Precipitation Module (TC-PRISMA) User Guide

Thermo-Calc Version 2019b

Thermo-Calc Software
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Introduction to the Precipitation Module (TC-PRISMA)

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About the Precipitation Module (TC-PRISMA)

TC-PRISMA is no longer a standalone program. It is integrated into the Thermo-Calc Graphical Mode and considered an add-on module called the Precipitation Module. It is also available for all platforms (Windows, Mac and Linux). If you have older versions of the TC-PRISMA software that you want to uninstall, follow the instructions to remove this program component as described in the Thermo-Calc Installation Guide.

The Precipitation Module, previously referred to as TC-PRISMA, is an add-on module to the core Thermo-Calc software. The Precipitation Module itself is a general computational tool for simulating kinetics of diffusion controlled multi-particle precipitation processes in multicomponent and multiphase alloy systems.

Precipitation, formation of particles of a second phase, or second phases from a supersaturated solid solution matrix phase, is a solid state phase transformation process that has been exploited to improve the strength and toughness of various structural alloys for many years. This process is thermochemically driven and fully governed by system (bulk and interface) thermodynamics and kinetics.

Typically, a precipitation process has three distinctive stages: nucleation, growth, and coarsening. However, under certain conditions, these can also happen at the same time. With the Precipitation Module, the kinetics of concurrent nucleation, growth, and coarsening can be simulated by calculating the evolution of the probability distribution of the particle number densities, usually called particle size distribution (PSD). The simulation results can be used to understand and guide how to obtain desirable precipitates with certain PSD or to avoid undesirable precipitations during heat treatments of alloys such as aging and tempering. A summary for the input and output of the Precipitation Module is shown.
Input and Output of the Precipitation Module

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The Precipitation Module relies on CALPHAD-based software tools and databases to provide the necessary bulk thermodynamic and kinetic data for phases in multicomponent systems. The CALPHAD approach has been developed for more than 50 years and is routinely applied to design new alloys and optimize existing materials within various metal industries, such as steels and alloys of nickel, titanium, aluminum and magnesium.

The power of this approach is due to the adopted methodology where free energy and atomic mobility of each phase in a multicomponent system can be modeled hierarchically from lower order systems, and model parameters are evaluated in a consistent way by considering both experimental data and ab-initio calculation results. The Precipitation Module is directly integrated into Thermo-Calc, a CALPHAD-based computer program for calculating phase equilibrium. Another add-on module, the Diffusion Module (DICTRA) is available for diffusion controlled phase transformation in multicomponent systems.

With Thermo-Calc and the accompanying thermodynamic and mobility databases, almost all fundamental phase equilibrium and phase transformation information can be calculated without unnecessary and inaccurate approximations. For example you can calculate:

- Driving forces for nucleation and growth
- Operating tie-lines under local equilibrium conditions
- Deviations from local equilibrium at interfaces due to interface friction
- Atomic mobilities or diffusivities in the matrix phase
In addition to bulk thermodynamic and kinetic data, a few other physical properties, such as interfacial energy and volume, are needed in precipitation models. These additional physical parameters can be obtained by experiments or other estimation models or first principles calculations. Volume data for steels and nickel-based alloys have already been assessed and included in TCFE, TCNI, and TCAL databases. The Precipitation Module has an estimation model available for interfacial energy.

This guide is a supplement to the full Thermo-Calc documentation set. It is recommended that you use the Online Help: From the main menu in Thermo-Calc choose Help → Online help.

See Help Resources to learn how to access this information if you have not already done so.

Available Options

The Precipitation Module, previously referred to as TC-PRISMA, is an add-on module to the core Thermo-Calc software. A separate license is required to perform calculations for more than three elements. Without it you are able to use the module in Demo Mode.

Demonstration (Demo) Mode

PRECIPITATION SIMULATION TEMPLATE

A Precipitation Simulation template is available to all Thermo-Calc users.

If you are accessing the Precipitation Module in Demo Mode, see Demonstration (Demo) Mode for what is available to you.

Using the Template

When you first open Thermo-Calc in Graphical Mode, on the My Project window, click the Precipitation Simulation button to add a System Definer, Precipitation Calculator and Plot Renderer to the Project tree.

Click the Precipitation Simulation button in the templates section to add these nodes to the Project.
Creating a Project from a Template

**PRECIPITATION CALCULATOR**

A Precipitation Calculator allows you to set the conditions for, and perform, a precipitation calculation.

**DEMO DATABASE PACKAGES FOR THE EXAMPLES COLLECTION**

Both a thermodynamic and mobility database are required to run the Precipitation Module simulation. If you have a Precipitation Module (TC-PRISMA) license you can run all the examples as the demonstration database packages are included with your installation. Select the database packages from the System Definer → Configuration window to run a simulation.

If you are using the Precipitation Module in Demo Mode, see Demonstration (Demo) Mode to learn more.

