

The DFT-D method includes the dispersion energy by adding an extra density-independent term to the energy density functional. With this formalism the energy becomes:

$$E_{tot} = E_{DFT} + E_{disp}. \quad (2.11)$$

The E_{disp} term accounts for the long range interaction between a pair of atoms which decays as $-1/r^6$ with the atomic separation r . The full expression for E_{disp} is:

$$E_{disp} = - \sum_{A,B} C_6^{AB} / r_{AB}^6 \quad (2.12)$$

which includes the dispersion coefficients C_6^{AB} that depend on the nature of atoms A and B . This interaction is isotropic and these coefficients are taken as being constant during the calculation, hence they do not depend on the environment of the atoms. Obtaining a good universal choice for them is difficult as it relies on experimental parameters which may not be available for some elements. Other problems with this method include the neglect of many body dispersion effects and higher order (C_8/r^8 , C_{10}/r^{10}) terms. Also for small r the energy diverges.

2.1.3.2 DFT-D2

The DFT-D2 method proposed by Grimme in 2006 offers an improvement to the DFT-D method [7]. In this formalism the dispersion energy contribution is modified (see below) and the C_6 coefficients are calculated from the product of the ionisation potentials and the static polarisabilities of isolated atoms. This allows coefficients for a greater number of elements to be included. However in some cases the coefficients can not be correctly derived from this expression and instead averages from other elements are used.

In order to prevent the divergence of E_{disp} which occurs at small r a damping function $f(r_{AB}, A, B)$ is added into the DFT-D2 E_{disp} expression:

$$E_{disp} = - \sum_{A,B} f(r_{AB}, A, B) C_6^{AB} / r_{AB}^6. \quad (2.13)$$

One choice of the damping function is the Fermi function,

$$f(r_{AB}, A, B) = \frac{1}{1 + e^{-d(r_{AB}/R_r - 1)}} \quad (2.14)$$

where r_{AB} is the distance between two atoms A and B , R_r is the sum of atomic vdW radii and d is the steepness of the damping function. The choice of the damping function is important and must be constructed so that it fits with reference data. It can be chosen so that it includes the effect of higher order (C_8/r^8 , C_{10}/r^{10}) terms [8]. Its form will also be dependent on the type of exchange-correlation functional to be used alongside this correction.

2.1.3.3 DFT-D3 and vdW(TS)

A problem with the DFT-D2 method is that the C_6 coefficients still have no dependence on the environment of the atom. The DFT-D3 and vdW(TS) methods improve on this by allowing the dispersion coefficient to depend on the effective volume of the atom. If an atom is effectively squeezed by other atoms then the C_6 coefficient is made smaller. In DFT-D3 the number of neighbours that a particular atom has is calculated and used to adjust the coefficient [8]. For a large number of neighbours the effective volume is assumed to be smaller and therefore C_6 is reduced. In this way the coefficients can be adjusted throughout the calculation. In the vdW(TS) method (proposed by Tkatchenko and Scheffler) effective atomic volumes are used [9]. The total electron density of a molecule is split between its individual atoms and this is then compared to the density of a free atom. The C_6 coefficient is scaled depending on the difference.

2.1.3.4 vdW-DF

The van der Waals density functional (vdW-DF) method calculates the dispersion from the electron density [10, 11]. For this the exchange correlation energy functional is divided into the original exchange term and a new correlation term,

$$E_{xc}[\rho(\mathbf{r})] = E_x^{GGA}[\rho(\mathbf{r})] + E_c^{new}[\rho(\mathbf{r})]. \quad (2.15)$$

$E_x^{GGA}[\rho(\mathbf{r})]$ is the exchange functional as determined by a GGA technique and $E_c^{new}[\rho(\mathbf{r})]$ is a non-local correlation function which includes vdWs interactions. This in turn can be divided into two different contributions:

$$E_c^{new}[\rho(\mathbf{r})] = E_c^0[\rho(\mathbf{r})] + E_c^{nl}[\rho(\mathbf{r})]. \quad (2.16)$$

$E_c^0[\rho(\mathbf{r})]$ can be approximated with the LDA correlation function $E_c^0[\rho(\mathbf{r})] \approx E_c^{LDA}[\rho(\mathbf{r})]$. $E_c^{nl}[\rho(\mathbf{r})]$ represents the long ranged non-local interactions which give rise to vdWs. It has the form of:

$$E_c^{nl}[\rho(\mathbf{r})] = \frac{1}{2} \int d^3\mathbf{r} \int d^3\mathbf{r}' \rho(\mathbf{r}) \Phi(\mathbf{r}, \mathbf{r}') \rho(\mathbf{r}') \quad (2.17)$$

where $\Phi(\mathbf{r}, \mathbf{r}')$ is an integration kernel. A problem with vdW-DF is that it tends to overestimate the long ranged interactions. The choice of the $E_x^{GGA}[\rho(\mathbf{r})]$ functional can also have an effect on the accuracy of the result. The vdW-DF method is more expensive than the Grimme-like methods. Furthermore a “universal” vdW functional does not currently exist [12].

2.2 Basis-Sets

Before solving the Kohn–Sham equations first the form of the wavefunctions, $\psi_i(\mathbf{r})$ must be chosen. The wavefunction is expanded into a set of basis functions, ϕ_j with coefficients c_{ij}

$$\psi_i = \sum_j c_{ij} \phi_j. \quad (2.18)$$

The type of the basis set is important as it affects how computationally expensive it is to converge the system with the required accuracy. The choice of the basis set is also dependent on the type of system. For a crystalline solid the basis set will obey Bloch’s theorem since the system is periodic. Due to the periodicity the potential $V(\mathbf{r})$ will have the form

$$V(\mathbf{r}) = V(\mathbf{r} + \mathbf{R}) \quad (2.19)$$

where $\mathbf{R} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3$ is the direct lattice vector, with $\mathbf{a}_{1,2,3}$ the unit cell vectors of the system. Based on this the basis functions $\phi_{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}e^{i\mathbf{k}\cdot\mathbf{r}}$ will satisfy the relation

$$\phi_{\mathbf{k}}(\mathbf{r} + \mathbf{R}) = e^{i\mathbf{k}\cdot\mathbf{R}}\phi_{\mathbf{k}}(\mathbf{r}) \quad (2.20)$$

where $\mathbf{k}$ is the reciprocal space wave vector and $u_{\mathbf{k}}$ are arbitrary functions that obey the periodicity of the lattice. A set of plane waves fulfil this condition and are commonly used for a system with periodic boundary conditions [13]. Then the one-electron wavefunctions ψ_i can be expanded in them:

$$\psi_{i,\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} c_{i,\mathbf{k}}(\mathbf{G})e^{i(\mathbf{G}+\mathbf{k})\cdot\mathbf{r}} \quad (2.21)$$

Here $\mathbf{G} = m_1\mathbf{b}_1 + m_2\mathbf{b}_2 + m_3\mathbf{b}_3$ is the reciprocal lattice vector and $c_{i,\mathbf{k}}(\mathbf{G})$ are expansion coefficients. The advantages of using plane waves is that they are orthogonal and Fast Fourier Transforms can be used in the calculation of the coefficients $c_{i,\mathbf{k}}(\mathbf{G})$. However when using a plane wave basis set for large systems many plane waves are needed. Also the wavefunctions oscillate within the core region and as a result the use of pseudopotentials is required (see Sect. 2.3).

