Chapter 2

Atomistic Simulation

Despite the steady increase in computer power, we are not yet able to model all physical processes. For example, it is still not possible to tackle a large system of atoms (i.e. $> 10^3$) quantum mechanically, except under specific circumstances, so methods employing inter atomic potentials are still very useful. For the same purpose of extending capabilities, cellular automata methods based on atomistic simulation are being used today [29].

The first UO_2 defect calculations using the Born [32] model of the ionic solid were performed by Tharmalingam [33] in the Materials Department of Imperial College. He used a method by Boswarva and Lidiard [34] in which the crystal was divided into two regions. Region I contained the defect, and the positions of its ions were minimized to zero force (see section 2.2). Polarisation of region II in response to the defect in region I was calculated using the Mott-Littleton approximation (equation 2.43).

The problem Tharmalingam encountered was that he had to correct his calculations by a 7% factor (derived from NaCl calculations) in order to get sensible results.

Later studies by Catlow and Lidiard in 1974 employed a core-shell model [24], allowing ion polarisation. They also divided region II in two parts (region IIa and IIb), in order to obtain a smooth transition from the region I-II boundary to the non-relaxed region IIb. This method produced more reliable results.

In this chapter, we shall take a close look at the perfect lattice and the simulation of defects therein. We shall see how we can derive useful data from the simulations. However, this description of the techniques is by no means complete, nor does it describe what the programs implementing these methods do, exactly, since they have, over the years, become very complex, and employ additional algorithms to increase performance.

2.1 The perfect lattice

Considering only pairwise ionic interactions, — in our case Coulombic and short-range, $\Phi(r_{ij})$, interactions — the lattice energy, E_L, per (single atom, i) unit cell can be calculated from:

$$E_{L,i} = \frac{1}{8\pi\epsilon_0} \sum \frac{q_i q_j}{r_{ij}} + \frac{1}{2} \sum \Phi(r_{ij}) \quad i \neq j, \tag{2.1}$$

where q_i is the charge of ion i, and r_{ij} is the distance between ions i and j and ϵ_0 is the dielectric constant. The first summation concerns the Coulombic or electrostatic energy of the lattice, and the second deals with the short range interactions between the ions. Although formally there is nothing wrong with this summation, it can not be solved directly. The $1/r$ dependence of the Coulombic potential combined with the summation over three-dimensional space forces us to use a mathematical construction to calculate the lattice energy.

Fortunately, the Coulombic part of the lattice energy can be written as a sum

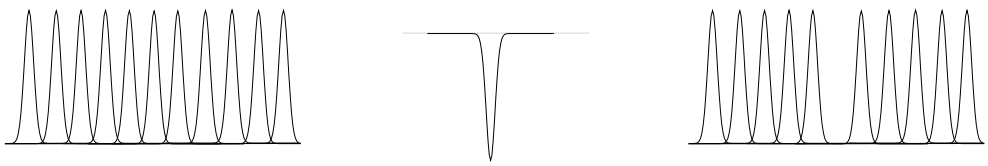
over charge times potential, $\phi(\vec{r_i})$:

$$E_{CL,i} = \phi(\vec{r_i})q_i, \tag{2.2}$$

which reduces the problem to that of calculating the potential at the ion site (or sites in the case of a more complex unit cell), but does not take away the convergence problem.

The convergence problem is solved by using the Ewald method, a mathematical construction which allows the calculation of the energy of an infinite array of Coulombic charges. Presented here is the principle of the Ewald method for a hypothetical single atom unit cell material. The observant reader will note that the lattice energy for our hypothetical system is infinite, but the method, when applied to a normal neutral ionic system, results in a finite lattice energy.

The Ewald method divides the potential into two parts; ϕ_1 and ϕ_2. ϕ_1 (Figure 2.1) is based on a lattice of positive Gaussian charge distributions, minus one Gaussian at the position $\vec{r_i}$ of reference ion i; ion i does not feels its own electrostatic potential.



(a) ϕ_L (b) $-\phi_i$ (c) $\phi_1 = \phi_L - \phi_i$

Figure 2.1: Construction of ϕ_1 from a lattice of Gaussians minus a Gaussian at a reference point as used in the Ewald approximation.

