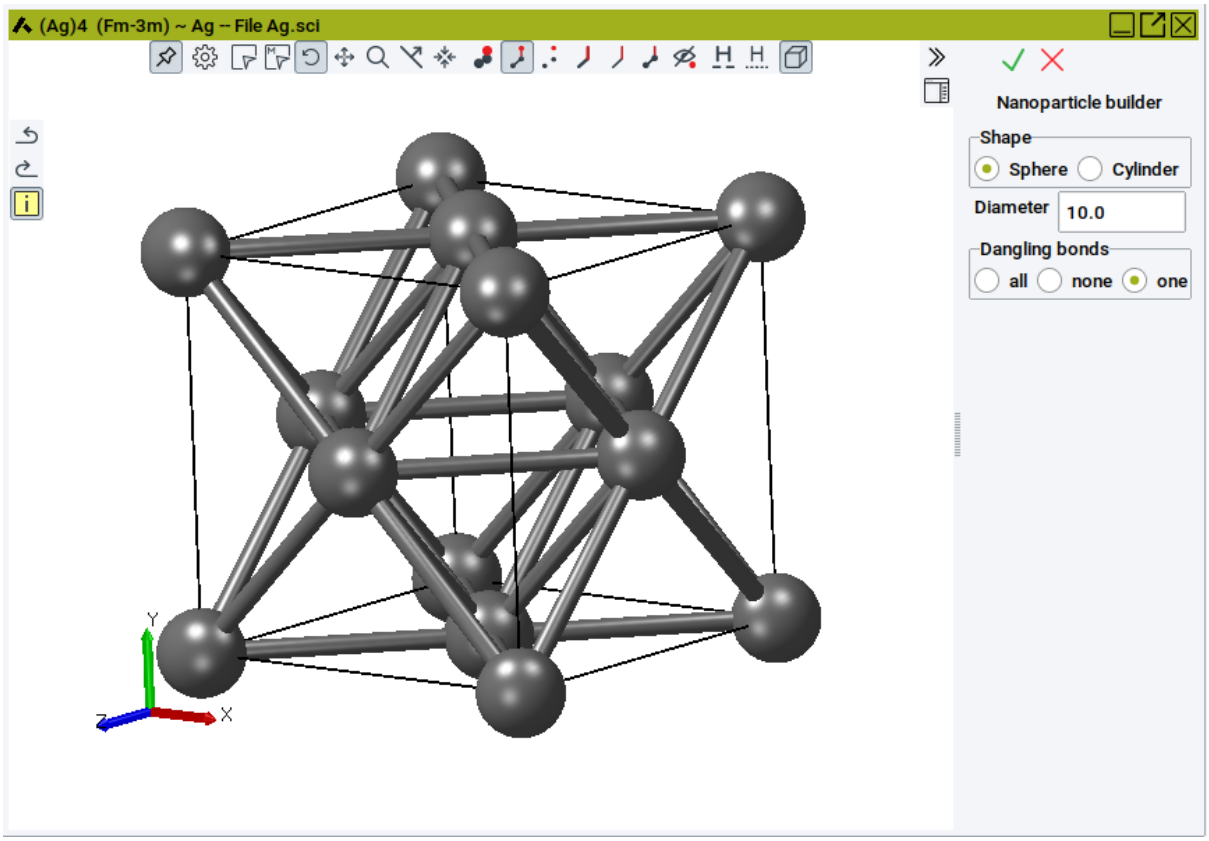
MedeA Builders: Building Complex Structures with Ease

Contents

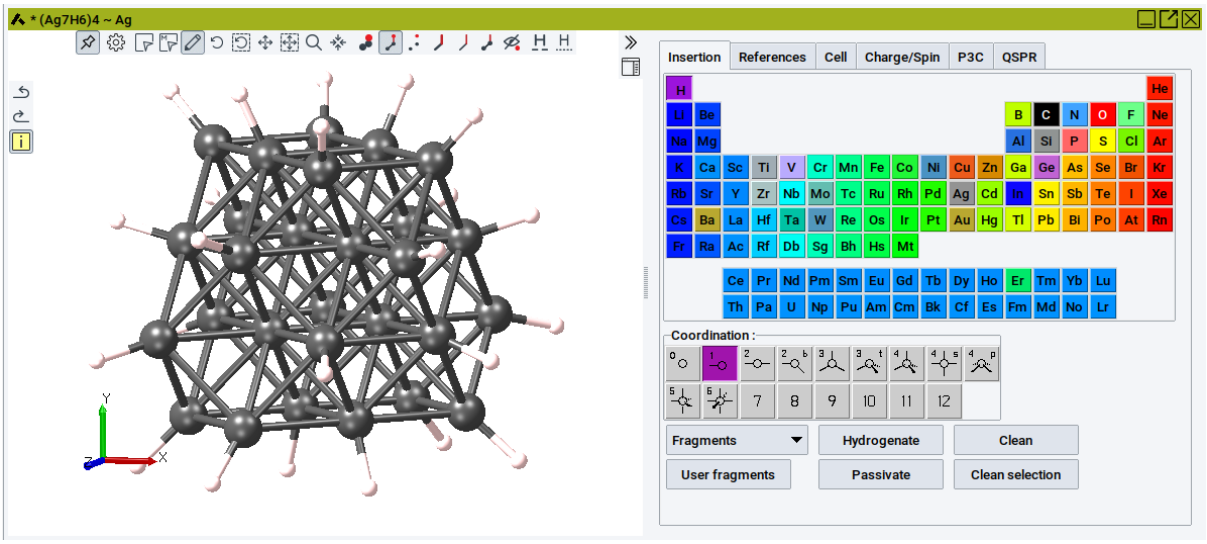
1 Nanoparticles

Builders >> Nanoparticles... creates a spherical or cylindrical nanoparticle based on an existing periodic model and opens the molecular editor to fine-tune the termination and set a cell size.



You need to specify the shape as *sphere* or *cylinder*, and set the size by diameter and length (for cylinder). Dangling bonds allows you to keep *all* existing bonds at the boundary, keep only *one* (for passivation) or *none*.

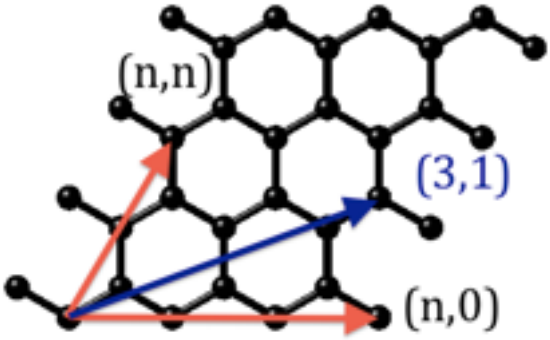
The initial nanoparticle is passed to the molecular editor (more details can be found in the Edit in Molecular Builder chapter), as you still have to decide on cell size, in case you want to continue with a periodic model. You can passivate the dangling bonds with hydrogen, functional groups, or with another element and continue passivating to build a bigger particle.



In the illustration below a spherical Ag nanoparticle with 10 Å diameter is passivated with hydrogen (with one-fold coordination).

2 Nanotubes

The Nanotube builder Builders >> Nanotubes... in *MedeA* creates periodic and isolated nanotubes from a flat sheet of graphene or related structure such as BN. You define basic requirements such as periodicity along the tube direction, packing in the perpendicular plane, and the number of nested nanotubes. *MedeA* calculates the size of the resulting cell before building a system.

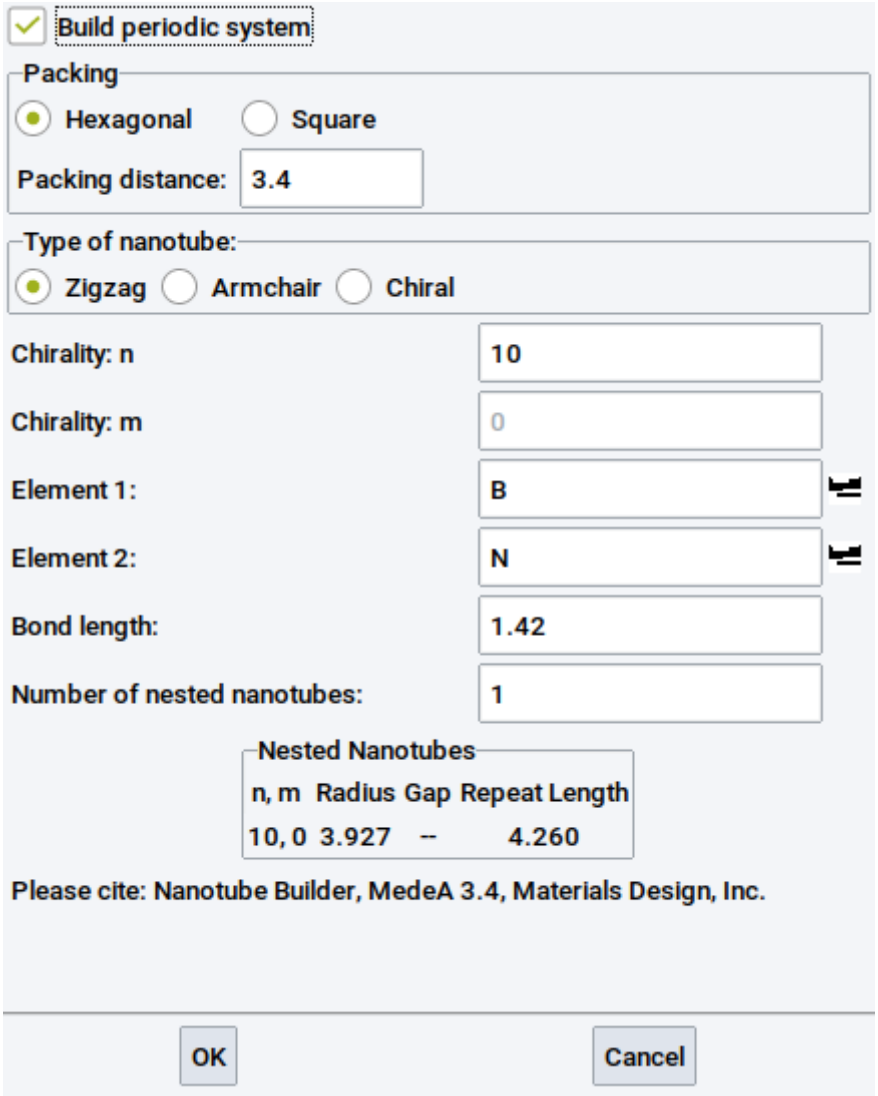


Type of nanotube : Nanotubes are defined by a chirality vector (*n,m*) which corresponds to how you fold a sheet of graphene into a tube. The two simplest nanotube orientations are *armchair (n,n)* and *zigzag (n,0)* and the corresponding chirality vector is shown in red.

Anything in between with *0*<*m*<*n* is called chiral, for example, the (*3,1*) direction is shown in blue. The Chirality vector *m* is set, but not editable, once you choose the *zigzag* or armchair type.

2.1 Periodic models

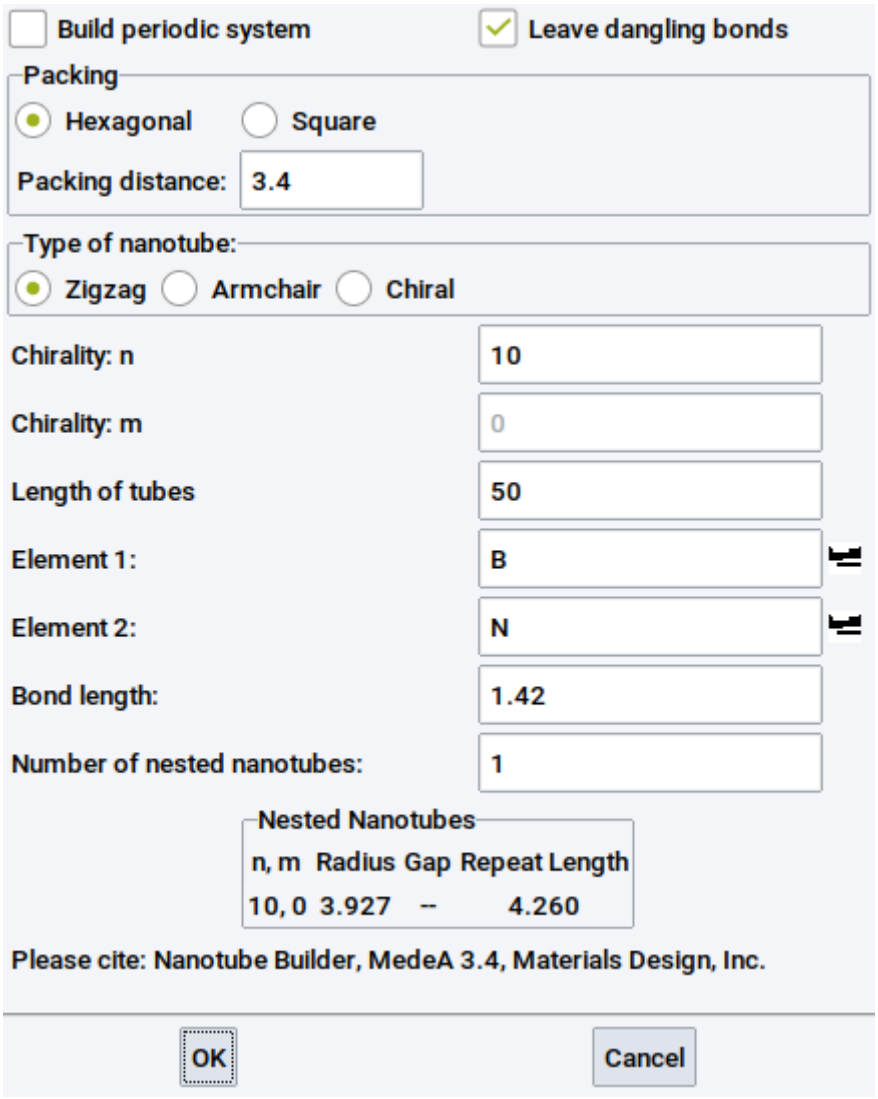
Check Build a periodic system to create infinitely long nanotubes of any type, otherwise you cut a nanotube of a defined *length of tube*.



Packing : You can select *hexagonal* or *cubic* packing in the plane normal to the nanotube direction. The distance between nanotubes is defined by *Packing distance* (in Angstrom).

Number of nested nanotubes : With *armchair* and *zig-zag* orientation it, is easy to stack nanotubes of similar chirality, as they share the periodicity along the tube direction. For any other *chirality MedeA* requires that *build periodic system* is inactive. Otherwise the input field *Chirality: m* is inactive and only *zig-zag* and *armchair* orientations can be chosen for nested nanotubes with periodicity.

2.2 Aperiodic models



You can still stack arbitrarily oriented nanotubes if you sacrifice the periodicity along the tube direction.

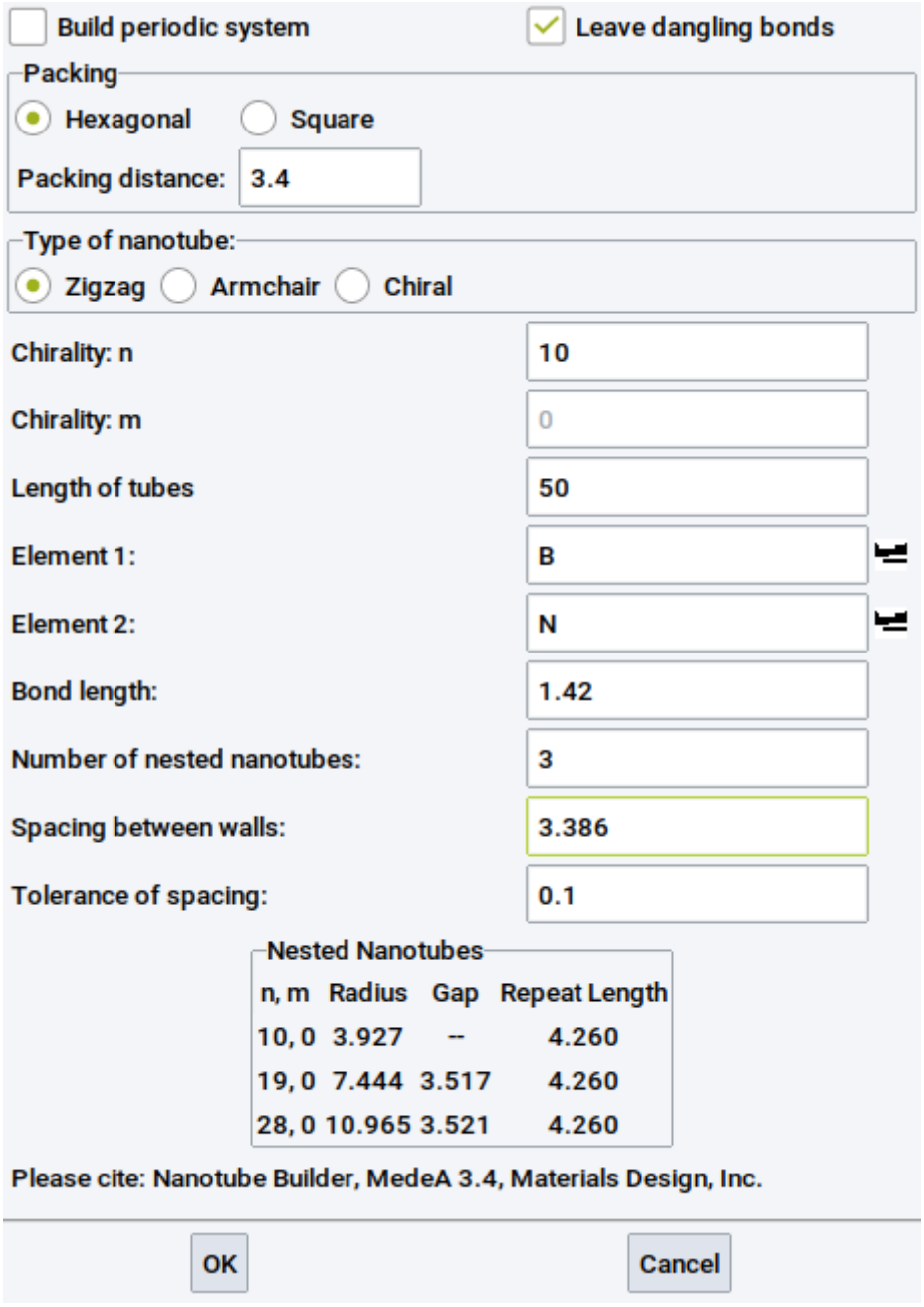
In this case, you need to specify the Length of tubes (in |AA|) and decide how to terminate the nanotubes.

Check Leave dangling bonds if you want to terminate with hydrogen.

Nested nanotubes are defined by a *spacing between walls and a tolerance of spacing*.

The Nested Nanotube panel shows the defined sequence.

For non-periodic systems with fewer constraints, you can select any of the suitable nanotubes within the given Tolerance of spacing from the list.



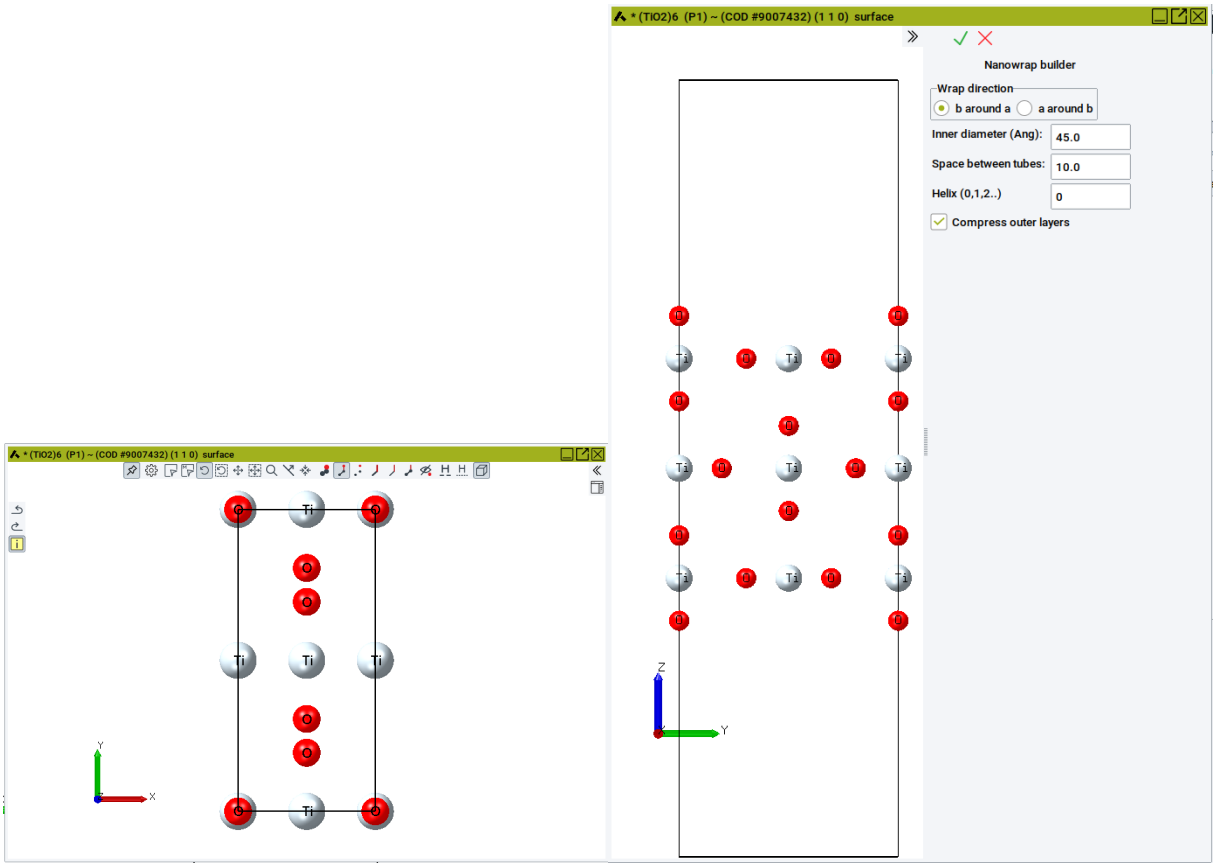
You can easily create nanotubes of BN by changing the Element and Bond length.

2.3 Naming convention

CNT-(n,m). For periodic nanotubes, *MedeA* appends the label *metallic* or *semiconductor* to the name. Metallic nanotubes have (*2n+m*) or (*n-m*) divisible by 3.