Another choice of basis set is a linear combination of atomic orbitals (LCAO). Atomic orbitals decay to zero at infinite distances in the same way as the wavefunction of an isolated atom or molecule. Therefore these are a good choice of basis function. They have the form:

$$\phi_j(\mathbf{r}) \rightarrow \chi_{nlm}(\mathbf{r}) = R_{nl}(r)S_{lm}(\mathbf{r}) \quad (2.22)$$

where $S_{lm}(\mathbf{r})$ is a spherical harmonic function [13], $R_{nl}(r)$ is the radial function and n, l, m are the usual quantum numbers for atomic orbitals. A minimum basis set is constructed, formed of the minimum necessary number of atomic orbitals for the system. However this minimum basis set fails at describing the chemical bonding and converging the energy of the system. To account for this diffuse atomic orbitals can be added to increase the basis set expansion and give a better representation of the charge density.

A further problem of LCAOs is the basis set superposition error (BSSE). This occurs when two species with different basis sets approach one another and one species may utilise the basis sets of the other species (or vice versa) to describe its electron distribution. This will improve the description of both species when they are interacting. However this description can now not be compared with when they are non interacting at large separations and hence the treatment is inconsistent. The BSSE can be corrected for by calculation of the counterpoise correction [14]. Furthermore there is a so-called Pulay correction to the atomic forces when LCAOs are used [13] due to the fact that the positions of the AOs depend explicitly on atomic positions.

The radial part of the atomic orbital may have the form of a Slater type orbital, $R_{nl}(r) \sim e^{-\xi r}$ or a Gaussian type orbital $R_{nl}(r) \sim e^{-\alpha r^2}$. Despite the fact that many Gaussian type orbitals are needed in order to get a good representation, they are computationally less expensive than Slater type orbitals and are therefore the favourable

choice. Compared to plane waves, less Gaussian type orbitals are required in order to represent the wavefunction. To represent the basis set, minimal (one basis function per AO), double zeta (two basis functions per AO), triple zeta (three basis functions per AO) or a split valence (one basis function per core AO, and more for the valence AOs) basis sets may be used.

Different electronic structure codes use different choices for basis sets. For example, the Vienna *ab initio* simulation package (VASP) [15, 16] uses a plane wave basis set whereas the CP2K code relies on both Gaussians and plane waves (GPW) [17]. The wavefunction is described using a combination of Gaussian type orbitals, but the electron density is expanded in plane waves to facilitate the calculation of the Coulomb potential; the exchange-correlation energy then is calculated on a grid. For large systems this method scales as $O(N_M^2 M)$ where M is the number of basis functions and N_M is the number of molecular orbitals.

2.2.1 *K-Point Sampling*

So far the quantities discussed have been considered for an infinite k-space sampling in the first Brillouin zone. However in practice the size of the k-mesh is limited. In order to integrate a function over the Brillouin zone, k-point sampling must be used. For example the electron density is given by

$$\rho(\mathbf{r}) = \frac{1}{\Omega_{BZ}} \sum_n^{occ} \int_{BZ} |\psi_n(\mathbf{r})|^2 d^3\mathbf{k} \quad (2.23)$$

where the sum is performed over all occupied states in the Brillouin zone and Ω_{BZ} is the volume of the Brillouin zone. Only a finite number of k-points are possible, and the number required depends on the system in question. Usually k-points are determined using the Monkhorst-Pack method [13, 18].

VASP allows the use of a k-mesh for integrating over in reciprocal space (k-space) to calculate properties. For larger cells a smaller k-mesh is required, and inversely small cells need a greater number of k-points. Metals in particular need more k points as the interaction between the conduction electrons are long ranged. In VASP small real space (r-space) cells may be used, as the k-points can compensate for the size of the cell. As the computation time scales linearly with number of k-points but to the order of N_A^3 for number of atoms this is a much cheaper alternative. By examining the convergence of total energy with k-points the size of the k-mesh can be determined. In CP2K only the gamma point is used, therefore there is not a well defined k-mesh for the integration. To compensate for this large r-space cells must be used so that the k-space sampling size is reduced.

2.3 Pseudopotentials

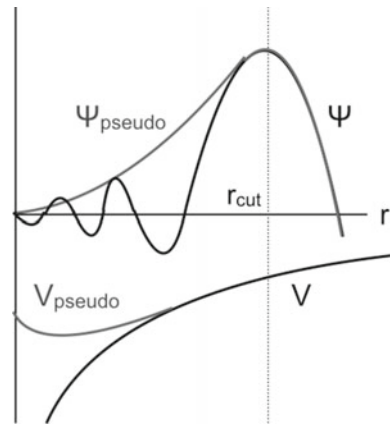
The electrons in atoms can be considered in terms of two groups: inner core electrons and valence electrons. The inner core electrons are tightly bound to the nucleus and play a limited part in the chemical bonding with other atoms. The valence electrons are screened from the effects of the nucleus by the core electrons and are involved in bonding. During bonding the wavefunctions of the core electrons are only slightly affected as they remain strongly localised around their cores and therefore they can be considered as essentially inert. These electrons along with the nucleus can be treated with non-variational wavefunctions to simplify the method. This is known as the frozen core approximation.

In addition to this, a problem arises due to the fact that the valence electrons are required to be orthogonal to the core electrons within the core region. This causes the spin orbitals of the valence electrons to oscillate in the core region and as a result of these oscillations many basis functions are needed in order to describe them correctly. Therefore, when using a plane wave basis set, a large value of the cutoff radius, G_{max} is required (see Eq. (2.21)), with a high energy cutoff E_{cut} for the wavefunctions $E_{cut} = \hbar^2 G_{max}^2 / 2m$. This increases the computational effort.

To reduce the number of basis sets needed, pseudopotentials are used to describe the Coulomb potential of the valence electrons as shown in Fig. 2.1. These are modified to ensure that the pseudo-wavefunctions are the same as the actual wavefunctions outside the core radius and smooth inside the core radius.

Common forms of the pseudopotentials include the norm-conserving, ultrasoft and the projected-augmented wave method (PAW) [13]. The PAW method (used in VASP) allows an effectively all-electron calculation with frozen core orbitals (the other methods are based on valence pseudo-wavefunctions) [13]. It works by splitting the valence electron function ϕ_v into three parts, such that $\phi_v = \tilde{\phi}_v + \chi_v + \tilde{\chi}_v$. $\tilde{\phi}_v$ is smooth everywhere and equal to ϕ_v outside the core (augmented) region, whereas χ_v is equal to the true orbital ϕ_v in the core region and smooth outside it. The net differences are included in $\tilde{\chi}_v$. $\tilde{\phi}_v$ is used to represent the pseudo-wavefunction.

Fig. 2.1 The pseudopotentials V_{pseudo} replaces the Coulomb potential V and as a result the oscillating core wavefunctions ψ are replaced by the pseudo-wavefunctions ψ_{pseudo} which are smooth inside the core region



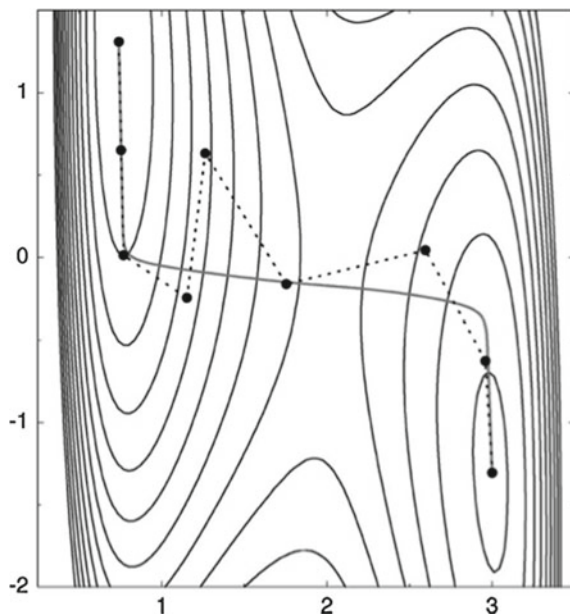
The Goedecker-Teter-Hutter (GTH) [19] method is used in the CP2K calculations of this thesis. Here the pseudopotentials are separated into local and non-local parts. The pseudopotentials are represented in an analytical form, with the parameters required to characterise each element in the form of Gaussians functions. This improves the efficiency.

