TYC Materials Modelling

Dorothy Duffy

Interatomic Potentials

Aim:

Give an overview of commonly used interatomic potentials for all classes of material

Overview

- Part 1
- Advantages / limitations of classical potentials
- Physics based potentials the relation to bonding
- 2-body potentials
- Case study: Phase transitions in ferroelectric crystals

• Part 2

- Multibody potentials for organic molecules and biomolecules
- Many body potentials for metals (embedded atom model, Finnis Sinclair)
- Many body potentials for covalent solids (Tersoff)
 - C
 - Si
- Part 3
- REAXFF potentials to describe complex chemistry (bond breaking and formation)
- Choosing a potential
- Summary

Why use interatomic potentials?

- Advantages
 - Efficient MD and MC simulations
 - Extended length (μ m) and time (ns) scales
- Limitations
 - Always approximate
 - "All models are wrong but some are useful" (George E P Box)
 - May not be reliable outside fitting range
 - Transferability
 - No information about electronic structure

Advantages

- Large length scales
 - Alloys
 - Disordered materials
 - Complex surfaces
 - Adsorbates on surfaces
 - Extended defects
 - Grain boundaries
 - Domain walls
 - Dislocations
 - Polymers/proteins
 - Nanoparticles
- Long time scales
 - Diffusion
 - Fracture
 - Thermal conductivity
 - Free energy surfaces (metadynamics)
 - Protein folding

Types of material

Ceramics

(Ionic & covalent bonding):

Large bond energy high T_m large E (Young's modulus) small α (thermal expansion) brittle

Metals

(Metallic bonding):

Variable bond energy moderate T_m moderate E moderate α ductile

Polymers

(Covalent & Secondary):



 $\begin{array}{c} \mbox{Directional Properties} \\ \mbox{Secondary bonding dominates} \\ \mbox{low } T_m \\ \mbox{small E} \\ \mbox{large } \alpha \\ \mbox{Ductile/Brittle} \end{array}$

2- Body potentials

- $E_{coh} = \sum_{i,j>i} V(r_{ij})$
- Lennard Jones
 - Inert gasses
 - Intermolecular interactions in polymers/ biomolecules
- Morse
 - Covalent bonds in small molecules
- Buckingham + Coulomb interaction
 - Ionic crystals

Lennard Jones - gasses and polymers

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

- 2 parameters
 - Bond strength ε
 - Atom/molecule size σ



Morse potential – small moelcules

- Covalent bonds in small (di/tri atomic) molecules
 - Anharmonic effects
 - Bond breaking

•
$$V(r) = D_e [1 - exp(\alpha(r - r_e))]^2$$

- 3 parameters
 - Bond strength
 - *D*_e
 - Bond length
 - *r*_e
 - Shape of well
 - α



Ionic crystals – Buckingham + Coulomb

• Coulomb interactions

$$V_{Coulomb}^{ij}(r) = \frac{q_i q_j}{4\pi\varepsilon_0} \frac{1}{r_{ij}},$$

$$V(r) = Aexp\left(-\frac{r}{\rho}\right) - \frac{C}{r^6}$$



Distance (Å)

Ionic Crystals – shell mode



- Ions are intrinsically polarizable
- Relevant properties can be captured using the shell model
- Assign +ve charge (q_c) to core and –ve charge (q_s) to shell
- Attach core and shell with a spring
 - Spring constant k related to polarizability
- Core and shell separate by r_{cs} under application of an electric field
- Potential energy $V(r_{cs})=1/2 kr_{cs}^2$

Example 1– Buckingham Potentials $PbZr_{1-x}Ti_{x}O_{3}(PZT)$

- PZT is a ferroelectric with exceptional piezo electric response
 - Large dipole induced by small strain
- Solid solution of PbTiO₃ and PbZrO₃
- Perovskite crystal structure
- Applications
 - Sensors
 - Ultrasonic transducers
 - Ceramic capacitors
 - AFM transducers



PZT – Phase diagram



Gindele et al. "Shell Model force field for Lead Zirconate Titanate $Pb(Zr_{1-x}Ti_x)O_3$ " J. Phys. Chem. C 2015, 119, 31, 17784-17789