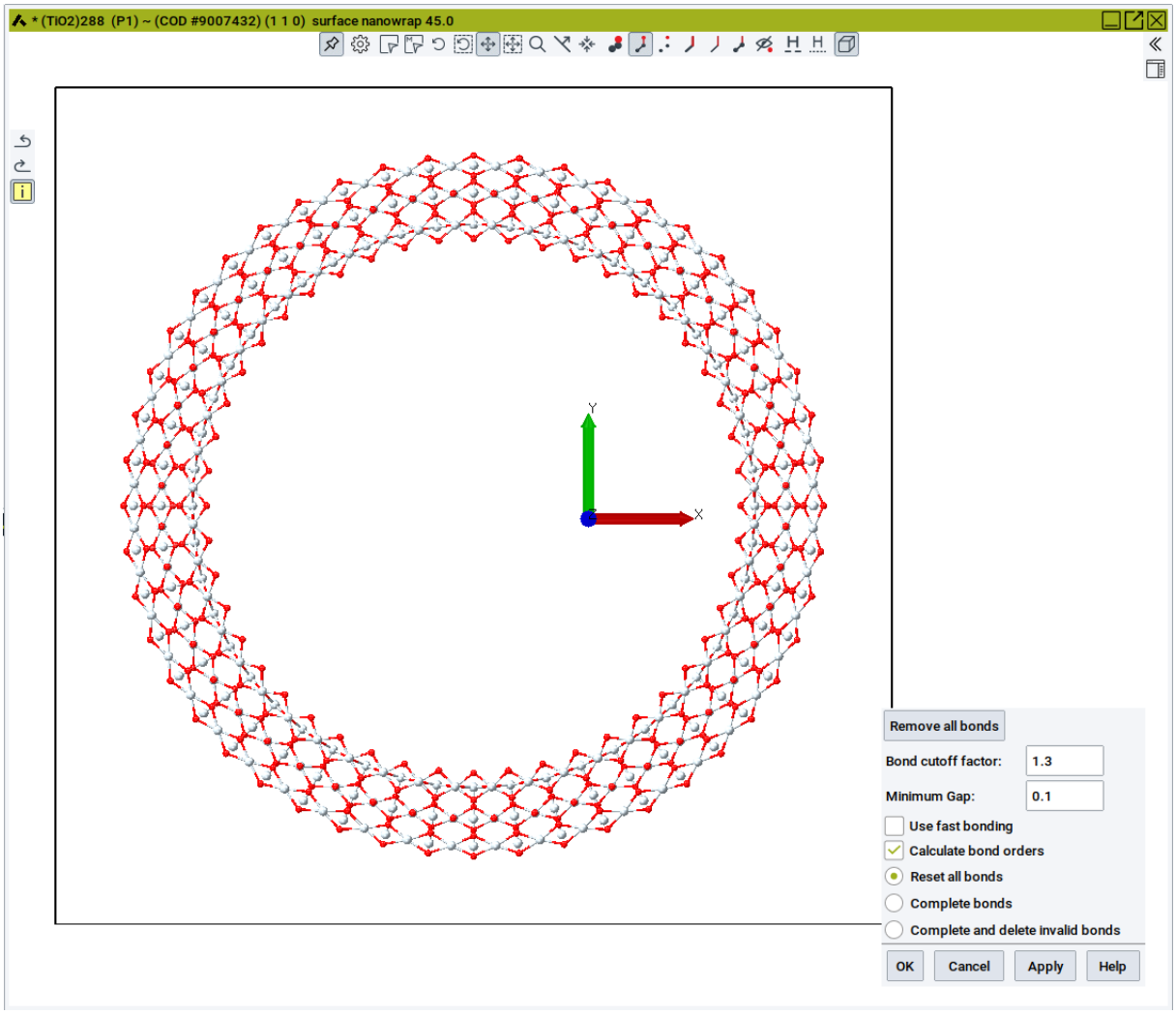
3 Nanowrap

Build making use of Builders >> Nanowrap... a nanowrap in a cylindrical shape. This tool works on periodic "surface" cells, where the vacuum of at least 4 Å separates the top from the bottom.



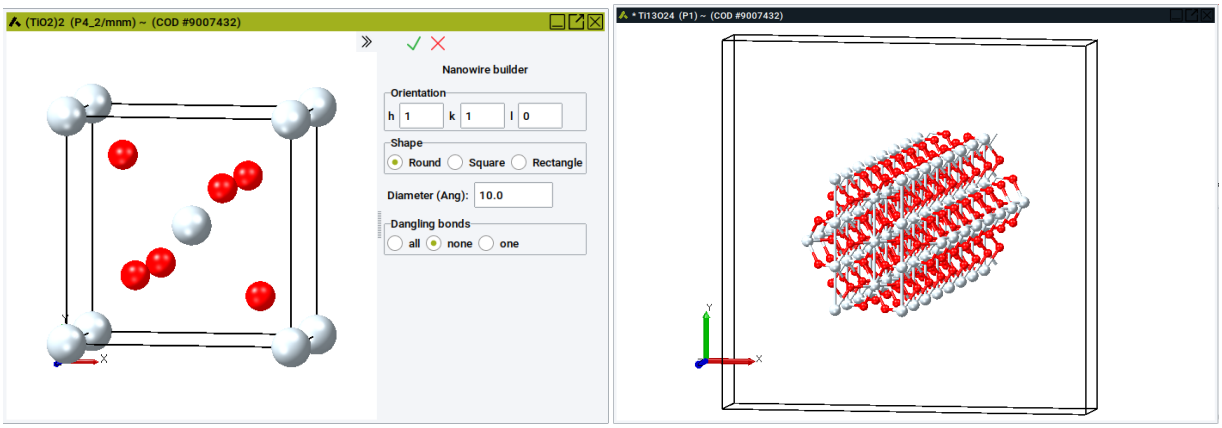
The top surface is going to be inside of a tube, the bottom surface outside. You have two choices to wrap a_around_b or b_around_a .

Having VASP in mind, the default choice is to create the nanowrap with the least number of atoms, so the suggested default is the shorter vector **b** as the direction of the tube and wrap the longer vector **a** as a supercell around a circle, so that the inner diameter (including the vacuum on top) is at least the requested 15 Å.



4 Nanowire

Nanowire building is accomplished by invoking Builders >> Nanowire... for a periodic bulk structure model. The control panel allows you to specify the wire's Orientation <hkl> through the bulk crystal lattice, whether the Shape should be *round*, a *square*, or a *rectangle*, and allows you to enter the Diameter of the wire in units of Å. The Dangling bonds choice allows you to keep all existing bonds at the boundary, keep only *one* (for passivation), or *none*. The resulting nanowire structure model is of molecular type, which can be transformed into a stack of wires by selecting Create a periodic copy from the context menu that comes up when right-clicking into structure window.

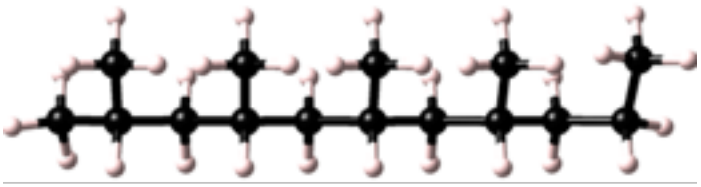
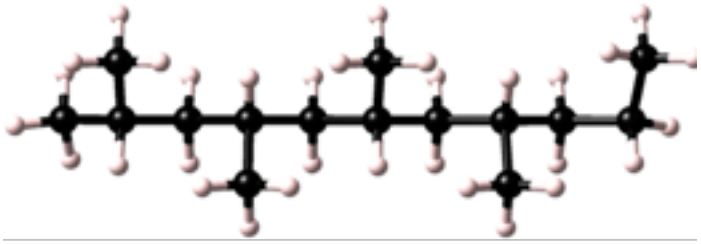
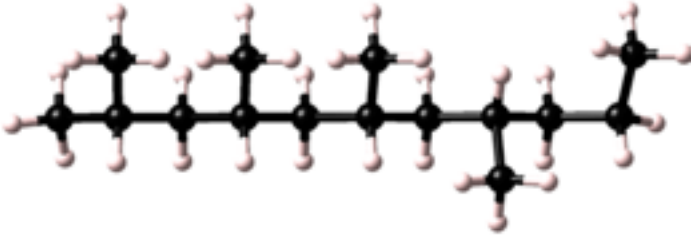


5 Polymer Builder

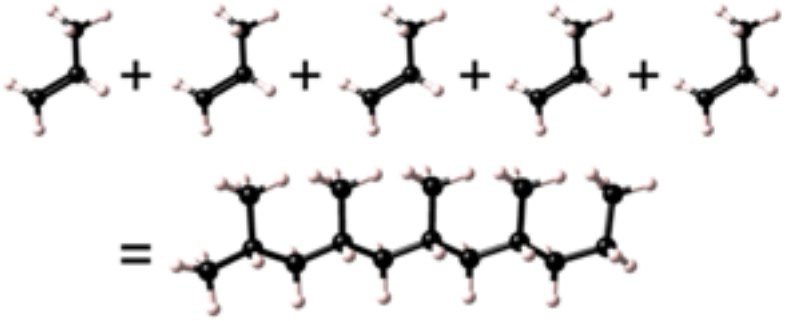
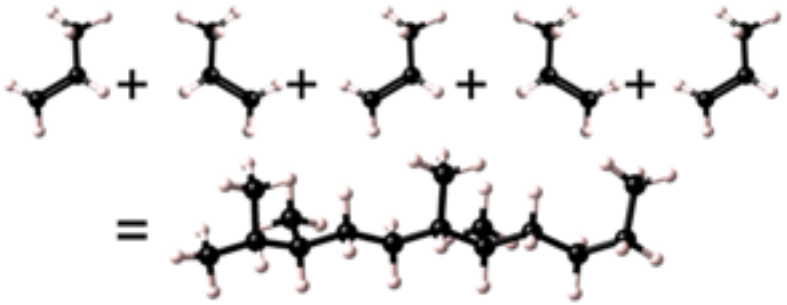
5.1 Features and Algorithm

The *MedeA Polymer Builder* constructs polymer models based on defined repeat units and rules concerning composition, orientation, and stereochemistry. A comprehensive collection of repeat units is supplied within *MedeA*, covering frequently encountered monomers, and repeat units may also be user-defined, constructed in the *Molecular Builder*, and incorporated into polymeric systems using the *Polymer Builder*, allowing the construction of any desired polymer.

Polymers possess a great variety of possible microstructures. For example a simple polymer, based on a single repeat unit type, may be isotactic, syndiotactic, or atactic.

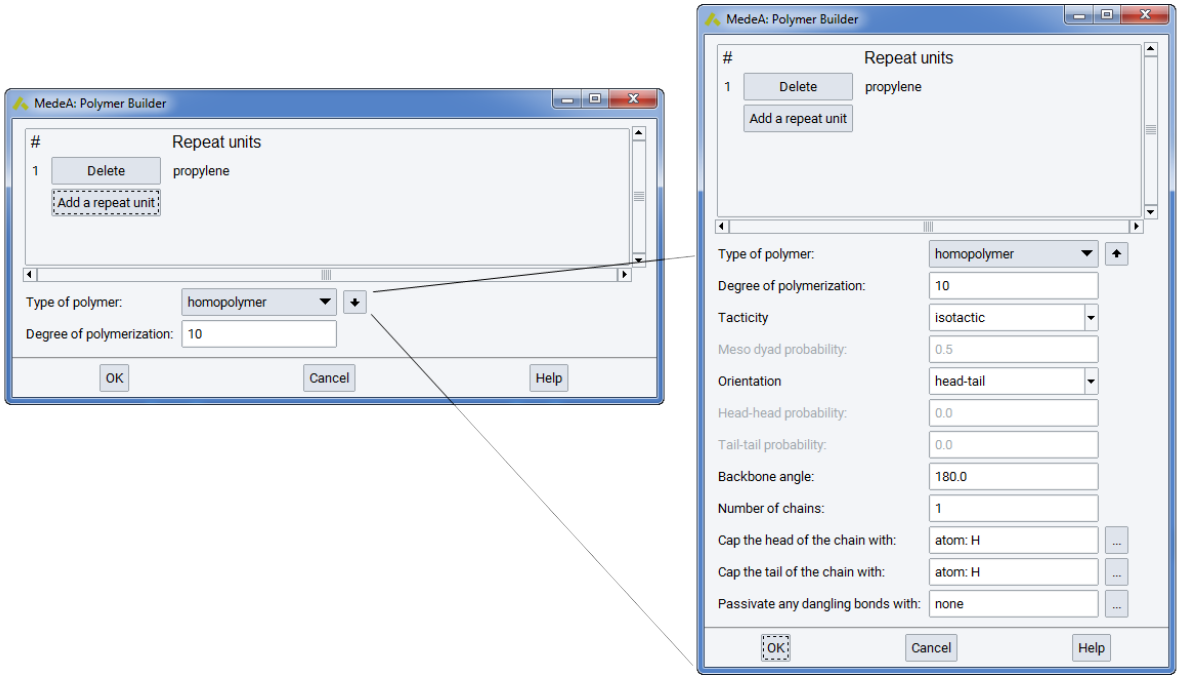
isotactic	
syndiotactic	
atactic	

Polymerization may occur in either a head to tail, head to head (and tail to tail), or in a random sense.

Head to tail	
Head to head	

Additionally, the polymer backbone formed by the polymerization process possesses a conformation defined by a sequence of dihedral angles, and the ends of the chain may be terminated by capping groups or atoms (e.g., initiator and terminator fragments). Furthermore, when several repeat units are simultaneously polymerized, the composition of the polymer must be specified.

To accommodate these diverse building options intuitively, the *Polymer Builder* provides an interface, which progressively exposes options based on preceding selections. Hence, if a homopolymer (i.e., a polymer-based on a single repeat unit) is to be constructed, options relating to copolymers are not presented in the user interface. Conversely, if multiple repeat units are specified, only options relating to copolymer formation are made available in the user interface, so that appropriate input may be provided. Hence the *Polymer Builder* allows complex polymers to be built with only the required options and settings presented to the user. Reasonable default options are provided whenever possible so that realistic polymer chains can be constructed straightforwardly.



By default, the *Polymer Builder* presents the user interface shown in the figure below, which is invoked from the Polymers... menu item of the Builders menu of *MedeA*. This allows you to construct simple polymers and copolymers with minimal input information, making use of default settings. Additional input parameters may be selected through the 'additional options' button: ↓. When the extended interface is selected, the 'additional options' button changes to ↑, and clicking this arrow will remove the additional options from the *Polymer Builder* dialog box.

Algorithmically the *Polymer Builder* employs a construction process similar to that used by the *Molecular Builder* in combining molecular fragments, tuned for efficient construction of large polymers. At each stage in construction the fragment to be added to the growing polymer chain is translated and rotated to the required position, as defined by the existing backbone configuration and specified dihedral angle, and the appropriate bond created to add the repeat unit to the chain. This addition process is repeated for each repeat unit to match the specified input options.

When random copolymers are created the composition and stereochemistry of the polymer chain must be specified. This is accomplished through input parameters, which govern the fraction of each repeat unit expressed in the final polymer chain (which must sum to 1.0), and inversion and flip probabilities. The inversion probability describes the probability of pseudo chiral center inversion before polymerization, the flip probability describes the relative probability of head and tail connections occurring, for repeat units in which inversion of the connection direction causes differences in the resulting chain.

5.2 Usage

The steps required to create polymer models are as follows:

Select the required repeat unit, or units, from which the polymer is to be constructed

Select the type of polymer to be built; the options to choose between will depend on the number of repeat unit units selected. If a homopolymer (a single repeat unit) is selected, the required tacticity can be specified. If a copolymer (two or more repeat units) is selected, the appropriate copolymer type must be defined.

Select the degree of polymerization (the number of repeat units represented in the final polymer) or the block copolymer lengths.

Specify capping atoms or fragments, and additional build options such as any required passivation of active bonds.

Construct the polymer, by clicking OK .

5.3 Default Parameters

In general the *Polymer Builder* provides reasonable default parameters. For example, polymer chains are passivated with hydrogen atoms, no additional active bond passivation is carried out, backbone dihedral angles are set to 180 degrees, and a single chain is constructed.

5.4 Parameters Common to all Polymers

Type of polymer

If just one repeat unit has been specified, the only available option is homopolymer .

If more than one repeat unit has been added to the repeat unit list, the options are:

alternating copolymer : E.g., *ABABABAB...*, *ABCABCABC...* etc.

block copolymer : E.g., *AAAAAAABBBBBBB*, *AAAABBBBAAAA*, *AAABBBCCC* etc. (where block sequence lengths must be specified in the repeat units' list).

random copolymer : Completely random ('statistical') occurrence of repeat units, requiring specification of conditional probabilities for determining the probability p_{ij} that a repeat unit of type j attaches to a growing chain with repeat unit i at its end. See also section Parameters Specific to Copolymers for additional details)

Degree of polymerization : For a *homopolymer* or *random copolymer*, denotes the number of repeat units in the chain. For an *alternating copolymer*, denotes the number of times the alternating sequence is repeated. Note that for *block copolymers*, the number of repeats in each block is entered directly into the repeat unit window, and this entry field is not shown.

Backbone angle : Specifies the *dihedral angle* between successive repeat units. The convention is '180 degrees is trans'.

Number of chains : *Number of independent polymer chains* to build when the OK button is pressed.

Cap the head of the chain with : Specifies the *moiety* to be attached to the beginning/head of the chain. Options are 'H', the *name of a fragment*, or *'none'*.

Cap the tail of the chain with : Specifies the moiety to be attached to the end/tail of the chain. Options are *'H'*, the *name of a fragment*, or *'none'*.

Passivate any dangling bonds with : When repeat units contain internal dangling/uncapped bonds, specifies the moiety to be attached. Options are *'H'*, the *name of a fragment*, or *'none'*.

5.5 Parameters Specific to Homopolymers

Tacticity : For vinyl and other repeat units containing pseudochiral centers (e.g., -CH_2CXY-), specifies the stereochemical configuration about the center. Options are *isotactic*, *syndiotactic* and *atactic*.

Meso dyad probability : For *atactic* chains, in which the stereochemical configuration is random, specifies the probability of two consecutive repeat units having the same chiral arrangement.

Orientation : Where appropriate (e.g., in vinyl polymers) specifies whether successive repeat units are connected in a *head-to-tail*, *head-to-head/tail-to-tail* or *random* pattern.

Head-Head Probability : Specifies the probability of attaching the next repeat unit via its head atom, when the atom at the end of a growing chain is also a head atom.

Tail-Tail probability : Specifies the probability of attaching the next repeat unit via its tail atom, when the atom at the end of a growing chain is also a tail atom.

5.6 Parameters Specific to Copolymers

Parameters are entered directly into the various fields displayed when the desired copolymer type has been selected. Required input for each copolymer type is:

Random (statistical) Copolymers

If the copolymer composition, as specified in the *MedeA GUI* via File >> Preferences, is given in the form of:

Mole Fractions: Fraction : Denotes the mole fraction of the repeat unit listed in row i.

Conditional Probabilities : P1, P2, P3, etc. - Specifies the conditional probability that the repeat unit in row i will be attached to a growing chain with repeat unit 1, 2, 3, etc., at its end. Values in each row must sum up to 1.0.

Pinv : For repeat units containing pseudochiral centers (e.g., -CH $_2$CXY-), specifies the probability of inverting the stereochemical configuration about the center before adding the repeat unit to the growing chain.

Pflip : For situations in which repeat units can connect in head-to-tail or head-to-head arrangements (e.g., in vinyl polymers), specifies the probability of reversing the default head-to-tail mode of addition.

Block Copolymers

N : Indicates the number of repeat units of the type within each row/block.

5.7 Polymer Builder - Repeat Unit Dialog

The Repeat Unit dialog is displayed whenever the Add... button has been clicked in the *Repeat units* panel of the *Polymer Builder* dialog. Clicking on the selector button labeled Get the repeat unit from a allows repeat units to be obtained from one of three sources: repeat unit library, a Window in MedeA, or from a File.

repeat unit library : Choosing this option displays a selection hierarchy with repeat units organized in folders according to common classifications, such as acrylics, amides, dienes, etc. Navigating to and selecting the desired repeat unit causes it to be displayed in the Repeat unit entry field. Clicking OK closes the dialog and adds the repeat unit to the main dialog. Alternatively, double-clicking the repeat unit name closes the dialog and adds the repeat unit to the main dialog directly.

MedeA includes a large selection of common repeat units in its internal library. However, should it be desired to use a custom set of repeat units, these may be accessed by placing *MedeA*.sci files in a folder of the user's choosing. The location of this folder is determined by the value of the User repeat unit library parameter in the *MedeA GUI* dialog accessed by File >> Preferences... . The names of all `.sci` files in the user library folder are then displayed in a separate user folder appended to the repeat unit hierarchy dialog and may be used in the same manner as the repeat units provided with *MedeA*. Note that if the user's repeat unit library does not exist, or is empty, this user folder will not appear in the display.

Note: User repeat units must contain valid repeat unit definitions for them to be included in the list.

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window in MedeA : Choosing this option will inspect all current windows within *MedeA* for valid repeat units - defined as molecular fragments containing at least two 'active' bonds, one of which must have been designated as a 'head' atom, and the other as 'tail' (with only one head and tail permitted per repeat unit). Any valid repeat units can then be chosen.

file : This option allows the direct specification of a `.sci` file, without requiring that the repeat unit first be loaded into *MedeA*.

6 Defining Repeat Units

As noted, the *MedeA Polymer Builder* constructs polymer models from defined repeat units. A comprehensive library of predefined repeat units is accessible from the *Polymer Builder* interface. Additionally, repeat units can be constructed using the *MedeA Molecular Builder* and saved in a user repeat unit library for later use.

To define a repeat unit in the *Molecular Builder* you construct a molecular fragment with active bonds at the desired head and tail connection points of the repeat unit. You then select the head and tail atoms and use the Define repeat unit command which is accessible from the right-click context menu of the *Molecular Builder*, under Selection , to identify the polymer backbone and connection points for the repeat unit.

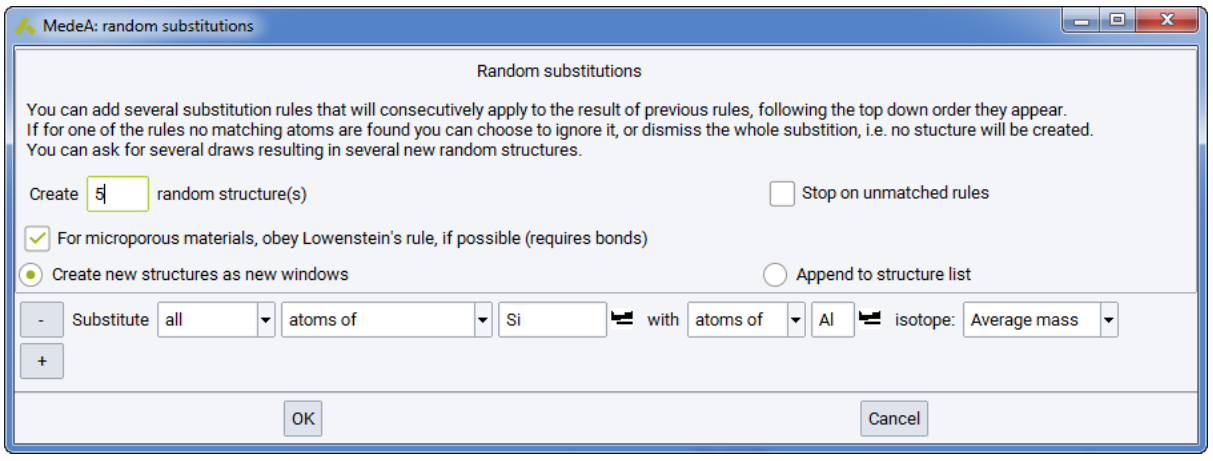
The Define repeat unit command is accessible when two atoms are selected in the *Molecular Builder*. These selected atoms must also have active bonds. With standard graphics settings, repeat units are rendered in the *MedeA* Environment with green and red active bonds for head and tail atoms, respectively. Additionally, after the execution of the Define repeat unit command, backbone atoms in the repeat unit will be highlighted, so the structural characteristics of the newly defined repeat unit may be viewed and checked.