2.4 The Nudged Elastic Band Method

The nudged elastic band method (NEB) is a valuable technique that finds the minimum energy pathway (MEP) between two minima on the potential energy surface [20–22]. This means that details of a transition from one state to another can be determined, such as the energy of the saddle point and its structure. This energy corresponds to the maximum energy point along the MEP and dictates the energy barrier that needs to be overcome during a transition. This technique is particularly useful for determining the rate of a processes within transition state theory using the Arrhenius equation (see Sect. 2.7.1).

During a NEB calculation an elastic band connecting the two minima is optimised to find the MEP. The optimisation acts as to minimise the force perpendicular to the band and the force along the band, which is treated as elastic with a spring constant k_{spring} . To begin, a number of images are constructed between the initial and final states which act as an initial guess for the path. For a simple case, such as the diffusion of an atom on a surface from one site to another, the images may be generated by linear interpolation (Fig. 2.2).

Fig. 2.2 The potential energy surface showing two minima connected by the initial energy pathway generated from interpolation (dotted line) and the optimised minimum energy pathway as calculated by NEB. Reprinted from [21], with the permission of AIP Publishing



During the NEB optimisation process the position of the images are adjusted. For $N + 1$ images, the position of each freely moving atom corresponds to a vector $[\mathbf{R}_0, \mathbf{R}_1, \dots, \mathbf{R}_N]$ (with fixed endpoints $\mathbf{R}_0$ and $\mathbf{R}_N$). The force on each image is calculated including the component of the spring force parallel to the tangent of each image and the component of the true force perpendicular to the tangent. The tangent for each image is estimated from [21],

$$\hat{\boldsymbol{\tau}}_i = \frac{\mathbf{R}_{i+1} - \mathbf{R}_{i-1}}{|\mathbf{R}_{i+1} - \mathbf{R}_{i-1}|}. \quad (2.24)$$

The total force is then,

$$\mathbf{F}_i = \mathbf{F}_i^s|_{||} - \nabla V(\mathbf{R}_i)|_{\perp} \quad (2.25)$$

which is comprised of the perpendicular true force,

$$\nabla V(\mathbf{R}_i)|_{\perp} = \nabla V(\mathbf{R}_i) - \nabla V(\mathbf{R}_i) \cdot \hat{\boldsymbol{\tau}}_i \quad (2.26)$$

and the spring force,

$$\mathbf{F}_i^s|_{||} = k_{spring}[(\mathbf{R}_{i+1} - \mathbf{R}_i) - (\mathbf{R}_i - \mathbf{R}_{i-1})] \cdot \hat{\boldsymbol{\tau}}_i \hat{\boldsymbol{\tau}}_i. \quad (2.27)$$

The total force calculated for each image is applied to move their atomic positions at each step of the optimisation process and a projected velocity Verlet algorithm is used for the minimisation. The process continues until the force on the images has converged to zero.

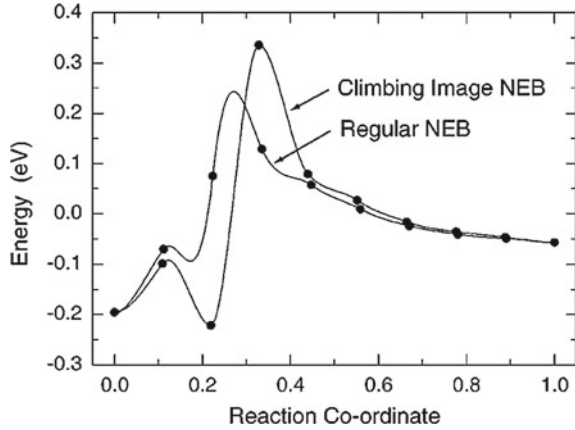
For NEB it is advised to use an odd number of images as one image (most likely in the middle) has a greater chance of finding the transition state, and will therefore give a more accurate value for the saddle point energy. Ideally many images should be used, as this will be able to give a better description of the minimum energy pathway. However adding images is computationally expensive since the number of processors required scales linearly with the number of images.

2.4.1 Climbing Image NEB

The climbing image method (CI-NEB) [20] improves the finding of the saddle point. The image with the highest energy is made to climb up the minimum energy pathway towards the saddle point and the spring constant across the band is varied so that the density of images is greatest near the saddle point. This is particularly useful when accurately determining the energy of the saddle point is required, such as when determining reaction rates (Fig. 2.3).

The CI-NEB method works by identifying the highest energy image after a few iterations. Then the force on this image is modified to,

Fig. 2.3 The energy profile of the elastic band calculated with CI-NEB compared to regular NEB. The climbing image converges to find the true saddle point. Reprinted from [20], with the permission of AIP Publishing



$$\mathbf{F}_{i_{max}} = -\nabla V(\mathbf{R}_{i_{max}}) + 2(\nabla V(\mathbf{R}_{i_{max}}) \cdot \hat{\tau}_{i_{max}})\hat{\tau}_{i_{max}}. \quad (2.28)$$

So that the force is inverted and the spring force component is completely removed. This force will now drive this image to eventually converge more closely to the saddle point.

2.5 Lattice Dynamics

Calculating the lattice dynamics of a system using DFT is a useful tool. It can be used to find the vibrational modes (phonons), and in turn find the phonon vibrational frequencies ω and the corresponding phonon density of states $D(\omega)$. The vibrational frequencies of a system are necessary for calculating the vibrational component of the free energy of a system. Furthermore, in transition state theory (Sect. 2.7.1) the pre-exponential factors A in an Arrhenius equation for the rate of a process $R = A \exp(-E/k_B T)$, with an energy barrier E , can be determined by finding the frequencies at the initial state and the transition state using the Vineyard equation [23] (see Eq. (2.43)). Finally, calculating the frequencies is needed in order to confirm convergence to the true saddle point since at this point there must be exactly one imaginary frequency.

In order to determine the lattice dynamics the dynamical matrix may be calculated using the frozen-phonon approximation [24]. The starting point for this is the Hamiltonian for the motion of atoms in a crystal. This is comprised of the kinetic energy and the potential energy,

$$H = \sum_{\alpha,k} \frac{p_{\alpha,k}^2}{2m_k} + \Phi \quad (2.29)$$

The potential energy Φ is the result of small atomic displacements. For a system of atoms in a unit cell with periodic boundary conditions applied, the displacement of an atom, κ , in a unit cell, l is given by, $\mathbf{u}_{l\kappa}(t)$. Therefore at a time t the position of a particular atom κl is given by $\mathbf{R}_{kl} = \mathbf{r}_k + \mathbf{r}_l + \mathbf{u}_{kl}(t)$.