ϕ_2 (Figure 2.2) is based on a complete lattice of negative Gaussians and positive point charges the total of which gives charge zero.

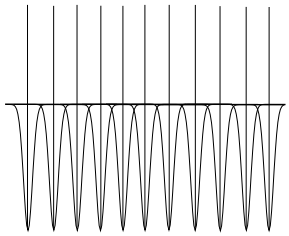


Figure 2.2: ϕ_2 as used in the Ewald approximation.

Summing ϕ_1 and ϕ_2 results in the potential at reference site i, $\phi(\vec{r}_i)$, caused by an array of point charges. Let us consider ϕ_1 first.

ϕ_1 Can be divided into two parts:

$$\phi_1(\vec{r}) = \phi_L(\vec{r}) - \phi_i(\vec{r}), \tag{2.3}$$

where ϕ_i is the potential caused by ion i and ϕ_L is the complete lattice potential, which can be represented by a Fourier series:

$$\phi_L(\vec{r}) = \sum_G c_G e^{\mathbf{i}\vec{G}\cdot\vec{r}}, \tag{2.4}$$

caused by a charge density

$$\rho(r) = \sum_G \rho_G e^{\mathbf{i}\vec{G}\cdot\vec{r}}. \tag{2.5}$$

In these equations, G is the set of possible reciprocal lattice vectors. The relation between c_G and ρ_G is evident using Poisson's relation between the electrostatic potential and the charge density:

$$\rho_G = G^2 c_G. \tag{2.6}$$

A Gaussian charge density for a single atom of charge q_i and half width $\sqrt{\frac{ln2}{\eta}}$ is:

$$\rho_i(r) = q_i(\eta/\pi)^{3/2} e^{-\eta r^2}. \tag{2.7}$$

Now equations 2.7 and 2.5 can be evaluated by multiplying with $e^{-\mathbf{i}\vec{G}\cdot\vec{r}}$ and integrating 2.7 over the whole crystal and 2.5 over the unit cell. These integrations should be identical:

$$\int_{V_C} \sum_G \rho_G e^{\mathbf{i}\vec{G}\cdot\vec{r}} d\vec{r} = V_C \rho_G, \tag{2.8}$$

consequently

$$V_C \rho_G = \int_{V_\infty} q_i (\eta/\pi)^{3/2} e^{-\eta r^2} e^{-\mathbf{i}\vec{G}\cdot\vec{r}} d\vec{r} = S(\vec{G}) e^{\frac{-G^2}{4\eta}}, \tag{2.9}$$

where $S(\vec{G})$ is the structure factor $\sum_t q_t e^{-i\vec{G}\cdot r_t}$ (in case a unit cell containing more than 1 ion is considered). Using relation 2.6 and substituting result 2.9 in equation 2.4 we get:

$$\phi_L = \sum_G \frac{S(\vec{G})}{V_C} e^{\frac{-G^2}{4\eta}}. \tag{2.10}$$

The contribution of ϕ_i to the field is:

$$\phi_i = \int \frac{1}{\epsilon_0} r^2 \frac{\rho(\vec{r})}{r} d\vec{r} = \frac{1}{2\epsilon_0} q_i \frac{\eta^{1/2}}{\pi^{3/2}} \tag{2.11}$$

so with 2.3 we have:

$$\phi_1 = \sum_G \frac{S(\vec{G})}{V_U} e^{\frac{-G^2}{4\eta}} - \frac{1}{2\epsilon_0} q_i \frac{\eta^{1/2}}{\pi^{3/2}} \tag{2.12}$$

For ϕ_2 we consider the point charges and gaussians and use $\epsilon_0 \nabla \cdot E = \rho$ for spherical geometry to split the Gaussians in two parts, $r < r_j$ and $r > r_j$:

$$\phi_2 = \frac{1}{4\pi\epsilon_0} \sum_j q_j [\frac{1}{r_j} - \frac{1}{r_j} \int_0^{r_j} \rho(\vec{r}) d\vec{r} - \int_{r_j}^{\infty} \frac{\rho(\vec{r})}{r} d\vec{r}] \tag{2.13}$$

$$= \frac{1}{4\pi\epsilon_0} \sum_j \frac{q_j}{r_j} erfc(\eta^{1/2} r_j), \tag{2.14}$$

and finally:

$$\phi = \sum_G \frac{S(\vec{G})}{V_U} e^{\frac{-G^2}{4\eta}} - \frac{1}{2\epsilon_0} q_i \frac{\eta^{1/2}}{\pi^{3/2}} + \frac{1}{4\pi\epsilon_0} \sum_j \frac{q_j}{r_j} erfc(\eta^{1/2} r_j), \tag{2.15}$$

which is a function which depends on the value of η for its convergence behaviour.