Buckingham Potential with anharmonic core-shell interaction

$$V_{Buckingham}^{ij}(r) = A_{ij} \exp\left(\frac{-r_{ij}}{\rho_{ij}}\right) - \frac{C_{ij}}{r_{ij}^6}.$$

$$V_{Coulomb}^{ij}(r) = \frac{q_i q_j}{4\pi\varepsilon_0} \frac{1}{r_{ij}},$$

Use shell model to reproduce polarization effects



 $V_{\text{core-shell}}^{ij}(r) = (1/2)k_2r_{ij}^2 + (1/24)k_4r_{ij}^4$

 $k_2 = 0.99 + 1000 r_{ij}^5$

~harmonic for r_{ij} <0.1 Å r_{ij}^{5} necessary to prevent large core shell separations

Fitting

- GULP start with PbTiO₃ parameters from existing potential
- Optimised to DFT calculated parameters for PbZrO₃ antiferroelectric and cubic phases
 - fitting the charges, lattice parameters, and atomic positions simultaneously
 - Leave Pb/O; O/O parameters unchanged
- Reparameterize for optimal fit to DFT calculated of other reference structures simultaneously,
 - tetragonal and cubic phases of PbTiO₃;
 - the *rhombohedral* and *cubic* phases of PbZrO₃
 - the ordered *tetragonal* phase of PbZr_{0.5}Ti_{0.5}O₃
- Finally fit to Born effective charges, elastic constants, and piezoelectric coefficients obtained by DFT calculations.

Set Initial FF (A_i), weights (w_i^0), observables (f_i^{ref}) and acceptable error tolerance (e_i^{target})



J. Chapman; PhD thesis, UCL

Parameters

species	<i>A</i> (eV)	ρ (Å)	$C (\mathrm{eV}^6)$	
Pb - O	25223.874	0.229	2.566	
Ti - O	1419.097	0.313	32.850	
Zr - O	1479.996	0.328	39.360	
O - O	13728.834	0.241	100.718	
species	$q_c(e)$	$q_s(e)$	$k_2 ({\rm eV}^{-2})$	$k_4 ({\rm eV}^{-4})$
Pb	11.697	-10.224	274.079	1023162.3
Zr	11.229	-8.279	43803.694	127868.5
Ti	7.997	-5.047	36926.634	132998.8
0	2.467	-3.941	221.301	67027.9

Phase transitions



- a) PbZrO₃
- b) PbTiO₃
- c) PbZr_{0.5}Ti_{0.5}O₃
- d) Polarization

O. Gindele; PhD thesis, UCL

Nanodomains in PbTiO₃ thin films

Chapman et al. Phys. Chem. Chem. Phys., 2017,19, 4243-4250



Tensile strain

Compressive strain

Novel domain formation in PTO thin films as strain and temperature are varied

Combining potentials - mixing rules

- Various rules for combining potentials for alloys or solutions
- LJ Lorentz Berthelot mixing rules
 - Arithmetic mean and geometric mean for LJ
 - $\varepsilon_{ab} = (\varepsilon_{aa} \varepsilon_{bb})^{1/2}$: $\sigma_{ab} = 1/2(\sigma_{aa} + \sigma_{bb})$
- Widely used for organic molecules
- Buckingham use following form:

$$u(r_{ij}) = \epsilon \left[\frac{6}{\alpha - 6} e^{-\alpha \left(\frac{r}{r_m} - 1\right)} - \frac{\alpha}{\alpha - 6} \left(\frac{r}{r_m}\right)^{-6} \right]$$

• Use with care!