The potential energy can be Taylor expanded in terms of the atomic displacements about the equilibrium positions of the atoms:

$$\Phi = \Phi_0 - \sum_{\alpha'l'k'} \Phi_{\alpha'l'k'} u_{\alpha'l'k'} + \frac{1}{2} \sum_{\alpha l k, \alpha' l' k'} \Phi_{\alpha l k, \alpha' l' k'} u_{\alpha l k} u_{\alpha' l' k'} + \dots \quad (2.30)$$

where the displacement direction, α is one of the cartesian components x, y, z. The first order term,

$$\left(\frac{\partial \Phi}{\partial u_{\alpha l k}} \right)_0 = -\Phi_{\alpha' l' k'} \quad (2.31)$$

becomes zero, since at equilibrium the forces are zero. Hence the potential (in the harmonic approximation) becomes

$$\Phi = \Phi_0 + \frac{1}{2} \sum_{\alpha l k, \alpha' l' k'} \Phi_{\alpha l k, \alpha' l' k'} u_{\alpha l k} u_{\alpha' l' k'} \quad (2.32)$$

where $\Phi_{\alpha l k, \alpha' l' k'}$ is the force constant matrix

$$\Phi_{\alpha l k, \alpha' l' k'} = \left(\frac{\partial^2 \Phi}{\partial u_{\alpha l k} \partial u_{\alpha' l' k'}} \right)_0 \quad (2.33)$$

which describes the force on an atom kl in the direction α due to the motion of an atom $k'l'$ displaced in the direction α' . Based on the force constant matrix and its symmetry, $\Phi_{\alpha l k, \alpha' l' k'} = \Phi_{\alpha' l' k', \alpha l k}$, the equation of motion for the system is

$$M_k \frac{\partial^2 u_{\alpha l k}}{\partial t^2} = - \sum_{\alpha' l' k'} \Phi_{\alpha l k, \alpha' l' k'} u_{\alpha' l' k'} \quad (2.34)$$

with M_k the atomic mass. This can be solved by seeking solutions of the form, $u_{\alpha l k} = 1/\sqrt{M_k} c_{\alpha l k} \exp(-i\omega t) \exp(-ikR)$, to give,

$$\omega^2 c_{\alpha l k} = \sum_{\alpha' l' k'} \frac{\Phi_{\alpha l k, \alpha' l' k'}}{\sqrt{M_k M_{k'}}} c_{\alpha' l' k'} \quad (2.35)$$

This can be expressed in matrix form as an eigenvalue and eigenvector problem:

$$\omega^2 \mathbf{c}_k = \mathbf{D}_k \mathbf{c}_k \quad (2.36)$$

with $\mathbf{c}_k = (c_{\alpha l k})$ a matrix of amplitudes, and $\mathbf{D}_k$ the dynamical matrix with elements:

$$D_{\alpha l k, \alpha' l' k'}(k) = \frac{1}{\sqrt{M_k M'_k}} \sum_{\alpha' l' k'} \Phi_{\alpha l k, \alpha' l' k'} \exp(-ikR). \quad (2.37)$$

Determining the dynamical matrix is achieved by the calculation of the force constant matrix. This contains $(3N)^2$ elements due to the cartesian components for each atom. By displacing each atom sequentially in the different directions and then calculating the resultant forces on the atoms, the individual elements can be calculated. For example, for an atom a displaced along the x-direction the force on atom b in the y direction gives rise to the force constant element $\Phi_{ax,by}$. This force constant component is given by,

$$\Phi_{ax,by} = \frac{F_{b,y}(a, +x) - F_{b,y}(a, -x)}{2\Delta} \quad (2.38)$$

where $F_{b,y}(a, +x)$ and $F_{b,y}(a, -x)$ are the forces on atom b in the y-direction, due to the displacement of atom a in the positive and negative x-directions respectively, and Δ is the length of the displacement. The value of Δ must be small with respect to the inter-atomic distance.

Once the force constants are found the eigenvalue problem Eq. (2.36) is solved to find the $3N$ eigenvalues ω^2 , which are the vibrational frequency modes. These may be used to determine the Arrhenius pre-factors in transition state theory as described in Sect. 2.7.1, or to calculate the vibrational free energy.

2.5.1 Vibrational Free Energy

The vibrational free energy due to the phonons in a system can be calculated using the harmonic approximation. The partition function for a harmonic solid with N atoms is simply the product of multiple single harmonic oscillators,

$$Z_N = \prod_{i=1}^{3N} \frac{e^{-\beta\epsilon_i/2}}{1 - e^{-\beta\epsilon_i}}. \quad (2.39)$$

where $\beta = 1/k_B T$ and $\epsilon_i = \hbar\omega_i$ is the energy of an individual phonon with frequency ω_i . The free energy $F_{vib} = -k_B T \ln(Z_N)$, is then given by,

$$F_{vib} = \frac{1}{2} \sum_{i=1}^{3N} \epsilon_i + k_B T \sum_{i=1}^{3N} \ln(1 - e^{-\beta\epsilon_i}). \quad (2.40)$$

Once the vibrational frequency modes are known, the vibrational free energy can then be calculated.

2.6 Core Level Binding Energies

X-ray photoemission spectroscopy experiments are performed by measuring the binding energy of a core electron. This electron is excited from the core by the x-ray photon and its kinetic energy left after leaving the surface (i.e. spent on the work function) is measured to determine its binding energy [25].

The core level binding energy of an electron in a particular atom can be calculated approximately with DFT methods. In this method the electron is removed from the core to the valence band. To calculate the binding energy the energy difference between a system with all electrons in the unexcited ground state, and the system with the electron excited from the core is determined. This is given by the energy difference,

$$E_{CLS} = E(n_c - 1) - E(n_c) \quad (2.41)$$

where $E(n_c)$ is the energy of the ground state with core electrons n_c , and $E(n_c - 1)$ is the energy of the excited state with $n_c - 1$ core electrons. The excited state is considered by removing the electron from the core and then relaxing the remaining core electrons, during which the core ionic PAW potential is created. The calculation is approximate as the core electron is not completely removed from the system. This would result in the system being charged, which is undesirable in calculations with periodic boundary conditions.

Calculating the core binding energy is useful as it allows experimental XPS spectra to be analysed. Each atom in a different environment will have a different core level binding energy. Based on this different species can be identified. It is worth noting that the calculated core binding energies can not be compared directly to the experimental binding energies and some relative shift will need to be applied to the energies in order to compare the data.

2.7 Kinetics

In order to determine the kinetics of various important chemical processes it is necessary to be able to evolve the dynamical motion of an atomic system in time. A simple way to do this is with molecular dynamics (MD) simulations. The forces on each atom are determined (classically or with DFT) and then the Newtonian equations of motion are solved to evolve the system (see Sect. 2.8). However this becomes problematic when the particular processes of interest occur infrequently. In order to resolve the atomic vibrations the MD time step must be of the order of femtoseconds but these infrequent events may only occur on average every microsecond, thus requiring impractically long simulation times. A way to overcome this problem is to coarse-grain the frequent events and so only consider the transitions corresponding to infrequent events. This is the principle of kinetic Monte Carlo simulations, as illustrated in Fig. 2.4.