Work by Catlow and Norgett [35] suggests that a good value for convergence is:

$$\eta = (\frac{s\pi^3}{V_U^2})^{1/6}, \tag{2.16}$$

where s is the number of atoms in the unit cell and V_U is the unit cell volume.

Now we know that it is possible to calculate the lattice energy of an array of point charges, let us consider how we can manipulate the lattice to obtain the minimum lattice energy.

2.2 Minimizing the Lattice Energy

Most programs which model ions as static species allow minimization of the lattice at constant volume or pressure. The constant volume option means that the unit cell dimensions do not change, only the arrangement of the atoms inside the cell are allowed to assume a minimum energy geometry. A constant pressure calculation varies the lattice vectors as well as the atom positions. We can define the lattice energy as a function of a set of N new ion coordinates, r', which have changed from the original set, r, by:

$$U(r') = U(r) + g^T \cdot \delta + \frac{1}{2}\delta^T \cdot W \cdot \delta, \tag{2.17}$$

where δ and g are vectors of dimension $3N + 6$, N being the number of ions in the unit cell. The $3N$ components of δ are the displacements of r' relative to r. The remaining 6 components of δ are the independent bulk strain components, $\delta\varepsilon$, of the

symmetric strain matrix, $\mathbf{E}$:

$$\mathbf{E} = \begin{pmatrix} \delta\varepsilon_1 & \frac{1}{2}\delta\varepsilon_6 & \frac{1}{2}\delta\varepsilon_5 \\ \frac{1}{2}\delta\varepsilon_6 & \delta\varepsilon_2 & \frac{1}{2}\delta\varepsilon_4 \\ \frac{1}{2}\delta\varepsilon_5 & \frac{1}{2}\delta\varepsilon_4 & \delta\varepsilon_3 \end{pmatrix} \tag{2.18}$$

and thus the set of coordinates r' is related to the set r by:

$$r' = \mathbf{E} \cdot (r + \delta r). \tag{2.19}$$

Thus, $\mathbf{E}$ is the Voigt matrix representation of the vector $\delta\varepsilon$. The vector g refers to the first derivative of the lattice energy with respect to the ion displacements and the strain components,

$$g = (\frac{\partial U}{\partial r}, \frac{\partial U}{\partial \delta\varepsilon}). \tag{2.20}$$

The matrix $\mathbf{W}$ contains the corresponding second derivatives:

$$\mathbf{W} = \begin{pmatrix} \frac{\partial^2 U}{\partial r \cdot r} & \frac{\partial^2 U}{\partial r \cdot E} \\ \frac{\partial^2 U}{\partial E \cdot r} & \frac{\partial^2 U}{\partial E \cdot E} \end{pmatrix} = \begin{pmatrix} W_{rr} & W_{Er} \\ W_{rE} & W_{EE} \end{pmatrix}. \tag{2.21}$$

2.2.1 Minimizing to Constant Volume

When minimizing to constant volume, the strain in the ion coordinates is removed, so that at equilibrium,

$$\frac{\partial U}{\partial \delta r} = 0 (= g). \tag{2.22}$$

Combining equations 2.17 and 2.22 and neglecting the bulk strain components of the vectors g and δ, gives:

$$0 = g + W_{rr} \cdot \delta r, \tag{2.23}$$

so the optimum displacement of an ion at point r from equilibrium is:

$$\delta r = -W_{rr}^{-1} \cdot g. \tag{2.24}$$

If the energy of the system were perfectly harmonic with respect to the strain, equation 2.24 would give the value of r, and hence the lattice energy, at the minimum. However, this is generally not the case, so equation 2.24 must be solved by an iterative procedure.