2- Body potentials - Summary

Carefully parameterized potentials can model complex phenomena

- Very efficient for ionic crystals
 - Multimillion atom simulations
 - Nanosecond timescales
- Complex materials
- Large scale features and defects
- Long timescale processes

Part 2: Multi-body and Many body Potentials

Materials in which cohesive energy poorly described by sum of pair potentials Multi-body – Organic molecules and organic solids Many body – metals and covalent solids

Multibody potentials

- Typically used to model large covalently bonded molecules
 - Polymers, lipids, amino acids, proteins
- Generally a sum of 2, 3 and 4 body terms

 $E = E_{bond} + E_{angle} + E_{dihedral}$

- Intermolecular interactions
 - LJ potentials with mixing rules
 - Coulomb interactions
- Harrison et al. Appl. Phys. Rev. 5, 031104 (2018)



Multibody potentials

- Standard forcefields associated with MD packages:
 - GROMOS GAFF for small molecules (UA)
 - AMBER CGenFF for small molecules (UA and AA)
 - CHARMM (UA and AA)
 - OPLS (UA and AA)
- MD codes
 - AMBER
 - GROMACS
 - NAMD
 - CHARMM
- Typically include parameters for atoms (C,N,O,P ..) in a wide variety of chemical environments



$$E = \sum_{bonds} K_b (b - b_0)^2 + \sum_{angles} K_\theta (\theta - \theta_0)^2 + \sum_{dihedrals} K_{\phi,n} [1 + \cos(n\phi - \delta_n)] + \sum_{dihedr$$

$$+\sum_{impropers}K_{\phi}(\phi-\phi_0)^2+\sum_{i\neq j}\left(\frac{q_iq_j}{r_{ij}}\right)+E_{LJ}.$$

Example 2 – Multibody potentials SARS-CoV2 Spike protein

• Arantes et al. ACS Cent. Sci. 2020, 6, 10, 1654–1656



SARS-CoV2 spike protein

 1.7 M atoms
Realistic environment glycan shield water
~3 μs

Initiated in both open and closed conformation

Find crucial structural role of 2 N linked glycans in NTD

- holds in open conformation

Disrupted by alanine mutation - 40% reduction in binding to ACE2



SARS-CoV2 in Aerosol droplet (*Marr et al. Virginia Tech*)



1.3 billion atoms! ~10 ns

Aerosol consists of water, Mucins, surfactants, deep lung fluid

https://www.nytimes.com/interactive/2021/12/01/science/coronavirus-aerosol-simulation.html

Many body potentials - Metals

- Interaction between any 2 atoms depends on the positions of *all* other atoms
- Atom is embedded in electronic density of valence electrons
- Embedded Atom Model (EAM)
 - M. S. Daw and M. I. Baskes, <u>Phys. Rev. B 29, 6443 (1984)</u>.
 - M. S. Daw and M. I. Baskes, Phys. Rev. Lett. 50, 1285 (1983)

$$E_{\text{tot}} = \sum_{i} F_{i}(\boldsymbol{\rho}_{i}) + \sum_{i>j} \phi(r_{ij}),$$

 $\rho_i = \sum_{j(\neq i)} f(r_{ji}).$

Electron density

Embedding energy 2 body potential

 $F(\rho), \phi(r), f(r)$ Can take different functional forms or be tabulated



Many body potentials

- Finnis Sinclair
 - $F(\rho) = -A\sqrt{\rho}$
 - Origin of square root is simple tight binding theory of metallic cohesion
 - Parabolic variation of cohesive energy across 3d-4d series explained by filling a d-band with rectangular DOS
 - Local electronic bond energy varies as \sqrt{z}
- MEAM
 - Builds a directional dependence into how the electron density at a site is calculated
 - Less physically motivated than EAM

EAM potentials - properties

- The variation in strength of bonds in different local environments enables accurate description of:
 - Elastic constants
 - Cauchy relation ($C_{12}/C_{44}=1$; G=3/5B) for all pair potentials
 - Does not hold for metals
 - Plastic flow
 - Enhanced compared to pair potentials
 - Vacancy energies
 - significantly overestimated by pair potentials
 - Surface properties
 - Surface relax outwards for pair potentials
 - Phonon dispersion

Covalent solids – Environment Dependant Interatomic Potentials (EDIP)

- Modulate strength of attractive potential according to local environment
 - Number of neighbours and angles between neighbours

$$E_b = \sum_i \sum_{j>i} \left[E^R(r_{ij}) - b_{ij} E^A(r_{ij}) \right] * f_c(r_{ij}).$$

Bond order term Cutoff function



Tersoff

The simplest and fastest carbon potential. Based on a bondorder treatment, it *modifies the strength of the bonds according to the number of neighbours*.