The initial selection of the head and tail atoms depends on the construction order of the molecular fragment, and if desired you may reverse the head and tail atoms with the Reverse repeat unit head and tail atoms command, which is also accessible from the *Molecular Builder* context menu, under the Selection command group.

Chiral and pseudochiral centers along the repeat unit backbone are identified by the Define repeat unit command, and this information is employed when the newly created repeat unit is used in the *Polymer Builder* to construct a polymer chain.

Structures with defined backbone flags can be saved for future use with the *Polymer Builder* by exporting *MedeA* `.sci` format files to your `~/MD/Structures/RepeatUnits` folder. (Note, the name and location of this folder can be altered using the File >> Preferences... command). Hence any desired repeat unit can be constructed, saved, and employed in the *MedeA Polymer Builder*.

7 Random Substitutions



Use Random substitutions... to replace atoms and atomic masses in the current model. Any existing symmetry is reduced to P1.

- Generate a derived single structure (the default) or
- generate a set of derived structures (number of structures).

In framework structured materials Lowensteins rule can be imposed. With this setting *MedeA* will try to avoid the next nearest neighbor substitution. For example, when substituting silicon with aluminum it will

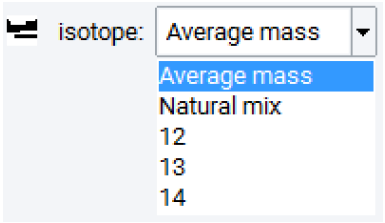
avoid replacing Si-O-Si with Al-O-Al linkages instead only allowing for Al-O-Si linkages. This functionality requires that bonds are present in the structure.

The substitutional rules employed are specified by applying the appropriate keywords in the set of rules shown on the dialog box. For example, by default the command exchanges all C atoms for Si atoms. This can be adjusted using the appropriate fields so that either a percentage of C atoms are substituted, or a defined number of C atoms. You can also substitute atoms for vacancies and you can set the appropriate isotopic masses for any substitutions that you make.

Identical Random substitutions... dialogs are employed in the *MedeA GUI* and the *MedeA* flowchart editor.

Note: The *MedeA HT-Launchpad* license allows for the generation of sets of derived structures as *Structure Lists* for use in high throughput calculations.

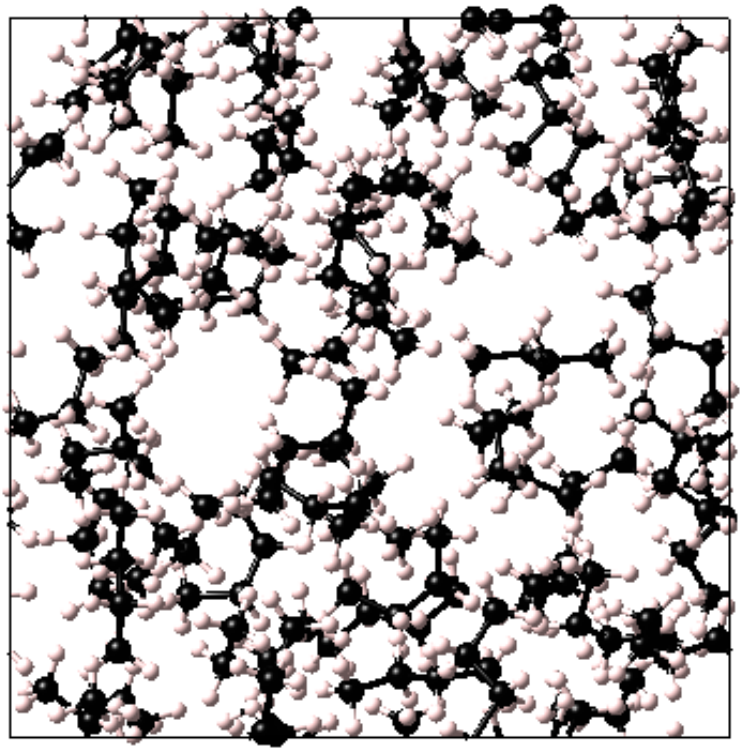
The isotope selector, shown here for Carbon, allows assigning *known isotopes*, *average mass*, or the *natural mix*. This can be quite important to break the artificial periodicity for thermal conductivity computations; in this case, perform substitutions for all atoms with the same element, but the *natural mix* for isotopes. Depending on the isotope distribution, the system size can be quite rather large to show some randomness in a given model.



8 Amorphous Materials Builder

The *MedeA Amorphous Materials Builder* is designed to aid in preparation of equilibrated models of disordered or partially ordered (oriented) organic or inorganic materials. Examples of typical systems are as follows:

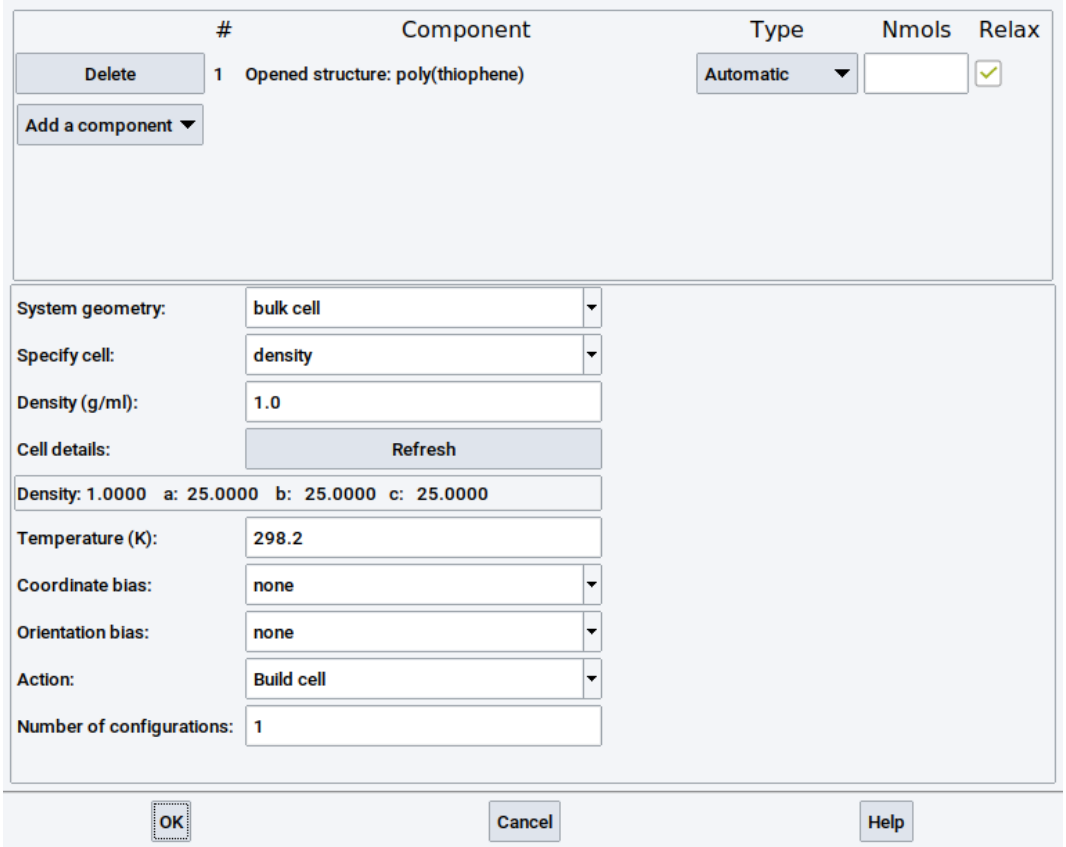
- Molecular liquids and liquid mixtures
- Bulk rubbery or glassy polymers
- Polymer solutions and blends
- Lipid-like monolayers comprised of surfactants, counter ions, and solvent, etc.
- Slab-geometry film layers suitable for incorporation into interphase models
- Small molecule or polymeric systems with nematic liquid crystalline order
- Gas penetrant-organic or inorganic systems as encountered in membrane and coating applications
- Oxide and mixed-oxide inorganic glasses



Systems may contain an arbitrary number of components, each of which may consist of a system comprised of one or more atoms or ions, or a non-infinite fully-bonded molecule obtained either from a standard *MedeA* `.sci` file, or from a model window in the current session. Note that partly-built molecules with open bonds, under construction using the molecular builder, or loaded from the fragment library, are not acceptable as input components and must either be hydrogenated or passivated before they can be combined together in an amorphous model.

Individual components may be non-periodic systems or periodic models with P1 symmetry. The overall molar composition is controlled by specifying the number of moles of each of the components and options are provided to control whether molecules are treated as flexible, with rotatable backbone bonds, or as completely rigid units. Additionally, models may be prepared in the form of periodic infinite bulk cells, or with a confined layer geometry suitable for further manipulation to create monolayers or interfaces between dissimilar materials.

Main Dialog - Control Parameters



System geometry : Permits specification of whether the builder will create a 3-D periodic 'bulk cell', or a periodic 'layer' system in which the Z-coordinates of atoms are biased to lie mostly within the current 'c' cell dimension. Note that in the latter case, since there is no absolute requirement that molecules reside entirely within the specified layer following the model building stage, a LAMMPS calculation using a Compress Layer stage must be performed to complete the preparation and force all atoms to lie within the layer before using other building tools such as Stack layers. . . to create models of interfaces.

Specify cell : Provides a variety of options for controlling the size of the amorphous models produced by the builder. Thus, for example, choosing density will produce cubic cells in which the cell edges are determined based on the overall composition and density. Similarly, choosing Specify cell density,c will create tetragonal cells based on the density and specified c dimension, while choosing a,b,c creates orthorhombic cells using a, b and c lengths provided (in which case the density cannot be specified independently since it is fixed by the composition).

Control of cell dimensions can be useful when building a layer which will be used to create an interface with another layer whose cell edges are fixed (e.g. a crystal substrate). For convenience, the Cell details - density and edge lengths a, b, c - are displayed in a non-editable panel in the main dialog.

The full set of options for Specify cell . . . is as follows:

- density
- density,a
- density,b
- density,c
- density,a,b
- density,a,c
- density,b,c
- a,b,c

Density : Define the desired density of the amorphous system in g/cm3. This is required for all *specify cell* options except *a,b,c*.

Cell length (a OR b OR c): Length of the given edge in Angstroms. Must be a positive real number.

Refresh : Click this button to update the cell dimensions based on any modification of the constituents (components) and amount of them, the cell parameters, and the defined density, respectively.

Temperature : Temperature, in degrees Kelvin, for which the builder will attempt to create configurations which would be found with high probability in an equilibrium ensemble.

Coordinate bias : Indicates that the positions of a pre-defined group of atoms, defined via an atom subset, will be biased to lie close to a specified set of grid points. Available options are as follows:

- none - Disables the coordinate bias option.
- 2D-grid - Randomly positions atoms from the specified subset on a two-dimensional grid displaced along the Z-axis of the cell by a user-specified distance. This feature can be used, for example, to locate surfactant head groups and/or associated counter ions in an approximately planar arrangement (note that building such monolayers would usually also involve use of the layer System geometry control, together with the uniaxial Orientation bias option to preferentially align the tails of individual molecules).
- 3D-grid - Randomly positions atoms from the specified subset on a three-dimensional array of grid points arranged symmetrically in the cell.

Usage of the coordinate bias option is subject to the following restrictions:

- *All components of the system must be of type 'Rigid' or 'Pre-existing' (see components panel parameter description below)*
- *Individual molecules in the list of components should contain only one (or zero) atoms from the subset used to define the coordinate bias atoms*

Grid dimensions : For 2-D grids, the grid contains nx*ny points, symmetrically arranged parallel to the XY plane of the cell, and displaced a distance z-offset along the Z-axis. 3-D grids contain *nx ny nz* points arranged symmetrically in the cell.

Coordinate bias subset : Specifies the name of a subset identifying the atoms whose positions will be biased towards the positioning grid during model building. Note that the total number of subset atoms in all components included in the coordinate bias subset must not exceed the total number of available grid sites (nx*ny, or nx*ny*nz, as appropriate).

The subsequent equilibration of the partially-ordered models, using LAMMPS minimization and dynamics, will generally include an initial simulation stage in which the positions of the atoms in the coordinate bias subset are held fixed, to preserve the integrity of the ordered arrangement during the early stages of the equilibration.

The subset will normally have been defined within *MedeA* by selecting a single bias atom in each component to which coordinate bias will be applied (e.g. the sulfur of a sulfonate group), right-clicking to display the context menu, and selecting the Subsets >> Create subset from selection . Specification of a Subset name and clicking Apply will then complete the definition of the subset for the given component. If molecules in other component windows contain atoms to be positioned using the same grid, the procedure is repeated, giving the same subset name.

Finally, if biasing using different grids is desired, the model building would be performed in two steps, with the first positioning one set of atoms, and the second incorporating the first model as a component of type Pre-existing , and applying the position bias to a second set of atoms using a different grid specification (to avoid later confusion, the second component's bias subset would be given a different unique name). As an example, a monolayer model containing a surfactant and its counter ions can be created by running the builder twice, such that the polyatomic anions are first incorporated by placing the head group atoms on a two-dimensional grid with z-offset value of, say, 6 angstroms (using the orientation option to align the tails), with a second invocation of the builder placing the appropriate cations on a grid with z-offset set to 2 angstroms, ensuring that the counter ions are located in reasonable proximity to the charged head group.

Orientation bias : Applies an energy bias during system building to control the placement of specified groups of atoms. Available options are as follows:

- none : Disables the orientation bias option.
- uniaxial orientation : Biases the orientation of groups of atoms based on the specification of a pair of atoms that effectively define the orientation of the group as a whole (such as the first and last carbon atoms of each alkyl chain in the tails of rigidly-placed surfactant molecules, or atoms 4 and 4' in the aromatic rings of the 1,1'-biphenyl group found in many liquid crystals).
- Direction :When 'uniaxial orientation' bias is selected, specifies any vector along the preferred orientation direction. The vector does not necessarily need to be of unit length. Thus, for example, specifying values of 1.0, 1.0 and 0.0 for the 'x', 'y' and 'z' components will preferentially bias the orientation of parts of the molecules parallel to the XY face diagonal of the resulting periodic cell; similarly, specifying values of 0.0, 0.0, and 1.234 or 0.0, 0.0, and 1.0 will both bias the alignment along the Z direction.

Orientation bias pair subset : Specifies the name of a set of atom pairs defining the intramolecular vectors desired to be preferentially aligned along the specified direction. Note that subsequent equilibration using LAMMPS must use this same subset in a protocol that preserves the original orientation to avoid the possibility of a loss of the orientation in some situations, such as equilibration at elevated temperatures or application of volume-changing methods such as NPT dynamics. Note that if the system contains more than one component, there is no requirement that the intramolecular vectors referenced by the given subset name should correspond to chemically identical units in the different components.

The pair subset will normally have been defined within *MedeA* by right-clicking, followed by choosing Subsets >> Create to display the Create a subset dialog, within which a subset of *length* 2 (i.e. a pair subset) can be defined by specifying the criterion used to identify *atom 1* and *atom 2* of the subset (usually the *Name* of each atom will be the best unique criterion to use). See the subsets documentation for a detailed explanation.

Action : This parameter specifies one of three actions to be taken when the OK button is clicked, as follows:

- Build cell : This is the default action, which instructs the builder to create one or more configurations of the amorphous system defined via the dialog parameters.
- Save system definition only : Selecting this option will ask the user to provide the name of a file after the OK button is clicked. When possible, the default location of the file will use the folder *~MedeA/AmorphousSpec*, which will be created if it doesn't exist, though you may change this to use any location. The supplied file will then be used to store all information pertinent to the model building, such as components, composition, cell, and density information, together with any information pertaining to a pre-existing component, such as a zeolite host,
- Save and build : This option will present the user with a save file dialog as above, and will then proceed to create one or more configurations as specified in the dialog.

The *save system definition* feature is particularly useful when it is desired to fine-tune model building interactively, followed by use of a *MedeA* flowchart to create a large batch of models with the same overall composition but different spatial configurations, as is frequently required to obtain statistically meaningful ensemble averages of properties. See the help text associated with the *Amorphous Materials Builder* flowchart stage for details on using these system composition files.

Number of configurations is the number of statistically independent configurations of the amorphous system to create (each displayed in a separate window in *MedeA*). Generating a large number of configurations, whose properties can subsequently be averaged, may be essential when working with molecules whose conformations change infrequently during molecular dynamics simulation. This will generally be the case for high molecular weight polymers under ambient temperature conditions at which there is insufficient energy to overcome backbone or side chain rotational (i.e., torsional) barriers on the usual molecular dynamics time scales. Conversely, when simulating low molecular weight liquid and liquid mixture systems, generating a single configuration will be adequate, since in such cases, molecular dynamics will usually explore a region of phase space sufficient to obtain meaningful average properties.

Hint: When specifying the build density for a molecular system containing stiff molecules with multiple aro-

matic rings embedded within a molecular backbone or side chain, the efficiency of the initial structure building can often be made considerably more computationally efficient if the specified build density is reduced somewhat below the ultimate anticipated density of the bulk material.

This is because the a priori probability of introducing ring catenations in a dense system can be quite high when there are few rotational (torsional) degrees of freedom available for the builder to explore to generate the required catenation-free model. Therefore, when working with stiff, ring-containing molecules such as polycarbonates or polystyrenes, specifying a build density of 0.4 or lower will usually be beneficial. The initial model can then be compressed to its final density by including an NPT molecular dynamics stage in the equilibration that must always be performed after building any 'raw' amorphous structure.

Main Dialog - Components Panel

The Components panel located at the top of the main Amorphous Builder dialog is used to specify a list of individual components that will be combined to create the amorphous model. Each component may be obtained from an already created existing model displayed on the *MedeA* screen, or from a previously-created model stored in a structure file of type `.sci`. For each component, the following information must be provided:

Component denotes the name of the component in the form of the name of an acceptable model contained in a *MedeA* window, or the name of a `.sci` file stored on the file system.

Type components may each be one of four types:

- Rigid : During model building, all molecules of this type of component will be inserted as rigid units. If the Coordinate bias option is not used, the positions of molecule centers of mass will be chosen randomly. Otherwise, the atoms contained in the Coordinate bias subset are placed according to the selected grid. Similarly, if Orientation bias is not used, molecule orientations are chosen randomly, as opposed to being subjected to the specified orientation bias. In all cases of rigid placement, internal bond conformational angles remain exactly as in the original component.
- Flexible : In the case of flexible molecules with many internal torsional degrees of freedom, it is generally desirable to sample all energetically reasonable dihedral angles within a component molecule. Unless the component is found to contain zero rotatable bonds, this option will force the sampling of all internal dihedrals formed by all sequences of non-hydrogen atoms within the component.
- Auto : Specification of this component type indicates that the builder should decide automatically whether intramolecular dihedral angles will be sampled during model building.
- Pre-existing : This option is used whenever the new system is to be created by adding more material to an already created existing model - e.g., adding small penetrant molecules to an amorphous model for diffusion studies, or solvating a system with a much larger quantity of solvent to create a dilute solution or interfacial model. Note that inclusion of a pre-existing model in the list of components will automatically select *a,b,c* in the Specify cell mode, and set the number of copies of the component, *Nmols*, to 1. The *a,b,c* parameters of the pre-existing model then define the cell parameters of the new model. Finally, note that in contrast to the restrictions applicable to components of type *rigid*, *flexible*, and *auto*, a pre-existing component type may include infinite covalent networks such as those created using the *MedeA Thermoset Builder*.

Hint: In extreme cases where a molecule contains almost no rotatable bonds and many aromatic or aliphatic rings, as with asphaltenes and kerogens, treating that species as of type rigid is recommended.

Nmols : Specify the number of moles of the component in the final amorphous model (i.e., per mole of cells). Note, that if the component is of type Pre-existing , the number of moles of this component will be set automatically to 1, since multiple spatially identical copies of components are not permitted.

Relax : Following the initial building, the amorphous model will normally be subjected to a short pre-equilibration ('cleaning') to prepare for subsequent comprehensive full equilibration and production simulations using *MedeA* LAMMPS. It is recommended that the full equilibration be performed using a flowchart beginning with a LAMMPS stage containing at least a Minimize stage followed by an NVT stage. If the initial

model has been created at reduced density, these stages may optionally be followed by an NPT stage. Note that for the most robust LAMMPS equilibration, the Nonbond method within the Initialization stage should be set to Cutoff. The PPPM or Ewald nonbond methods may then be used for later production stages after the model equilibration has been completed.

If desired, unchecking the Relax toggle in the amorphous builder itself may be used to disable the relaxation during pre-equilibration. This will prevent changes in coordinates of atoms whose original positions should be preserved. Examples include hybrid systems consisting of an immovable crystalline component interfaced with a mobile liquid or amorphous solid phase, and building of dissolved systems in which the dissolved molecule must be left in its original conformation.

Hint: If fixing of atoms is to be used in subsequent simulations, it may be helpful to define the fixed portions of the system as one or more atom subsets before amorphous model building.

---

9 Thermoset Builder

The models created by the amorphous builder are the starting point for creating thermosets. Since the bonding topology and local packing within individual crosslinked models will vary widely between configurations, statistically meaningful averages of parameters characterizing both the crosslinking process itself and behavior of the resulting material will typically require generation of a batch of models (e.g., 50-100 to obtain precise estimates of the small strain elastic constants of a model containing of the order of 10000 atoms). The crosslinking process involves creation of bonds between user-specified sets of atoms (*sites*), achieved in a series of crosslinking cycles through the growth of a *capture sphere* about each site. During each cycle, bonds are created between each site and designated atoms lying within the site's capture sphere until the maximum allowed number of connections specified for each site has been reached. After cleaning to remove high energy interactions, each cycle is completed by performing structural relaxation using a small number of iterations of molecular dynamics followed by minimization. The process continues through growth of the capture sphere until either a maximum capture radius has been reached, or until other specified conditions prevail (exceeding a maximum number of cycles, maximum *conversion extent* of a user-specified site type, threshold strain energy in the system, or detection of catenations between small rings).

Note that the Thermoset Builder operates on a principle similar to that of the polymer builder with one minor difference. Thus, whereas the polymer builder operates by connecting together polymer *repeat units* rather than monomers (e.g., -(CH $_2$-CH $_2$)- as opposed to H $_2$C=CH $_2$ for polyethylene), the *Thermoset Builder* creates crosslinks in a pre-equilibrated system of fully hydrogenated *network segments* (e.g., H $_2$N-R-NH $_2$ and H $_3$C-CH(OH)- CH $_2$-O-R'-O-CH $_2$-CH(OH)-CH $_3$ for an epoxy resin system, in which the terminal nitrogens of the amine are sites capable of making up to two connections and the terminal carbons of the diglycidyl ether fragment are sites each capable of making a single new connection). In the case of thermoset model building, the need to begin with a mixture of components that has been well-equilibrated using a forcefield means that any necessary removal of hydrogen atoms from components takes place after rather than before the bond formation step. Consequently, when working with fully atomistic hydrogen-containing models, if it is determined that none of the atoms defined as a given site type contains attached hydrogens, crosslinking with that site type will not be possible and the builder will not proceed until the situation has been rectified (an example would be attempting to define ether oxygens as a site).

Note: The conversion extent of a given site type is the total number of crosslinks formed at/by sites of that type (e.g., type 'A'), divided by the total number of crosslinks possible at those sites, with the latter being equal to the product of the total number of sites of a given type and the maximum number of bonds that can be created at the site defined by, for example, Site A max connections.

Whenever the conversion extent criterion is exceeded for a user-specified site type at the end of a crosslinking cycle, the builder will stop.

