

# TYC Materials Modelling Course: Interatomic Potentials

Professor Dorothy Duffy

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## 1 Introduction

Interatomic potentials, also commonly referred to as forcefields, are widely used in the materials modelling community for simulating processes and calculating structural properties. They have been employed for several decades in a range of modelling methods, including molecular dynamics, Monte Carlo and, more recently, in rare event methods, such as umbrella sampling and metadynamics, discussed in previous lectures of this course.

The primary reasons for the popularity and success of methods employing interatomic potentials are their computational efficiency. Simulations of hundreds of millions of atoms are now commonplace and molecular dynamics timescales of tens of nanoseconds, or even microseconds, are achievable on high performance computing platforms. Extending simulation length and time scales is a universal aim of materials modellers, as they endeavor to close the gap between modelling and experiment.

The main disadvantage with employing interatomic potentials is, of course, that the results are sensitive to the model. While this is true to some extent for density functional theory calculations, the sensitivity to the model is much stronger in interatomic potential methods. A second significant limitation is that the methods provide no information about electronic structure, therefore calculations of electronic properties, such as band gaps, are inaccessible. Nevertheless, carefully parameterised potentials are an invaluable tool for exploring time and length scale regimes currently inaccessible to quantum based modelling methods.

Examples of large length scale calculations include:

- Alloys and disordered materials
- Complex surfaces
- Large molecules on surfaces
- Extended defects such as grain boundaries, domain walls, and dislocations
- Polymers and proteins.

Examples of long time scale simulations include:

- Diffusion
- Fracture

- Free energy calculations
- Protein folding

Classical interatomic potentials are often physics based - that is they encode the physics of the interatomic bonding and, by implication, the electronic structure, into the functional form of the potential. By capturing the properties of the bonds they are able, with careful fitting procedures, to reproduce materials properties with a high degree of accuracy. Materials are classified by the chemical bonding (metals, ceramics, polymers etc.) therefore, unsurprisingly, the functional forms used for a particular material is related to the bonding type. Functional forms range in complexity from simple two body potentials, such as the well known Lennard Jones potentials, where the interaction energy can be decomposed into a sum between pairs of atoms, to complex many body potentials in which the interaction energy between a pair of atoms is influenced by the positions of the surrounding atoms.

The overall objectives of this lecture are to give an overview of the most common interatomic potentials for a range of classes of materials and to enable an informed choice of the appropriate interatomic potential for a particular application. The sections below describe interatomic potentials with increasing complexity and the types of bonding or material that is relevant to that potential type.

## 2 Two Body Potentials

For some materials the total cohesive energy,  $E_{coh}$  can be decomposed into the sum of the interaction energies between all pairs of atoms, and the interaction energies depend only on the distance between the atom pairs, as in equation 1.

$$E_{coh} = \sum_{i,j>i} V(r_{ij}) \quad (1)$$

Here  $i$  and  $j$  label the atoms,  $r_{ij}$  is the distance between atoms  $i$  and  $j$  and  $V(r_{ij})$  is the interaction energy between atoms  $i$  and  $j$ .  $V(r_{ij})$  has a number of different function forms which reflect the type of bonding between the atoms of the materials.

The simplest, and perhaps the most famous, 2-body potential is the Lennard Jones potential, equation 2.

$$V(r) = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right] \quad (2)$$

Here  $\epsilon$  and  $\sigma$  are fitting parameters which determine the strength and the range of the interaction between 2 atoms. In common with many 2-body potentials, the Lennard Jones potentials consist of a long range attractive term  $-\left(\frac{\sigma}{r}\right)^6$  and a short range repulsive term  $\left(\frac{\sigma}{r}\right)^{12}$ . The  $r^{-6}$  attractive term captures the effect of the attractive dispersion or van der Waals interaction, that is a dipole-dipole interaction between atoms or molecules. The  $r^{-12}$  repulsive term approximates