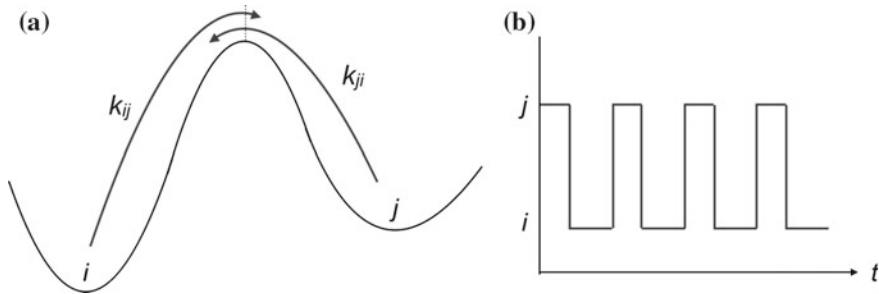


Fig. 2.4 An infrequent event as described by **a** molecular dynamics and **b** kinetic Monte Carlo. The event taking state i into state j has a low escape probability and hence the system will spend a long time in state i before the transition occurs. In molecular dynamics simulations this would result in long simulation times which is inefficient. In kinetic Monte Carlo the system is coarse-grained in terms of the atomic vibrations and only discrete events are considered

In order to coarse-grain and evolve only the infrequent events a Markov chain Master equation describing transitions out of a state is constructed. The rate of change in probability for being in a state i is found from the probability difference of entering the state from another state j , and leaving the state to another state j

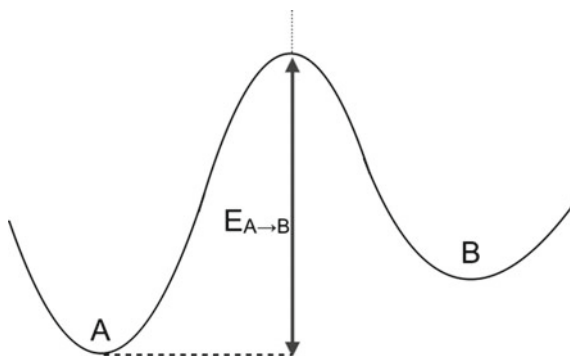
$$\frac{dP_i}{dt} = - \sum_{j \neq i} k_{i \rightarrow j} P_i(t) + \sum_{j \neq i} k_{j \rightarrow i} P_j(t) \quad (2.42)$$

Here the rate constants $k_{i \rightarrow j}$ give the average escape rate from state i to another state j . The sum is taken over all states j . If the possible transitions and their rate constants are known then evolving the system is simply achieved by solving the set of equations (2.42). This can be achieved numerically using a kMC simulation, whereby an ensemble of trajectories is created, and then the system is evolved from state to state via the allowed trajectories. The probability for being in a state $P_i(t)$ can then be determined from averaging over many trajectories.

2.7.1 Transition State Theory

Transition state theory (TST) allows the calculation of the rate constant for a particular transition. For an infrequent transition between two states A and B (as shown in Fig. 2.5) the rate constant is given by the equilibrium flux through the dividing surface between the states. This approximation requires that the transitions are classical, and that there no subsequent re-crossings of the barrier. Transitions must be rare so that the system has enough time to equilibrate at the minimum and there should be no correlated dynamical events, i.e. it is assumed that the system spends long enough time vibrating in a basin that it has no memory of previous transitions. Once

Fig. 2.5 For transition from $A \rightarrow B$ transition state theory can be used to determine the rate constant, $k_{A \rightarrow B}$ in terms of the energy barrier at the saddle point, $E_{A \rightarrow B}$ and the vibrational frequencies at the initial state and the saddle point (Eq. 2.43)



the system is at the dividing surface it is presumed that it will make the transition into the next state and not return to the original state. In fact this may lead to an overestimation in the rates [26, 27].

To further simplify transition state theory the harmonic approximation can be used (hTST) [23, 28]. The transition at the dividing surface is characterised by the saddle point which corresponds to the maximum along the transition pathway. Furthermore the potential energy at the minimum and at the saddle point are approximated by second-order potentials which correspond to the harmonic approximation. With this description the rate constant for the transitions from A to B can be given by

$$k^{hTST} = \frac{\prod_i^{3N} \nu_i^{min}}{\prod_i^{3N-1} \nu_i^{sad}} \exp(-E_{A \rightarrow B}/k_B T) \quad (2.43)$$

where $E_{A \rightarrow B}$ is the energy barrier given by the energy difference between the saddle point of the transition and the minimum of state A and k_B is the Boltzmann constant, T is the temperature. The pre-exponential factor is given by the ratio of the products of the $3N$ vibrational frequencies at the minimum and the $3N - 1$ frequencies at the saddle point i.e. with the imaginary frequency at the saddle point excluded, where N is the total number of atoms in the system. This ratio picks out the frequency at the minimum associated with the transition. Often the pre-exponential factor for a transition will be in the range of $10^{12} - 10^{13} \text{ s}^{-1}$.

Assuming both the initial and final states of a transition are known then the saddle point (and its energy barrier) can be found using the nudged elastic band method. Providing the saddle point is found accurately, the pre-exponential factors can also be determined by calculating the vibrational frequencies at the saddle point and either of the two minima. This allows the rate constant for a process to be found. In order to accurately simulate the kinetics of a system it is necessary to predetermine all possible processes and their energetics in this way. If certain transitions are overlooked then the correct reaction mechanisms may be excluded from the simulation, resulting in different outcomes to reality. This is one of the main obstacles for performing infrequent event simulations accurately.

2.7.2 Rate Equations

Consider a system of a gas of many reacting species. The evolution of this system can be calculated in a simplistic way using Eq. (2.42). In the limit of a large number of species then in Eq. (2.42) the probability of a state P_i can be approximated as the relative concentration of the reacting state constitutes N_i . For unimolecular reactions ($A \rightarrow B + C$) this is simply proportional to the reactant concentration N_A . For bimolecular reactions ($B + C \rightarrow A$) the probability of having the reacting state AB can be approximated as proportional to the product of the concentrations of the two reactants $N_A N_B$. This assumes that the probability for A and B to meet is equal to $N_A N_B$, which is independent of any spatial effects such as their diffusion. For instance, for a simple model system described by $A + B \leftrightarrow C$ with the rates of the forward and reverse processes given by $k_{AB,C}$ and $k_{C,AB}$ respectively, the Master equations describing the change in concentration for each species become:

$$\frac{dN_A}{dt} = N_C k_{C,AB} - N_A N_B k_{AB,C} \quad (2.44)$$

$$\frac{dN_B}{dt} = N_C k_{C,AB} - N_A N_B k_{AB,C} \quad (2.45)$$

$$\frac{dN_C}{dt} = N_A N_B k_{AB,C} - N_C k_{C,AB} \quad (2.46)$$

Here rate equations for the change in concentration of each species have been constructed. For a simple system like the one above the equations can be solved analytically. However for more complicated systems with many different species and processes it is necessary to evaluate the differential equations computationally. The concentration of each species is evaluated as the time is increased by a discrete time step value. Solving these ordinary differential equations simultaneously will determine the continuous kinetic evolution of each of the different species A, B and C depending on the rates $k_{AB,C}$ and $k_{C,AB}$. This method is based on only the relative concentrations of the species. All spatial information, such as their diffusion and effects present in the limit of high concentrations are neglected. In particular, the rate constants are independent on the species environment; this approximation breaks down at large concentrations. Therefore solving rate equations will only yield an accurate representation of the kinetics in the limit of a low concentration of species, considering that their diffusion is fast enough not to limit any of the bimolecular reactions.

The rate constants can be calculated assuming harmonic transition state theory (Eq. (2.43)) and using the NEB method to calculate the relevant energy barriers e.g. $E_{AB,C}$. Based on hTST the pre-exponential factor ν in all cases will be approximately $10^{12} - 10^{13} \text{ s}^{-1}$.