Thermoset Builder may be used to create a variety of types of crosslinked models, ranging from simple materials such as crosslinked polyethylene, in which the actual crosslink formation is effected by exposure

to radiation, through materials prepared by reaction of pairs of chemical functional groups as occurs with polyesters or epoxies crosslinked with various curing agents, to materials prepared from complex multicomponent mixtures in which pairs of groups may react chemically at very different rates.

To facilitate setting up the builder to create models of these widely varying materials, the *MedeA* graphical interface presents the user with a pair of tabbed panels, labeled *Parameters* and *Sites*. The former panel is used to specify building control parameters common to crosslinked materials ranging from the simplest to the most complex, and also to specify the nature of the types of sites that will be used to create the model - referred to as *single site*, *pairs* and *multi-site* types. The content of these tabbed panels is summarized in the following sections.

9.1 Parameters Tab

Input parameters are as follows:

Bonding site types : Choices available for this parameter are *single*, *pairs* and *multi-site*. The value chosen determines the layout of the associated *Sites* tabbed dialog, in which parameters specific to the material of interest are input. The single site type option would be chosen for materials such as radiation-crosslinked polyethylene, in which new covalent bonds are created between atoms belonging to identical types of site (e.g., -C-C-). The pairs option is most appropriate for materials such as polyesters and epoxies. In many such cases, the actual crosslinking process may involve only two components, such as an epoxy resin and an amine. Note however that the pairs option may also be used when creating models in which the formulations involve multiple components that react chemically at similar rates (e.g., two different epoxy resins and an amine can still be described by a single pair of site types - one for the different epoxy groups and one for the amine group). Choosing *multi-site* for this parameter will present a form of the *Sites* tabbed panel in which the user may specify multiple types of sites together with the relative probability that any specified pair of sites will form a connection. The *Sites* tabbed panel may be used for input when working with materials with up to ten different types of site. However, should it be desired to make use of a larger number of site types, the *Sites* tab may be disabled by clicking on the checkbox labeled *Sites and Connections from file*, in the main *Parameters* tab. In this case, all relevant connections and associated information may be provided using a text file, and no limit is imposed on the total number of site types.

Apply substitution effect probability when max connections > 1 : It may sometimes occur that during an actual chemical crosslinking process, a given atom will form bonds to more than one other atom. However, when this occurs, the probability of adding a second (or 3rd, etc.) crosslink to the atom may occur with a lower probability than formation of the first bond to that atom. In epoxy resin crosslinking, this is sometimes referred to as the *substitution effect* (or *induced unequal reactivity*). Checking this box will allow the user to impose reduced probabilities for formation of a second or third crosslink at a site, relative to formation of the first crosslink. See the individual *Sites* dialogs for further information.

Fixed atoms : This option allows specification of a subset of atoms whose positions should not be changed during the relaxation of the partially crosslinked material at the end of each crosslink formation cycle. This is useful, for example, when the crosslinking process involves creation of one or more bonds to atoms in a crystalline or partially-ordered substrate, such as a filler particle, whose structure must be preserved and unaffected by the thermoset model building process.

Beginning capture radius ; Specifies the capture radius in Angstroms applied at the start of the crosslinking process.

Capture radius increment : Denotes the amount by which the capture sphere radius is increased when no bondable pairs are found to lie within the current sphere for all sites.

Relaxation conditions : Indicates whether the relaxation dynamics applied at the end of each cycle are to be performed under constant volume (NVT) or constant pressure (NPT) conditions.

Relaxation iterations (per cycle) : Can be used to increase the total amount of structural relaxation applied for highly rigid systems.

Note: The use of large value ($>$10) will significantly increase the time taken to perform the crosslinking, and is best only changed for very rigid systems. The default value can be used in almost all cases.

Stop building when conversion extent of site: <sitename> exceeds ... Indicates that the building process will terminate if the conversion extent of the specified site exceeds the supplied value. By convention, sites are referred to as siteA, siteB, etc. (in the order specified in the *Sites* tabbed panel).

Maximum capture radius : Denotes the capture radius at which the building will stop.

Maximum acceptable bond strain : Indicates that crosslinking will stop if, following the relaxation performed after each bond creation cycle, the strain (l-l0)/l0 of any bond exceeds the specified value. A value in the range 0.1-0.2 is normally sufficient to generate realistic strain-free crosslinked models suitable for computing properties such as densities and elastic properties of rigid materials (e.g., glasses).

Note: Using a large value, say 1.0 or higher, is likely to result in structures containing unrealistic stretched bonds which at best cannot be relaxed to create an equilibrated structure during subsequent simulations, or at worst leads to failure of simulations as a consequence of extremely large forces on the atoms in the vicinity of the strained bonds.

Maximum crosslinking cycles : Can be used to reduce independently the number of cycles below that implicitly defined by the maximum, beginning, and capture radius increment.

Stop at gelation : Selecting this option will cause the building to terminate immediately after the formation of a 3-dimensional infinite network has been detected, overriding other termination parameters such as the Maximum conversion extent . This can be useful for studying the gel point itself, and for examining the properties of the network immediately after formation.

Reset Forcefield atom types : This checkbox is selected by default and indicates that forcefield atom types and partial charges will be reassigned following completion of the building, which will often be necessary before performing further LAMMPS simulations due to changes in the bonded environment of individual atoms resulting from crosslink formation. Uncheck the option if you wish to exercise complete control over atom types and partial charges.

Write structure after each cycle : If this checkbox is selected, the coordinates and topology of the relaxed structure at the end of each crosslinking cycle will be saved in a *MedeA* trajectory file for later visualization or further manipulation.

Control intramolecular ring formation : Enabling this option can be useful for studying how intramolecular reactions influence network structure and properties such as the gel point or behavior such as elastic constants and thermal conductivity of the final network.

Minimum ring size (atoms) : This parameter is only required when limiting intramolecular ring formation is to be applied. Typically, rings containing a small number of atoms are most likely to be formed (where allowable sizes are determined by the bonding topology of the reactants). Consequently, specifying a value equal to 'n+1', where 'n' denotes the number of atoms in the smallest ring, will exclude only those rings from the network. Conversely, specifying a large value will practically eliminate all intramolecular cycles.

9.2 Sites Tab (single site type)

Input parameters are as follows:

Site A subset : Denotes the *MedeA* subset name identifying the atoms belonging to the named site type.

Site A max connections : Denotes the number of new bonds between sites of type A. Note that after adding each new bond, a hydrogen atom is removed from the site A atom, if appropriate.

Site A substitution effect prob : This parameter only becomes available when Apply substitution effect probability when max connections > 1 has been ticked in the *Parameters* tab and the value for Site A max connections is larger than 1. It is used to specify the relative probability (or probabilities) of forming crosslinks at individual sites to which one or more bonds have already been added. The relative probabilities of adding new bonds at a site capable of making a total of N connections should be specified by providing a list of (N-1) probabilities.

9.3 Sites Tab (pairs option)

Input parameters are as follows:

Site A subset : Denotes the *MedeA* subset name identifying the atoms belonging to the first of a pair of subsets used for bond formation.

Site A max connections : Denotes the number of new bonds between sites of type A and other sites (of type A or B). Note that after adding each new bond, a hydrogen atom is removed from the site atom, if appropriate.

Site A substitution effect prob : This parameter only becomes available when Apply substitution effect probability when max connections > 1 has been ticked in the *Parameters* tab and the value for Site A max connections is larger than 1. It is used to specify the relative probability (or probabilities) of forming crosslinks at individual sites to which one or more bonds have already been added. The relative probabilities of adding new bonds at a site capable of making a total of N connections should be specified by providing a list of (N-1) probabilities, which will typically take the form of a list of decreasing values. Note that for common amine-cured epoxy thermosets, the relative rates of secondary and primary amine reactions often lies in the range 0.2-0.6 for aromatic amines, with larger values for aliphatic amines (see, for example, *"Cross-linking of Epoxy Resins", K. Dusek, in Rubber-modified thermoset resins ACS Adv. Chem. Ser. vol 208 (1984)*).

Site B subset : Specifies the name of the second of the pair of subsets used in bond formation.

Site B max connections : Denotes the number of new bonds between sites of type B and other sites (of type B or A). Note that after adding each new bond, a hydrogen atom is removed from the site atom, if appropriate.

Site B substitution effect prob : See explanation of the analogous parameter for sites of type A.

Allowed connections : These checkboxes denote the connections to be made between the atoms comprising the siteA and siteB subsets. Most commonly, this will only be between the different types of site (e.g., when building models of crosslinked polyesters or amine-cured epoxy resins).

9.4 Sites Tab (multi-site option)

This tabbed panel contains two frames, with the upper frame used to input a list of crosslink site types, and with the lower frame presenting a triangular matrix in which the relative probabilities of forming bonds between the sites must be specified.

Input parameters for the upper, *Site definitions*, frame are as follows:

Site subset : In each row of this column, the name of the *MedeA* subset identifying the site atoms should be specified, using values supplied in the drop-down list of subsets defined in the model.

Max connections : In each row of this column, the maximum connections to the specified site should be given. Note that if the value given is greater than 1, *and* if the *Apply substitution effect probability...* toggle has been checked on the *Parameters* tab, the fields of the adjacent *Substitution effect factor* column will be active.

Substitution effect factor : This column only becomes available when Apply substitution effect probability when max connections > 1 has been ticked in the *Parameters* tab. In each row of this column, the substitution effect probability factor(s) can be entered. Recall that the relative probabilities of adding new bonds at a site capable of making a total of N connections should be specified by giving a list of (N-1) factors, which will often take the form of a list of decreasing values. For common amine-cured epoxy thermosets, the relative rates of secondary and primary amine reactions often lies in the range 0.2-0.6 for aromatic amines, with larger values for aliphatic amines (see, for example, *"Cross-linking of Epoxy Resins", K. Dusek, in Rubber-modified thermoset resins ACS Adv. Chem. Ser. vol 208 (1984)*).

The lower, *Relative bond formation probability* frame consists of a lower triangular matrix with rows and columns labeled according to the letter representing the site type - i.e., *A* for *siteA*, *B* for *siteB*, etc. Note that these are relative probabilities which do not need to sum to unity. Thus, for example, whenever multiple choices exist for creation of a bond between an atom *i* and other atoms *j* within its capture sphere, the type

of site *i* and those of all potential bonding atoms *j* are checked, and the relative probabilities of the bond formation between the site type of atom *i* and the site types of all atoms *j* are used to determine which bond will actually be created. Note that the value specified for relative bond formation probability applies to the first connection made to a particular site *i*. If more than one connection has already been made to the site, and substitution effect factors are in effect, the base *Relative bond formation probability* is first multiplied (usually reduced) by the appropriate substitution effect factors for the sites identified as being candidates for bond formation before final determination of the connection to be created. Finally note that, by default, the relative probabilities of bond formation between atoms of the same type are set to 0.0.

As noted above in the description of options available from the main *Parameters* tab, complex systems involving more than ten different *types* of site may use a text file to specify the site definition and bond formation information. The format of the file referred to via the *Sites and Connections from file* option essentially mirrors that provided by the multi-site tabbed panel described above. Specifically, the format should follow the example given below:

```
#ThermosetBuilder 3.6 multisite data
#
#SITES
#site_label, subset_name, max_connections, subst_effect_factor (blank or list of␣
↪max_connections-1 values)
siteA, BISDIFUNC1, 2, 0.8
siteB, BISDIFUNC2, 2, 0.2
siteC, BISMONO1, 1
siteD, BISMONO2, 1
siteE, BISMONO3, 1
#END

#CONNECTIONS
#site-site_connection (hyphenated), base_probability
siteA-siteC, 1.0
siteA-siteD, 1.0
siteA-siteE, 1.0
siteB-siteC, 0.6
siteB-siteD, 0.6
siteB-siteE, 0.6
#END
```

Here, the first section describes a system with a total of five site types (subsets) in total. The first two site types refer to subsets BISDIFUNC1 and BISDIFUNC2, which might refer to two different molecular species, with each molecule containing two identical sites each capable of forming two bonds (e.g., as would be the case for two diamines). The second set of site types, defined through subsets BISMONO1 through BISMONO3, might refer to three different molecules, with each molecule containing two sites each of which can form a single connection (e.g., as with diglycidyl compounds). The second section then defines the allowed connections and associated relative probabilities.

9.5 Properties

This stage generates building-related information, including maximum bond strain, and dimensionality of the structure as a function of progress of the crosslinking (see `Progress.txt` and `bondEnergy.png` on the Job's page). A dimensionality of 3 denotes that the gel point has been exceeded and that a true 3-Dimensional network has been created. The lower and upper bounds of the gel point conversion are reported in the file `Job.out`, together with a list of *MedeA* variables created by the builder.

Note: Restarting crosslinking from a partially crosslinked system is not yet supported.

10 Stack Layers Builder

The *MedeA* Stack Layers Builder is designed for preparation of interfacial systems comprising two or more layers of materials. Individual layers may be amorphous or crystalline solids, liquids, partially-ordered liquid crystal systems, and vacuum regions (empty cells) if so desired. The layer builder itself can process any type of material - organic, inorganic or metallic, though the feasibility of subsequent simulations will require that the chosen simulation tool supports all components of the combined system (e.g., for classical simulations, the forcefield used must include coverage for all atoms and interactions within the model).

Warning: Each of the layers to be stacked must be orthorhombic, i.e., the cell angles have to be α = β = γ = 90 ^{o}.

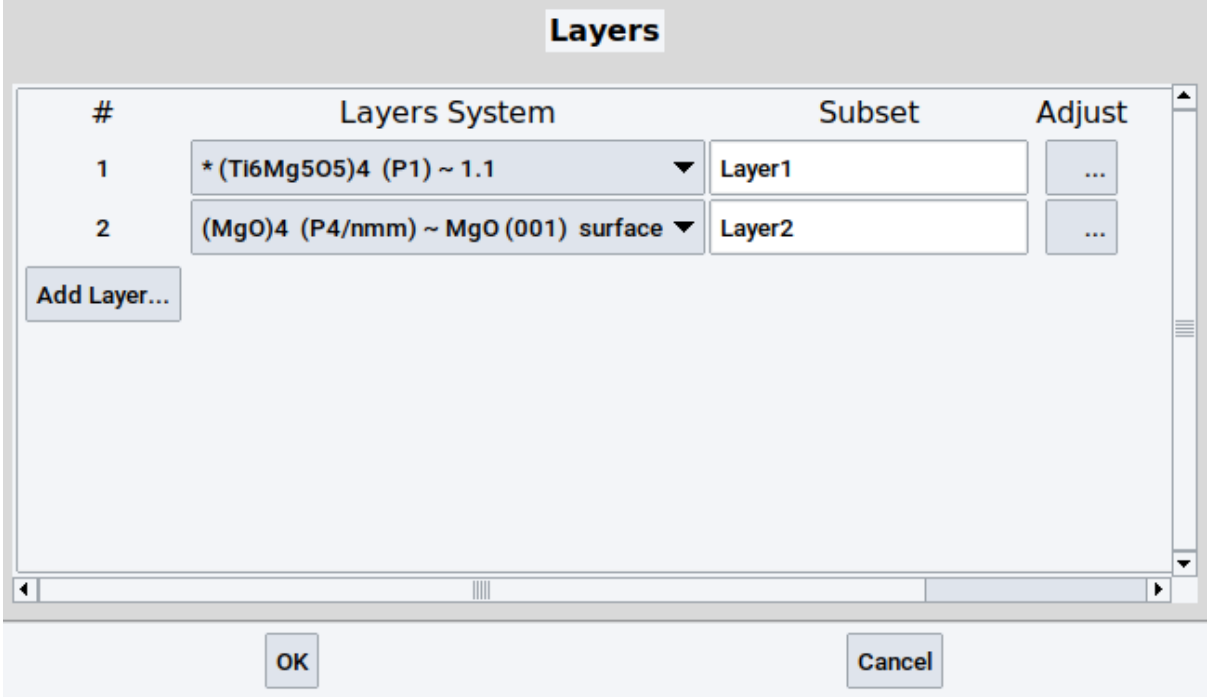
To use the stack layers builder, it is a requirement that none of the component layer systems contain bonds that cross the top/bottom faces of the cell. Suitable models can be prepared by combining the System geometry: layer option of the *Amorphous Materials Builder* with a Compress Layer LAMMPS equilibration flowchart stage. Note that the *Amorphous Materials Builder* layer option itself is not intended to create models completely free of bonds crossing the cell ab faces, rather it only applies a bias to confine material *mostly* within the layer; actual forcing of atoms to lie completely within the layer will be performed by the Compress Layer stage while the final equilibration is being performed. Alternatively, layer systems used as input to the stack layers builder can be created manually or using other *MedeA* tools such as Interfaces.

Regardless of the method used to create the component layer, it will usually be advantageous to ensure that all layers have been pre-equilibrated, since this will minimize the risk of disruption of the newly-created interface(s) during subsequent simulations owing to the presence of unduly large forces on atoms in the interfacial region(s).

When the Stack Layers Builder is first invoked for a periodic system from Builders >> Stack layers..., the dialog panel shows entries for two-component layers. By default, the currently-active *MedeA* model system is pre-selected as the first ('topmost') layer of the new system, though this can be changed if desired simply by clicking on the name and choosing a different system from the list provided. The second layer of the new system is then specified by clicking on 'Select System' and choosing from the list provided. Any number of additional layers may be added by clicking the Add Layer... button and repeating the selection steps. Finally, when the OK button is pressed the new layered system is created with layers in the order specified in the dialog and displayed on the screen with the Z-axis oriented vertically.

Main Dialog Parameters

DOCUMENTATION



The Layer System : specifies the system to be used to create individual layers. Clicking on this entry displays a list of eligible P1 models.

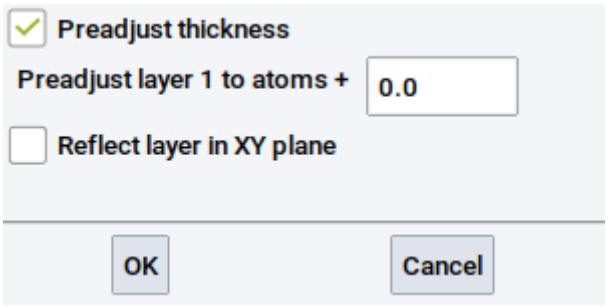
The Subset parameter specifies the name of a subset containing atoms from the layer that will be made part of the created layer model. If subsets are not required, this entry may be cleared and left blank.

Adjust offers precise control over the distance between the top most atom in a layer and the lowest atom in the layer immediately above. Clicking on ... will open the *Layer Data* dialog, which provides for adjustment of the layer prior to building the final multilayer system. Details of available adjustment options are given in the adjust parameters section below.

The Add Layer... adds a new row to the Layers panel. Parameters for each additional layer are then specified in the same manner as already performed for the layers higher in the stack. Layers beyond the second in the multilayer system include a *Delete* button for removal of the layer if necessary.

Layer Data Adjust Dialog Parameters

Click on ... : to apply additional options to each layer.



The Preadjust layer : allows input of additional data to control the thickness of the layer when the multilayer system is finally assembled.

The Preadjust layer to atoms + : specifies a distance in Angstroms which will be added to the thickness of the layer after first setting the thickness of the layer cell to the value defined by the difference between the highest and lowest Z-coordinates of atoms in the component layer. This can be useful to exert precise control over the minimum separation between atoms in two adjacent layers.

For example, specifying pre-adjustment distances of say 4 Angstroms in each of two adjacent layers will guarantee that in the resulting multilayer system, no atoms approach closer than this distance. Note that the

pre-adjustment space is apportioned equally at the top and bottom of the cell (i.e., the Z coordinates of the component layer atoms are effectively first centered in the cell, and then shifted upwards by one half of the distance specified).

Finally, note that if the pre-adjust option is used with an empty cell to insert a vacuum layer, since there are no atoms present, the thickness of the inserted layer will become that of the Preadjust layer to atoms + parameter itself.

11 Compress Layer Building

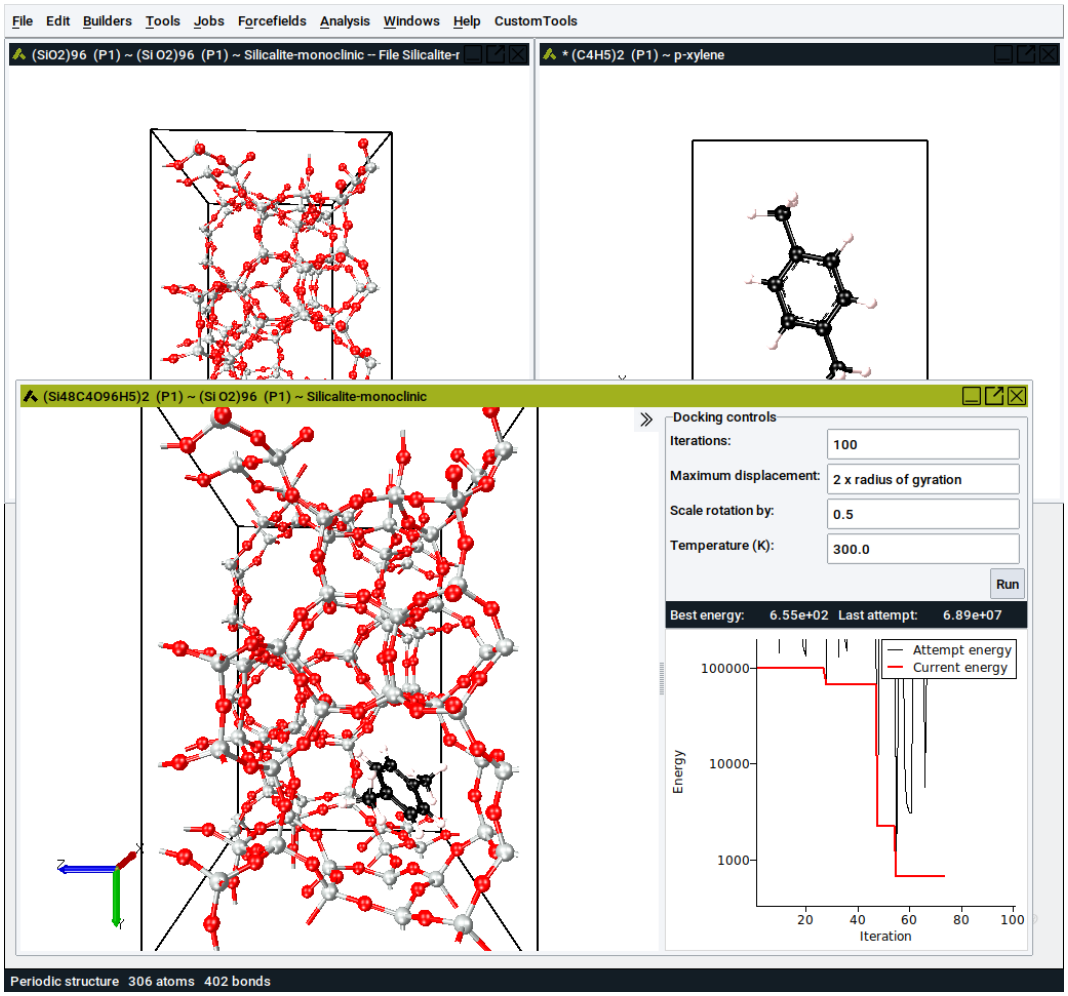
Compress Layer Building is performed by first creating a raw initial layer structure using the *Amorphous Materials Builder*, followed by a refinement and equilibration step performed using a LAMMPS stage. Please see Compress Layer for more details.