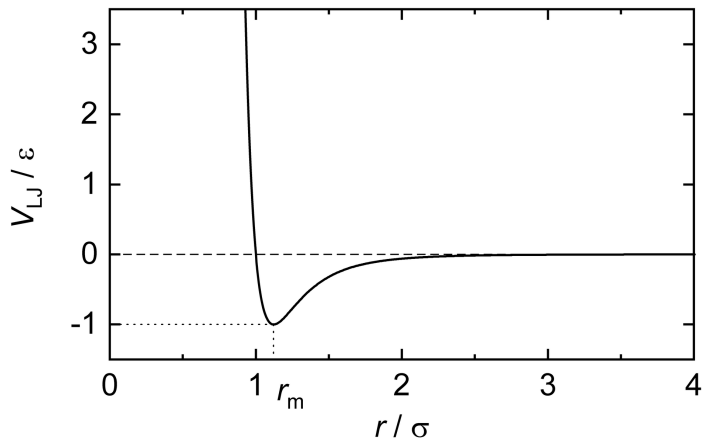


Figure 1: Lennard Jones Potential

the repulsive energy of Pauli exclusion caused by the overlap of atomic orbitals. A representation of a typical potential is shown in figure 1. The competition between the repulsive and attractive terms results in two important features of the potential, the depth and the position of the potential energy well. These are determined by the fitting parameters  $\sigma$  and  $\epsilon$  and, physically, they relate to the strength of the binding and the size of the atoms or molecules. The  $r^{-12}$  function has no physical justification, as it was originally chosen for computational efficiency. Nevertheless, the Lennard Jones potential functional form is still widely used for interactions between inert gasses and between organic molecules, as it captures the fundamental features of the interactions between closed shell molecules.

The Lennard Jones potentials does not capture the fundamental features of intramolecular bonds. For small molecules, such as  $N_2$  and  $CO_2$ , the Morse potential, equation 3 is often used.

$$V(r) = D_0 [1 - \exp(\alpha(r - r_e))]^2 \quad (3)$$

The Morse potential has 3 fitting parameters,  $r_e$ , which is related to the equilibrium bond length,  $D_0$ , related to the strength of the bond, and  $\alpha$  which is related to the anharmonicity of the potentials well, figure 2. All of these properties can be measured accurately experimentally, therefore the fitting procedure of Morse potentials for small molecules is relatively straight forward.

Modelling ionic crystals with classical interatomic potentials has a long and successful history. The dominating interaction in such crystals is the Coulomb interaction between the ions, described by equation 4.

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

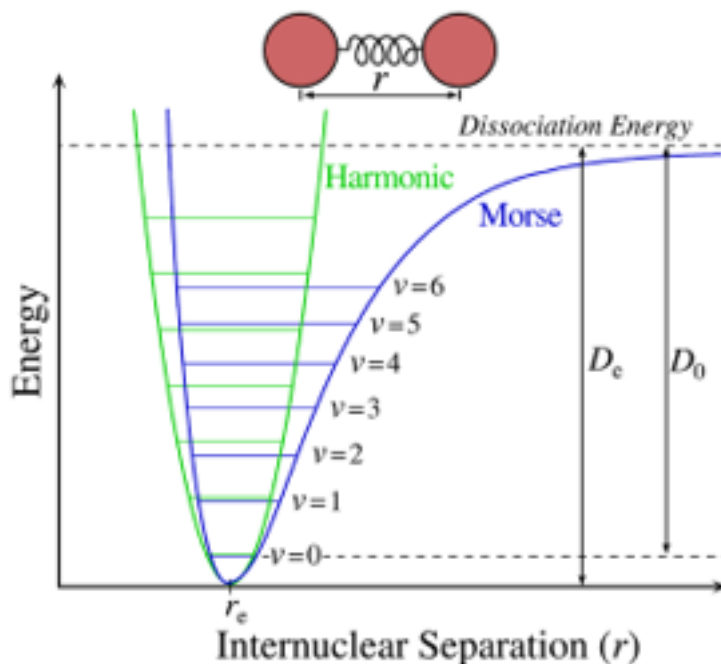


Figure 2: Morse Potential

Here  $q_i$  and  $q_j$  are the charges of ions  $i$  and  $j$ ,  $r_{ij}$  is the distance between  $i$  and  $j$  and  $\epsilon_0$  is the permittivity of free space. The charges  $q$  for the ions can either be formal charges (e.g. +2 for Mg and -2 for O) or they can be determined from quantum calculations.