$$\boldsymbol{\Phi} = \frac{1}{2} \sum_{i \neq j} \phi_{ij}(\boldsymbol{r}_{ij}), \tag{1}$$

$$\phi_{ij}(r_{ij}) = f_c(r_{ij})[A \exp(-\lambda_1 r_{ij}) - b_{ij}B \exp(-\lambda_2 r_{ij})], \qquad (2)$$

$$b_{ij} = (1 + \xi_{ij}^{\eta})^{-\delta}, \tag{3}$$

$$\xi_{ij} = \sum_{k \neq i,j} f_c(r_{ij}) g(\theta_{ijk}) \exp[\alpha (r_{ij} - r_{ik})^\beta], \tag{4}$$

$$g(\theta) = g_{\rm org}(\theta) = a \left\{ 1 + \frac{c^2}{d^2} - \frac{c^2}{d^2 + (h - \cos \theta)^2} \right\},\tag{5}$$

$$f_c(r) = \begin{cases} 1, & r \leq R_1, \\ \frac{1}{2} \left[1 + \cos\left(\pi \frac{r - R_1}{R_2 - R_1}\right) \right], & R_1 < r < R_2, \\ 0, & r \geq R_2, \end{cases}$$
(6)

Extensions to Tersoff for C-H and graphite

- Benner
 - Allows for changes in hybridization states for C
 - Good for hydrocarbons
 - Replace site additive energy with a bond additive energy
 - 2 terms added to take account of number of neighbours for each atom in a pair of bonded atoms
- AIREBO (Stuart)
 - Long range (van der Waals) interactions are included
 - Torsion term included
- For comprehensive review see
 - Harrison et al. Appl. Phys. Rev. 5, 031104 (2018)

Silicon potentials

B.-J. Lee / Computer Coupling of Phase Diagrams and Thermochemistry 31 (2007) 95-104

Table 4 Calculated structural properties of silicon, in comparison with experimental data and other calculations

		Exp./DFT	SW ^a (1985)	Tersoff ^a (1988)	EDIP (1998)	HOEP (2000)	Baskes (1989)	Present work
Diamond	E_c a	-4.63 5.43	-4.63 5.43	-4.63 5.43	-4.65 5.43	-4.61 5.43	-4.63 5.43	-4.63 5.43
Simple cubic	$\frac{\Delta E_c}{a}$	0.35 2.53	0.29 2.61	0.32 2.54	0.53 2.50	0.29	0.26 2.61	0.34 2.62
β-Tin	ΔE_c a c/a	0.27 4.82 0.55	0.21 4.97 0.56	0.33 4.91 0.52	0.67 4.76	0.31 - 0.56	0.38 4.83 0.62	0.35 5.04 0.52
Simple hexagonal	ΔE_c a c/a	0.29 2.64 0.94	0.40 2.83 0.92	0.47 2.70 0.97	- - -	0.23	0.38 2.75 0.95	- -
bee	ΔE_c a	0.53 3.09	0.30 3.25	0.43 3.08	1.59 3.24	0.72	0.45 3.25	0.49 3.14
fcc	$\frac{\Delta E_c}{a}$	0.57 3.89	0.42 4.15	0.76 3.90	1.84 4.08	0.70	0.34 4.19	0.57 3.98
hcp	ΔE_c a c/a	0.55 2.74 1.63	0.32 3.65 0.88	0.76 2.76 1.63	0.93 2.56 2.13	0.67 - 2.04	0.34 2.96 1.64	0.56 2.82 1.63

Si potentials

- Same paper also compares:
 - Defect energies
 - Surface structures
 - Surface energies
 - Melting point
 - Latent heat
 - Volume change on melting
 - Liquid coordination
 - Amorphous coordination
 - Liquid RDF
 - Amorphous RDF
 - Clusters

Part 2: Summary

Interatomic potentials encode the QM of bonding into the functional forms

- Many and multibody potentials are used for materials in which the cohesive energy cannot be expressed as a sum over the interaction energy between pairs of atoms
- Multibody potentials energy dependent on 4 atoms linked by covalent bonds
 - Covalently bonded molecules such as polymers and proteins
- Many body potentials interaction energy between 2 atoms function of the positions of all neighbouring atoms
 - Metals
- Bond order potentials bond energy function of the configuration of all other bonds linked to same atom
 - Covalent solids