2.7.3 Kinetic Monte Carlo

Kinetic Monte Carlo simulations differ from the rate equation approach described above in that instead of considering continuous concentrations of species that change in turn with time, the transition events are discretised. In this case instead of uniformly increasing the time, the time that has passed before a single transition can occur is calculated and then the system is evolved. For a system in state i there will be a rate constant that describes the probability of escape to any other state, k_{tot} . The probability, p_{ii} that the system remains in the same state i at time t is,

$$p_{ii}(t) = \exp(-k_{tot}t) \quad (2.47)$$

and hence the escape probability to have escaped after a time t' is $1 - p_{ii}(t')$. If the system was then to make an instantaneous transition to a state j the probability would be equal to the ratio of the rate constants for the transition to j and the total of all transitions, k_{ij}/k_{tot} . If the system remains in state i for a time t and then instantaneously makes a transition to state j then the probability is given by:

$$p_{ij} = \frac{k_{ij}}{k_{tot}} \exp(-k_{tot}t) \quad (2.48)$$

The time for the transition to occur Δt can be found from (2.47), assuming the probability can be considered as a random number (RN) between 0 and 1:

$$\Delta t = -\ln(RN) \frac{1}{k_{tot}} \quad (2.49)$$

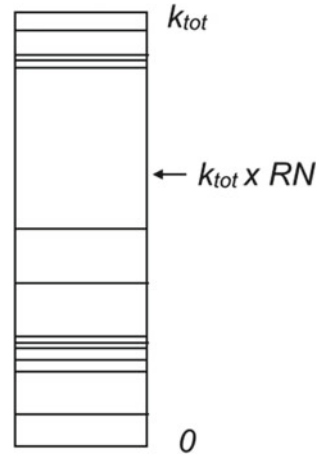
The escape rate for a system in state i is formed of the sum of the rate of all possible transitions, $k_{tot} = \sum_j k_{ij}$.

The Bortz, Kalos and Lebowitz (BKL) algorithm is used to determine which transition is successful [29]. The rate constants for each transition are ordered into a “stack” and joined end to end. Each has a length equal to their value. The total length of the “stack” will therefore be equal to k_{tot} . Drawing a random number between 0 and k_{tot} and selecting the transition that this number lands on ensures that transitions are selected with the correct probability. Only one random number is required for this selecting process. The chosen process p' will then fulfil the criteria,

$$\sum_{p=1}^{p'} k_{ip} \geq RN \times k_{tot} \geq \sum_{p=1}^{p'-1} k_{ip} \quad (2.50)$$

where the rates for each process p out of a state i are summed. The BKL algorithm is illustrated in Fig. 2.6.

Fig. 2.6 The BKL algorithm for choosing a process in kMC. The rate constants are stacked into a list, where the height of each process corresponds to its rate constant, and the total height of the stack is k_{tot} . A random number between 0 and 1 is drawn and multiplied by k_{tot} in order to chose a process with probability proportional to its rate constant



Once the transition has been chosen and the time step calculated the system is updated with the new move. A new list of transitions is generated based on the new state and the process is then repeated.

2.7.3.1 Time-Dependent kMC

The kMC algorithm outlined above assumes that the rate constants are independent of the time. However for simulations of the thermal evolution of a system, the change in temperature will naturally affect the rates, which will mean that calculation of the time step will be time-dependent. Calculating Δt using Eq. (2.49) does not work, since k_{tot} at time t will be different from k_{tot} at $t \rightarrow t + \Delta t$. Instead the time step has to be calculated taking into account the time dependence of the rates [30]. For the usual system in a state i the probability of the system being still in state i after a time dt is:

$$p_i(t + dt) = p_i(t)[1 - k_{tot}(t)dt] \quad (2.51)$$

where $k_{tot}(t)$ is the time dependent rate. Rearranging this and solving the differential equation gives:

$$\frac{dp_i(t)}{dt} = -k_{tot}(t)p_i(t) \quad (2.52)$$

$$\ln p_i(t + \Delta t) = - \int_t^{t+\Delta t} k_{tot}(\tau) d\tau \quad (2.53)$$

where Δt is the time which passes before the system can escape which is calculated from the time t of the previous step. For the time independent case, the right hand side simply becomes $k_{tot} \Delta t$ and Eq. (2.49) is recovered.

For time dependence, the time until escape, Δt , can be calculated from the integral,

$$-\ln(RN) = \int_t^{t+\Delta t} k_{tot}(\tau) d\tau \quad (2.54)$$

where RN is a random number between 0 and 1. Finding Δt then involves finding the upper limit of the integral over time. To do this the integral can be evaluated iteratively between t and $t + nt_i$, where $t_i \ll \Delta t$ and n is a positive integer so that the upper limit is increased gradually. Δt is found when the integral becomes greater than $-\ln(RN)$. This is when Δt has increased such that the probability of escape is certain.

2.7.4 Lattice-Based kMC

Another main difference between the rate equation approach and kMC is that spatial effects are included. In the case of reactions occurring on a surface simulations are carried out on a two-dimensional grid where the adsorbed molecules occupy grid sites. Molecules may diffuse between grid sites of the lattice during the simulation. Bimolecular reactions can only occur if the reacting molecules are located near to each other on the grid. This is dependent on whether the molecules can easily diffuse to meet each other. Likewise unimolecular decomposition reactions are only possible if there is the correct amount of empty space on the grid such that the product species can fit after a reaction. These reactions may become limited at high coverages where many sites are already occupied. For convenience, the simulations are run on a grid assuming that all species of interest can only occupy the grid vertices.

Local interactions between molecules can also be included with lattice-based kMC. The simplest way of achieving this is to consider nearest-neighbour interactions. For each different combination of neighbouring species the rate constant for reactions can be calculated depending on the location and the species of the nearest neighbour. For complicated systems with many different species this is unfeasible since there will be many different rates to calculate.

2.8 Molecular Dynamics

Molecular dynamics simulations are used to simply evolve the dynamical motion of a system of atoms or molecules over an incremental time interval. The motion of the a system of N atoms is simulated by evolving the Newtonian equations of motion at each time step dt . For a force F_i acting on atom i the motion will evolve with classical mechanics according to:

$$F_i = m_i \dot{v}_i \quad v_i = \dot{r}_i \quad (2.55)$$

The forces required for solving the equations of motion are derived from the atomic potential energy field. This may be determined using density functional theory or classically with empirical potentials. The equations of motion (2.55) are solved numerically for a finite time step dt by integration using, for example, the velocity Verlet algorithm [31]. The size of the time step must be of the order of femtoseconds in order to resolve atomic vibrations. This limits standard MD simulations to a total simulation time of microseconds when using empirical potentials and to picosecond when using DFT calculated forces.

For MD calculations different statistical ensembles can be used depending on the quantities of interest in the system. In the microcanonical ensemble (or NVE) the number of particles N , the volume V , and the total energy E are constrained. In this ensemble the exchange between kinetic energy and potential energy of the atoms can be followed, however the total energy is constant.

In some scenarios the canonical ensemble (or NVT) is more suitable as the temperature T may be constrained, but the pressure is allowed to vary. This is useful for replicating experimental scenarios where high temperatures may be required. It is also practical for dissipation of energy through a system. The size of the system itself will affect the size of the temperature fluctuations.

2.8.1 Canonical Ensemble: NVT

To maintain the correct temperature in the canonical ensemble a thermostat needs to be applied to all or some of the atoms in the system. This type of simulation corresponds to the one in which a fragment of the whole system is attached to the rest of it (very large), which is treated as a heat bath at constant T , and hence adding or removing energy from the boundaries of the system when necessary can be facilitated. When doing this it is important to preserve the correct thermodynamics of the system and ensure that the dynamics is realistic.

2.8.1.1 Velocity Rescaling and the Berendsen Thermostat

The simplest way to ensure that the system temperature is constrained to the desired value is to rescale the velocity of the atoms. In the velocity rescaling method the velocity is scaled at each time step in order to adjust the temperature of the system.

$$\mathbf{v}_{new} = \lambda \mathbf{v}, \quad \lambda = \sqrt{\frac{T}{T_{inst}}}, \quad T_{inst} = \frac{2E_{kin}}{3k_B} \quad (2.56)$$

This however does not capture energy fluctuations in the system and the correct thermodynamics is lost.