As with Lennard Jones materials, the dispersion and Pauli exclusion interactions must be included, in addition to the Coulomb interactions. For ionic materials, the Buckingham potential, equation 5, is generally employed.

$$V(r) = A \exp\left(-\frac{r}{\rho}\right) - \frac{C}{r^6} \quad (5)$$

Here there are 3 fitting parameters,  $A$ ,  $\rho$  and  $C$ . These are determined by fitting to either experimentally measured properties or quantum mechanical (Hartree Fock or density functional theory) calculations. The choice of ionic charges influences the optimum values for the fitting parameters.

Figure 3 shows a typical plot of a Buckingham potential. The plot highlights a potential issue with this potential that users should note. The potential becomes attractive a very small separations, which is clearly unphysical and potentially causes catastrophic failures of simulations. However, this feature will only cause problems in far from equilibrium situations, therefore a careful setup of the initial simulation conditions will generally avoid the atoms crossing the potential barrier and entering the unphysical region. The ions in ionic crystals

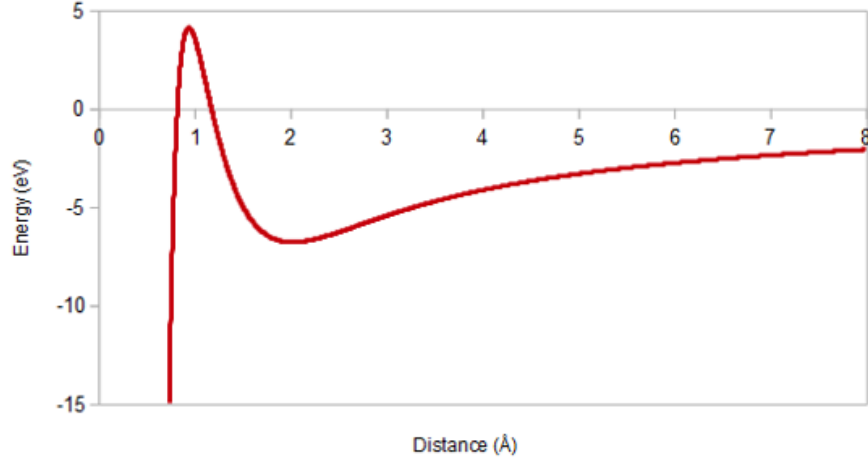


Figure 3: Buckingham potential

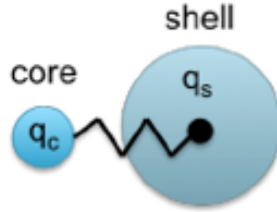


Figure 4: Core Shell model of an ion

are intrinsically polarizable, which implies that a dipole moment is induced by charge separation of the negative electrons and positive nuclei in response to an applied electric field. For some materials, and for some types of calculations, these effects are significant and must be included in the interatomic potentials. This is achieved by employing a shell model (figure 4) where the positive nucleus is surrounded by a negatively charged sphere, referred to as a shell. The nucleus and shell are connected by a spring, such that the potential energy when the core and shell are separated by a distance  $r_{cs}$ , in response to an electric field, is given by equation 6.

$$V(r_{cs}) = (1/2)kr_{cs}^2 \quad (6)$$

The charges assigned to the core and shell, and the spring constant  $k$ , are fitting parameters that aim to reproduce the polarizability of the material.

