

A new approach to molecular and lattice simulations with CrystalMaker[®]

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Appendix A Potentials functions

To perform relaxation and simulation, we need to know how atoms interact with each other. These are summarised by potential functions, which are a series of functions of atom distance and angles etc. In empirical force fields models, these functions are commonly categorised into short-range and long-range interactions.

A.1 Short range interactions

Short-range interactions are limited to atoms in close proximity. CrystalMake only considers these interactions for bonded atoms which include:

Bonded pair potentials: Keep pair atoms in a certain distance (Table A1). The short-range interactions decrease rapidly with increasing distance. Morse, Born-Mayer, Harmonic, Squared harmonic, and Stillinger-Weber two body potentials are all short-range potentials. Two body potentials also include long-range interactions which will be discussed in A.2.

Three-body potentials: Constrain angles between three atoms (Table A2).

Table A1 Two-body potentials

Potential	Formula	Units
Morse potential	$E = A \left[\left(1 - e^{-B(r-C)^2} \right) - 1 \right]$	A in eV, B in $1/\text{\AA}$, C in $\text{\AA}$
Buckingham	$E = Ae^{-r/B} - \frac{C}{r^6}$	A in eV, B in $\text{\AA}$, C in $\text{\AA}^6$
Born Mayer	$E = Ae^{(-r/B)}$	A in eV, B in $\text{\AA}$
Lennard-Jones(LJ)	$E = A \left[-2 \left(\frac{B}{r} \right)^6 + \left(\frac{B}{r} \right)^{12} \right]$	A in eV, B in $\text{\AA}$
Harmonic	$E = \frac{1}{2}A(r-B)^2$	A in eV/ $\text{\AA}^2$, B in $\text{\AA}$
Squared harmonic	$E = \frac{1}{2}A(r^2 - B^2)^2$	A in eV/ $\text{\AA}^4$, B in $\text{\AA}$
Stillinger-Weber(SW)	$E = A \left(\frac{B}{r^4} - 1 \right) \frac{C}{e^{r-cutoff}}$	A in eV/ $\text{\AA}^4$, B in $\text{\AA}$

Four-body potentials: These dihedral(also referred as torsional) shape and out of plane atom groups involving four atoms (Table A2).

Table A2 Three-body potentials

Potential	Formula	Units
Cosine harmonic	$E = \frac{1}{2}A(\cos\theta - B)^2$	A in eV, B is dimensionless
Linear three	$E = A(1 + \cos\theta)$	A in eV
Harmonic	$E = \frac{1}{2}A(\theta - B)^2$	A in my eV/rad ² , B in rad
Three cosine	$E = A + B\cos(C\theta) + D\cos(E\theta)$	A, B, D in eV. C and D are dimensionless
Stillinger-Weber(SW)	$E = A(\cos\theta - \cos B)^2 e^{\frac{C}{r_{ij}-E} + \frac{D}{r_{ij}-F}}$	A in eV, B in degree, C and D in $\text{\AA}$

Table A3 Four body potentials

Potential	Formula	Units
Torsion dihedral	$E = A[1 + \cos(B\phi - C)]$	A in eV, B is dimensionless, C in degree
Torsion expanded dihedral	$E = A[1 + \cos(B\phi - C)] + D[1 + \cos(E\phi - F)] + G[1 + \cos(H\phi - I)]$	A, D, G in eV, B, E, H are dimensionless, and C, F, I in degree.
Inversion planar	$E = A(1 - \cos\phi)$	A in eV
Inversion harmonic	$E = \frac{1}{2}A(\phi - B)^2$	A in eV, B in radian
Inversion squared.	$E = \frac{1}{2}A \frac{(\cos\phi - \cos B)^2}{(\sin B)^2}$	A in eV, B in degree.

A.2 long-range interaction and cutoffs

Long-range potential are the Coulomb interactions and $1/r^6$ attraction terms (also referred as $C6$ terms in dispersion interaction), this type of interactions converges

slowly in space and is computationally expensive to calculate directly. To solve this problem, CrystalMaker employs the Ewald Sum method, splitting these interactions into real and reciprocal space to speed up the calculations. The contribution of real and reciprocal space is controlled by factor η .