**DEMONSTRATION (DEMO) MODE**
The Precipitation Module, and some examples, are available to all Thermo-Calc users but only for simulations of alloys with up to three elements. If you do not have a license for the Precipitation Module then you are in *Demonstration Mode* when using the Precipitation Calculator or Precipitation Simulation template.

**Precipitation Simulation Template**

When you are in DEMO mode, in the **Templates** area this is indicated by the text under the logo.

![PQ2 Precipitation Simulation DEMO](image)

**Precipitation Calculator**

If you are experimenting with the Precipitation Calculator in Demo Mode, you may have access to a variety of databases based on your license. However, you can only define up to three elements for a demo simulation.

If you define more than three elements on the System Definer, when you go to the Precipitation Calculator, the **Perform** button is unavailable and the tooltip explains why. In this case one of the chosen elements needs to be removed and then the Perform button is made available.

![PQ2 Precipitation simulations in Demo mode limited to three elements only](image)

Even if you have more than three elements, the Plot Renderer or Table Renderer **Perform** button is still available. However, if you click the button and try to run the simulation the Event Log displays an error message.

**Network License Restrictions**

The Precipitation Module (TC-PRISMA) requires a separate license. If you are using a network client installation of Thermo-Calc, then you may not be able to use it even if you have access to a license server with a valid network license file. The reason for this is because other clients who are part of your network installation may have checked out all instances of the network license allowed to run simultaneously.
For users with a network license, you must exit Thermo-Calc to release the license for other users. The license is checked out as soon as you add a Precipitation Calculator and remains unavailable to other users until you exit the program.

With a network license, and if as per above you temporarily do not have access to a license, you are automatically put into Demo Mode. Then the Precipitation Calculator is available with three elements.

Search the online help or see the Thermo-Calc Installation Guide for more about network licenses.

**Selecting the Disordered Phase as a Matrix Phase**

The following information is about using disordered Fcc as a matrix phase with the following thermodynamic and mobility database packages:

- TCCU and MOBCU (Cu-based alloys)
- TCNI and MOBNI (Ni-based alloys)

In the TCNI/MOBNI and TCCU/MOBCU packages, the well-known order/disorder two-sublattice model is used to describe the Gibbs energy of both FCC_A1 and FCC_L12. With this treatment, FCC_L12 is becoming FCC_A1 if the site fractions of each element on both sublattices are identical, which means that FCC_A1 is only a special case of FCC_L12. Therefore, FCC_A1 is not shown in the phase list on the Phases and Phase Constitution tab on the System Definer activity and in subsequent equilibrium calculation results. Instead it is shown only as FCC_L12. The real ordered FCC_L12 is shown as FCC_L12#2.

In precipitation simulations, the matrix phase is quite often the disordered FCC phase. You can directly select FCC_L12 as the matrix phase and run a simulation. However, the speed is not optimal due to the sophisticated model used for both Gibbs energy and atomic mobilities. A better and more convenient way is to deselect FCC_L12 and FCC_L12#2 from the phase list on the Phases and Phase Constitution tab on the System Definer if the ordered phase is irrelevant in the alloy under investigation, such as in most Cu alloys. Once these are unchecked (i.e. not selected), the FCC_A1 phase is available and can later be selected as the matrix phase.

For Ni-based superalloys using the TCNI/MOBNI package, the ordered FCC_L12#2 (gamma prime) has to be included as the precipitate phase in most of calculations. In this case, you can select DIS_FCC_A1 from the phase list on the Phases and Phase Constitution tab and then select it as the matrix phase in the Precipitation Calculator.
Help Resources

'Online' Help: No Internet Required

To access online help in a browser, open Thermo-Calc and press <F1> on the keyboard, or select Help → Online Help.

The content opens in a browser but uses local content so you don't need an Internet connection except for links to external websites.

Context Help (Graphical Mode Only)

When you are in Graphical Mode, you can access feature help (also called topic-sensitive or context help) for the activity nodes in the tree.

1. In the Project window, click a node. For example, System Definer.

2. In the lower left corner of the Configuration window, click the help button 📜.

3. The Help window opens to the relevant topic.

The window that opens has the same content as the help you access in the browser. There are these extra navigation buttons in this view.

- Use the buttons on the bottom of the window, to navigate Back and Forward (these are only active once you have started using the help
Console Mode Help

Console Mode is for Thermo-Calc and the Diffusion Module (DICTRA).

In Console Mode at the command line prompt, you can access help in these ways:

- For a list of all the available commands in the current module, at the prompt type a question mark (?) and press <Enter>.
- For a description of a specific command, type Help followed by the name of the command. You can only get online help about a command related to the current module you are in.
- For general system information type Information. Specify the subject or type ? and the available subjects are listed. This subject list is specific to the current module.

Typographical Conventions

The following typographical conventions are used throughout the documentation, both online and in the PDF documents.