Buckingham potential models, in conjunction with the shell model, have been particularly successful in the field of materials modelling for studying both structural properties, such as surfaces and defects, and dynamic properties, such as phonons. An example of a complex ferroelectric will be presented during the

tutorial, demonstrating how careful parameterization of the interatomic potentials can reproduce complex phase diagrams and be used to calculate domain patterns and hysteresis in these important technological materials [1].

The strength of the interaction between a pair of atoms decreases as the interatomic distance increases (figures 1, 2 and 3), therefore it is unnecessary, and inefficient, to include interactions between atoms at large interatomic separations. In practice, a finite cutoff is implemented, and all interactions between atoms separated by distances larger than the cutoff are neglected. As always, there is a balance between accuracy and efficiency, as large cut offs result in more atom-atom interactions to be calculated.

Reliable two body potentials are not available for every possible pair of ions, however, in some cases it is possible to derive potentials for a pair of unlike species ( $a$  and  $b$ ) from the known potentials of the individual species, by employing mixing rules. The most commonly used mixing rules are the Lorentz Berthelot rules for the Lennard Jones potential. These involve the arithmetic mean of the  $\sigma$  parameter and the geometric mean for the  $\epsilon$  parameter, as shown in equations 7 and 8.

$$\sigma_{ab} = 1/2(\sigma_{aa} + \sigma_{bb}) \quad (7)$$

$$\epsilon_{ab} = \sqrt{\epsilon_{aa}\epsilon_{bb}} \quad (8)$$

The justification for the mixing procedure is that, since  $\sigma$  relates to the size of the individual atoms, the arithmetic mean should give a reasonable approximation for the equilibrium separation between  $a$  and  $b$ . Such mixing rules are widely used for the van der Waals intermolecular and intramolecular interactions in organic molecules, where the large number of atoms types makes it impractical to fit potentials for all possible atom type pairs.

Alternative mixing rules are available for other 2-body potentials (Buckingham and Morse), however, these are much less commonly used. Inorganic materials generally contain a small number of atom types therefore fitting parameter sets for each atom type pair in the materials of interest is a viable, and preferable, strategy.

### 3 Multibody Potentials

In the previous section we considered interatomic potentials in which the total cohesive energy of a solid could be written as the sum over the interaction energy of all pairs of atoms in the system. This is a good approximation for some materials but a very poor approximation in others. In this section we will consider interatomic potentials that include two, three and four body interactions. This model is appropriate for organic molecules such as polymers, amino acids and proteins. Such molecules contain multiple covalent bonds and the energy,  $E$ , of the molecule is described well by equation 9, that is the sum of the bond stretching energy  $E_{bonds}$ , a 2-body interaction, the bond bending energy,  $E_{angles}$ , a 3-body interaction and the torsion (dihedral) energy,  $E_{dihedrals}$  which is a 4-body interaction. The torsion energy refers to the energy cost of rotating

2 bonds around a central bond, and it depends on the positions of the atoms of the bonds connected to the central bond, hence it is a 4-body term.

$$E = E_{bonds} + E_{angles} + E_{dihedrals} \quad (9)$$

The individual components of the total energy are given by equations 10, 11 and 12 below.

$$E_{bonds} = \sum_{i,j>i} K_{bonds} [r_{ij} - r_0]^2 \quad (10)$$

$$E_{angles} = \sum_{i,j>i,k>j} K_{angles} [\theta_{ijk} - \theta_0]^2 \quad (11)$$

$$E_{dihedrals} = \sum_{i,j>i,k>j,l>k} K_{dihed} [1 + \cos(n\phi_{ijkl} - \delta_n)] \quad (12)$$

Here  $\theta_{ijk}$  is the angle between bonds  $ij$  and  $jk$ ,  $\theta_0$  is the equilibrium angle, and  $r_0$  is the equilibrium bond length.  $K_{bonds}$  and  $K_{angles}$  are harmonic force constants for bond stretching and bond bending respectively, and  $K_{dihed}$ ,  $n$  and  $\delta_n$  are parameters describing the energy variation with bond rotation.  $n$  is a measure of the number of local minima as the bond is rotated through  $2\pi$ .