12 *MedeA* Docking

The computational analysis of the preferred orientation of one molecule in the environment of a second structure, which may be a surface or a microporous material is generally termed 'docking' [1].

The *MedeA Docking* command, invoked from Builders >> Docking... for a periodic system, facilitates the creation of composite models. The command takes an existing bulk system and merges into this system a specified second structure.

[1] Thomas Lengauer and Matthias Rarey, "Computational Methods for Biomolecular Docking," Current Opinion in Structural Biology 6, no. 3 (June 1996): 402-406; D W Lewis, Clive M Freeman, and C Richard A Catlow, "Predicting the Templating Ability of Organic Additives for the Synthesis of Microporous Materials," Journal of Physical Chemistry 99, no. 28 (July 1995): 11194-11202; Dewi W Lewis, David J Willock, C Richard A Catlow, John Meurig Thomas, and Graham J Hutchings, "De Novo Design of Structure-Directing Agents for the Synthesis of Microporous Solids," Nature 382, no. 6592 (August 15, 1996): 604-606.



The docking algorithm employs the Metropolis Monte Carlo algorithm [2] to sample possible configurations for the second system relative to the specified host system. For each trial configuration the energy change required to create this configuration is used to compute a Boltzmann probability and this is compared with a random number between 0 and 1 to either accept or reject the changed configuration. Reducing the simulation temperature allows the docking process to reject energy increasing moves and increasing the temperature causes energy increasing moves to be accepted.

The energy of trial configurations is evaluated through the use of a simple 12-6 Lennard-Jones potential. This simple description allows the command to provide sterically plausible structures. The relative energy of possible configurations is only a first approximation and more elaborate forcefields or quantum mechanical methods should be employed in evaluating the energetic properties of composite systems.

12.1 Docking Dialog Input - Required Parameters

Guest : The guest system to be introduced to the current system by the docking process. The docking procedure creates a new system, with Host and Guest subsets. Note that if the current system already created possesses Host and Guest subsets, the current Host-Guest complex may optionally be refined.

Iterations : The maximum iterations to be employed in the Monte Carlo docking process.

Maximum displacement : The maximum displacement to be applied to the guest system in Angstroms.

Scale rotations by : A scale factor applied to randomly chosen Euler angles of rotation applied to the guest system at each iteration. The scale factor is applied to each rotation to limit angular sampling.

[2] Nicholas Metropolis, Ariana W Rosenbluth, Marshall N Rosenbluth, Augusta H Teller, and Edward Teller, “Equation of State Calculations by Fast Computing Machines,” Journal of Chemical Physics 21 (June 1953).

Temperature (K) : The temperature in degrees Kelvin employed in the Metropolis Monte Carlo procedure. Selecting a high temperature will cause high energy structures to be accepted in the Monte Carlo search process, and a low temperature will favor energy reducing configurations.

12.2 Docking - Notes

The initial configuration employed in *Docking* locates the guest molecule at the center of the Host system. This configuration may be of high energy and several iterations may be required to find more reasonable steric configurations.

Hint: Docking may be interrupted by clicking the Stop button. The final configuration is always that of the lowest energy configuration sampled during the current docking process.

The *MedeA* docking functionality can be employed in interactive building as described above. In addition, docking is implemented as a flowchart stage, which permits the combination of host structures with guest configurations obtained from molecular dynamics trajectories as a part of computational workflows employing flowcharts.

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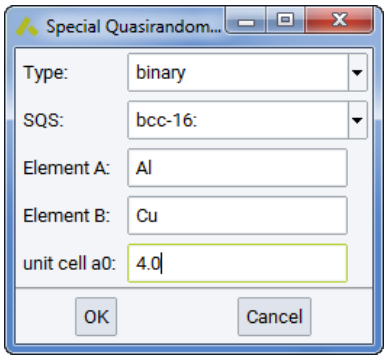
13 Special Quasirandom Structures

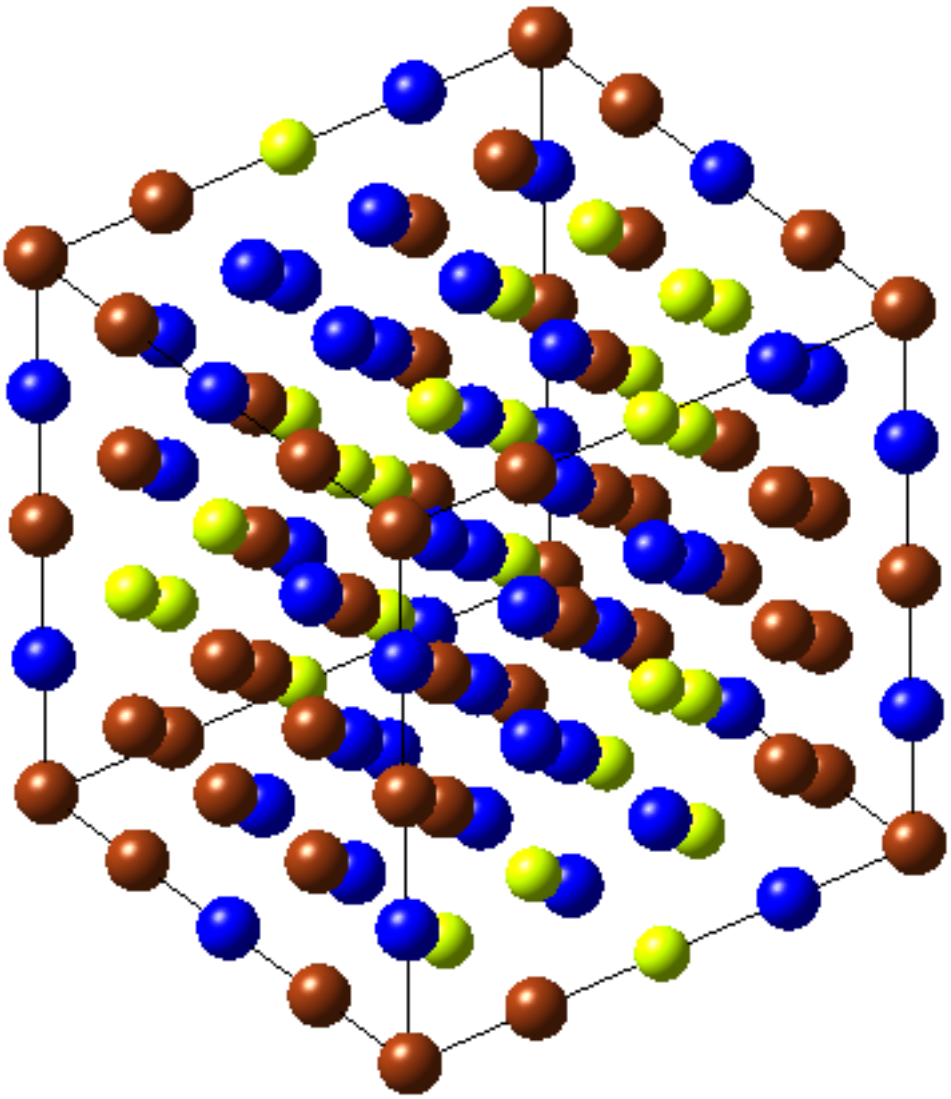
Special Quasirandom Structures SQS are good models for disordered alloys, as the coordination number in the different coordination shells are identical to or close to those of a random, disordered alloy with a given stoichiometry. *MedeA* allows building such structures from the Special Quasirandom Structures (SQS)... entry of the Builders menu.



The first selection is the Type of *binary*, *ternary* or *pseudoternary* alloy.

Then you select as SQS one individual structure (like the *A3B*) or an entire set for a given lattice type and size (the *bcc-16* series of bcc structures with 16 atoms).

The required inputs are elements A, B, and C (only for ternaries) and the lattice constant a_0.



Binary alloys: bcc, fcc, hcp

MedeA offers 8-atom models for *bcc* and *hcp* structures, 16-atom models for *bcc*, *fcc*, and *hcp*; 32-atom models for *fcc*. This means you create the *A3B*, *AB*, and *AB3* for a given lattice constant at once. That's even more impressing and time-saving with getting all 15 fcc models with 32 atoms each.

More details on these quasirandom structures in general and the binary structures are for example from Wolverton & Ozolins [4] and Zunger, Wei, Ferreira & Bernard [5].

Ternary alloys: fcc, bcc, B1

fcc: ABC (24 atoms) and A_2BC (24 atoms): Shin, van de Walle, Wang & Liu [6]

B2: A_2BC (8 atoms), and A_4B_3C (16 atoms): Jiang, Chen & Li [7]

bcc: ABC (36 atoms), A_2BC (32 atoms), $A_2B_3C_3$(64 atoms) and A_6BC (64 atoms): Jiang [8]

[4] C Wolverton and V Ozolins, "First-Principles Aluminum Database: Energetics of Binary Al Alloys and Compounds," Physical Review B 73, no. 14 (April 2006): 144104.
[5] Alex Zunger, SH Wei, LG Ferreira, and JE Bernard, "Special Quasirandom Structures," Physical Review Letters 65, no. 3 (1990): 353-356.
[6] Dongwon Shin, Axel van de Walle, Yi Wang, and Zi-Kui Liu, "First-Principles Study of Ternary Fcc Solution Phases From Special Quasirandom Structures," *Physical Review B* 76, no. 14 (October 2007): 144204.
[7] Chao Jiang, Long-Qing Chen, and Zi-Kui Liu, "First-Principles Study of Constitutional Point Defects in B_2NiAl Using Special Quasirandom Structures," Acta Materialia 53, no. 9 (2005): 2643-2652.
[8] Chao Jiang, "First-Principles Study of Ternary Bcc Alloys Using Special Quasi-Random Structures," Acta Materialia 57, no. 16 (2009): 4716-4726.

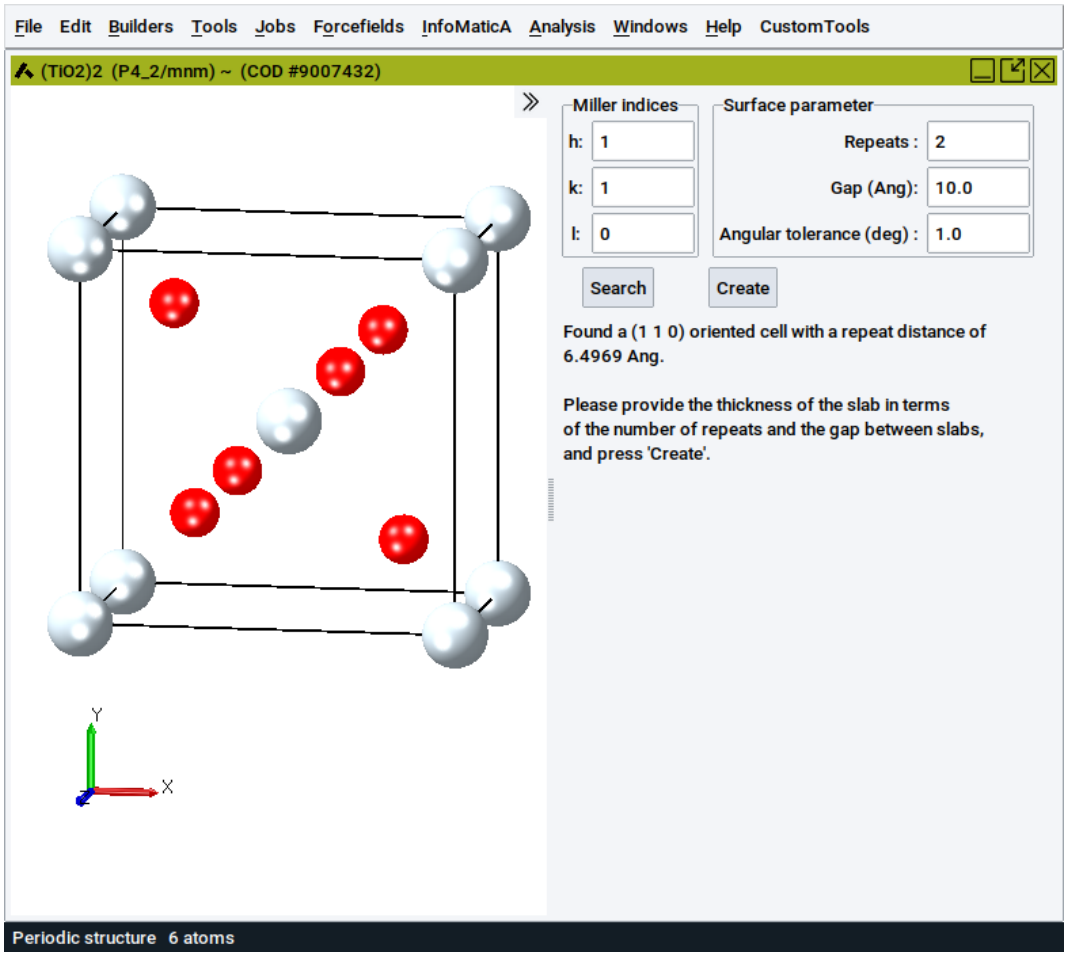
Pseudoternary alloys: Zincblende-64

A variety of different stoichiometries realized by structures with 64 atoms

14 Build Surfaces

The *MedeA Surface Builder* lets you build surfaces from bulk structures by defining a set of Miller indices.

- Start from a periodic bulk structure.
- Invoke surface builder through the *MedeA* menu entry: Builders >> Build Surfaces...
- Select Miller indices (e.g., 111) and press Search .
- Follow the instructions printed by the surface builder to build your surface model.



The following options and parameters are available:

14.1 Orientation and Thickness

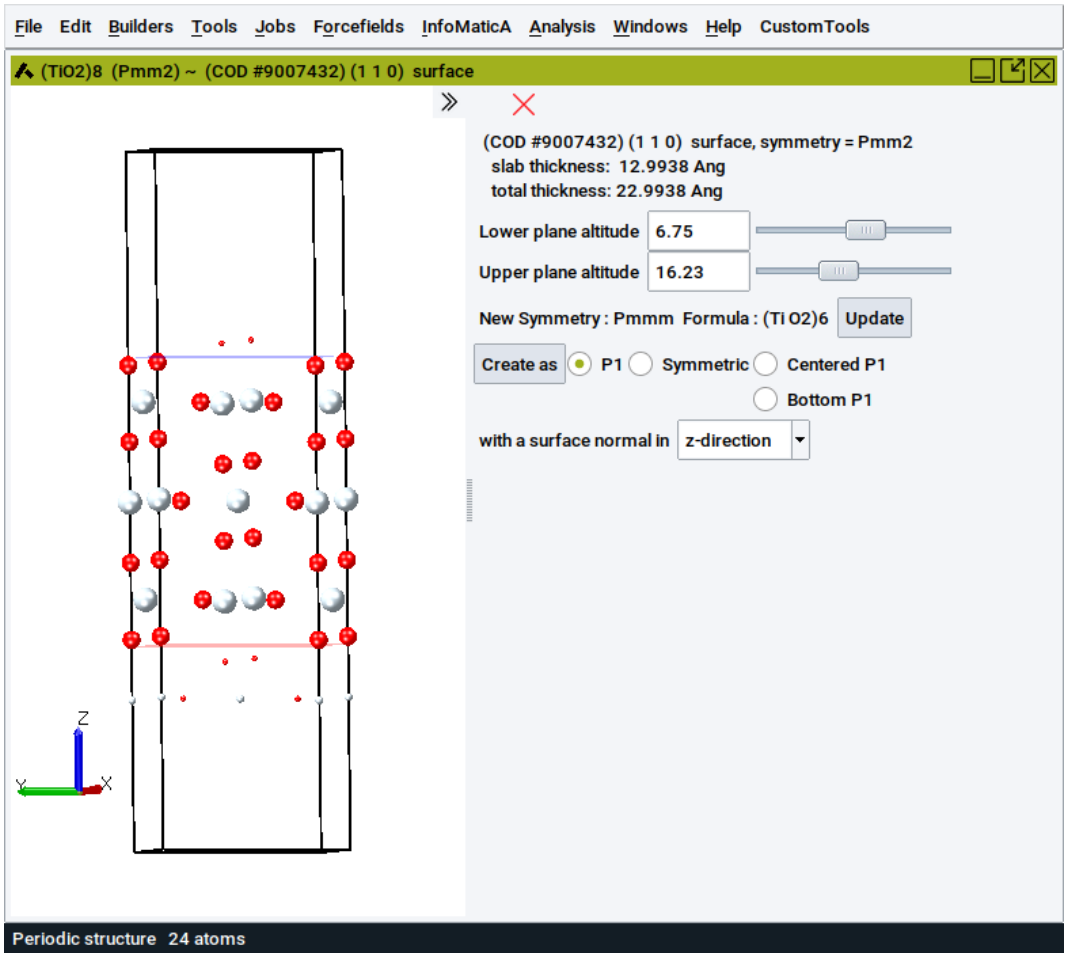
- The Repeats setting varies the material thickness by changing the number of cells to stack in the direction of the surface plane.
- The Gap setting sets the thickness of the vacuum layer. The default of 10 Å is a good value making sure that there's no interaction between surface layers within the periodic boundary model used, e.g., by VASP.

- The Angular tolerance setting sets the allowed deviation of the surface normal from the desired direction. This is needed for some bulk structures and surface as it is not possible to build a coherent cell accommodating the structure with correct stoichiometry.
- The Create button builds and displays a preview of the surface model/

MedeA now displays a preview window allowing you to set further parameters and to check the symmetry of the resulting system before building the final structure.

14.2 Surface Builder Preview Window

Here, you can verify the model, check its symmetry and possibly move the surface plane to cut parts of the structure away and modify terminations.



- Use the sliders Plane 0 and Plane 1 to remove surface layers. For example, in hexagonal ZnO above, you may decide to terminate both surfaces by just zinc atoms or by just oxygen.
- Click Update to display the current symmetry.
- Click Reset to return to the previous builder screen.
- Click P1, Symmetric or Centered P1 to choose in which symmetry to display the final system.
- Click Apply to create the final surface structure but keep the Preview window open
- Click OK to create the final structure and close the Preview window.
- Click Cancel to abandon the whole operation.

Note: Changing the termination of the slab model may change the stoichiometry and symmetry of the system. If your goal is to calculate the surface energy you should make sure that both surfaces present in the slab model are identical. Also, in polar systems, you may want to avoid creating a dipole by working with systems that have inversion symmetry.

What symmetry you choose for the final surface depends on your goals: For example, to calculate the surface energy of the above system you would like to use the full symmetry of the system. To add a molecule to the surface, you most likely would use P1, as you are going to further modify the structure.

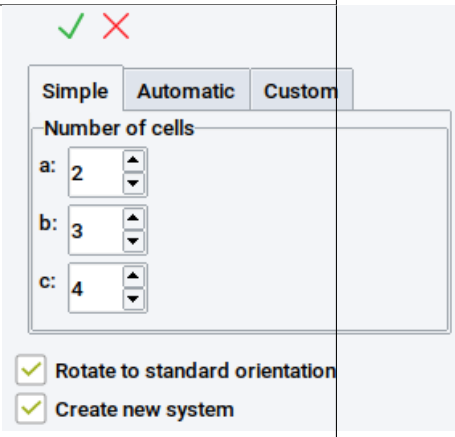
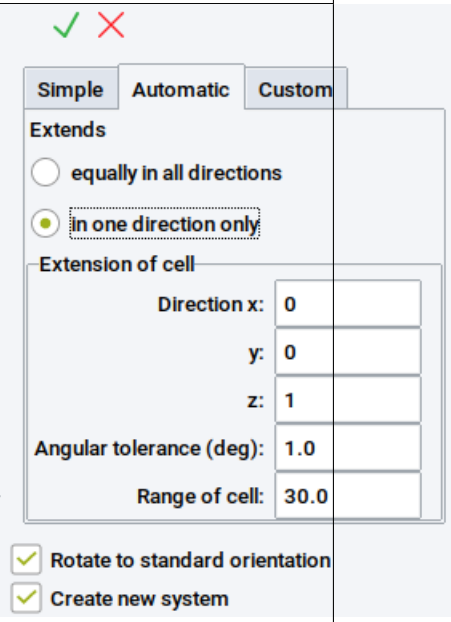
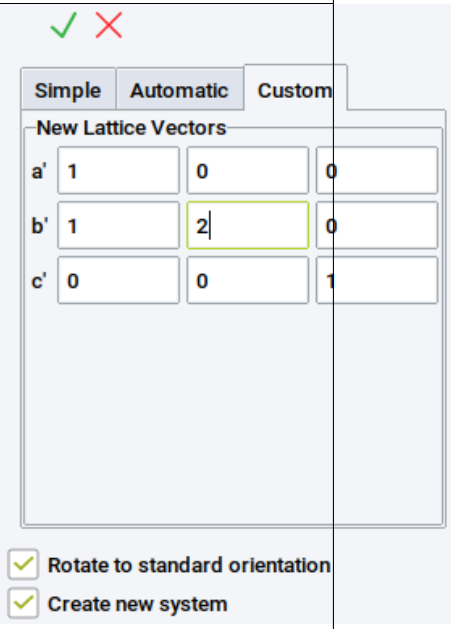
- Create as P1 creates a slab model exactly the way you see it on the screen.
- Create as Symmetric uses the new symmetry to set up the slab model, might change the cell shape.
- Create as Centered P1 creates a slab model as you see it on the screen, but re-centered to the middle.
- Create as Bottom P1 creates a slab model as you see it on the screen, but re-centered so that the bottom-most layer is at the bottom.

15 Build Supercells

The *Supercell Builder* lets you create a large cell starting from your initial periodic structure.

- Invoke the supercell builder from the *MedeA* Builders menu item Build Supercells. . . .

The following settings are available:

Mode	Description	
Simple	Increases lattice parameters in a, b, and c direction Also available as a flowchart stage	
Automatic	Uses range parameter to build a supercell: i. Extension equally in all directions ii. Extension in one direction	
Custom	Defines a new set of lattice parameters for supercell	

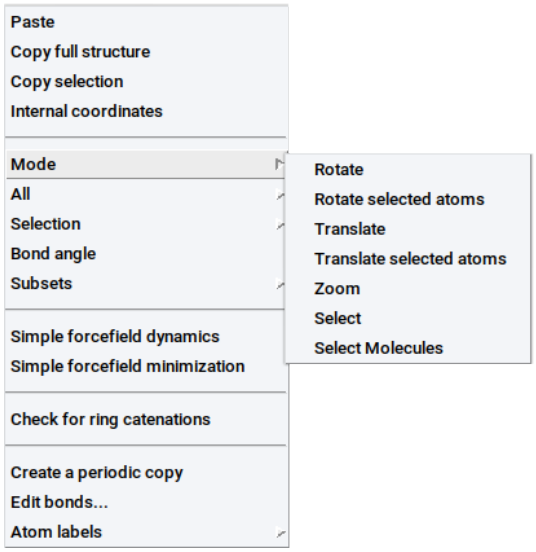
16 Context Sensitive Menu for Non-Periodic Structures

Right-clicking into the drawing area of the viewer interface brings up a context sensitive menu. The following list describes the available options:

The Mode menu

The mode menu lets you select an action mode. Current modes are Select, Rotate, Rotate selected atoms, Translate, Translate selected atoms, Zoom, Select, and Select Molecules. Alternatively, the Insert mode is invoked by selecting an element from the insert panel or by clicking the Insert icon in the *MedeA* menu bar.

Right-click to use context sensitive menus.