The Berendsen thermostat also involves rescaling the average velocity of the atoms in order to adjust to the correct temperature, however instead of rescaling at every time step the rescaling takes place with a time scale for the heat transfer, τ , via [32]

$$\lambda^2 = 1 + \frac{\delta t}{\tau} \left(\frac{T}{T_{inst}} - 1 \right). \quad (2.57)$$

As with velocity rescaling the Berendsen thermostat also fails to capture the correct thermodynamics.

2.8.1.2 Andersen Thermostat

In the Andersen thermostat the system is coupled to a heat bath, which allows effectively random stochastic forces to be applied to particles that are selected randomly [33]. The selected particle collides with the heat bath over a certain timescale and a new velocity is applied to it. The velocity is drawn from a Maxwell–Boltzmann distribution corresponding to the thermostat temperature. In the limit of an infinitely long simulation with many instances of velocity changes the canonical ensemble can be recovered. However once the velocity of the chosen particle is reassigned it will have lost all memory of its previous dynamics.

2.8.1.3 Nosé–Hoover Thermostat

In the Nosé–Hoover thermostat the temperature is regulated by the addition of an extra artificial degree of freedom, s to the equations of motion [34, 35]. This acts as a heat reservoir to exchange thermal energy with the system. The extra degree of freedom and the corresponding Hamiltonian are selected in such a way that the combined system is microcanonical; however, when the extra degree of freedom is integrated over, the system is exactly canonical. The Hamiltonian becomes:

$$H_{Nose} = \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m_i s^2} + U(\mathbf{r}^N) + \frac{p_s^2}{2Q} + nk_B T \ln s \quad (2.58)$$

where Q is an effective mass related to the additional degree of freedom s and n is the number of degrees of freedom, $n = 3N + 1$. It then follows that the momentum of s , p_s is equal to $Q\dot{s}$. The third and fourth terms in Eq. (2.58) are related to the kinetic and “potential” energy of the artificial degree of freedom, respectively. The choice of the effective mass Q is important as this controls the coupling of the system to the reservoir. If Q is too large the coupling with the bath is reduced and the correct temperature will only be obtained after a long time. If Q is too small the temperature will fluctuate appreciably.

2.8.2 Langevin Thermostat

In order to ensure realistic dynamics of the system the Langevin thermostat can be used. Here the motion of slow particles throughout a continuum of fast particles is considered [36]. The small particles cause friction on the larger particles and also have some kinetic energy that transfers some energy to the larger particles. Correspondingly a friction term and force driving stochastic term $\mathbf{F}_i$ are added to the equations of motion for the large particles:

$$m_i \dot{\mathbf{v}}_i = -\frac{\partial U(\mathbf{r}^N)}{\partial \mathbf{r}_i} - \gamma m_i \mathbf{v}_i + \mathbf{F}_i \quad (2.59)$$

The friction term depends on the damping parameter γ . The driving force term must be balanced by the friction, so that the canonical ensemble is recovered. The force is chosen randomly within a Gaussian distribution with a dispersion σ_i given by [37]:

$$\sigma_i = \sqrt{2\gamma m_i k_B T / \Delta t} \quad (2.60)$$

where Δt is the MD time step. The exact dynamics can be determined providing the choice for γ is sensible. A method for determining a value for the damping parameter is detailed below.

2.8.2.1 Determining the Damping Parameter

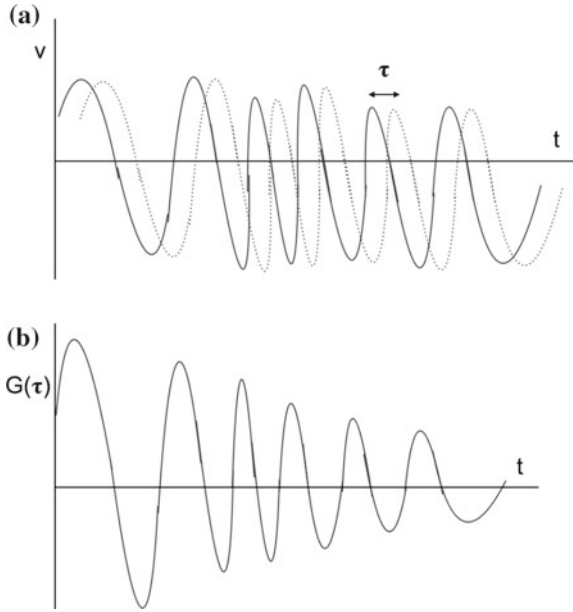
The value of the damping parameter in the Langevin thermostat has to be chosen so that the correct dynamics of the system is obtained. To do this it is possible to determine the phonon DOS of the system from the molecular dynamics with the thermostat applied to some of the atoms and then compare this to the phonon DOS as determined from lattice dynamics. The phonon DOS can be found from an MD simulation by calculating the velocity autocorrelation function of a selection of NVE atoms located within a system where the thermostat is applied to a different selection of NVT atoms. In this setup kinetic energy will be added and removed to the NVE atoms from the NVT atoms, while the NVE atoms maintain the proper dynamics. Taking the Fourier transform of the velocity autocorrelation function returns the phonon DOS.

The velocity autocorrelation function (VACF) determines how correlated the velocity of a system is at two separate times. For a velocity of a particle at a time t and at future time $t + \tau$ the correlation function will decay as τ is increased and the two velocities become further apart in time. This is illustrated in Fig. 2.7.

The VACF, $G(\tau)$ is given by

$$G(\tau) = \sum_i \langle v_i(t_0) v_i(t_0 + \tau) \rangle_{t_0} = \frac{1}{N} \sum_{i=1}^N \frac{1}{t_{max}} \sum_{t_0=1}^{t_{max}} v_i(t_0) v_i(t_0 + \tau), \quad (2.61)$$

Fig. 2.7 **a** The velocity of a particle at t_0 , $v_i(t_0)$ and shifted by τ , $v_i(t_0 + \tau)$ and **b** the corresponding velocity autocorrelation function $G(\tau)$



where v_i is the velocity of particle i . In Eq. (2.61) the velocity correlation function of each particle is found as τ is increased linearly until the end of the simulation time is reached t_{max} . A particle average is then taken by summing the individual velocity correlation functions and then dividing by the number of particles N .

By taking the Fourier transform of $G(\tau)$ the phonon DOS is recovered. By varying γ and monitoring the changes in the phonon DOS an optimum value for γ can be chosen where the calculated phonon DOS matches the features of a reference phonon DOS, as determined from lattice dynamics simulations.

2.9 Ir(111) Surface Parameterisation

The first step in any DFT calculation is to parameterise the system. For a bulk crystalline system this means determining the correct lattice constant given the basis set, basis set cut off energy and the pseudopotentials. Since periodic boundary conditions are applied, to construct a surface slab a vacuum gap must be introduced to separate adjacent layers. Parameterising the surface set up requires determining a suitable value for the vacuum gap, as well as the number of layers required to approximate the surface. More layers are favourable to get a more accurate result; however this increases the number of atoms in the simulation, and slows down calculations.

The calculations in this thesis are based on epitaxial graphene growth on the Ir(111) surface. For iridium the m-DVZP basis set [38], with a plane wave cut off energy of 300 Ry were used, along with the GGA-PBE exchange-correlation functional [39] and Goedecker-Teter-Hutter (GTH) pseudopotentials [19]. Van der Waals forces are included with the DFT-D3 method [8].