Equation 9 describes the energy of all the covalent bonds in an organic molecule, however, additional terms are required to account for non-bonding interactions, such as van der Waals and Coulomb interactions. For these the Lennard Jones potential, equation 2, and the Coulomb interaction, equation 4, are generally used. The atomic charges  $q_i$  and  $q_j$  are partial charges associated with each atom, which can be obtained from quantum calculations.

Multibody potentials have played a pivotal role in modelling biological materials such as drugs, peptides and proteins, therefore considerable resources and effort have been applied developing forcefields that reproduce diverse properties such systems. These are under continuous development therefore their accuracy improves over time. It should be noted, however, that the ability to describe the complex environment of all atoms in a molecule, such as a protein, by a relatively small number of parameters is necessarily limited, as the interaction between any 2 atoms in a bond is affected by the environment. Nevertheless, by ascribing different labels to atoms in different environments, such as singly, doubly and triply bonded carbon atoms, these organic forcefield parameter sets do a remarkable job in reproducing the properties of organic molecules.

The most commonly used forcefields for organic molecules are GROMOS, AMBER, CHARMM and OPLS. Some of these have separate parameterizations for small molecules. Most also have united atom (UA) versions, as well as all atom versions. In the UA versions the H atoms are not treated as separate species, but they are combined with another atom, such as carbon, to which it is bonded. The UA approach increases efficiency in two ways. First, it reduces the number of atoms in the simulation and second, it enables a longer timestep for the molecular dynamics simulation. The maximum simulation timestep is related to the vibrational frequency of the bonds in the simulation. H is a light

atom therefore the C-H bond has a high vibrational frequency compared to other bonds in the molecule, which reduces the maximum simulation timestep.

The various forcefields for organic molecules are described in detail in a comprehensive review article [2]

## 4 Many Body Potentials

### 4.1 Metals

So far we have discussed interatomic potentials suitable for ionic crystals and covalently bonded molecules, however, none of the functional forms discussed can successfully describe the properties of metallic materials. The interatomic potentials for metals need to capture the fundamental properties of metallic bonding, in which the atomic nuclei are embedded in a “sea” of electrons. The implication is that the energy of any atom depends on the local electronic density.

This effect is captured very successfully by embedded atom type interatomic potentials, first introduced by Daw and Baskes [3], [4]. The idea behind such models is that the local electronic density is determined by the positions of all the other atoms. The term “embedded” refers to the idea that each atom (technically, each ion because each atom donates valence electrons to the metal) is embedded in the environment established by all other atoms in the system. In practice this is implemented by equations 13 and 14.

$$V = \sum_i F_i(\rho_i) + \sum_{i>j} \phi(r_{ij}) \quad (13)$$

$$\rho_i = \sum_{j \neq i} f(r_{ij}) \quad (14)$$

Here  $F$  is the embedding energy which is a function of the local environment, or local density, determined by  $\rho$ .  $\rho$  is the local density built by adding contributions from all neighbouring atoms.  $\phi$  is a 2-body interatomic interaction which generally contains both a repulsive and an attractive component. The functions  $F$ ,  $\rho$  and  $f$  can take different functional forms, or they can be tabulated.

A very successful implementation of the embedded atom approach is the Finnis Sinclair model [5]. This model builds on the tight binding theory of metallic cohesion in which the cohesive energy is a function of the square root of the electron density. Applying this to the embedded atom model leads to equation 15.

$$F(\rho) = -A\sqrt{\rho} \quad (15)$$

Here  $A$  is a fitting parameter, chosen to reproduce the properties of the metal and  $\rho$  is a function of the position of the neighbouring atoms as in equation 14.