All other modes are selected through the context sensitive menu or through menu buttons in the non-periodic structure control bar. The cursor shape indicates the current viewing mode:

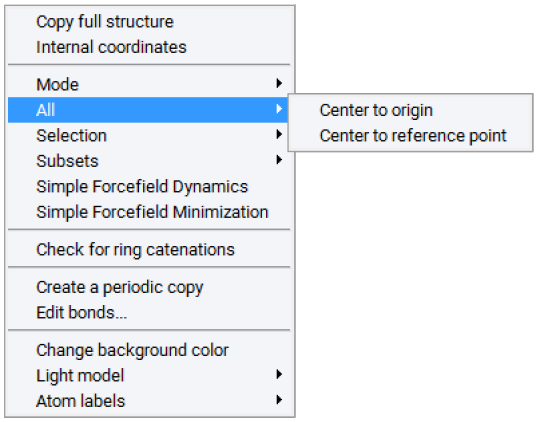
- for *Insert*
- for *Select* or *Select Molecules*
- for *Rotate* or for *Rotate selected atoms*
- for *Translate* or for *Translate selected atoms*
- for *Zoom*

In addition, the *MedeA* control bar displays buttons for selecting modes when a window is active:

Move your mouse cursor over these buttons to display a brief description of each mode.

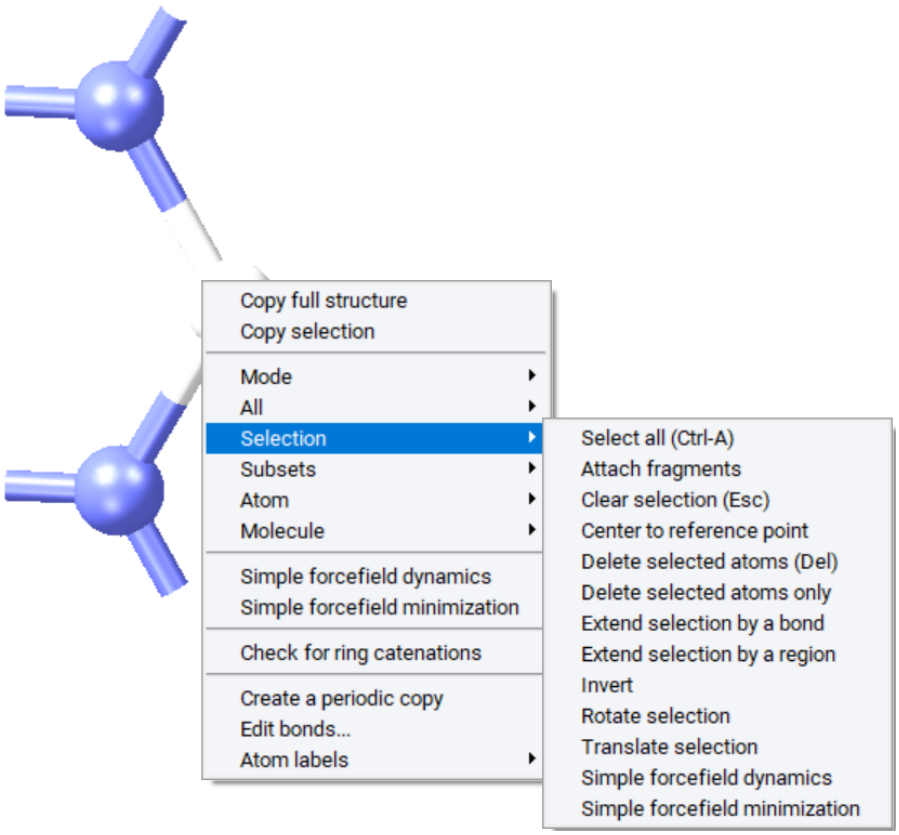
The All menu

The All menu lets you center all atoms in the drawing area to either the origin or to the origin or a reference point of your choice. Centering means **moving the center of the smallest box which envelopes all atoms (bounding box)** to the reference point/origin.



The selection menu

The Selection menu lets you perform a certain operation on a selection of atoms. Available operations depend on the number of selected atoms:

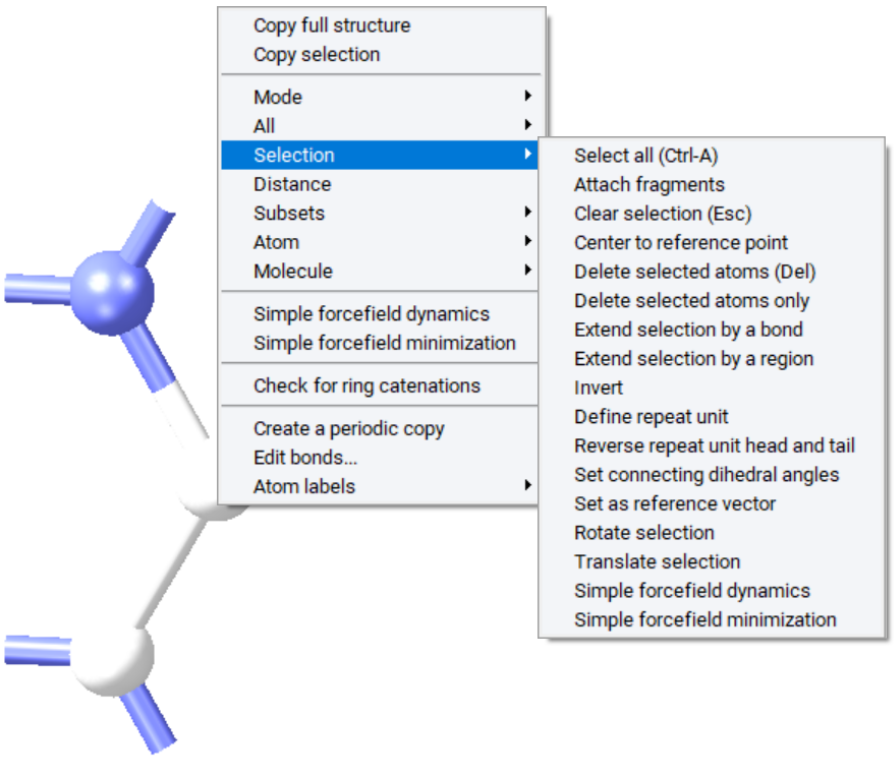


When one atom is selected

- Select all : Selects all atoms in the drawing area (shortcut Ctrl - Alt).
- Attach fragments : Attach a fragment to the selected atom. If dangling bonds exist then the fragemnt is attached to a dangling bond. Otherwise a new bond is created.
- Clear selection : Unselects all selected atoms. (shortcut Esc)
- Center to reference point : Moves all atoms present in the drawing area such that their geometric center comes to lie at the reference point. Defining a reference point.
- Delete selected atoms : Deletes all selected atoms. All bonds are also removed. (shortcut Del)
- Delete selected atoms only : Only deletes the slected atoms. Any bonds connecting the atoms to the the molecule are kept.

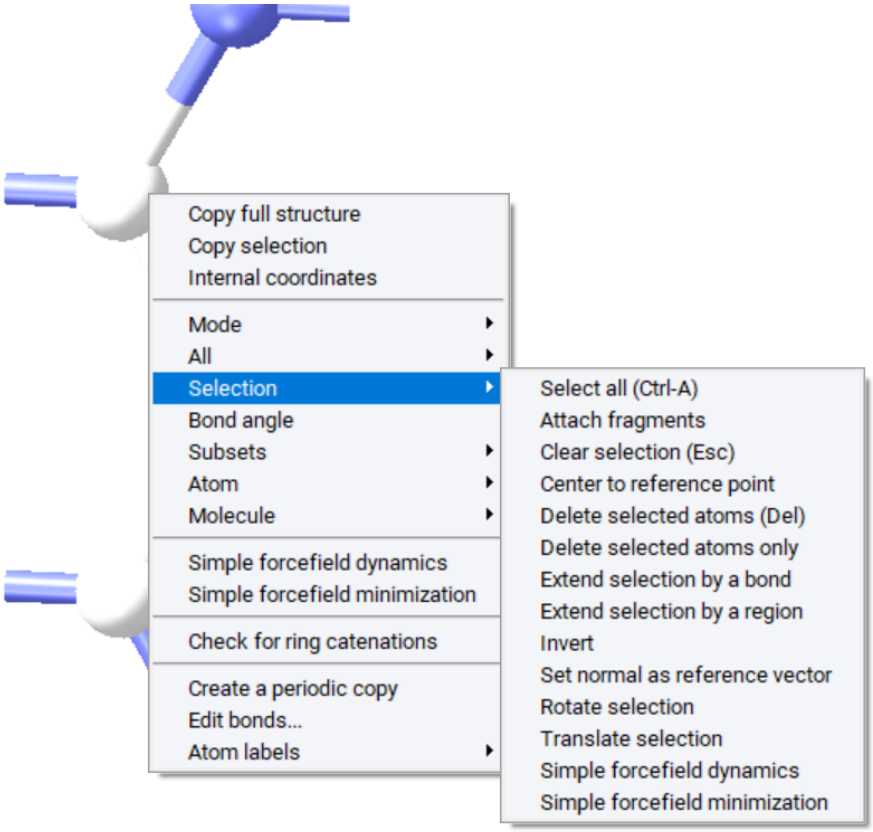
- Extend selection by a bond : Extend the selection by all atoms connected by a bond to the selected ones.
- Extend selection by region : Extend the selection by a definable region.
- Invert : Invert the selection.
- Rotate selection : Rotates the selected atom around the reference axis. A dialog will ask for the rotation angle.
- Translate selection : Translates the selected atom by norm (reference vector) along the reference vector.
- Simple forcefield dynamics : Performs a simplified forcefield dynamics on the selected atoms (see the section *simple forcefield minimization/dynamics*).
- Simple forcefield minimization : Perform a simple forcefield minimization on the selected atoms (see the section *simple forcefield minimization/dynamics*).

When two atoms are selected (only options not mentioned earlier are listed)



- Define repeat unit : Use this option when both atoms have at least one dangling bond to define a repeat unit.
- Reverse repeat unit heat and tail : Use this option when both atoms define a repeat unit to revers heat and tail.
- Set as a reference vector : Sets the bond connecting the two selected atoms as a reference vector.

Distance appears as entry below Selection. Use this to modify the distance between two atoms, choose which to move.

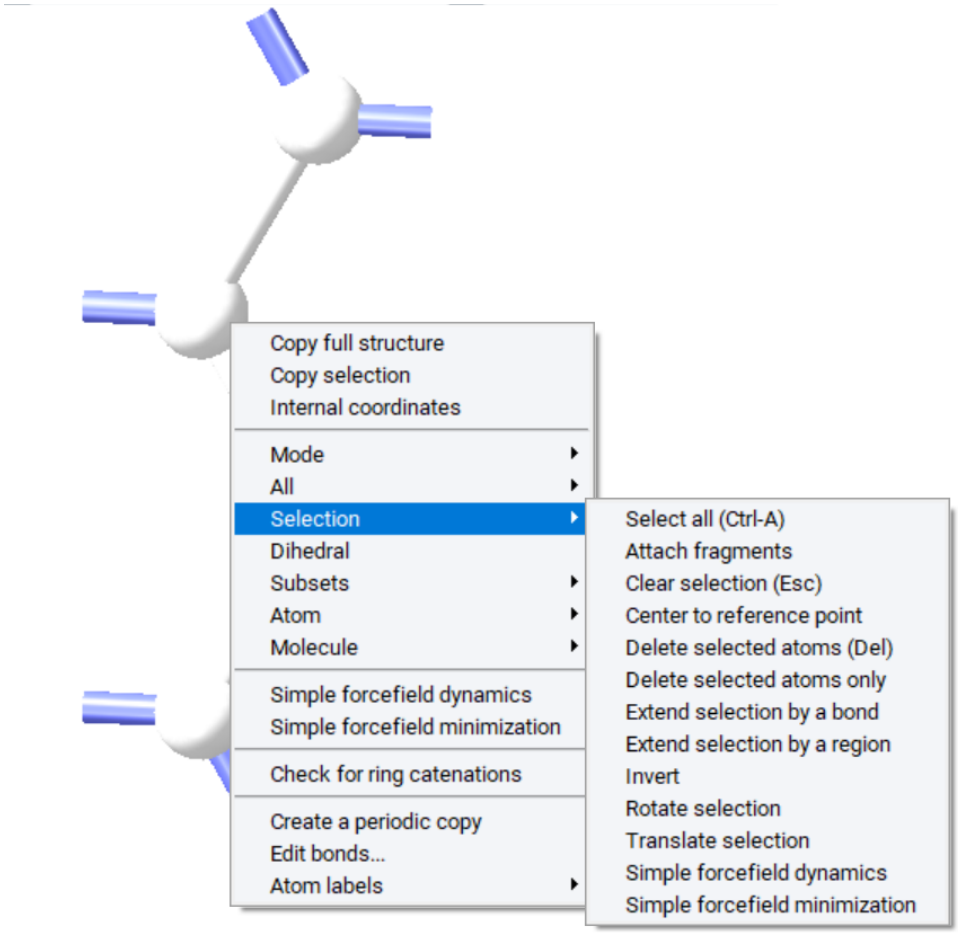


When three atoms are selected (only options not mentioned earlier are listed)

- Set normal as reference vector selects reference vector normal to plane spanned by three atoms

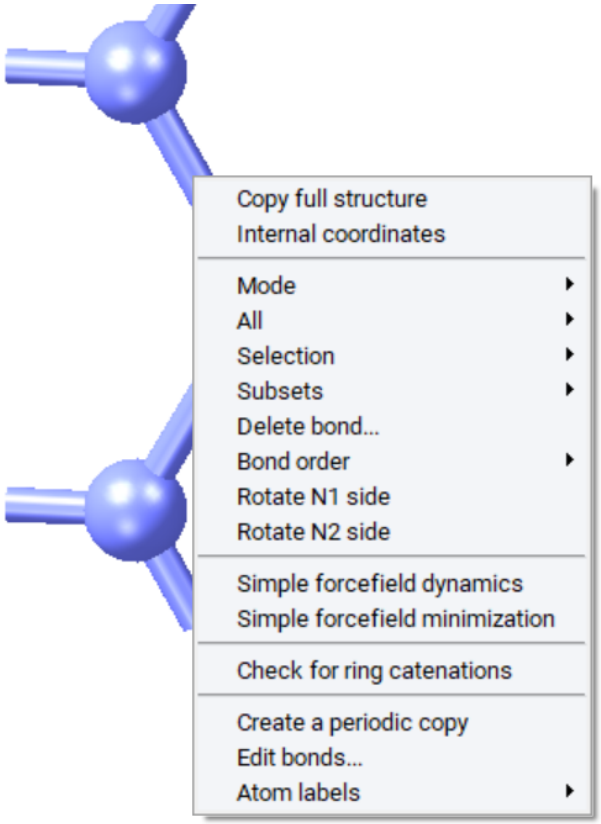
Bond angle appears as entry below Selection. Displays dialog to view and edit the bond angle including the option change which atom to displace when changing the angle.

When four atoms are selected

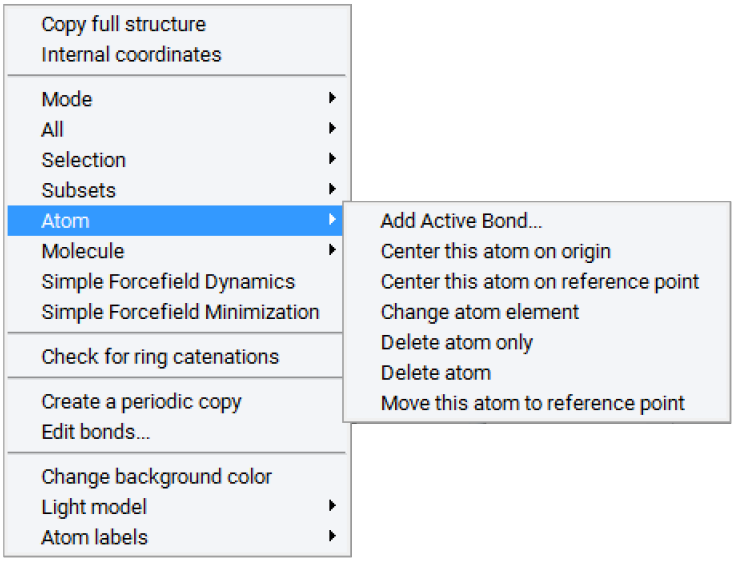


Dihedral appears as entry below Selection. Displays dialog to view and edit the dihedral angle including the choice which of the two atoms at the end of the chain to displace when changing the angle. This option requires 4 linearly bonded atoms.

Right-click when cursor hovers over a bond.



- Delete bond... : Deletes the bond.
- Bond order : Change the bond order. Available options are Single , Aromatic/Partial Double , Double , and Triple .
- Rotate <atom_number>side : Rotates the part of the molecule connected to <atom_number> around the bond (when atoms are selected).



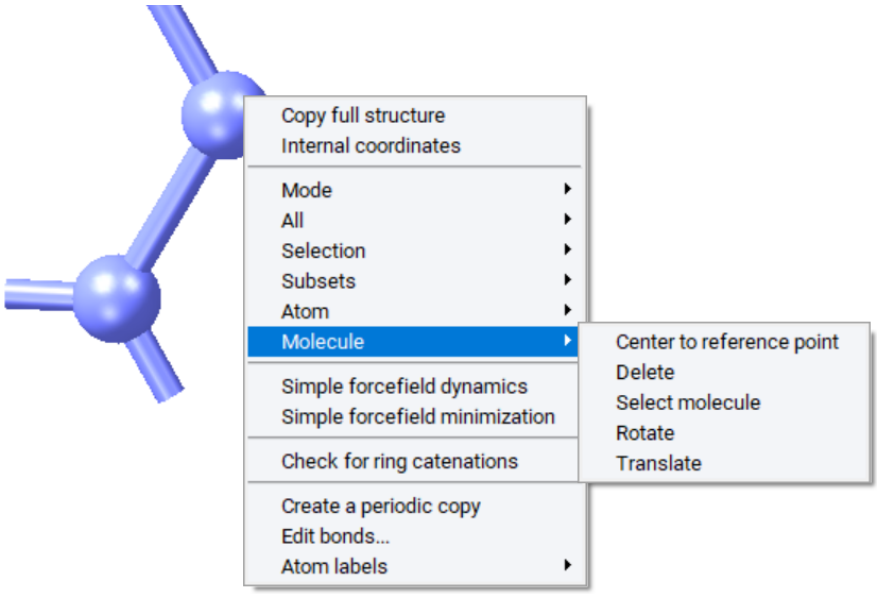
Right-click on an atom (only options not described earlier are listed) - Atom

- Add active bond : Creates an active bond perpendicular to the current viewing plane.
- Center this atom on origin : Moves all atoms such that the atom under the cursor comes to lie at the origin (0,0,0).

- Center this atom to reference point : Moves all atoms such that the atom under the cursor comes to lie at the reference point.
- Change atom element : replace the element under the cursor by the element currently loaded into the cursor.
- Delete atom only : Deletes the atom leaving the active bonds of the atom(s) bonded to this atom.
- Delete atom : Deletes the atom and all bonds connecting to this atom.
- Move this atom to reference point : Moves only the atom under the cursor to the reference point.

When right-clicking on an atom - Molecule

In the following, “Molecule” refers to all atoms connected to the one under the cursor.

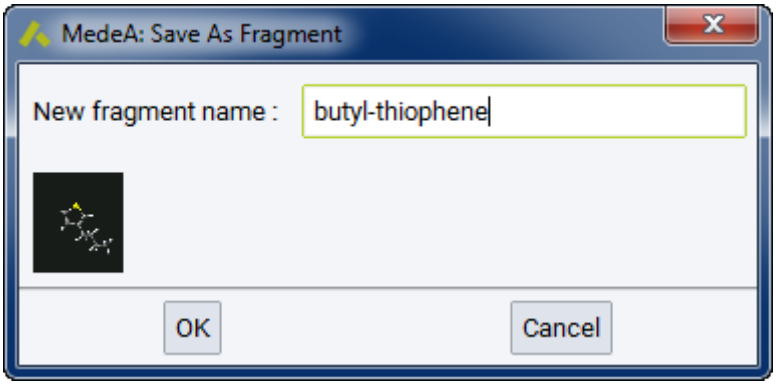


- Center to reference point : Centers the molecule to the reference point
- Delete : Deletes the molecule
- Select molecule : Selects the molecule
- Rotate : Rotates the molecule around the axis defined by Point and Vector
- Translate : Translates the molecule by the vector defined by Vector

Right-click anywhere in the structure - Create a periodic copy

Create a periodic copy of the non-periodic structure, which can be used as input for, e.g., VASP.

Right-click anywhere in the structure - Save as fragment



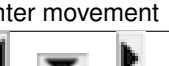
Save as fragment : Molecules that have exactly one active bond can be saved as fragments for later use as a building block for more complex structures. When saving a fragment make sure to choose a comprehensive name and in the graphics panel zoom in on the fragment beforehand. *MedeA* will save a snapshot of the structure along with its name

Tip: This option is shown only when the structure has exactly one active bond!