### TEXT

<table>
<thead>
<tr>
<th>Convention</th>
<th>Definition</th>
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</thead>
<tbody>
<tr>
<td>Forward arrow symbol →</td>
<td>The forward arrow symbol → instructs you to select a series of menu items in a specific order. For example, <strong>Tools → Options</strong> is equivalent to: From the <strong>Tools</strong> menu, select <strong>Options</strong>.</td>
</tr>
<tr>
<td><strong>Boldface</strong> font</td>
<td>A <strong>boldface</strong> font indicates that the given word(s) are shown that way on a toolbar button or as a menu selection. For example, if you are told to select a menu item in a particular order, such as <strong>Tools → Options</strong>, or to click <strong>Save</strong>.</td>
</tr>
<tr>
<td><strong>Italic</strong> font</td>
<td>An <em>italic</em> font in the body of the text indicates the introduction of important terminology. Expect to find an explanation in the same paragraph or elsewhere in the guide.</td>
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<tr>
<td>Convention</td>
<td>Definition</td>
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<tr>
<td><strong>COMMAND</strong></td>
<td>For features in Thermo-Calc that use Console Mode (i.e. the command line), this font and all capital letters indicates that this is a Console Mode COMMAND. Examples of how you can use a command are written with code font. For example: Use <code>DEFINE_ELEMENTS</code> followed by a list of the elements that you want in your system. (To list the elements that are available in your current database, use <code>LIST_DATABASE</code> and choose <code>Elements</code>).</td>
</tr>
<tr>
<td><strong>HELP</strong></td>
<td>Text in blue and underline and a page number is a link to another topic in the current or referenced guide. Command names are often also topics. Clicking the link takes you to more detail about a particular command or subject in the PDF or documentation set.</td>
</tr>
<tr>
<td><code>&lt;Enter&gt;</code></td>
<td>Text with &lt;angle brackets&gt; indicates a keyboard entry. Usually to press <code>&lt;Enter&gt;</code> (or Return) or to use a series of keys such as <code>&lt;Ctrl + S&gt;</code>.</td>
</tr>
<tr>
<td><strong>code and code bold</strong></td>
<td>A code font shows a programming code or code example. The code bold font highlights the entry.</td>
</tr>
<tr>
<td><strong>click vs press</strong></td>
<td>In general, you <strong>click</strong> with the mouse to perform an action on the screen (e.g. click <strong>Save</strong>) and you <strong>press</strong> keys on a keyboard to enter a set of commands (e.g. press <code>&lt;Ctrl + S&gt;</code>). When working in Console Mode, you can use keyboard shortcuts. Sometimes a window opens where you have the option to <strong>Save</strong>, <strong>Cancel</strong> or <strong>Open</strong> a file, for example. In these cases the instructions might say <strong>click Save</strong>, whereas you would need to <strong>press</strong> the applicable keys to perform the action.</td>
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### ICONS

<table>
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<tr>
<td><strong>Important</strong></td>
<td>Provides important information. It is recommended that you read the text or follow the link.</td>
</tr>
<tr>
<td>Convention</td>
<td>Definition</td>
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<tr>
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</tr>
<tr>
<td>Note</td>
<td>The information can be of use to you. It is recommended that you read the text or follow the link to more information.</td>
</tr>
<tr>
<td>Also see</td>
<td>Go to the link or guide to see more general information about the topic being discussed. Usually includes both text and a link.</td>
</tr>
<tr>
<td></td>
<td>The small blue arrow is used when there is one (sometimes two) cross reference and no text describing the link. Often used in settings pages to link you to accompanying theory or extra detail.</td>
</tr>
<tr>
<td>Tip</td>
<td>This is general information that can be of use but is not required knowledge.</td>
</tr>
<tr>
<td>Examples</td>
<td>Go to the example collection to learn more.</td>
</tr>
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<td>Console Mode</td>
<td>This note relates specifically to something in Console Mode.</td>
</tr>
<tr>
<td>Graphical Mode</td>
<td>This note relates specifically to something in Graphical Mode.</td>
</tr>
<tr>
<td>Diffusion Module</td>
<td>This indicates that the information relates to the add-on Diffusion (DICTRA) Module.</td>
</tr>
<tr>
<td>Precipitation Module</td>
<td>This indicates that the information relates to the add-on Precipitation Module.</td>
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Using the Precipitation Calculator

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Precipitation Calculator

A Precipitation Calculator allows you to set the conditions for, and perform, a precipitation calculation. You can add the calculator to the System Definer directly (right-click and select it from the Create New Successor menu) or use the Precipitation Simulation template.

Once you have added a Precipitation Calculator, the Configuration window has these settings tabs:

- **Conditions**: Set the conditions for your calculation that define the Matrix and Precipitate phases. Choose the Calculation Type.
- **Options**: Modify Numerical Parameters that determine how the conditions are calculated. The Growth rate model can be set to Simplified or Advanced mode.

Define the Precipitation Calculator

1. Add a Precipitation Calculator node to the System Definer. If you used the Precipitation Simulation template, click the node to display the Configuration settings window.
2. In the Precipitation Calculator Configuration window, enter the settings described in Conditions Tab Settings. Additional advanced options settings are also available and described Option Tab Settings.
3. Once you have finished defining the Precipitation Calculator, you also choose settings on the Plot Renderer. Some additional settings are specific to the Plot Renderer.