The embedded atom and Finnis Sinclair models have been very successful for reproducing the fundamental properties of metals which are not possible



to achieve with 2-body potentials. Examples include elastic properties, surface structure, defect energies and plastic flow. They have been particularly successful for face centered cubic metals in which the bonding is predominately metallic. Body centered cubic structured metal have some degree of covalent bonding, the directional nature of which is not captured by the standard embedded atom approach. Extensions to the model, referred to as the modified embedded atom model (MEAM) have been developed to take account of covalent effects. Thus there are now EAM type potentials for many elementary metals and for some, such as Fe, several different models exist, as the drive to develop ever more accurate parameterizations for different properties and processes continues.

One of the main advantages of EAM potentials is their efficient implementation in MD models. The density function is effectively a sum over 2-body terms, therefore computational cost of the energy and force calculations are comparable those of 2-body potentials. Multi-million atom simulations of metals are commonplace, allowing investigation of processes such as fracture, diffusion and radiation effects.

## 4.2 Covalent Solids

In section 3, multibody potentials were introduced to model covalent molecules. Such potentials are not, however, appropriate for covalently bonded solids, such as diamond and silicon, which consist of a continuous network of bonds. The appropriate potentials for such materials are environment dependent interatomic potentials (EDIPs). As with metals, in these materials the interaction energy between two atoms depends on the positions of the neighbouring atoms, hence the name "environment dependent". The complex dependence in covalently bonded solids is challenging to capture with classical interatomic potentials, however, the technological importance of these materials has driven an enormous effort in the development of successful potentials.

The general form of an EDIP potentials is shown in equation 16.

$$E = \sum_i \sum_{j>i} [E^R(r_{ij}) - b_{ij}E^A(r_{ij})]f_c(r_{ij}) \quad (16)$$

Here  $E^R(r_{ij})$  and  $E^A(r_{ij})$  are 2-body repulsive and attractive interactions, respectively, between atoms  $i$  and  $j$ , separated by a distance  $r_{ij}$ . The environment dependence is introduced by the term  $b_{ij}$ , known as the bond order term, which modifies the strength of the attractive interaction in response to the positions of the neighbouring atoms, that is the number of neighbours and the angle between the neighbours. The function  $f_c$  is a switching function, which varies smoothly from 1 to 0 as  $r_{ij}$  increases, to ensure only nearest neighbour atom pairs contribute to the bond energy.

One of the first EDIP potential to reproduce the most fundamental properties of silicon was the Tersoff potential [6], in which the functional forms of the

terms in equation 16 are given by equations 17 to 22.

$$E^R = Aexp(-\lambda_1 r_{ij}) \quad (17)$$

$$E^A = Bexp(-\lambda_2 r_{ij}) \quad (18)$$

$$b_{ij} = (1 + \zeta_{ij}^n)^{-\delta} \quad (19)$$

$$\zeta_{ij} = \sum_{k \neq i, j} f_c(r_{ik}) g(\theta_{ijk}) exp[\alpha(r_{ij} - r_{ik})^\beta] \quad (20)$$

$$g(\theta) = a \left[ 1 + \frac{c^2}{d^2} - \frac{c^2}{d^2 + (h - \cos(\theta))^2} \right] \quad (21)$$

$$f_c(r) = \begin{cases} 1 & : r < R_1 \\ \frac{1}{2} \left[ 1 + \cos \left( \pi \frac{r - R_1}{R_2 - R_1} \right) \right] & : R_1 \leq r \leq R_2 \\ 0 & : r > R_2 \end{cases} \quad (22)$$

The bond order term  $b_{ij}$  modifies the strength of the attractive interaction between  $i$  and  $j$ , depending on the length of all bonds connected to  $i$  and the angles between all pairs of bonds connected to  $i$ . Equations 17 to 22 have a large number of fitting parameters:

