

Forcefield fitting with GULP: SnO₂ library derivation

Purpose: Explains how to use the Forcefield fitting task in GULP to obtain new potential parameters or to refine the existing ones.

Modules: Materials Visualizer, GULP

Time:  

Prerequisites: None

Introduction

The current libraries in GULP do not have parameters to describe the SnO₂ bulk structure. Therefore, to be able to model this material and to calculate its different properties with GULP, new forcefield parameters have to be derived. The Forcefield fitting task in GULP can be used to obtain those. The bulk modulus, some elastic constants and the experimental structure of SnO₂, have been used as observables in the forcefield fitting procedure.

This tutorial covers:

- [Getting started](#)
- [To define the forcefield types and functional forms](#)
- [To define the observables used in the fitting](#)
- [Fitting procedure](#)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the [Creating a project](#) tutorial for instructions on how to restore default project settings.

1. Getting started

Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **ff_library** as the project name, click the **OK** button.

The new project is created with *ff_library* listed in the Project Explorer. You will load the crystal structure of the system you will be studying later.

2. To define the forcefield types and functional forms

The first step when performing a forcefield fitting task is to define the forcefield types and functional forms that describe the different interactions in the system. For the case under consideration, you need to define Buckingham parameters for the O-O, Sn-O and Sn-Sn two body terms.

When creating a new library you can proceed in two different ways, you can create a new library file (.lib) from scratch or you can modify an existing one. In this tutorial you will create a new library from scratch for the SnO₂ case. A library is just a text document, so you must open a text document.

Click the **New** button  on the toolbar and select **Text Document** from the dropdown list. **Rename** the new text file to **SnO2.lib**.

You will be prompted that changing the extension may make the file unusable.

Click the **Yes** button to change the file extension.

Click the **GULP** button  on the **Modules** toolbar and choose **Calculation** from the dropdown list.

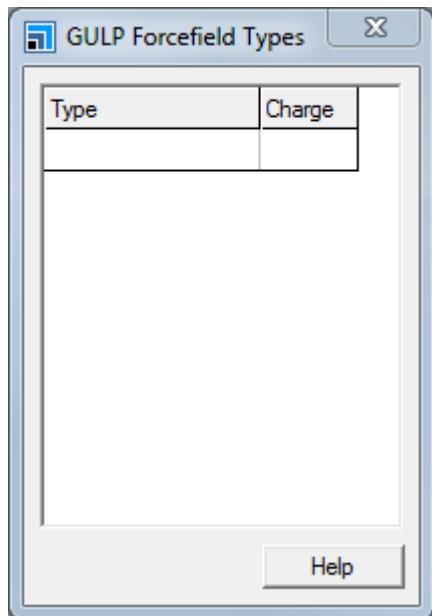
This opens the GULP Calculation dialog.

Change the **Task** to **Fit Forcefield**. Select **Browse...** from the **Forcefield** dropdown list to open the Choose GULP Forcefield dialog, then choose **SnO2.lib** from the dropdown list. Change the **Charges** to **Forcefield assigned** and click the **More...** button.

This opens the GULP Fit Forcefield dialog, before entering the potentials parameters, the atom types should be defined.

Click the **Types...** button.

This opens the GULP Forcefield Types dialog which lists atom types and charge definitions.

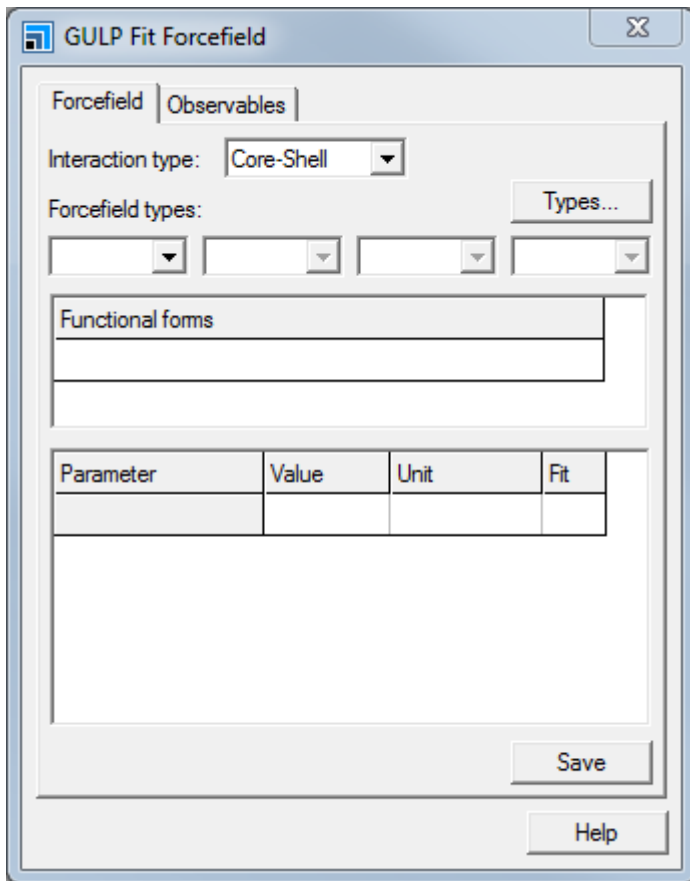


GULP Forcefield Types dialog

You are going to add two new atom types, Sn core and O core, with appropriate charges.