Shortcuts

A number of shortcuts are available to simplify operations:

Table1: Summary of very useful key combinations

Key combination	Action
Crtl + m	invokes the *Molecular Builder* to build a new system
Crtl + n	invokes the *Crystal Builder* to build a new system
Crtl + o	open a structure from file
Crtl + j	open a structure from a job
Crtl + z	undo the last action
Crtl + y	revert undo actions
Crtl + a	select all atoms of the active structure
Esc	clear the atom selection
Del	delete selected atoms
z +  , or pointer movement	increase or decrease the size of the entire structure in small steps
Shift + z +  , or pointer movement	increase or decrease the size of the entire structure in large steps
t +  , or pointer movement	**translation** of the **entire structure** by **0.1** Å along the **vertical** and **horizontal** axes of the screen
Shift + t +  , or pointer movement	**translation** of the **entire structure** by **1.0** Å along the **vertical** and **horizontal** axes of the screen
s + t +  , or pointer movement	**translation** of **selected atoms** by **0.1** Å along the **vertical** and **horizontal** axes of the screen
Shift + s + t +  , or pointer movement	**translation** of **selected atoms** by **1.0** Å along the **vertical** and **horizontal** axes of the screen
Alt + t +  , or pointer movement	**translation** of the **entire structure** by **0.1** Å along the axis **perpendicular** to the screen
Alt + Shift + t +  , or pointer movement	**translation** of the **entire structure** by **1.0** Å along the axis **perpendicular** to the screen
r +  , or pointer movement	**rotation** of the **entire structure** by **1.0 degree** around the **vertical** and **horizontal** axes of the screen
Shift + r +  , or pointer movement	**rotation** of the **entire structure** by **10.0 degrees** around the **vertical** and **horizontal** axes of the screen
Alt + r +  , or pointer movement	**rotation** of the **entire structure** by **1.0 degree** around the axes **perpendicular** to the screen
Alt + Shift + r +  , or pointer movement	**rotation** of the **entire structure** by **10.0 degrees** around the axis **perpendicular** to the screen
s + r +  , or pointer movement	**rotation** of **selected atoms** by **1.0 degree** around the **vertical** and **horizontal** axes of the screen
Shift + s + r +  , or pointer movement	**rotation** of **selected atoms** by **10.0 degrees** around the **vertical** and **horizontal** axes of the screen

17 Substitutional Search

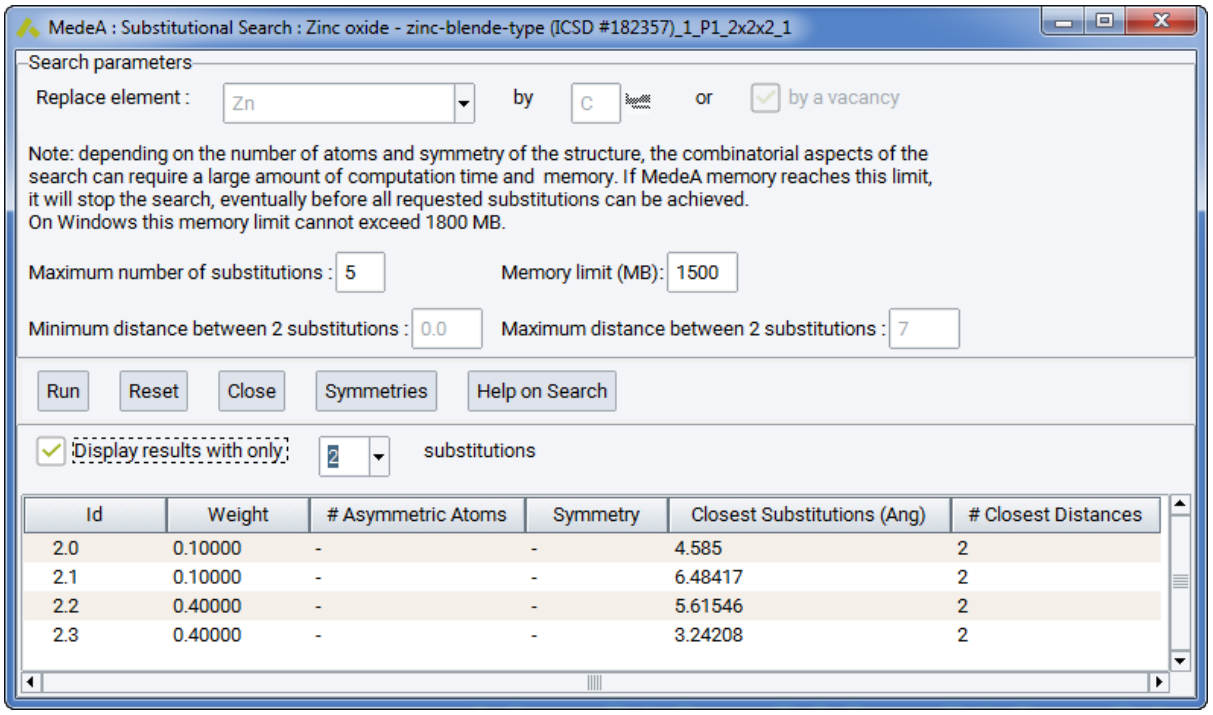
17.1 Features and algorithm

MedeA's *Substitutional Search* takes the active structure window as an input and searches all symmetrically different systems obtainable by substituting an element in the system by an other element at the same site. A vacancy can be chosen as the type. The maximum number of allowed substitutions is half the number of atoms of the type already created present in the system.

The search algorithm proceeds as follows: First, a single substitution is made for each symmetrically independent site A, hereby generating a set of new structures. The structures resulting from this operation are grouped by their new symmetries. Next, for each element of the new set of structures, a second substitution is performed on each symmetrically independent site; again the resulting structures are regrouped according to symmetry, and the process is repeated up to the desired number of substitutions.

17.2 Usage

To bring up the Substitutional Search interface, select the periodic structure window you would like to perform the search in and select Substitutional Search from the Builders menu:



To start with, select which element to replace (here: Zn) and select an element to replace by (here: vacancy). You can use additional parameters to limit the search, e.g. by defining a minimal or maximal distance between two substitutions.

- Run : Starts the Search.
- Reset : Resets the search without changing the parameter settings.
- Symmetries : Calculates the symmetries for all structures displayed in the results table.
- Help on Search : Brings up help text.

In the previous example of up to two vacancies in ZnO having a maximum distance between two substitutions of 7 Å clicking Symmetries creates information on the number of asymmetric atoms per cell and the cell symmetry:

Id	Weight	# Asymmetric Atoms	Symmetry	Closest Substitutions (Ang)	# Closest Distances
2.0	0.10000	9	P-42m	4.585	2
2.1	0.10000	11	P-4m2	6.48417	2
2.2	0.40000	20	Cmc2_1	5.61546	2
2.3	0.40000	26	Cmm2	3.24208	2

Search results are listed in the results table and classified by an id number giving the number of substitution in the system followed by an index. For example, Id = 2.1, 2.2, 2.3, 2.4 means that 4 symmetrically different systems with two atoms replaced by atoms have been found.

The displayed results can be filtered by the number of substitutions per system, check Display results with only [n] substitutions and select a number for substitutions.

The table can be sorted by right-clicking on a column header and selecting a sorting criterion.

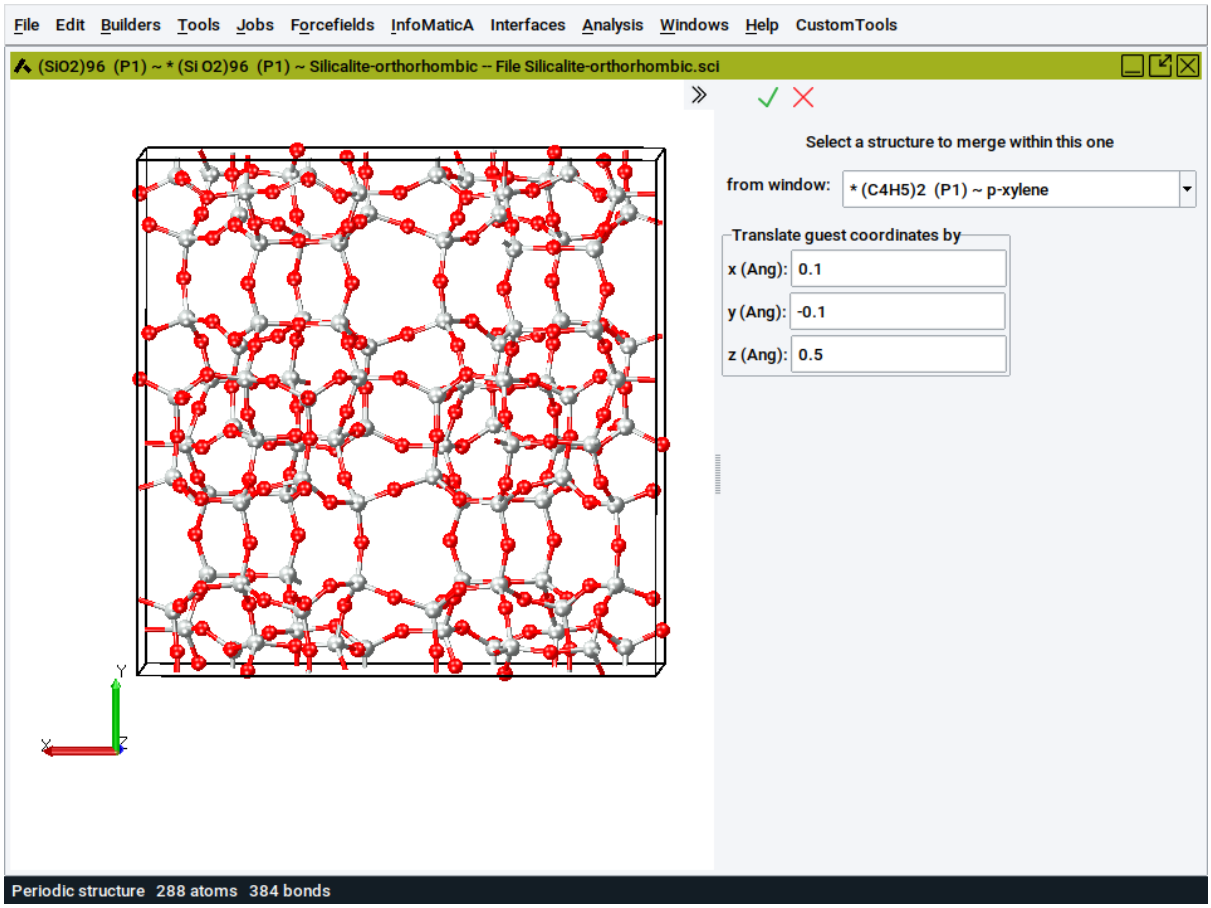
- Right-click on a structure entry to view a structure, compute its symmetry or copy the system to an internal buffer for later pasting to a spreadsheet.

  Other Search options are:

- Replace element [ ] by [ ] : Element to be replaced () and element to substitute with ().
- Maximum number of substitutions to be performed (*default=5*).
- Memory limit (MB) : The memory limit in MB to be imposed for the search (see explanation in the panel text).
- Minimum distance between 2 substitutions : Only systems having a distance between substitutions larger than this parameter are considered (*default=0*).
- Maximum distance between 2 substitutions : Only systems having a distance between substitutions smaller than this parameter are considered (*default= not set*).

18 Merge

Merge combines the contents of two periodic structures, and is invoked from Builders >> Merge... for the larger model. The second model is translated by *x*, *y*, and *z* (units in Angstrom).



If the two models don't share the same lattice vectors, you can shift the second system in the bigger first system, as defined by a translation vector. Please take care that the second system has smaller or equal dimensions than the first model.

19 Building Interfaces

19.1 Features and Algorithm

The *MedeA Interface Builder* takes one or two surfaces slab structures as an input. It then searches for a relative orientation of these two surfaces such that the lattice mismatch of the resulting system is minimized.

- For each of the surfaces, loop over the allowed range of cells, creating new cells that are multiples of the original cell: *a' = ma + nb*, *b'=oa + pb* where *a* and *b* are the original in-plane lattice vectors and *m*, *n*, *o* and *p* are integers from *-max* to *+max*
- For each cell find the reduced cell, which gives a standardized list of possible cells
- Find the matches between the two lists of reduced cells that meet the requested tolerances for the mismatch of the *area*, *lattice parameters* and *angle*
- Build the surface structures for the reduced cells that match, testing for and removing duplicates. These are saved in the subdirectory *surfaces*
- Build the trial interfaces from the surface structures
- Find the reduced cells for the interfaces, looking for translational symmetry
- Compare the reduced interface with previous ones and remove duplicates

As a result Interface Search produces:

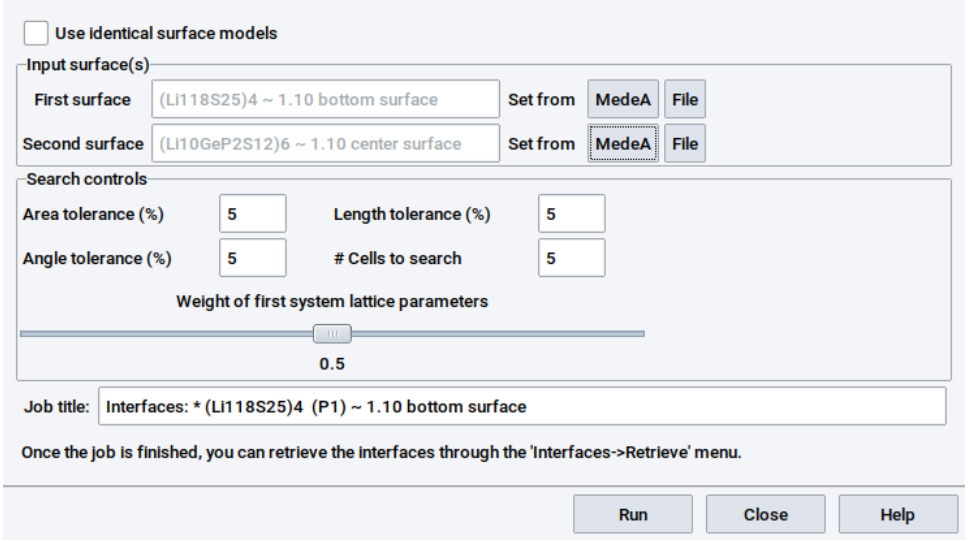
- A spreadsheet of interface structures with geometrical parameters that can be used for visualization, further geometry and symmetry analysis and as an input for computations
- A subdirectory ./interfaces (in the job directory, accessible through Jobs) containing all interfaces using default parameters for gap sizes and γ-surface shifts
- A subdirectory ./surfaces containing all surface structures built from the reduced cells that matched the tolerance criteria

19.2 Usage

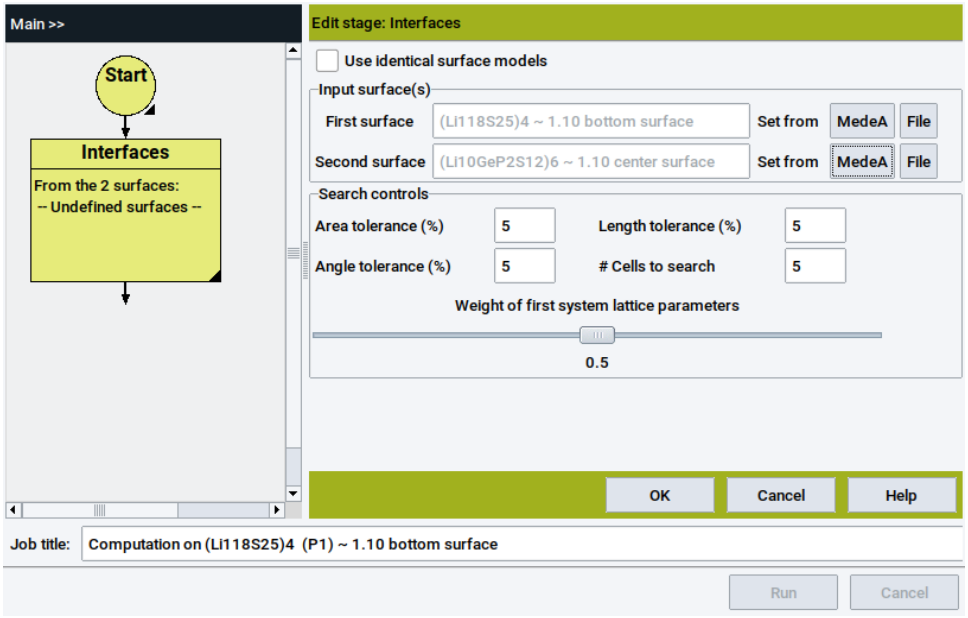
The *MedeA Interface Builder* is either accessible via the Tools menu of the *MedeA GUI* and as a flowchart stage in the flowchart editor. To open the dialogue of the *Interface Builder* tool use the menu sequence Tools >> Interfaces to activate this tool and then Interfaces >> Define and run to access the interface. The dialogue of the *Interface Builder* flowchart stage is accessible in the flowchart editor:

1. Jobs >> New Job...
2. In the area of the flowchart editor on the right side scroll to the section Building and Editing and click on Interfaces
3. Open the dialogue either with right-click on the flowchart stage >> Edit... or with a double-click on the stage

Both dialogues are very similar as they have same options. However, the dialogue of the *Interface Builder* tool has one option more, namely to enter a title just for the task to build an interface between two selected structures:



If you want to use the *Interface Builder* flowchart stage to build interface model then you can enter the title for the job in which the entire flowchart is processed by the JobServer:



Note: The *Interface Builder* flowchart stage can be combined with other flowchart stages to, e.g., analyse and extract particular created interfaces. Hence, you may be want to enter job title that briefly describes the entire workflow and not only the interface building stage.

The steps required to create a set of interfaces are:

1. Prepare surface models using the *MedeA Surface Builder* whereby the surface normals must be parallel to the z-axis.
2. Keep the created surface structures either in the structure windows of the *MedeA GUI* or save the structures of the surface models to disk, preferable in the *MedeA* internal format `.sci`.
3. Open one of the two *Interface Builder* dialogues
4. By default you can define two structures that should form the interface; alternatively you can also define one surface model to build an interface with itself
5. If necessary modify the options in the pane Search controls

#. In the *Interface Builder* flowchart stage confirm the settings with OK

1. Enter an informative job title and submit the *Interface Builder* workflow with Run

19.3 Default search parameters

By default, the algorithm looks for interfaces between the defined structures with a maximum tolerance of 5% for the misfit of the area, length, and angle.

A plane which is in-plane with the selected surfaces area(s) and has the size of 5×5 the original surface cell(s) will be searched for Bravais-type lattice vectors making up the new cell and complying with the mismatch tolerances.

To make a coherent cell, the in-plane lattice parameters of the two cells need to be adjusted. By default, the interface builder weighs the lattice parameters of each system with a factor 0.5, meaning both systems will be dilated/constrained by the same amount. In general, you may choose a weighting factor depending on your knowledge about the elastic properties of the two materials involved.

19.4 Description of Search parameters

First surface : Defines one of the two surface models that should form the interface.

Second surface : Defines the other of the two surface models that should form the interface.

Use identical surface models : If this option is marked then the *Interface Builder* dialogue lets you define only a structure for the first surface.

MedeA : Opens a dialog to select a structure from the structures currently open in *MedeA*.

File : Opens a dialog to select a structure data file stored on disk; supported file formats are those which are displayed upon expanding the pull-down menu of Files of type .

Area tolerance (%) : The tolerance for the deviation between the two native surface areas making up the interface. Here, “native” means “by construction”, that is before applying any strain to fit the two surfaces together.

Length tolerance (%) : Tolerance for mismatch of the natural in-plane lattice parameters of the two surface cells.

Angle tolerance : Tolerance for the mismatch of the natural in-plane angles of the two surface cells.

#cells to search : How many multiples of the original cell to use for constructing new surfaces during step 1 of the search procedure (see algorithm above).

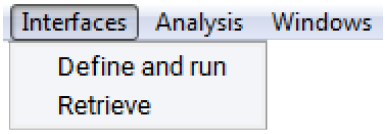
Weight of first system : Determines how much strain (between 0 and 1) is applied to the first system, when fitting the two surfaces together to form an interface. The remaining weight will be applied to the second system.

Click Run to submit the interface search job.

Building the new surface structures, finding the reduced cells and symmetries and constructing and comparing the interfaces may take a considerable amount of CPU time. Depending on input symmetry, search space and system size, time to completion can vary between minutes and hours.

19.5 Display of results

In order to access the results of a completed interface job, invoke Retrieve from the Interfaces menu entry.



Select the interface job in question from the file selection dialog and click Insert and then OK . You will get a spreadsheet-like window showing the data of those systems that fulfill your tolerance criteria. The screenshot below shows an example of Interfaces default output for (100) Ni twist grain boundaries. The following table summarizes the parameters given in the output:

- **Identical Interfaces**: (Yes/No) Indicates if the two interfaces present in the cell are identical. Using a structure model having identical interfaces allows for direct calculation of e.g. the interface energy. Given that the Interface Search works with 3D period or crystalline structures, a slab model of an interface has to have two actual interfaces in a unit cell.
- **ID**: Counts the class of the interface, followed by another index, if there are different interfaces in this class. In the example below, the class 1 has two interfaces with different symmetry.
- **nAtoms**: The number of atoms in the interface unit cell.
- **Space group**: Symmetry of the resulting interface unit cell.
- **Area (AA)**: Area of the interface in $\mathrm{\AA}^2$.

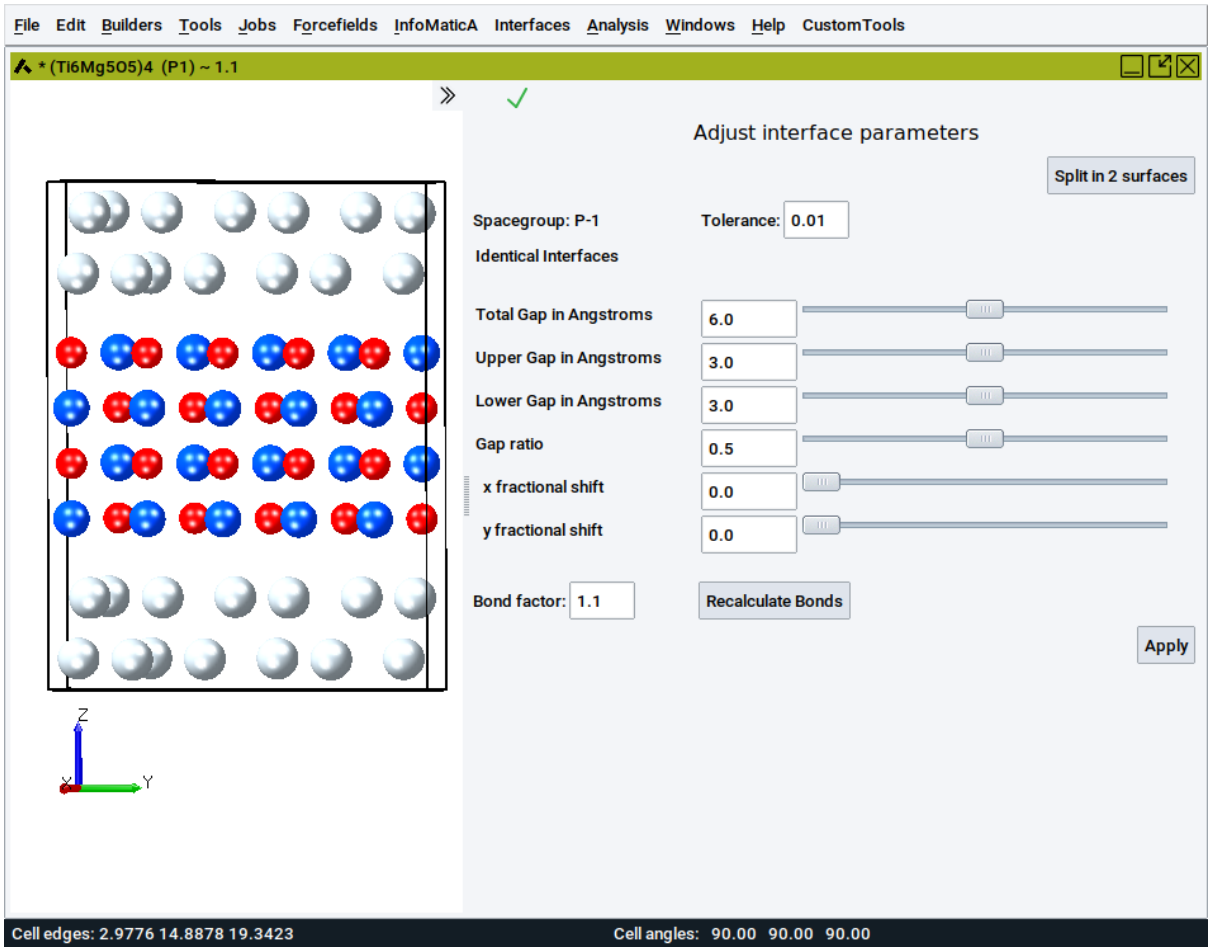
- **dA**: Area mismatch of the two natural surfaces making up the interface.
- **A, B, dA, dB**: A and B lattice parameter of the interface, the mismatch of the original (natural) lattice parameters A and B in %.
- **Theta, dTheta**: The angle of the 2-D cell (in-plane angle), the mismatch of the original (natural) in-plane angles.
- **Bed angle**: The angle between the *a'* vectors of the new surface layers making up the interface.