The main drawback associated with this method of minimization is the storage and inversion of the $3N \times 3N$ matrix $\mathbf{W}$. The time required for inversion of the $\mathbf{W}$ matrix can be reduced by using the method of Norgett and Fletcher [36] whereby the $\mathbf{W}^{-1}$ matrix is updated by an approximate method and only occasionally recalculated explicitly. In the $(k+1)^{th}$ iteration, the new coordinate positions are given by:

$$r_{k+1} = r_k - g_k \cdot \mathbf{H}_k, \tag{2.25}$$

where

$$\mathbf{H}_k = (W_{rr})_k^{-1}. \tag{2.26}$$

$\mathbf{H}_k$ is known as the Hessian matrix and an estimate for the next iteration step can be obtained from the approximations of Davidon [37] and Fletcher and Powell [38] :

$$\mathbf{H}_{k+1} = \mathbf{H}_k + \frac{\delta r \cdot \delta r^T}{\delta r^T \cdot \delta g} - \frac{\mathbf{H}_k \cdot \delta g \cdot \delta g^T \cdot \mathbf{H}_k}{\delta g^T \cdot \mathbf{H}_k \cdot \delta g}, \tag{2.27}$$

or

$$\mathbf{H}_{k+1} = \mathbf{H}_k - \frac{\delta g^T \cdot \mathbf{H}_k}{\delta r^T \cdot \delta g} - \frac{\mathbf{H}_k \cdot \delta g \cdot \delta r^T}{\delta r^T \cdot \delta g} + (1 + \frac{\delta g^T \cdot \mathbf{H}_k \cdot \delta g}{\delta r^T \cdot \delta g}) \cdot \frac{\delta r \cdot \delta r^T}{\delta r^T \cdot \delta g}, \tag{2.28}$$

where $\delta r = r_{k+1} - r_k$ and $\delta g = g_{k+1} - g_k$. Therefore, this approach only requires the recalculation of the forces g after initial calculation of $\mathbf{H}$. For most of the systems studied in this thesis, it was sufficient to perform one initial matrix inversion, followed by approximate updating and occasional full inversion, to achieve convergence.

2.2.2 Constant Pressure

For constant pressure calculations, the energy is minimized with respect to the ion coordinates as for the constant volume case, but in addition the bulk strains acting on the cell are removed by adjusting the lattice vectors. The bulk strains, $\delta\varepsilon$ are defined so that they transform every vector r in the lattice to r', where:

$$r' = (\mathbf{I} + \mathbf{E}) \cdot r. \tag{2.29}$$

Here $\mathbf{I}$ is the identity matrix and $\mathbf{E}$ is the symmetric strain matrix defined in equation 2.18. The strains are calculated assuming Hooke's law (i.e. the strain is proportional to the stress on the crystal), with a constant of proportionality given by the elastic constant tensor. The stress is the first derivative of the lattice energy with respect to strain. Hence, the bulk strains, $\delta\varepsilon$, are given by:

$$\delta\varepsilon = \frac{\partial U}{\partial \delta\varepsilon} \cdot \mathbf{C}^{-1}, \tag{2.30}$$

where $\mathbf{C}$ is the elastic constant matrix. The elastic constants are defined as the second derivatives of the lattice energy with respect to strain, normalized to the unit cell volume. If equation 2.17, at equilibrium ($g = 0$), is expanded into its two components we obtain:

$$U(r') = U(r) + \frac{1}{2}\delta r^T \cdot W_{rr} \cdot \delta r + \delta r^T \cdot W_{rE} \cdot \delta\varepsilon + \frac{1}{2}\delta\varepsilon \cdot W_{EE} \cdot \delta\varepsilon. \tag{2.31}$$

Also at equilibrium,

$$\frac{\partial U}{\partial \delta r} = 0 \tag{2.32}$$

so that

$$\delta r = -W_{rr}^{-1} \cdot W_{rE} \cdot \delta\varepsilon. \tag{2.33}$$

Substituting this equation into 2.31 gives the total energy as:

$$U(r') = U(r) + \frac{1}{2}\delta\varepsilon \cdot (W_{EE} - W_{Er} \cdot W_{rr}^{-1} \cdot W_{rE}) \cdot \delta\varepsilon. \tag{2.34}$$

Thus, it follows that the elastic constant matrix is given by:

$$\mathbf{C} = \frac{1}{V_C}(W_{EE} - W_{Er} \cdot W_{rr}^{-1} \cdot W_{rE}), \tag{2.35}$$

where V_C is the volume of the unit cell. Using 2.34 and 2.35, expression 2.30 may now be substituted into equation 2.29 to give the new lattice vectors and ionic coordinates. As the energy is not harmonic, the bulk strains must be removed over several iterations. In practice, an efficient method for removing both the basis and the bulk strains is, within each iteration, to first perform a constant volume minimization and then to minimize with respect to the cell vectors.