In the **Type** box enter **O core** and in the **Charge** box enter **-1.025**. On the next line, enter **Sn core** and **2.050**. Close the **GULP Forcefield Types** dialog.

You can now define the potential parameters on the GULP Fit Forcefield dialog.



GULP Fit Forcefield dialog, Forcefield tab

You need to define the functional form for each combination of potentials, O core - O core, Sn core - Sn core, and Sn core - O core.

Change the **Interaction type** to **Two-body**. In the **Forcefield types** section select **O core** as the first forcefield type and **O core** also for the second. In the **Functional forms** section, select **Buckingham (buck)** from the dropdown list.

Repeat this for the **O core - Sn core** and **Sn core - Sn core** combinations.

Next, you need to enter the following parameters for each case (these initial values are taken from *Bandura et al. J. Phys. Chem. B 2006, 110, 8386-8397*):

| Potential Pair | A (eV) | rho (Å) | C (eV*Å ⁶) | rmax (Å) |
|-------------------|---------|---------|------------------------|----------|
| O core - O core | 5000 | 0.273 | 48.7 | 15.0 |
| O core - Sn core | 100000 | 0.169 | 16.0 | 15.0 |
| Sn core - Sn core | 1000000 | 0.205 | 6.3 | 15.0 |

Change the **Forcefield types** back to **O core** and **O core**. Choose the **Buckingham(buck)** functional form. Scroll down the **Parameter** box and enter the values for the parameters as listed above. Repeat this for **O core - Sn core** and **Sn core - Sn core**.

Initially you will only fit the A parameters for the three two-body terms. You will then use the obtained A parameters to fit the rho parameters, and finally those to fit the C ones. You need to indicate that the A parameters are the ones you want to fit.

For each pair potential, in the **Fit** column check the corresponding box for the Buckingham **A parameter**. Click the **Save** button.

A new `.lib` file (`SnO2_2.lib`) with all the defined atom types and parameters is created, containing:

```
species
Sn core 2.05
O core -1.025
```

```

buck 1
Sn core Sn core 1000000.0000000000 0.2050000000 6.3000000000 &
0.0000000000 15.0000000000 1 0 0
Sn core 0 core 100000.0000000000 0.1690000000 16.0000000000 &
0.0000000000 15.0000000000 1 0 0
0 core 0 core 5000.0000000000 0.2730000000 48.7000000000 0.0000000000 &
15.0000000000 1 0 0

```


Close the **GULP Fit Forcefield** dialog.

3. To define the observables used in the fitting

To obtain the Buckingham parameters for the SnO₂ library, the following observables have been used in the fitting:

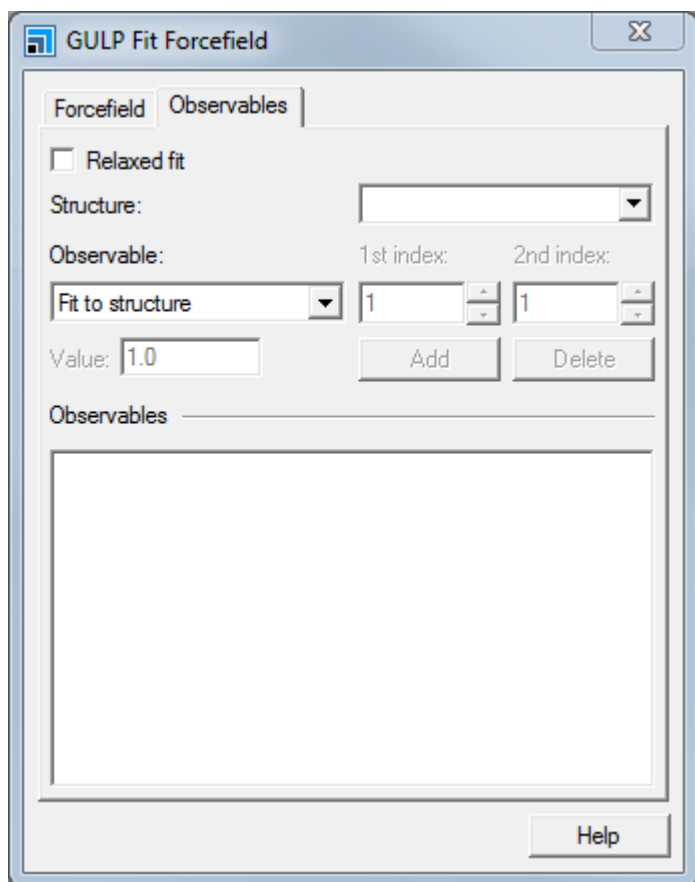
1. Experimental SnO₂ structure
2. Experimental bulk modulus: 212.3 GPa
3. Experimental elastic constants: C11 = 261.7, C33 = 449.6, C44 = 103.1, and C66 = 207.4 GPa.