$(A, B, \lambda_1, \lambda_2, n, \delta, \alpha, \beta, a, c, d, h, R_1, R_2)$  therefore fitting such potentials to reproduce the properties of materials is challenging. Nevertheless reliable sets of Tersoff potentials have been developed for C, Si and SiC. For Si, the potentials have been fit to both experimental data and to theoretical calculations of both real and hypothetical structures. The resulting potentials are able to reproduce properties of amorphous, liquid and diamond structured Si, including the observed density increase on melting. It should be noted that for SiC, each set of 3 bonds requires a different parameter set (i.e. Si-C-Si is different from C-Si-C) and, as there are 8 such combinations for a binary compound, 8 parameter sets are required for such materials.

The Tersoff potential has been hugely successful but, as with all potentials, it has limitations. In the case of carbon based materials these limitations include the neglect of hybridization effects and van der Waals interactions and it is not, therefore, appropriate for hydrocarbons or graphite. The problem lies with the functional form, in which the cohesive energy is written as a sum over atomic sites. The Brenner potential addresses these issues by replacing the sum over sites by a sum over bonds. Two additional terms are required to take account of the number of neighbours of each atom in a pair of bonded atoms. The Brenner potential [7] approach has been very successful for modelling hydrocarbons, and carbon nanostructures (graphene and nanotubes). Graphite requires the addition of van der Waals interactions between the graphene layers and these are included in the AIREBO potentials [8].

The technological importance of Si has resulted in an enormous effort in the development of interatomic potentials for this material, with varying degrees of success. One measure of success is the ability of a potentials to reproduce the cohesive energies of a range of real or hypothetical structures, either measured

experimentally or calculated using density functional theory. These have been compared for a number of commonly used Si potentials in reference [9]. Of course, such properties are only a small subset of the important properties of a simulated material and, in any case, they are often used in the fitting procedure so they are not a reliable measure of success. Other properties that should be reproduced accurately by an interatomic potential include defect energies, surface structures, surface energies, melting point, latent heat, volume change on melting, liquid and amorphous coordination numbers, and liquid and amorphous radial distribution functions. These properties are also compared for a range of potentials in [9], which enables the reader to select the potential the most accurately reproduces the properties of interest. All potential forms discussed above are included in the LAMMPS molecular dynamics code.

## 5 ReaxFF Potentials

One of the significant drawbacks of interatomic potentials is the lack of transferability, that is potentials developed for one material or scenario do not work for different scenarios, therefore new sets of potentials are required for each new application. This, and the inability to model chemical interactions, was the motivation behind the development of ReaxFF potentials in 2001 [10]. Such potentials bridge the gap between expensive, but relatively accurate, quantum calculations and classical potentials. They are transferable across phases (solid, liquid, gas) and different chemistries, so an O atom is treated with the same formalism whether it is in  $O_2$  gas, liquid  $H_2O$  or solid  $SiO_2$ . In addition they can also be used to model chemical interactions. They have a general, but complex, functional form where the total cohesive energy is given by the sum of the bond stretching energy  $E_{bond}$ , bond bending energy,  $E_{angle}$ , torsion energy  $E_{torsion}$ , van der Waals energy  $E_{vdw}$  and Coulomb energy  $E_{coul}$ . In addition to these familiar terms, there is an energy penalty term  $E_{over}$  for deviation from the ideal coordination and a term  $E_{spec}$  to take account of effects not included in the other terms. The bond stretching, bending and torsion terms are all functions of the bond order,  $BO$ , which is a function of the interatomic separations between  $i$  and  $j$ ,  $r_{ij}$ , in a similar way to the Tersoff potential. This term modifies the strength and angle dependence of the bond, depending on the number and length of neighbouring bonds. For example, the bond order term for carbon is given by the sum of contributions from single, double and triple bonds ( $BO_{ij}^\sigma$ ,  $BO_{ij}^\pi$  and  $BO_{ij}^{\pi\pi}$  respectively), as shown in equations 23 and 24.