Ewald sum cutoffs: A proper value for η is required for sufficient accuracy when:

$$\exp(-\eta r_{max}^2) = 10^{-12} \quad (A1)$$

The results would be accurate enough for most crystalline systems. Here we define an accuracy factor in form of η :

$$f = \eta r_{max}^2 \quad (A2)$$

From Eq.3, we have $f = -\ln(10^{-12}) = 27.631021115..$

$$r_{max} = 2\sqrt{f\eta}, k_{max} = 2\sqrt{f\eta} \quad (A3)$$

in which, r_{max} and k_{max} are the cutoffs in real and reciprocal space, respectively.

$$\exp(-\eta r_{max}^2) = 10^{-12} \quad (A4)$$

The cost of computation in both real space and reciprocal space is also controlled by η . In our software, η is chosen for the minimum number of terms calculated in real space and reciprocal space in total. Coulomb interaction and C6 terms are calculated respectively. These cut-offs in real space speed up greatly with the size of unit cell, especially for large systems like ZIFs and complicated molecular crystals such crystalline benzenes, naphthalenes and paraterphenyl. Large cutoffs made the optimisation and simulation process possible for these large systems.

The repulsive energy in van der Waals's energy: short-range interactions that converges very quickly with r . Hence the repulsive energy and real space energy can be calculated together to save computation time.

Appendix B Potential library

CrystalMaker[®] carries its own in-built selection of potential parameter libraries for use in simulations, negating the need for the user to have to find or create potentials of their own. The potentials are assigned automatically depending on the structure type and local bonding environment. Most of the potentials are transferable, which helps expand the pool of simulation models to more complicated system. So far, our potentials library are divided into two categories: organic molecules and solid crystals.

Organic molecules The organic molecules and organic molecular crystals (composed mainly of C, O, N and H), CrystalMaker uses "Molecular Mechanics 3" (MM3)[1-4] potentials to keep the molecule shapes. MM3 is widely used to simulate organic structure and dynamics due to its comprehensive coverage of most of the short range interactions: bonded pair, three-body and torsion potentials.

Although the MM3 model does provide potentials for describing long-range dispersion interactions, previous experience within M T Dove has found that the MM3 dispersion parameter set does not describe these forces well. As a result, CrystalMaker[®]

does not incorporate them, and instead it relies on Williams potentials[5] for dispersion interactions in organic systems. The atomic charges are from the work of Dove et al.[6] based on the Distributed Multipole Analysis(DMA)[7] method. When non-organic elements are present in a molecular crystal file, the program falls back to Universal force fields (UFF)[8], which includes all short and long-range interactions.

To improve computational efficiency, the Ewald Sum for long-range dispersion interactions is switched off. A cutoff of 10 Å is applied with the sacrifice of long-range dispersion interaction accuracy. 10 Å is a reasonable value maintains structural integrity and dynamics while reducing computation costs.

Inorganic and hybrid materials Compared with organic molecules, inorganic crystals involve a diverse range of elements and bonding types. There is no one unified empirical potential library for the large number of solids. However, specific types of systems, such as oxides[9–12], silicates[9], semiconductors[13, 13–16], Zeolitic Imidizolate Frameworks(ZIFs)[17] have been modelled. So far, there are more than 30 references included in our potential library. CrystalMaker detects the structure type(e.g., molecular crystal, inorganic solids, frameworks et.) and process to analyse the local bonding environments around each sites, assigning the most appropriate potentials. The references and type of materials covered are listed in Table B4.

As shown in Table B4, there is a substantial body of work on oxides, which include 50 elements in the periodic Table, including common metals, transitional metals, metalloids, most of the lanthanides and one Actinides: Uranium. CrystalMaker automatically goes through the library and chooses the most widely used reference, such as Catlow[18–22] and Alfonso Pedone’s[9] set as default options for common oxides in the program. The ones that are not set as default is listed in the brackets. Catlow’s, Pedone’s and Bush’s work combined together have covered most of the oxides.

Although the parameters of inorganic are transferable to similar composition systems, a set of parameters might work for one symmetry but not for others. When this happens, this indicates that the parameters might need to be tweaked for specific system. In most cases, this will work with a bit attempts of adjusting the values of the parameters for a better fitting without reinventing the wheel of a new set of force fields model.