Before defining all the above observables in the GULP Fit Forcefield dialog, you need to open the SnO₂ structure.

Click the **Import** button  on the toolbar to open the Import Document dialog. Navigate to the **Structures\metal-oxides** folder and double-click on **SnO2.msi**.

Once you have imported the structure, you can proceed to define all the observables in the dialog.

On the **GULP Calculation** dialog, check that the **Forcefield** is **\SnO2_2**. Open the **GULP Fit Forcefield** dialog and select the **Observables** tab.



GULP Fit Forcefield dialog, Observables tab

You will perform a relaxed fitting to obtain the SnO₂ library. The relaxed fit option fits to structural displacements on relaxation rather than to the derivatives. This also means any observables are fitted to the optimized rather than experimental structure.

Check the **Relaxed fit** checkbox. Select **SnO2.xsd** from the **Structure** dropdown list. To define the experimental structure as observable select **Fit to structure** from the **Observable** dropdown list.

As you want to fit to the structure, you need to add it to the observables.

Click the **Add** button.

The SnO₂ structure will appear in the Observables list on the GULP Fit Forcefield dialog. Now you will add the other observables that you want to fit to.

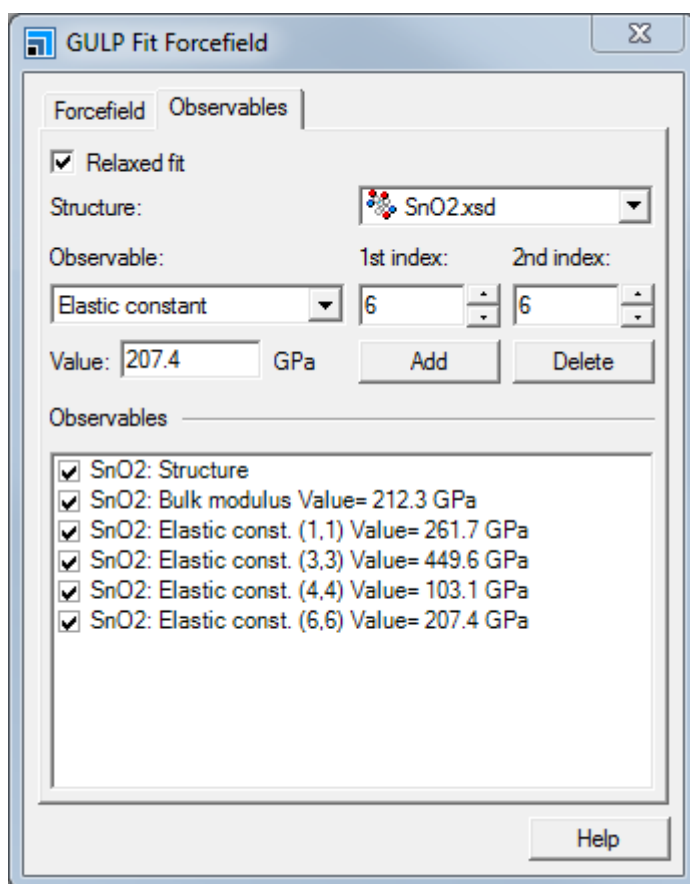
Change the **Observable** to **Bulk modulus**. Set the **Value** to **212.3** and click the **Add** button.

Change the **Observable** to **Elastic constant**. Ensure that the **1st Index** is set to **1** and the **2nd Index** is set to **1**. Set the **Value** to **261.7**. Click the **Add** button. Repeat this for:

1st Index = 3, 2nd Index = 3 and Value = 449.6

1st Index = 4, 2nd Index = 4 and Value = 103.1

1st Index = 6, 2nd Index = 6 and Value = 207.4.



GULP Fit Forcefield dialog Observables tab with values set as required

Close the **GULP Fit Forcefield** dialog and leave the GULP Calculation dialog open.

4. Fitting procedure

Now that the functional forms and observables have been defined, you can run the fitting calculation.

Click the **Run** button on the **GULP Calculation** dialog.

When the calculation is finished, the results of the fitting can be found in the **.gout** file. The new library is returned in the **.lib** file.

Open the GULP output file, **SnO2_2.gout**.