- Selecting the Disordered Phase as a Matrix Phase

Conditions Tab Settings

Below are details about the settings available from the Conditions tab.
You can change these settings locally for a specific Precipitation Calculator or globally for some defaults in the Options settings. To open the Options window: From the main menu select Tools → Options. Click the Graphical Mode tab then click Precipitation.

**SHOW OR HIDE DETAILS**

Click Show details (found to the right of the section) to view some of the additional settings listed below. You can also set the default to display in Phase view mode under Tools → Options → Graphical Mode, then click the Precipitation node.
**Composition Unit**

Choose from **Mass percent**, **Mole percent**, **Mass fraction** or **Mole fraction**.

**Matrix Phase**

**Phase**

Only phases with kinetic data can be selected as the matrix phase. If the list is empty, go to the System Definer to confirm that both thermodynamic and kinetic databases are selected and defined.

Choose a **Phase** from the list. The list is based on the settings for the System Definer. When setting up a system, choose a matrix phase with kinetic data available in the database.

**Elastic properties**

**Homogeneous Nucleation**

Choose **Disregard** to ignore the elastic properties.

Default elastic constants for **Isotropic** or **Cubic** are based on the major element of the alloy system. The elastic properties can affect nucleation rate, nuclei size, and particle shape.

- For **Isotropic**, enter values for **Shear modulus** (in GPa) and **Poisson's ratio** as required.
- For **Cubic**, enter values for **c11**, **c12** and **c44** as required. **c11**, **c12**, **c44** are the elastic constants.

**Molar volume**

Use the **Database** value (if the molar volume for the phase is defined in the thermodynamic database) or select **User-defined** to enter another value.

**Grain size**
The **Grain size** value changes the available nucleation sites when **Grain boundaries, Grain edges**, or **Grain corners** is selected along with **Calculate from matrix settings** in the Precipitate Phase. Enter a numerical value and choose a unit from the list. The default is 1.0E-4 m.

See Precipitation Morphology and The Number of Available Heterogeneous Nucleation Sites for more information.

**Grain aspect ratio**

The **Grain aspect ratio** value changes the available nucleation sites when **Grain boundaries, Grain edges**, or **Grain corners** is selected along with **Calculate from matrix settings** in the Precipitate Phase. Enter a numerical value. The default is 1.0.

See Precipitation Morphology and The Number of Available Heterogeneous Nucleation Sites for more information.

**Dislocation density**

The **Dislocation density** value changes the available nucleation sites when **Dislocations** is selected along with **Calculate from matrix settings** in the Precipitate Phase. Enter a numerical value. The default is 5.0E12 m\(^{-3}\).

See Precipitation Morphology and The Number of Available Heterogeneous Nucleation Sites for more information.

**Mobility enhancement prefactor**

A parameter that multiplies to the mobility data from a database. This value scales the mobility by a constant amount. This can be useful, for example, when the material has a higher than normal vacancy concentration at the start of the precipitation simulation. (e.g. from a prior solutionizing and quenching treatment).

**Mobility enhancement activation energy**

A value that adds to the activation energy of mobility data from a database. This value scales the mobility by a temperature dependent amount. Similar usage as mobility enhancement prefactor.

**Precipitate Phase**

**Phase**
The phases available to choose have both thermodynamic and kinetic data. If the list is empty, go to the System Definer to confirm that both types of databases are selected and defined.

**System Definer**

Choose a Phase from the list. The list is based on the System Definer settings.

**Nucleation sites**

- **Homogeneous Nucleation and Heterogeneous Nucleation**

  The number of different nucleation sites is dependent on the shape and size of grains in the matrix. Choose one of the following from the list:

  - **Bulk, Grain boundaries, Grain edges, Grain corners, or Dislocations.**
  - **For Grain boundaries, Grain edges and Grain corners, enter the Wetting angle (0-90)** in addition to the matrix settings. Wetting angle defines the deviation from spherical shape (or dihedral angle).

  Click to select the Calculate from matrix settings check box if you want to calculate the number density of sites from the matrix grain size or dislocation density.

  To enter a specific value for the number of Nucleation sites, deselect the check box.

**Interfacial energy**

- **Estimation of Coherent Interfacial Energy and Interfacial Energy Anisotropy**

  Choose Calculated to use the estimated value. To adjust the estimate, enter a different prefactor or choose User-defined to enter a value in J/m². For the User-defined option, you can also enter it as a function of radius (r) and temperature (T).

**Growth rate model**

Select Simplified, General, Advanced, Paraeq or NPLE. All models treat a particle (precipitate) of stoichiometric composition or with negligible atomic diffusivity. Local equilibrium or paraequilibrium at the precipitate-matrix interface is assumed. See Growth for more information.
Morphology

Precipitation Morphology

Choose the particle shape: **Sphere** (default), **Cuboid**, **Plate** or **Needle**. Options are based on the Elastic properties selected for the Matrix phase:

- For **Cubic**, **Sphere**, **Plate**, **Needle** and **Cuboid** are available.
- For **Isotropic**, **Sphere**, **Plate** and **Needle** are available.