The force fields from different libraries are not comparable. This only works for the systems that use the potentials from the same potential pool - standardised parameters from one resource. This is because the potentials are developed based on relative energy instead of absolute energy. One good example is periclase MgO (space group Fm-3m), with cell parameter 4.2462 Å relaxed using Catlow’s force fields, energy is -161.700708 eV per cell. The cell parameter is 4.2393 Å optimised using Pedone’s force fields. The cell structure is kept well with both force fields. However the cell energy calculated with Pedone’s force fields is -66.306664 eV, which is totally different from Catlow’s one.

When no potential can be applied to a solid crystal, UFF is applied as a fall back for the solids. This includes the pure metals, Ag, Cu, Fe etc. To use UFF, sensible bonds are required for short range interactions, two-body and three-body interactions. long-range interactions (Coulomb and van der Waals) are excluded from the bonded pairs.

Table B4 List of potential library

Material type	References	Covered elements
Oxides	Catlow[18–22]	Na, K, Sr, Ni, Al, Fe, Ti, Mg
	Pedone[9]	Li, Be, Ca, Sr, Ba, Sc, Zr, Cr, Mn, Co, Cu, Ag, Zn, Si, Ge, Sn, P, Nd, Gd, Er, (Na, K, Sr, Ni, Al, Fe, Ti, Mg)
	Bush[10–12]	Pr, Po, Rb, Ta, Tl, U, V, Sb, Ga, Y, La, Eu, Yb, Ce, Nb, Pb, Lu, Ru(Li, Na, K, Mg, Ca, Sr, Ba, Fe, Ti, Al, Nd, Gd, Ag, Co, Cu, Fe, Ge, Mn, Sn, Zr, Ni, Er)
	Hope[23]	Kr (Si)
	Grimes[24–26]	Sm, Mo(Ce, Lu, Yb, Er, Y, Gd, Eu, Nd, La, Ti, Ru, Sn, Zr, Pb)
	Winch[27]	HgO (BaO)
	Fisher[28]	In(Ba) and BaIn2O5
	Cherry and Catlow[29]	Ca, La, Cr, Mn, Ga, Ti
	Post[30]	Na, Mg, Al, Si, K, Ca, Ti, Sr, Ba
	Dove and Redfern[31]	Ca, Co, Zn, Cd, Ni, Mn, Sr, Mg, Fe, Ba, Pb
	Gastreich[32]	B, Si
	Atwood[33]	Li, Na, K, Rb, Cs
	Diller[14]	Li, Na, K, Rb
	Post[30]	Si, Na, Al, Ca
	Baram and Parker[34, 35]	Si, O-H
Oxides with O-H surface		
Carbonates	Dove and Redfern[31]	Ca, Co, Zn, Cd, Ni, Mn, Sr, Mg, Fe, Ba, Pb
Aluminosilicate minerals	Winkler and Dove[36]	Si, Al, K, Mg, Ca, O, H
Nitrides with H	Gastreich[32]	B, Si
Halides	Atwood[33]	Li, Na, K, Rb, Cs
	Diller[14]	Li, Na, K, Rb
	Post[30]	Si, Na, Al, Ca
Florides	Jackson[37]	La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu
Chlorides	Post[30]	Si, Na, Al, Ca
Other solids	Fan[13]	CdS-CdSe-PbS-PbSe system
II-VI	Zhou[15]	Zn, Cd, Hg, S, Se, Te
III-V	Han[16]	InAs, InP, GaAs, GaP
Sulphides	Diller[14]	Na2S
	Wright[38]	CdS, ZnS
Gallium phosphate	Girard[39]	GaPO ₄
ZIFs	Gao[17]	ZIFs, ZIF-zni, ZIF-1 to ZIF-11, with -N ₂ C ₃ H ₃ - ligand only

One should be aware of the huge difference between organic molecules and crystalline solids, which are differentiated by the bonds in CrystalMaker. The molecules consist of atoms bonded to each other, while solid crystals are represented with no bonds at all or represented as infinite framework. In crystalline solids, long-range potential plays an important role in maintaining the structure.

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