ID	Identical Interfaces	nAtoms	Spacegroup	Area	dArea	A	dA	B	dB	theta	dTheta	BedAngle
1.1	Yes	64	P-1	44.33	-2.0	2.978	0.9	14.888	-2.9	90.0	0.0	-30.00
2.1	Yes	128	P-1	88.66	-2.0	8.422	-5.0	10.736	0.9	101.3	-4.6	44.04
2.2	Yes	128	P-1	88.66	-2.0	8.422	-5.0	10.736	0.9	101.3	-4.6	44.04
3.1	Yes	164	P-1	115.26	1.9	10.736	0.9	10.736	0.9	90.0	-2.4	49.79
3.2	Yes	164	P-1	115.26	1.9	10.736	0.9	10.736	0.9	90.0	-2.4	49.79
3.3	Yes	164	P-1	115.26	1.9	10.736	0.9	10.736	0.9	90.0	-2.4	72.41
3.4	Yes	164	P-1	115.26	1.9	10.736	0.9	10.736	0.9	90.0	-2.4	72.41
4.1	Yes	176	P-1	124.12	2.9	10.736	0.9	12.277	4.0	109.7	3.3	44.04
4.2	Yes	176	P-1	124.12	2.9	10.736	0.9	12.277	4.0	109.7	3.3	44.04
4.3	Yes	176	P-1	124.12	2.9	10.736	4.9	12.277	-4.6	109.7	-3.4	14.04
4.4	Yes	180	P-1	124.12	-3.2	10.736	0.9	12.277	-4.6	109.7	-0.8	30.14
4.5	Yes	180	P-1	124.12	-3.2	10.736	0.9	12.277	-4.6	109.7	-0.8	-2.07
5.1	Yes	192	P-1	132.99	-2.0	10.736	0.9	12.633	-1.8	101.3	4.0	49.79
5.2	Yes	192	P-1	132.99	-2.0	10.736	0.9	12.633	-1.8	101.3	4.0	17.59
6.1	Yes	200	P-1	141.85	4.5	10.736	4.9	13.316	-1.5	97.1	-3.8	33.69
6.2	Yes	200	P-1	141.85	4.5	10.736	4.9	13.316	-1.5	97.1	-3.8	33.69
6.3	Yes	200	P-1	141.85	4.5	10.736	0.9	13.316	3.5	97.1	-0.2	49.79
6.4	Yes	200	P-1	141.85	4.5	10.736	0.9	13.316	3.5	97.1	-0.2	17.59
6.5	Yes	204	P-1	141.85	-0.9	10.736	0.9	13.316	-1.5	97.1	2.0	49.79
6.6	Yes	204	P-1	141.85	-0.9	10.736	0.9	13.316	-1.5	97.1	2.0	17.59
7.1	Yes	216	P-1	150.72	-0.0	10.736	0.9	14.888	0.9	109.4	3.1	49.79
7.2	Yes	216	P-1	150.72	-0.0	10.736	4.9	14.888	-4.7	109.4	0.3	33.69
8.1	Yes	232	P-1	159.58	-3.8	10.736	0.9	14.888	-4.7	93.2	0.2	49.79
8.2	Yes	232	P-1	159.58	-3.8	10.736	0.9	14.888	-4.7	93.2	0.2	17.59
9.1	Yes	240	P-1	168.45	1.6	10.736	4.9	16.035	-2.4	101.9	2.9	33.69
9.2	Yes	240	P-1	168.45	1.6	10.736	4.9	16.035	-2.4	101.9	2.9	33.69
9.3	Yes	244	P-1	168.45	-2.9	10.736	0.9	16.035	-2.4	101.9	4.8	49.79
9.4	Yes	244	P-1	168.45	-2.9	10.736	0.9	16.035	-2.4	101.9	4.8	17.59
10.1	Yes	252	P-1	177.32	2.3	10.736	0.9	16.844	2.5	101.3	4.2	49.79
10.2	Yes	252	P-1	177.32	2.3	10.736	0.9	16.844	2.5	101.3	4.2	17.59
11.1	Yes	264	P-1	186.18	2.9	10.736	4.9	17.362	-1.9	92.7	3.0	33.69
12.1	Yes	264	P-1	186.18	2.9	12.277	4.0	15.183	-1.0	92.7	3.0	-15.96
13.1	Yes	288	P-1	203.91	4.0	10.736	4.9	19.066	-1.5	95.0	-2.7	33.69
13.2	Yes	288	P-1	203.91	4.0	10.736	4.9	19.066	-1.5	95.0	-2.7	-26.31
13.3	Yes	292	P-1	203.91	0.2	10.736	0.9	19.066	-1.5	95.0	-3.7	-10.21
14.1	Yes	304	P-1	212.78	0.8	12.277	4.0	17.865	-3.1	104.0	0.1	-15.96

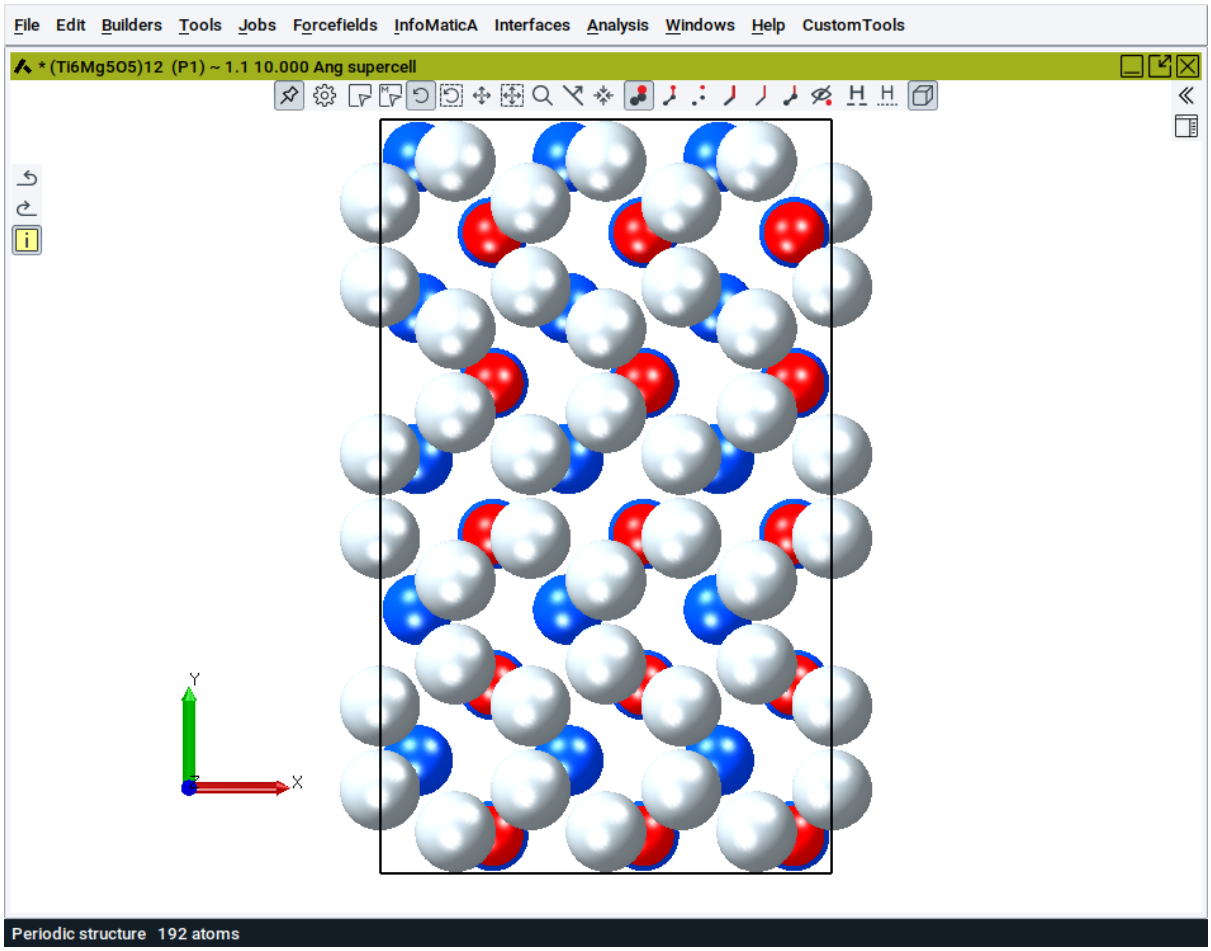
Select a row

Close

To create an interface for one of the listed structure parameters, select a row in the spreadsheet, right-click and select Create interface to bring up a preview window with a number of additional options for the construction of the final interface structure.



The above preview window provides a number of additional options for building the final interface structure:



Split in two surfaces : Lets you split the interface into the two corresponding subsystems (surfaces). Use this option when calculating, e.g., the work of separation for an interface.

Spacegroup/Tolerance : Shows the current symmetry and lets you modify the tolerance used to calculate symmetry. Click Apply to recalculate symmetry.

Identical interfaces : Indicates if the two interfaces present in the cell are identical.

Total/upper/lower gap/Gap ratio : Allows you to define two independent gaps for the upper/lower interface.

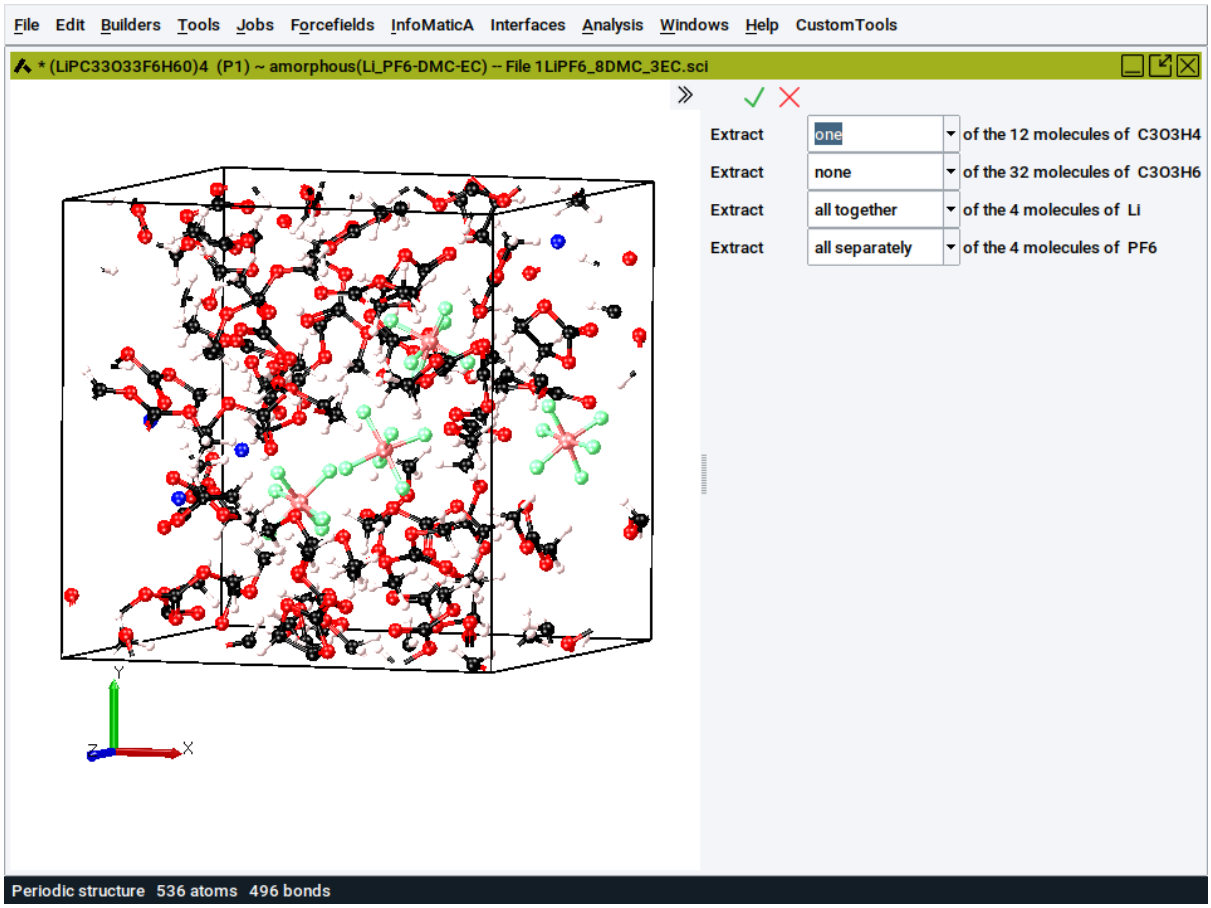
x,y fractional shifts : Lets you move the two substructures making up the interface in a plane parallel to the interface. Use this option to create additional points on the so-called γ -surface.

Bond factor / Recalculate bonds : Lets you apply a bond factor and recalculate bonds for the interface.

Apply : Applies changes to the interface structure.

20 Split Into Molecules

This feature is very useful to decompose a structure into its constituents, i.e. single atoms, atoms that are connected with and bonded to other atoms to form molecules, etc. To decompose a structure into its constituents invoked Builders >> Split Into Molecules .



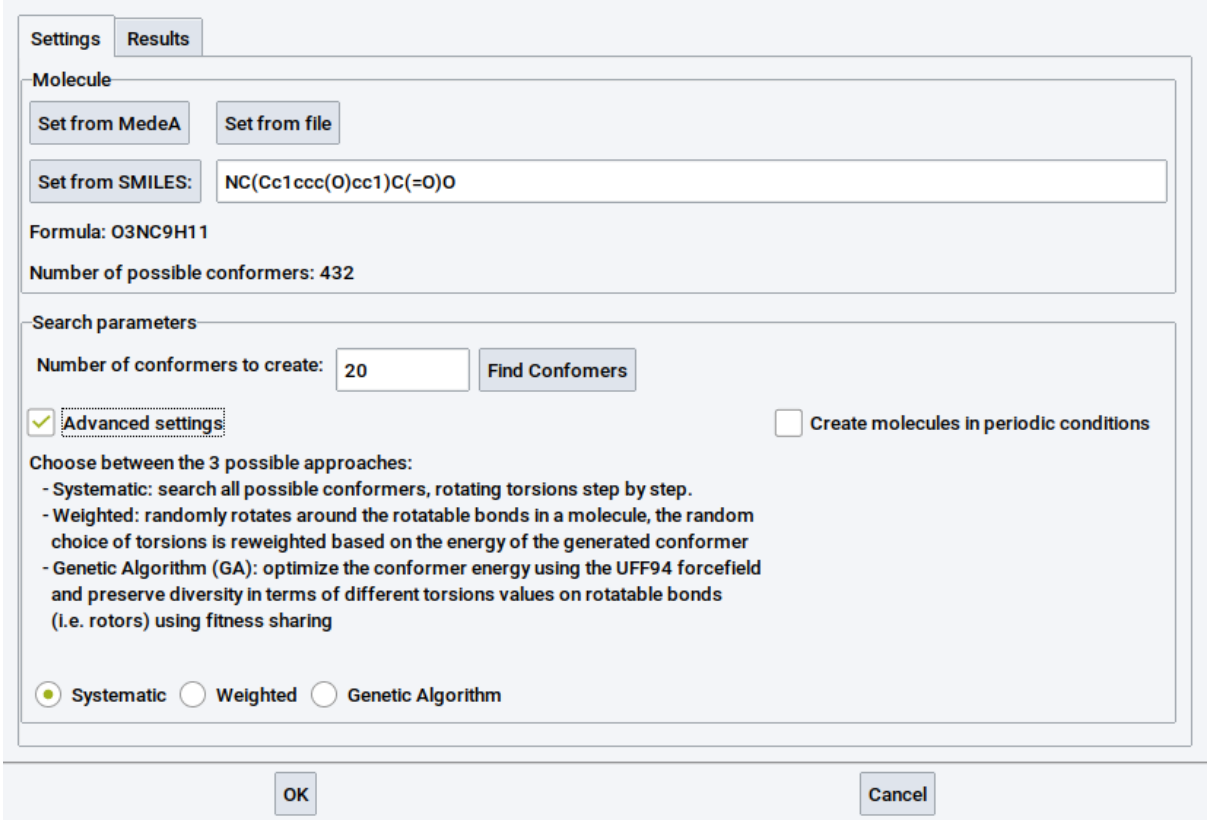
The panel on the right side shows the different constituents and let's you select to extract

- one moiety of constituents in a new structure window,
- none, no moiety of constituent,
- all together, collect all moieties of a constituent in one new structure window,
- all separately, create for each moiety of a constituent a new structure window.

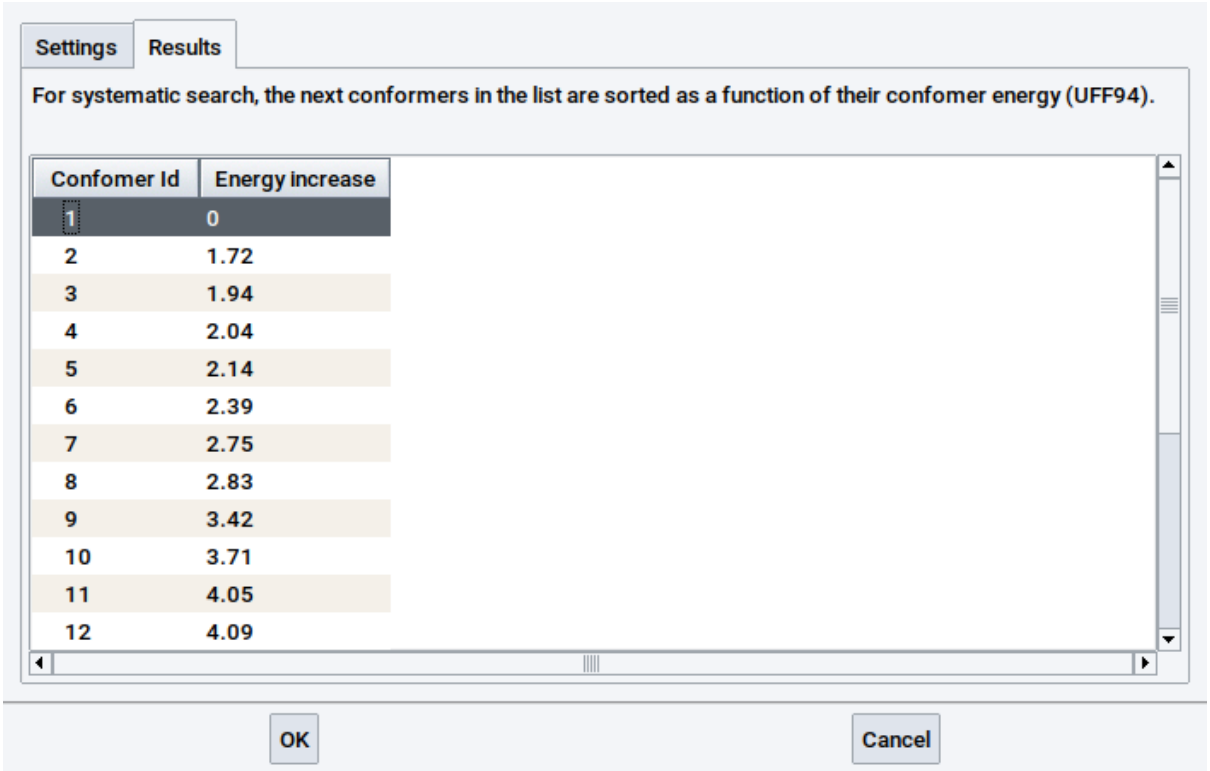
21 Conformers Search

Computing some properties may require considering all molecule conformers or at least a set of most representative conformers when they are too numerous. Identifying the interesting conformers of a molecule or set of molecules requires specific search and minimization routines. This tool is invoked from Builders >> Conformers search... and allows you to search molecule conformers, that can be chosen from *MedeA* windows or a file, containing a single molecule.

As an alternative, a SMILES string, that is quite commonly used and a convenient way to describe a molecule. SMILES stands for Simplified Molecular Input Line Entry Specification: specification in the form of a line notation for describing the structure of chemical molecules using short ASCII strings. The dialog allows you to type in or copy a SMILES string.



Once the molecule of interest is provided, the number of possible conformers is indicated (if this number is higher than 100,000,000 it will be simply mentioned so). According to this number, a search strategy is automatically set and one just needs to press " Find Conformer ". The search time depends on the complexity of the molecule, depending on the number of rotatable bonds and their number of local energy minima they have. When completed the resulting list of conformers is displayed in a table in the Results tab. The first of the list is the most stable conformer found.



The SMILES conversion and conformer search are performed by a separate program called automatically by *MedeA*. This program is built with the OpenBabel library (see http://openbabel.org) and is licensed

under the GPL conditions. This program follows the conditions of this license. The forcefield used for the search is the UFF94 that applies to a wide variety of molecules, so the conformers energies have to be understood relatively to this forcefield.

The available conformer search strategies are the following:

- Systematic : Search all possible conformers, rotating torsions step by step. This is suited for a small number of conformers.
- Weighted : Randomly rotates around the rotatable bonds in a molecule, the random choice of torsions is reweighed based on the energy of the generated conformer.
- Genetic Algorithm (GA) : Optimize the conformer energy using the UFF94 forcefield and preserve diversity in terms of different torsions values on rotatable bonds.

When the number of possible conformer is small, *MedeA* will select automatically the systematic search, if not the GA will be selected. But one can freely select the parameters through the advanced options.

For systematic or weighted search, the conformers in the list are sorted as a function of their conformer energy (UFF94). For the GA search, the following conformers are added according to their similarity with the previous conformers in the list. The similarity is a distance, which is defined by the number of different torsion values with respect to previous conformers. Similarity of 0 means identical.

Additional column provides:

- Similarity to first : Similarity to the most stable conformer.
- Average similarity : Average similarity to all other conformers in the list.
- Minimum similarity : Minimum similarity to all other conformers in the list.

22 Generic simple Forcefield (Minimization and Dynamics)

A generic simple forcefield is defined in *MedeA* to add the ability to clean (remove local stresses caused during building or construction) the active system. It is of a very generic form, covers all elements, and works with any system in *MedeA*.

It is defined with the following components:

- bonding potential : When 2 atoms are bonded, a reference bond length is defined as the sum of the valence radii, and the potential is proportional to the square deviation. If the bond order is aromatic, double , or triple a reducing factor is applied to the reference length.
- bond angles potential : The potential is proportional to the square deviation from a target angle. The target bond angle is determined generically according to the number of bonds and order, e.g. 120 degrees for 3 single bonds.
- improper torsion : Only defined for atoms having 3 bonds, will be minimal when the atom is in the same plane as its 3 connected atoms.
- non bonds interaction : Following a Lennard-Jones 6-12 form. Parameters are adjusted to fit the sum of Van der Walls radii
- electrostatic charge : A small positive charge is added creating an additional repulsive potential.

Because of their simplicity, these potentials cannot be effectively fitted (individually or as a whole) to reflect actual energy values. The default constants are determined empirically to maintain a good overall balance.

The generic simple forcefield is used for structure clean-up and optimization in two different manners, both available from the right-click context menu of a molecular or periodic P1 structure, and as a flowchart stage:

Simple forcefield minimization : perform a fast and interactive geometric optimization to avoid close distances or long bonds. This will not necessarily provide highly accurate geometries but in most cases it will provide a good starting point to search for it.

Simple forcefield dynamics : start with a pseudo molecular dynamics (not strictly defined temperature since the forcefield uses a crude energetic presentation only) for a limited number of steps followed by a geometric optimization. It can be applied repeatedly and displays intermediate conformations to illustrate the current geometry of the system. This option can be useful to relax a set of molecules or a single large molecule.

Note: If the result of simple forcefield minimization or simple forcefield dynamics does not match expectations, one can simply undo with (ctrl-Z) any structural changes.