For **Plate** or **Needle**, select the **Calculate aspect ratio from elastic energy** check box or enter a numerical value in the **Aspect ratio** field to provide a constant aspect ratio. See **Particle Shape Determination** for information.

*Figure 1: The cuboid shape is described by a supersphere. Cuboids have six faces, which form a convex polyhedron.*
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**Figure 2:** The plate is described as oblate spheroid. Oblate spheroids have rotational symmetry around an axis from pole to pole.

**Figure 3:** The needle shape is described as prolate spheroid. A prolate spheroid is a surface of revolution obtained by rotating an ellipse about its major axis.

**Transformation strain**

Choose **Disregard** to ignore the transformation strain. When **Isotropic** or **Cubic** is chosen in **Elastic properties** in Matrix Phase, you can also choose **Calculated from molar volume** to obtain a purely dilatational strain. If **Plate** or **Needle** is selected as the **Morphology**, you can alternatively choose **User-defined** and enter the properties for $\varepsilon_{11}$, $\varepsilon_{12}$, $\varepsilon_{13}$, $\varepsilon_{22}$, $\varepsilon_{23}$, and $\varepsilon_{33}$. See **Particle Shape Determination** for more information.

**Molar volume**

Use the **Database** value (if the phase molar volume is defined in the thermodynamic database) or select **User-defined** to enter another value.

**Phase boundary mobility**

A parameter that accounts for interface-controlled growth. Only effective if a very small, positive value is used. Use with caution due to a tentative treatment. See **Simplified Growth**
Rate Model for more information.

**Phase energy addition**

An energy value that adds to the Gibbs free energy of the precipitate phase from a database. See Simplified Growth Rate Model for more information.

**Approximate driving force**

Select the check box to include this if simulations with several compositions sets of the same phase create problems. See Nucleation Theory for more information.

**Preexisting size distribution**

Select the check box to include this. Click Edit particle size distribution to open the Preexisting Particle Size Distribution window where you can edit the parameters and view a graph comparing the radius and number density for the selected component.

Press F1 and search for "Particle Size Distribution (PSD)" for detailed instructions.

See examples P_10 and P_11

**Calculation Type**

**Isothermal**

Use an Isothermal calculation type to do a precipitation simulation at constant temperature. Choose a unit of measurement and enter a numerical value for the Temperature and Simulation time.

See examples P_01, P_02, P_04, P_05, P_08 and P_09

**Non-isothermal**

Nucleation During a Non-isothermal Process

Use a Non-isothermal calculation type to do a precipitation simulation with a user-defined temperature profile. Select a Temperature unit and Time unit from the lists. Enter a numerical value for the Simulation time.
Click **Edit thermal profile** to enter thermal profile **Temperature** and **Time** coordinates into a table. A minimum of two points is required. You can also **Import** to add your own **Thermal profile** from a text file in *.xls, *.xlsx, or *.csv* formats.

![Edit Thermal Profile](image)

See example [P_06](note).

**TTT diagram**

Use a **TTT-diagram** to calculate the time-temperature-transformation (TTT) curve for the formation of the precipitate phase.

- **Temperature**: Enter **Min**, **Max**, and **Step** numerical values and choose a temperature **Unit**.
- **Max annealing time**: Enter a numerical value and choose a time **Unit**.
- **Stop criteria**: Choose **Volume fraction of phase** or **% of equilibrium fraction** and then enter a numerical value. For each temperature, the simulation stops when the stop criteria is fulfilled or if the maximum annealing time is reached, whichever happens first.

See example [P_03](note).

**CCT diagram**

Use a **CCT-diagram** to calculate the continuous-cooling-transformation (CCT) curve for
Precipitation

- **Temperature**: Enter Min and Max numerical values and choose a temperature **Unit**.
- **Cooling rate(s)**: Enter a range of values in the field, e.g., .01 .1 1 10 100. These values are equal to K/s, °C/s or °F/s per second based on the temperature **Unit** selected.
- **Stop criteria**: Enter a numerical value for the **Volume fraction of phase**. For each temperature, the simulation stops when the stop criteria is fulfilled.

See example **P.07**.

**Particle Size Distribution (PSD)**

See examples **P.10** and **P.11**

On the Precipitation Calculator you can set the pre-existing particle size distribution (PSD) parameters in the **Show details** section. The size distribution can be entered as a pre-defined distribution, by importing a file, or by manually entering information into a table.

**Accessing the 'Pre-existing size distribution' settings**

1. To the right of the **Precipitate Phase** settings fields, click **Show details**.

2. Click to select the **Preexisting size distribution** check box.
3. Click **Edit particle size distribution** to open the window as in example P_10.

![Image of particle size distribution window]

**Defining the Preexisting size distribution**

1. Under **Compositions**, choose a **Dependent component** from the list and enter the composition for the other component.