Part 3: Reactive forcefields

Interatomic potentials that allow for:

- Bond breaking/forming
- Chemical reactions

ReaxFF: Motivation

- To develop potentials for accurate simulations of chemical interactions
 - Combustion
 - Catalysis
- Transferrable across chemistries and phases
 - O atom same in O₂, H₂O, SiO₂ etc.
- Model different classes of material (ionic and covalent) with same functional form
 - Bond order for covalent bonding
 - Partial charge which varies in different chemical environments for ionic interactions

ReaxFF potentials

$$\begin{split} E_{\text{system}} &= E_{\text{bond}} + E_{\text{over}} + E_{\text{angle}} + E_{\text{tors}} + E_{\text{vdWaals}} + E_{\text{Coulomb}} \\ &+ E_{\text{Specific}}. \end{split}$$

- E_{bond} continuous function of r
 - Bonds not defined a priori
 - No switching functions
- $E_{bond} E_{angle} E_{tor}$ modified by bond order term
- Bond order function of *r* only (not angles)
- *E*_{over} energy penalty for deviation from ideal coordination
- Uses electronegativity equalization to distribute charges according to electronegativity differences
 - Charge determined iteratively
 - Continuously calculated during simulation
- *E*_{specific} captures properties specific to particular systems
 - Lone pairs



Senftle et al. npj Computational Materials (2016) 15011





npj Computational Materials (2016) 15011



ReaxFF development tree, where parameter sets on a common 'branch' are fully transferable with one another.

npj Computational Materials (2016) 15011 42

ReaxFF potentials - Summary

- First developed introduced in 2001 functional form stable since 2005
- Suitable for both ionic and covalently bonded materials
 - Bonded and non-bonded interactions
 - Bond order dependence for covalent interactions
 - Polarizable charge for ionic interactions
- Accurately predicts transition barriers
 - Long range covalent interaction
 - Suitable for chemical interactions
- Can model reactive chemistry with accuracy comparable to QM
- Review: npj Computational Materials (2016) 15011

Applications of ReaxFF

- Nanoscale phenomenal in complex systems
- Heterogeneous catalysis
 - Ni Catalysed C nanotube growth
 - Vanadia catalysts interaction of hydrocarbons with V₂O₅
- Atomic layer deposition
- Reduction of graphene oxide
- Ultrafast resistance switching
- Proton diffusion membranes
- Nanoindentation

Example 3 - ReaxFF Graphene growth on SiC

Zhang and van Duin, Chem. Mater. 2020, 32, 19, 8306-8317

Optimizing growth conditions for synthesising high quality, large scale graphene Investigate

Different temperatures

Different substrate facets

Thermal decomposition and CVD strategies

Studied defect and grain boundary structures of grown films



Graphene growth on SiC Thermal decomposition

• Chem. Mater. 2020, 32, 19, 8306-8317



Graphene growth on SiC - CVD

• Chem. Mater. 2020, 32, 19, 8306-8317



ReaxFF – Codes

- LAMMPS (open source)
- PuReMD (open source)
- ADF (SCM)
- Materials Studio (Accelerys)

Choosing a potential

- Comprehensive literature search of modelling of your system
- Which properties have different potentials been fit to?
- Which properties are most important for your application?
 - Thermal properties melting T; heat capacity
 - Mechanical properties
 - Defect properties
- Which code(s) do you want to use?

Open KIM

- https://openkim.org
- Interatomic potential repository for making molecular simulations reliable, reproducible and portable
- Click on an element to find interatomic models for that species
- Support for GULP, DL_POLY, LAMMPS

Where next for interatomic potentials

- Machine learning?
 - Flexible functional forms
 - ML techniques to fit PES to electronic structure calculations
 - Large number of parameters
- Very successful for systems with complex QM effects
 - Stability of Si(111) surface reconstructions
- Requires large number of high level electronic structure calculations