Tip: The contents of your output file may vary from this example.

In the .gout calculation you will find the new A parameters and also the value of the sum of squares, which gives an indication about the quality of the fitting, for example:

**** Fit completed successfully ****

Final sum of squares = 4.302300

Final gradient norm = 0.000286

Final values of parameters :

| Parameter No. | Parameter Original | Parameter Final | Parameter Type | Species |
|---------------|--------------------|-----------------|----------------|---------|
| 1 | 1000000.000000 | 404423.175101 | Buckingham A | |
| 2 | 100000.000000 | 88619.438577 | Buckingham A | |
| 3 | 5000.000000 | 4053.048025 | Buckingham A | |

Final values of numerical parameter gradients :

| Parameter No. | Parameter Gradient | Parameter Type | Species |
|---------------|--------------------|----------------|---------|
| 1 | -0.000013 | Buckingham A | |
| 2 | -0.000182 | Buckingham A | |
| 3 | -0.000220 | Buckingham A | |

Final values of residuals :

| Observable no. | Type | Observable | Calculated | Residual | Error(%) |
|----------------|---------------|------------|------------|----------|----------|
| 1 | Bulk modulus | 212.30000 | 211.95855 | 0.11659 | -0.161 |
| 2 | Elastic Const | 261.70000 | 268.06136 | 0.40467 | 2.431 |
| 3 | Elastic Const | 449.60000 | 448.42642 | 0.01377 | -0.261 |
| 4 | Elastic Const | 103.10000 | 97.62695 | 0.29954 | -5.308 |
| 5 | Elastic Const | 207.40000 | 203.19004 | 0.17724 | -2.030 |
| 6 | Structure | 4.73727 | 4.68035 | 3.24018 | -1.202 |
| 7 | Structure | 3.18638 | 3.18995 | 0.01269 | 0.112 |
| 8 | Structure | 0.30700 | 0.30506 | 0.03762 | -0.632 |

Comparison of initial and final observables :

| Observable no. | Type | Observable | Initial | Final |
|----------------|---------------|------------|-----------|-----------|
| 1 | Bulk modulus | 212.30000 | 198.30781 | 211.95855 |
| 2 | Elastic Const | 261.70000 | 255.18258 | 268.06136 |
| 3 | Elastic Const | 449.60000 | 457.46019 | 448.42642 |
| 4 | Elastic Const | 103.10000 | 97.16571 | 97.62695 |
| 5 | Elastic Const | 207.40000 | 188.18899 | 203.19004 |
| 6 | Structure | 4.73727 | 4.76579 | 4.68035 |
| 7 | Structure | 3.18638 | 3.27295 | 3.18995 |
| 8 | Structure | 0.30700 | 0.30498 | 0.30506 |

The .lib document will also be updated with the optimized value of A.

Open **SnO2_2 GULP Fit\SnO2_2.lib**.

The value for A has changed from 5000 to 4053.048.

As stated above, you will use the results obtained here for the A parameters to fit the rho parameters, and then again to obtain the C parameters. To this end, you need to modify the `.lib` file used in the calculation, you should define the parameters obtained here as new values for the calculation and indicate which parameters you want to fit.

Open the **GULP Calculation** dialog. Select **Browse...** from the **Forcefield** dropdown list to open the **Choose GULP Forcefield** dialog. Select the **SnO2_2.lib** document in the **SnO2_2 GULP Fit** folder.

The new forcefield document is imported.

Open the **GULP Fit Forcefield** dialog and check that the **Forcefield types** are **O core** and **O core**. Scroll down to the fitted parameters.

The value for A has been updated to 4053.

Note: The value for your forcefield may not be exactly the same as this example due to minor differences in calculations, this is expected.

Check the **Fit** checkbox for the **rho** parameter. Repeat this for the **O core - Sn core** and **Sn core - Sn core** pair potentials. Click the **Save** button.

A new forcefield, `SnO2_2 GULP Fit\SnO2.lib`, is created.

On the **GULP Calculation** dialog, change the **Forcefield** to **SnO2_2 GULP Fit\SnO2.lib** and click the **Run** button.

Once the calculation is complete, you need to fit for C.

Repeat the last few steps, opening the newly optimized forcefield and fitting for C.

The final library obtained for SnO₂ after fitting A, rho and C, is:

```
species
O core -1.025
Sn core 2.05

keyword
buck 1
O core O core 4053.0480000000 0.2729750000 43.4236690000 0.0000000000 & 15.0000000000 0 0 0
O core Sn core 88619.4390000000 0.1689920000 16.2778010000 & 0.0000000000 15.0000000000 0 0 0
Sn core Sn core 404423.1800000000 0.2049250000 39.3054100000 & 0.0000000000 15.0000000000 0 0 0
```

This is the end of the tutorial.