2. Under **Size Distribution** define the following:
   a. Choose a **Length unit**: m, μm, or nm.
   b. Choose a **Distribution**: LSW (Lifshitz-Slyozov-Wagner), **Normal**, **Log normal** or **From file**. You can also manually enter numbers into the table instead of importing a file.

   ![Image of particle size distribution table]

   c. For **LSW**, **Normal** and **Log normal**, enter a **Mean radius**.
   d. For **Normal** and **Log normal**, enter a value for the standard deviation (**Std**).
   e. For **From File**, click **Import** and navigate to the file containing the required information and click **Open**. This file can be in .xls, .xlsx, .csv or .txt formats. The
file should consist of two columns with values where the first column contains **radius** data and the second contains **number density** data.

f. For all options, choose an **Amount of phase**: **Volume percent** or **Volume fraction** and then enter a number in the field.

g. Once the **Distribution** is defined, click **Generate**.

**Option Tab Settings**

These settings are for the Precipitation Calculator and are located on the **Configuration** window → **Options** tab.

💡 You can change these settings locally for a specific Precipitation Calculator or globally in the **Options** settings. To open the Options window: From the main menu select **Tools → Options**. Click the **Graphical Mode** tab then click **Precipitation**.

**Numerical Parameters**

Click **Options** to go to these settings.

💡 For equations and details about these settings, see **Numerical Method**.

**Max time step fraction**

The maximum step time allowed for time integration as fraction of the simulation time. The default is 0.1.

**No. of grid points over one order of magnitude in radius**

Default number of grid points for every order of magnitude in size space. The default is 150.0.

**Max no. of grid points over one order of magnitude in radius**

The maximum allowed number of grid points in size space. The default is 200.0.

**Min no. of grid points over one order of magnitude in radius**

The minimum allowed number of grid points in size space. The default is 100.0.

**Max relative volume fraction of subcritical particles allowed to dissolve in one time step**
The portion of the volume fraction that can be ignored when determining the time step. The default is 0.01.

**Max relative radius change**

The maximum value allowed for relative radius change in one time step. The default is 0.01.

**Relative radius change for avoiding class collision**

Set a limit on the time step. The default is 0.5.

**Max overall volume change**

This defines the maximum absolute (not ratio) change of the volume fraction allowed during one time step. The default is 0.001.

**Max relative change of nucleation rate in logarithmic scale**

This parameter ensures accuracy for the evolution of effective nucleation rate. The default is 0.5.

**Max relative change of critical radius**

Used to place a constraint on how fast the critical radium can vary, and thus put a limit on time step. The default is 0.1.

**Min radius for a nucleus to be considered as a particle**

The cut-off lower limit of precipitate radius. The default is 5.0E-10 m.

**Max time step during heating stages**

The upper limit of the time step that has been enforced in the heating stages. The default is 1.0 s.

**Maximum relative solute composition change at each time step**

Set a limit on the time step by controlling solute depletion or saturation, especially at the isothermal stage. The default is 0.01.
Plot Renderer

The following is information about the settings available for a Plot Renderer when it is a successor to a Precipitation Calculator.

▶ In Thermo-Calc press F1 and search for "Plot Renderer".

There are also specific settings related to non-isothermal simulations that are detailed in this topic.

Plot Settings

Legend option
Select whether the diagram’s legend displays On or Off.

Axis variable
Set the state variable you want plotted along the X-axis and the Y-axis.

Select the Separate multimodal PSD check box to enter settings for Points, Excess kurtosis, Valley depth ratio and Minimum peak.

▶ See Non-Isothermal Simulations for definitions.

Axis type
Select the type of axis scale: Linear, Logarithmic, Logarithmic 10 or Inverse.

Limits
Specify the range along the axis to show in the plot. In the fields, enter the minimum and maximum values of the axis variable. You can also determine the step size between the tick marks along each axis.

Select the Automatic scaling check box to allow the program to set the limits.

Unit (Time X Axis)
Choose a Unit: Seconds, Hours, or Days.

Add an axis and Remove this axis buttons
Use the Add an axis and Remove this axis buttons to add additional X- and/or Y-axes to a
plot or to merge plots (to overlay one plot with another in the same diagram). When merging plots, you define this variable as the Z-axis.

**Axis Variables**

- **Mean radius**: Spherical radius of average volume of all particles for a specific phase and nucleation type, regardless of their actual shapes.
- **Critical radius**: Spherical radius of critical nuclei for a specific phase and nucleation type.
- **Matrix composition**: Instantaneous compositions of the matrix phase.
- **Precipitate composition**: To track the instantaneous composition of precipitate particles. In particular, it is useful to distinguish different composition sets of the same phase (for example, FCC_A1#2 and FCC_A1#3). Further choose **Solutions or All**.
- **Number density**: Instantaneous number of particles per unit volume for a specific phase and nucleation type.
- **Size distribution**: Number of particles varying with their sizes per unit volume per unit length, for a specific phase and nucleation type, at a specific time.
- **Number density distribution**: Retrieve the number density (number of particles per unit volume) of precipitates distributed in different particle sizes.
- **Volume fraction**: Instantaneous volume fraction for a specific phase and nucleation type.
- **Nucleation rate**: Instantaneous number of nuclei per unit volume per unit time for a specific phase and nucleation type.
- **Normalized driving force**: Instantaneous nucleation driving force per unit mole of elements for a specific phase and nucleation type. It is normalized with RT and therefore, dimensionless.
- **Mean cubic factor**: Average cubic factor of cuboid particles. Available only when cuboid is selected as the **Morphology**.

