

## Chapter 2

# Atomic Interactions

### 2.1 Introduction

The simulations contained in this work make use of a pair-wise description for atom interactions. Two groups are of interest: ionic interactions, when studying defects in crystal lattices (i.e. a Born-type model [8]); and non-ionic Lennard-Jones interactions [9], when studying the behaviour of gas atoms on a surface.

In addition to purely electrostatic forces, the energy of an interaction between pairs of atoms arise from changes to the wave functions as the atoms approach. The resulting energy can be considered in terms of two components: a long range interaction,  $\Phi_{lr}$ , and a short range interaction,  $\Phi_{sr}$ . The sum of these these interaction energies gives the total energy,  $\Phi$ , for the interaction as a function of the atom separation,  $r$ . Thus,

$$\Phi(r) = \Phi_{lr}(r) + \Phi_{sr}(r) \quad (2.1)$$

The sum of all such interactions gives the total energy of the system.

The mathematical form chosen to represent  $\Phi_{lr}$  and  $\Phi_{sr}$  will depend on the physics of the system modelled. The method of calculating interactions for an entire system will

depend on the type of information required and the nature of the system.

### 2.1.1 Simulation of Ionic Lattices

When simulating ionic lattices both long range and short range interactions are accounted for. The energy of the lattice is evaluated by series summation of all interactions, although for the long range terms approximate techniques are necessary as series convergence is slow. Energy minimisation can then be used as a basis with which to find the global energy minimum of the lattice. Lattice defects may be introduced, allowing a variety of defect energies to be calculated.

### 2.1.2 Simulation of Gas Layer Evolution onto a Surface

When simulating noble gas atom interactions with a surface there are no long range, slowly converging, terms. The longest range terms converge quickly and can therefore be summed directly. Attachment energies are calculated and a stochastic method used to simulate adsorption and desorption of gas atoms onto a surface.

## 2.2 Fundamental Atomic Interaction Principles

In a given system there may be many atoms interacting with each other such that the interaction is normally expressed as a series summation of interactions between increasing numbers of atoms,

$$\Phi(r) = \sum_{ij} \Phi_{ij}(r) + \sum_{ijk} \Phi_{ijk}(r) + \sum_{ijkl} \Phi_{ijkl}(r) + \dots \quad (2.2)$$

where  $ij$  refers to all atom pairs,  $ijk$  to all atom triplets, etc.

The interactions of interest in the systems studied here should be highly isotropic

and so the majority of the interaction can be approximated by pair potentials (i.e.  $\Phi(r)$  is approximated to  $\Phi_{ij}(r)$ ).

### 2.2.1 The Long Range Interaction

Now that the situation is simplified to a set of pair-wise interactions the form for the long range and short range interactions can be discussed. In an ionic system if a pair of ions  $i$  and  $j$ , are separated by a distance,  $r_{ij}$ , there is a coulombic interaction energy found by solving:

$$\Phi_{lr}(r_{ij}) = \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} \quad (2.3)$$

where  $q$  is the charge on the ion and  $\epsilon_0$  is the permittivity of free space. In non-ionic systems this interaction will not be present and only short range interactions need be considered.

### 2.2.2 The Short Range Interaction

While the origin of the long range coulombic interaction is easy to understand the short range interaction is more complex. Electron cloud overlap leads to strong short range repulsive forces since electron density, and therefore nuclear shielding, is reduced. This in turn increases the coulombic repulsion between the positively charged nuclei. It is this force partly that prevents a crystal lattice from collapsing in on itself. However, before the nuclear repulsion becomes significant there is also a quantum mechanical effect because the electrons are forced to occupy a smaller portion of space. Since the electrons must maintain orthogonal orbitals, the energy states increase in energy. This is known as the orthogonalisation or Pauli repulsion. There is a contrasting longer range attractive interaction at larger interatomic distances arising from the formation of instantaneous dipoles between adjacent electron clouds. This effect, known as the van der Waals interaction, is

clearly also quantum mechanical in origin.