$$BO_{ij} = BO_{ij}^\sigma + BO_{ij}^\pi + BO_{ij}^{\pi\pi} \quad (23)$$

$$= \exp \left[ p_{bo1} \left( \frac{r_{ij}}{r_o^\sigma} \right)^{p_{bo2}} \right] + \exp \left[ p_{bo3} \left( \frac{r_{ij}}{r_o^\pi} \right)^{p_{bo4}} \right] + \exp \left[ p_{bo5} \left( \frac{r_{ij}}{r_o^{\pi\pi}} \right)^{p_{bo6}} \right] \quad (24)$$

The parameters  $p_{bo1}, p_{bo2}, p_{bo3}, p_{bo4}, p_{bo5}, p_{bo6}$  and  $r_o^\sigma, r_o^\pi, r_o^{\pi\pi}$  are all fitting parameters.

All pairs of atoms have non-bonded interactions so there is no requirement for switching functions. However, these terms become unphysically large at

short distances therefore it is necessary to include shielding functions to both the Coulomb and van derWaals terms to compensate. One special feature of the ReaxFF potential, that is essential for the simulation of chemical interaction and transferability, is the dynamic calculation of atomic charges during the simulation. The method employs electronegativity equalization to distribute charges according to electronegativity differences. The charges are determined iteratively during the simulation and they are distributed so that electronegativity is equalized for a given atomic configuration. This is a powerful attribute, but it has the disadvantage that it is computationally expensive. Nevertheless it may be used to model some processes, such as catalysis, with comparable accuracy with density functional theory, using a fraction of the computational resources.

The original aim of the ReaxFF methodology was to develop a set of potentials for all elements that would be completely transferable between systems. This has proved unfeasible so there are currently three branches (combustion, independent and aqueous) and the elements in each branch are completely transferable within the branch, but not between branches. The ReaxFF formalism has been particularly successful in modelling processes such as heterogeneous catalysis and atomic layer deposition, due to the ability to model interactions between gas molecules and surfaces. Other applications include, but are not limited to, reduction of graphene oxide, ultrafast resistance switching, proton diffusion membranes and nanoindentation. The potentials can be employed in both molecular dynamic and Monte Carlo simulations. The excellent 2016 review [11] gives a comprehensive overview of the ReaxFF potentials and their applications.

## 6 Summary

Atomistic scale simulations based on empirical interatomic potentials remain a powerful tool for exploring the properties of established and novel materials. Interatomic potentials have been developed for all classes of materials, from simple 2-body potentials for inert gasses and ionic crystals, to complex potentials that aim to model chemical processes at solid surfaces. The essential feature of all the potentials covered in this lecture is that the functional forms employed aim to capture the underlying quantum mechanics of the electronic bonding. Thus different classes of materials are described by different functional forms and some are, necessarily, more computationally efficient than others. Obtaining successful parameter sets for a particular material is achieved by fitting to a range of properties, which have either been measured experimentally or calculated with accurate quantum mechanical methods. Fitting parameter sets is challenging, and often described as an art rather than a science. Fortunately, there are parameter sets for hundreds of materials in the scientific literature so the starting point for any research project should always be a comprehensive literature search. Where, as is often the case, there are several examples for the material of interest, the choice should be made on the basis of how well the po-

tential does in calculated the most relevant properties (elastic properties, defect energies, melting point) for the process to simulated. The Open KIM project (<https://openkim.org/>) is an excellent resource for locating interatomic potentials and their properties. OpenKIM is an interatomic potential repository and an online framework for making molecular simulations reliable, reproducible, and portable.

Machine learning is becoming a very popular methodology for interatomic potential development. This methodology uses flexible functional forms which have no basis in the physics of bonding of the material. Machine learning methods use neural networks to fit potential energy surfaces to quantum calculations. The advantage is that the methods can be used for materials without making any assumptions about the bonding but the disadvantage is that the links to the underlying physics is lost.

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