2.2.3 Physical Properties

The previous sections have described the methods for the calculation of the equilibrium lattice energy, cell parameters and elastic constants. It is also possible to obtain the dielectric constant matrices.

At equilibrium the net force acting on each ion is zero i.e. $g = 0$. Therefore in the presence of an external field, e_{ext},

$$U(r') = U(r) + \frac{1}{2}\delta^T \cdot \mathbf{W} \cdot \delta - q^T \cdot r^\alpha \cdot e_{ext}^\alpha \tag{2.36}$$

where r is the zero field configuration, q^T is an N-dimensional vector which contains the ionic charges and α implies the summation is over all components. Using definition 2.21 equation 2.36 can be expanded to give:

$$U(r') = U(r) + \frac{1}{2}\delta^T \cdot W_{rr} \cdot \delta + \delta\varepsilon \cdot W_{Er} \cdot \delta r + \frac{1}{2}\delta\varepsilon \cdot W_{EE} \cdot \delta\varepsilon - q^T \cdot \delta^\alpha \cdot e_{ext}^\alpha \tag{2.37}$$

Applying the equilibrium condition that $\partial U(r)/\partial r = 0$, to the differential of this equation and multiplying by the inverse matrix W_{rr}^{-1}, gives:

$$\delta r^\alpha = -[W_{rr}^{-1} \cdot W_{rE} \cdot \delta\varepsilon]^\alpha + [W_{rr}^{-1}]^{\alpha\beta} \cdot q \cdot e_{ext}^{\alpha\beta} \tag{2.38}$$

The dielectric displacement field, D, is defined by;

$$D^{\alpha} = e^{\alpha}_{ext} + \frac{4\pi}{V_C} q^T \cdot [W^{-1}_{rr}]^{\alpha\beta} \cdot q \cdot e^{\alpha\beta}_{ext} - \frac{4\pi}{V_C} q^T \cdot [W^{-1}_{rr} \cdot W_{rE} \cdot \delta\varepsilon]^{\alpha}. \tag{2.39}$$

Thus, from the definition:

$$D^{\alpha} = \sum_{\beta} k^{\alpha\beta} e^{\beta}_{et} + \sum_{i} \gamma^{\alpha} \varepsilon_i, \tag{2.40}$$

the dielectric tensor $k^{\alpha\beta}$, and the piezoelectric tensor, γ^{α}, are given by:

$$k^{\alpha\beta} = \delta^{\alpha\beta} + \frac{4\pi}{V_C} q^T \cdot [W^{-1}_{rr}]^{\alpha\beta} \cdot q \tag{2.41}$$

and

$$\gamma^{\alpha}_{i} = -\frac{4\pi}{V_C} q^T \cdot [W^{-1}_{rr} \cdot W_{rE}]^{\alpha}_{i}, \tag{2.42}$$

where $\delta^{\alpha\beta}$ is the Krönecker δ.

2.3 Defects

A considerable contribution to the formation enthalpy of a charged defect is the relaxation of the surrounding lattice. Thus, computational constraints dictate that we can only consider lattice atoms near the defect. Computationally, the simulated defective lattice is divided into three parts (Figure 2.3),

- the spherical centre, Region I, containing the defect and a number of surrounding atoms (typically over 500),
- an interface shell, Region IIa, which lies between the defect and the remaining lattice (typically containing over 1000 atoms)
- Region IIb which extends, mathematically, to infinity.

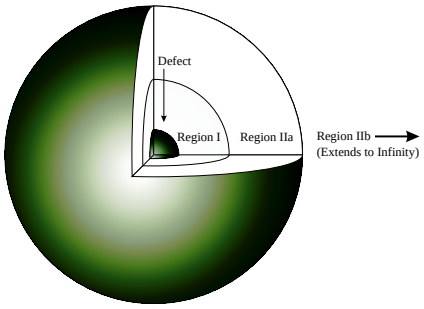


Figure 2.3: The lattice surrounding a defect is split up into three regions.