Formal charges are assumed for lattice simulations and gas surface interactions are non-ionic, thus, the short range potential is the only simulation variable throughout. As such, great care over the form and parameters of the short range interactions must be exercised. It is interesting to note that the long range term makes up the great majority of the total interaction energy. Despite this, by only adjusting the much smaller short range contribution the whole spectrum of crystal structures can be reproduced. Below some of the possible descriptions for the short range interaction are discussed.

The most basic form would be a simple harmonic interaction,

$$\Phi_{sr}(r_{ij}) = \frac{1}{2}K(r_{ij} - r_0)^2 \quad (2.4)$$

where  $r_{ij}$  is the distance between two atoms  $i$  and  $j$ ,  $r_0$  is the equilibrium bond distance and  $K$  is the harmonic force constant. This model is quite sufficient for systems that only deviate slightly from  $r_0$  and for which interactions can realistically be confined to adjacent pairs of ions. However, for systems where large deviations may be expected (e.g. defective systems) alternative potential forms must be employed.

For example, a Morse potential can be used to describe wider ranges of separation,

$$\Phi_{sr}(r_{ij}) = D_{ij} [1 - \exp(-\beta_{ij}\{r_{ij} - r_0\})]^2 \quad (2.5)$$

where  $D_{ij}$  is the disassociation energy of the bond and  $\beta_{ij}$  is a variable parameter that can be determined from spectroscopic data. This type of model is particularly useful in chemical systems to model bonded covalent interactions and the O-H species [9].

The Lennard-Jones potential,

$$\Phi_{sr}(r_{ij}) = \frac{A_{ij}}{r_{ij}^{12}} - \frac{B_{ij}}{r_{ij}^6} \quad (2.6)$$

where  $A_{ij}$  and  $B_{ij}$  are the variable attractive and repulsive parameters respectively, is often used to model non-bonded interactions such as rare gas solids [9]. In this form the

$r^{12}$  term represents the short range repulsive electron cloud interaction and the  $r^6$  term the intermediate range van der Waals energy.

If the  $r^{12}$  term in the Lennard-Jones potential is replaced by a more complex dual parameter exponential term the Buckingham potential form results,

$$\Phi_{sr}(r_{ij}) = A_{ij} \exp\left(\frac{-r_{ij}}{\rho_{ij}}\right) - \frac{C_{ij}}{r_{ij}^6} \quad (2.7)$$

where  $A_{ij}$  and  $\rho_{ij}$  describe components of the repulsive interaction and  $C_{ij}$  describes the attractive interaction.  $A_{ij}$  and  $\rho_{ij}$  are thought to relate to the number of electrons and the electron density respectively, while  $C_{ij}$  is meant to represent the van der Waals interaction. In the case where ions have small polarisabilities the  $C$ -term is often omitted giving rise to a Born-Mayer potential [10, 11],

$$\Phi_{sr}(r_{ij}) = A_{ij} \exp\left(\frac{-r_{ij}}{\rho_{ij}}\right) \quad (2.8)$$

The Buckingham and Born-Mayer potentials have been used successfully in the excellent work of Grimes [12–16] and co-workers to model a wide range of crystal structures and ionic species.

Finally it is worth mentioning the original simple short range potential for ionic systems due to Max Born [17],

$$\Phi_{sr}(r_{ij}) = \frac{A_{ij}}{r_{ij}^n} \quad (2.9)$$

where  $A_{ij}$  is a variable parameter and the optimum value of  $n$  was determined to be approximately 9.

The classification of the short range interaction used here is somewhat generalised since the van der Waals interaction will operate over several atomic distances. However, it is often convenient to think of it as a short range interaction since it reduces rapidly with  $r_{ij}$ . As such, the interaction is often considered zero beyond a sensible cut-off distance.