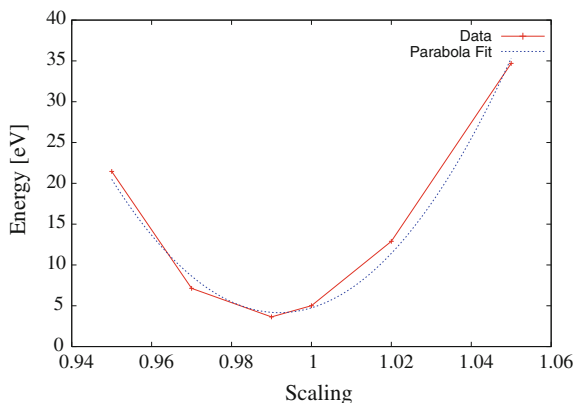
2.9.1 Bulk Lattice Constant

The unit cell for iridium is face-centered cubic. The experimental lattice constant is 3.84 Å and hence the basic lattice vectors for the unit cell are: $\mathbf{a}_1 = (0, 0.5, 0.5)a$, $\mathbf{a}_2 = (0.5, 0, 0.5)a$ and $\mathbf{a}_3 = (0.5, 0.5, 0)a$, where a is the lattice constant.

In CP2K only the gamma point is used, therefore there is not a well defined k mesh for the integration. To compensate for this large real-space cells must be used to take into account long range interactions. To begin with, a $4 \times 4 \times 4$ cell of iridium atoms with a lattice constant of 3.84 Å is constructed. This lattice constant is the experimentally calculated value, however the actual value of the lattice constant that minimises the energy of the atomic lattice may vary slightly from this. This will be affected by the choices of the basis set, local interactions and pseudopotentials.

To determine the value of the lattice constant of the bulk Ir the unit cell is scaled and the energy calculated. By fitting a parabola to the results and finding the minimum, the optimum lattice constant value is found. Based on the results in Fig. 2.8 the lattice constant for iridium is 3.81 Å. This is very close to the experimental value, and suggests that the calculation set up accurately describes the system. Correspondingly, the Ir lattice is rescaled to this calculated lattice constant value.

Fig. 2.8 The total energy of the Ir bulk lattice for different scaling applied to the primitive unit cell. The dotted line is an interpolation of the calculated energies with a parabola



2.9.2 Ir(111) Surface

From the Ir bulk an Ir(111) surface slab can be created by dissecting along the (111) Miller indices of the unit cell and introducing a vacuum gap to produce slabs that are separated from each other in each unit cell. Since CP2K requires a large unit cell size, and to ensure molecules placed on the surface are well separated an 8×8 unit cell is used for a single Ir(111) layer.

Creating a surface with a large number of layers gives the most accurate representation, however this is too computationally expensive. Therefore only a few layers may be used, however they must still be able to represent the properties and behaviour of a surface with many layers. These include the surface energy, the electronic properties (DOS and band structure) and its interaction with any surface species placed onto it.

First the change in surface energy with the number of layers is determined. The surface energy per atom is defined as:

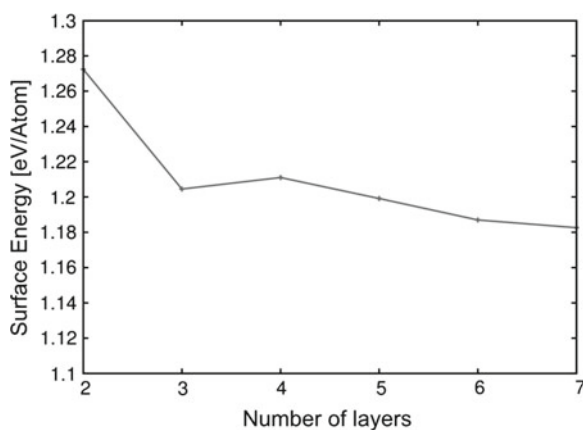
$$E_{surf} = \frac{1}{2N}(E_{slab} - NE_{bulk}), \quad (2.62)$$

where E_{slab} is the total energy of the slab, E_{bulk} is the energy of a single bulk atom (in the case of Ir) and N is the total number of atoms in the slab. In this calculation both the upper and the lower surfaces are allowed to relax.

As the number of layers increases this energy will converge when the top and bottom surfaces are far enough apart and do not interact with each other. This gives an idea of how many layers should be used. The surface energy for the Ir(111) surface with varying number of layers is shown in Fig. 2.9. The vacuum gap is greater than 15 Å.

For more than three layers the surface energy varies by less than 0.05 eV/Atom. Therefore more than two layers should be used in order to get an accurate result (less

Fig. 2.9 The surface energy per surface atom of an 8×8 Ir(111) surface cell for different numbers of layers



than 0.05 eV error). Even with only two layers the energy is still within 0.1 eV of its converged value. As adding an extra layer to the system requires 64 more atoms it is computationally expensive to consider many layers. For the surface calculations in this thesis four layers are used unless stated. Two layers were used initially for expensive calculations such as NEBs. To obtain more accurate values for the energy barriers this was increased to up to 7 layers, where necessary. This is detailed in the Appendix A. In all cases the vacuum gap is greater than 15 Å.

In order to preserve the bulk geometry in the surface slab a number of the bottom layers must be fixed to the bulk lattice constant, while the upper layers are free to relax. The number of layers which are fixed to the Ir bulk geometry may be varied. The system must have enough of these to be similar to the bulk, but near the top of the surface some layers must be allowed to relax so that it can behave correctly near the vacuum gap so that it can interact with any molecules which may be added to it.

2.9.3 Plane Wave Cutoff Energy

The plane wave cutoff energy E_{cut} dictates the cut off for the largest plane waves vectors G_{max} where $E_{cut} = \hbar^2 G_{max}^2 / 2m$, where m is the electron mass. Choosing a large enough value is crucial in order to include enough plane waves to give accurate results. The convergence of the total energy of the system can be monitored as the cutoff energy is increased until the energy converges.

Energy differences will converge with E_{cut} much faster than total energies. Since only the relative energy differences are of interest (e.g. adsorption energies, energy barriers, binding energies and formation energies) it is possible to take a lower value for the energy cutoff. The calculated formation energy for a vacancy defect in the iridium bulk and the adsorption energy for a CH₂CH molecule on the Ir(111) surface are shown in Table 2.1 for a variety of energy cutoffs. To determine the formation energy of the vacancy defect in the bulk Ir the energy difference between the energy

Table 2.1 The variation of energy differences with energy cutoff E_{cut} for the formation energy of an Ir bulk defect and the adsorption energy of CH₂CH on a Ir(111) surface with 3 layers

E_{cut} [Ry]	E_f (Ir bulk defect) [eV]	% Error	E_{ads} (CH ₂ CH) [eV]	% Error
200	-14.154	0.07	-3.802	0.05
300	-14.155	0.06	-3.802	0.05
350	-14.155	0.06	-3.802	0.05
400	-14.161	0.02	-3.803	0.02
450	-14.164	<0.01	-3.805	0.02
500	-14.164	<0.01	-3.804	<0.01
600	-14.164	<0.01	-3.804	<0.01

of the defective cell E_{defect} plus the energy of a single Ir atom E_{atom} and the energy of defect-free cell E_{bulk} is calculated:

$$E_f^{defect} = [E_{defect} + E_{atom}] - E_{bulk} \quad (2.63)$$

The adsorption energy of the CH_2CH molecule on the Ir(111) surface is given by:

$$E_{ads} = E_{\text{Ir}+\text{CH}_2\text{CH}} - [E_{surf} + E_{\text{CH}_2\text{CH}}] \quad (2.64)$$

In each case the geometries are relaxed. Overall the error in the energies due to the cutoff is very small (less than 1%). Almost any of the tried values could be taken for the energy cutoff. In the calculations of this thesis a value of 300 Ry is used.

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