The following settings are available as indicated when **Needle, Plate** or **Cuboid** are selected as the **Morphology** in the **Precipitate Phase** section on the Precipitation Calculator.

- **Cubic factor distribution**: Variation of cubic factor with particle size at a specific time. Available with a cuboid morphology.
- **Mean aspect ratio**: Average aspect ratio of non-spherical particles. Available with a
needle or plate morphology. Note that this is always larger than 1, where 1 = a sphere.

- **Mean particle length**: Diameter of non-spherical particles along the longer axis. Available with a needle or plate morphology.
- **Aspect ratio distribution**: Variation of aspect ratio with particle size at a specific time. Available with a needle or plate morphology.

### Non-Isothermal Simulations

When doing non-isothermal simulations it is common that particles grow in different generations. This results in multi-modal size distributions. To correctly estimate the properties of these different generations of particles you need to separate the peaks of multi-modal distributions.

#### Separate multimodal PSD

When the **Separate multimodal PSD** check box is selected on a Plot Renderer activity for the Precipitation Calculator, the size distribution is evaluated at the given time steps and checked for multi-modal peaks. These are separated and used to calculate the specified property.

![Separate multimodal PSD](image)

It can be applied on the following plot properties:

- Mean radius
- Size distribution
- Number density
- Volume fraction

### Points

This field is available when **Mean radius, Number density** or **Volume fraction** is selected as the **Axis variable**. Since the evaluation of multi-modality at each time step is costly, you can specify how many evaluation **Points** to use. The points are geometrically distributed over the
time scale where nucleated particles are found. The default is 40 points.

**Time**

This field is available when Size distribution or Number density distribution is selected as the Axis variable. Enter one or a series of numbers in the field, separated by a space.

For example, if you enter 100.0, 1000.0 and 1.0E7 in the field:

![Graph showing size distribution over length with different time values plotted]

When you click Perform the times are plotted:

**Excess Kurtosis**

The Excess kurtosis number specifies the sensitivity when the program evaluates whether a curve is bimodal or not. The evaluation process calculates the excess kurtosis of the given size distribution and compares it with the input value. If the value is lower than the given value, the distribution is split. The excess kurtosis is a statistical measure that measures how peaked and how heavy tail a distribution has. For the definition used see [http://en.wikipedia.org/wiki/Kurtosis](http://en.wikipedia.org/wiki/Kurtosis). The default is 25.0.

**Minimum Separation Limit (Valley Depth Ratio)**
The Minimum Separation Limit is a rough method to prevent that noise or wiggles are interpreted as different distributions. If a local minima is encountered above this value the following peak is not interpreted as a new distribution. The valley depth ratio is the ratio of the minimum separation limit to the peak value. The default is 0.01.

**Minimum Peak**

Any separated peak below the entered Minimum peak value is removed. The default is 100000.0.

**Pause, Resume and Cancel Precipitation Calculations**

Precipitation calculations are often complex simulations that take some time to complete. Sometimes you may want or need to pause or resume a calculation, or make adjustments to your compositions and start again. You pause and resume from the Precipitation Calculator Configuration window.

**To Pause and Resume a Job**

1. Run the job (i.e. click Perform Tree). In the Scheduler, you can see the job listed and in the Event Log you can follow the progress of the calculation.

2. In the Project window, click the Precipitation Calculator node.

3. In the Configuration window at the bottom, click Pause. If there are intermediate
results available these will be listed in the **Event Log**.

4. When ready, click **Continue** to resume your calculations from the last time step or click **Discard** to discard the calculation (then click **Yes** or **No** on the window that opens).

**To Cancel a Job**

- In the **Scheduler** window, right-click the job you want to cancel and select **Cancel Job**.
Theoretical Models and Numerical Methods

In this section:

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Introduction to the Theory

Based on the theory from Langer-Schwartz (1980)¹ Precipitation Module (TC-PRISMA) adopts Kampmann-Wagner numerical (KWN) (1991)² method to simulate the concomitant nucleation, growth, and coarsening of precipitates in multicomponent and multiphase alloy systems. The KWN method is an extension of the original Langer-Schwartz (LS) approach and its modified (MLS) form, where the temporal evolution of the mean radius and particle density over the whole course of precipitation are predicted by solving a set of rate equations derived with certain assumptions for the rates of nucleation and growth, as well as the function of particle size distribution (PSD). The MLS approach differs from the LS with respect to the Gibbs-Thomson equations used for calculating equilibrium solubilities of small particles. The former applies the exact exponential form, whereas the latter takes the convenient linearized version. Instead of assuming a PSD function a priori and working with rate equations for determining only mean radius and particle density, the KWN method extends the LS and MLS approaches by discretizing the PSD and solving the continuity equation of the PSD directly. Therefore, the time evolution of the PSD and its \( n^{th} \) moment (0: number density; 1st: mean radius; 3rd: volume fraction) can be obtained altogether during the simulation. The key elements of the KWN method are the models for nucleation and growth under the mean field mass balance condition and the numerical algorithm for solving the continuity equation of the PSD. Coarsening comes out naturally without any ad hoc treatment.