Region I is relaxed explicitly, using the minimization techniques described in the previous section. In Region IIb the interactions with the defect region are considered to be weak enough to allow treatment with a method based on continuum theories. For a cubic crystal the response of the lattice at a distance r from the defect centre of charge q is described with the Mott-Littleton [39] approximation:

$$P = \frac{V_C}{4\pi} \frac{qr}{|r|^3} (1 - \frac{1}{\epsilon^0}), \tag{2.43}$$

where P is the polarisation of the crystal, per unit cell, and ϵ^0 is the static dielectric constant of the crystal. Moreover, the electrostatic potential of region IIb ions on ions in regions I and IIa is included by virtue of an Ewald summation.

The total energy of the system is written as:

$$E = E_1(r) + E_2(r, \zeta) + E_3(\zeta) \tag{2.44}$$

where E_1 is the energy of region I, arising from displaced ions at positions r in this region; E_3 is the energy of region II for which ζ is the vector of coordinate displacements for this region; and E_2 is the interaction energy between regions I and II. $E_3(\zeta)$ cannot be be calculated exactly since it involves an infinite number of displacements. However, it is assumed that since displacements in region II will be small, the harmonic approximation is valid so that E_3 is a quadratic function of the displacements, i.e.:

$$E_3(\zeta) = \frac{1}{2}\zeta^T \cdot A \cdot \zeta, \tag{2.45}$$

where A is the force constant matrix. If we now differentiate the total energy with respect to the displacements in region II, ζ, and apply the equilibrium condition, $\partial E/\partial\zeta = 0$ we obtain:

$$(\frac{\partial E_2(r, \zeta)}{\partial \zeta})_{r,\zeta=\zeta'} = -(\frac{\partial E_3(\zeta)}{\partial \zeta}), \tag{2.46}$$

where ζ' are the equilibrium values of ζ. Thus, from equation 2.45,

$$(\frac{\partial E_2(r, \zeta)}{\partial \zeta})_{r,\zeta=\zeta'} = -A \cdot \zeta'. \tag{2.47}$$

Substituting 2.47 into 2.46 and then into 2.44, we obtain:

$$E = E_1(r) + E_2(r, \zeta) - \frac{1}{2}(\frac{\partial E_2(r, \zeta)}{\partial \zeta})_{r,\zeta=\zeta'} \cdot \zeta. \tag{2.48}$$

This removes any dependence of the energy, E on E_3. Thus, in principle the defect energy, E, could be found by minimizing the energy through solving equation:

$$\frac{dE}{dr} = 0. \tag{2.49}$$

However, this would involve the explicit differentiation of the outer region displacements, ζ, with respect to r, which is difficult to do analytically because of the complicated structure of E. We can solve this problem by only requiring zero force on the ions of the inner region:

$$(\frac{\partial E}{\partial r})_{\zeta=constant} = 0. \tag{2.50}$$

If the region II atoms are in equilibrium, these two approaches are equivalent. In practice, this method leads to negligible differences with full energy minimization.

2.4 Interionic Interactions: Short Range Potentials

In reality, the quality of the atomistic calculation depends on the short range potentials, which, together with the Coulombic potential, define the system forces. Short range potential descriptions can be two (Φ_{ij}), three (Φ_{ijk}) or many ($\Phi_{i..z}$) body potentials. Three body potentials are often used when modeling covalent systems, but they are not used in this study.

The form of our short range two-body potential (not including the Coulombic interaction) is usually the Buckingham form:

$$\Phi_{ij}(r_{ij}) = A_{ij}e^{\frac{-r_{ij}}{\rho_{ij}}} - \frac{C_{6,ij}}{r_{ij}^6}. \tag{2.51}$$

The A_{ij} and ρ_{ij} parameters define the repulsive exponential part of the potential and the $C_{6,ij}$ defines an attractive van der Waals or dispersive interaction.

The parameters A_{ij}, ρ_{ij} and $C_{6,ij}$ for pair potential 2.51 can be derived by using different methods:

- via quantum mechanical calculations on the system
- electron gas calculations
- Empirical fitting to experimental results
- a combination of the above methods

The quantum mechanical method consists of first calculating the total energy of an array of atoms, varying the interatomic spacing, recalculating the total energy and repeating this to form a potential energy surface. The parameters of the potentials such as equation 2.51 are then fitted (using for example least squares) to reproduce the potential surface.

2.4.1 Electron Gas Method

The electron gas method [40, 41] approximates the interaction between the ions by calculating the energies associated with the overlap of the electron gas densities surrounding two atoms. The method assumes a spherical charge distribution, which can be calculated quantum mechanically. The interaction between two ions then becomes:

$$E_T = E_{Elec} + E_{KE} + E_{Exch} + E_{Corr} + E_{Disp}, \tag{2.52}$$

where E_{Elec} is the electrostatic interaction (nucleus-nucleus, nucleus-electrons and electrons-electrons) between the two different ions. E_{KE} is the kinetic energy of the electrons. E_{Exch} is the exchange energy, E_{Corr} is the correlation energy and E_{Disp} is the dispersive contribution. A more detailed description of the terms in equation 2.52 can be found in Harding and Harker [42] or Mackrodt and Stewart, 1979 [43]. If E_T is calculated at different inter ionic separations, a Buckingham potential form can be fitted to the resulting inter ionic interaction data.

2.4.2 Empirical Method

Empirical potentials are derived by fitting to physical properties: observed crystal structures, dielectric tensors and elastic properties. One of the reasons why the empirical technique is successful, is that the theoretical derivation techniques usually do not appreciate the dynamic behaviour of atoms, while the empirical method fits to macroscopic properties which include the full behaviour of the ensemble of atoms. Furthermore empirical potentials are not subject to the approximations inherent in the quantum mechanical simulations. In addition, it has recently become possible to fit to the properties of multiple structures simultaneously. This means that the potentials are fitted over a number of interatomic separations rather than to just one and are therefore more reliable at modelling distortions of the lattice [44, 45]. In addition any experimental errors in the fitting data may be averaged out.

One of the most reliable ways of deriving potentials consists of first determining the parameters using a quantum mechanical (QM) technique and using this as a basis for empirical fitting. Blind fitting may produce apparently "good" potentials, which might reproduce the lattice structure and elastic and dielectric behaviour, but there exists a multitude of possible potentials which reproduce these observable properties. It is therefore important to have a good basis for the individual inter-ionic potentials especially when displacements may be significant.

2.5 Ionic Polarizability

Especially when charged defects are considered, the polarization of ions surrounding the defect is significant. Ion polarisation opposes the average electric fields in a crystal, causing the extent of a defect's electrostatic interaction to be reduced.

When calculating dynamic properties of ions (i.e. diffusion or vibration behaviour) the polarization of the ion in question is important. An early method of modeling polarization behaviour was the Point Polarizable Ion (PPI) model, which assumes a dipole moment linear with the electric field. Because the simulation method we employ uses short range interactions which do not influence the local electric field directly, the PPI model does not give satisfactory results. However, the core-shell model, proposed by Dick and Overhauser [24] is a more useful description. In this model, a charged shell, which can be thought to be associated with the valence electrons of an atom, is bound to a charged core by a central force spring. The total charge of the shell and core is the ion charge. Displacements from the equilibrium position induce a dipolar electric field around the pair. The interaction energy between the pair is only the spring energy. A Coulombic interaction between the pair is not used, because the spring constant is fitted to model the pair's interaction as a whole. In treating polarisability, only the displacement of the shell and a virtual equal counter charge is considered.

If we consider a shell with a charge Q_Y round an opposite countercharge $-Q_Y$, the relation between the polarisability and the force constant is:

$$\alpha = \frac{Q_Y^2}{k}, \tag{2.53}$$

where $\alpha[C^2m^2J^{-1}]$ is the polarisability, $k[Nm^{-1}]$ is the force constant, and $Q_Y[C]$ is the charge of the shell.

Since the polarisability, α, is often [46] given in Å^3, and k is used in eVÅ^{-2}, we can substitute the "units" into equation 2.53 and rewrite it as follows:

$$\alpha = 14.3\frac{Q_Y^2}{k}, \tag{2.54}$$

where Q_Y is in the unit of electron charge.