The key elements of the KWN method and their relationship as implemented in the Precipitation Module (TC-PRISMA).

Integration of the Precipitation Module into Thermo-Calc

Precipitation Module (TC-PRISMA) is integrated with Thermo-Calc in order to directly get all necessary thermodynamic and kinetic information required in the KWN method. For industry relevant multicomponent alloys, thermodynamic and kinetic databases and calculation tools have to be used in order to obtain various quantities in the multicomponent models for nucleation and growth, such as the driving forces for the formation of embryos and their compositions, the atomic mobilities or diffusivities in the matrix, the operating interface compositions under local equilibrium conditions, the Gibbs-Thomson effect, and the deviation from local equilibrium due to interface friction etc. With Thermo-Calc and the Diffusion Module (DICTRA) as well as the accompanying databases, all these properties and effects can be calculated without unnecessary and inaccurate approximations.

In the following topics, various models and numerical methods implemented in Precipitation Module (TC-PRISMA) are introduced. Unless specified, spherical particles are assumed in the discussion.
Nucleation Theory

Precipitation starts from the nucleation of clusters that can be considered as embryos of new phases with distinctive structures or compositions. In a perfect single crystal, nucleation happens homogeneously. In an imperfect crystal or polycrystalline materials, nucleation tends to occur heterogeneously due to the presence of dislocations, grain boundaries, grain edges, and grain corners. These imperfections or defects reduce the nucleation barrier and facilitate nucleation. However, if supersaturation or driving force is very large homogeneous nucleation is also possible since all sites including those inside a grain can be activated.

The following sections further elaborate on this theory.

- Homogeneous Nucleation
- Heterogeneous Nucleation
- Nucleation During a Non-isothermal Process

Homogeneous Nucleation

The classic nucleation theory (CNT) [Kashchiev (2000)\(^1\) and Russell (1980)\(^2\)] has been extended for the purpose of modeling nucleation in multicomponent alloy systems. The time dependent nucleation rate \(J(t)\) is given by

\[
J(t) = J_s \exp \left( \frac{-\tau}{t} \right)
\]

[Eq. 1]

where

- \(J_s\) is the steady state nucleation rate,
- \(\tau\) is the incubation time for establishing steady state nucleation conditions, and
- \(t\) is the time.

The steady state nucleation rate \(J_s\) is expressed by

\[
J_s = Z\beta^* N_0 \exp \left( \frac{-\Delta G^*}{RT} \right)
\]

[Eq. 2]

where

---

• \( Z \) is the Zeldovich factor.
• \( \beta^* \) is the rate at which atoms or molecules are attached to the critical nucleus.
• \( N_0 \) is the number of available nucleation sites (of a particular type) per unit volume. In the case of homogeneous nucleation, each atom in the mother phase is a potential nucleation site.
• \( \Delta G^* \) is the Gibbs energy of formation of a critical nucleus.
• \( k \) is Boltzmann’s constant.
• \( T \) is absolute temperature.

The Gibbs energy of formation of a critical nucleus is expressed as

\[
\Delta G^* = \frac{16\pi \sigma^3}{3\left(\Delta G^{\alpha \rightarrow \beta}_{m} / V_m^\beta\right)^2}
\]

[Eq. 3]

where

• \( \sigma \) is the interfacial energy,
• \( \Delta G^{\alpha \rightarrow \beta}_{m} \) is the molar Gibbs energy change for the formation of the \( \beta \) precipitate of the critical composition \( X_i^\beta \) from the \( \alpha \) matrix, i.e. the maximum driving force for the \( \alpha \rightarrow \beta \) phase transformation
• \( V_m^\beta \) is the molar volume of the \( \beta \) precipitate phase.

If elastic strain energy is excluded, \( \Delta G^{\alpha \rightarrow \beta}_{m} \) is the chemical driving force for nucleation. There are two ways to calculate the nucleation driving force \( \Delta G^{\alpha \rightarrow \beta}_{m} \) and the critical composition \( X_i^\beta \), as shown in Figure 1 for a prototype binary system. The standard calculation, shown in Figure 1 (a), is to obtain the maximum driving force by finding the parallel tangent lines or surfaces passing through the alloy composition of the matrix, which is a routine calculation in the Thermo-Calc software. The approximate calculation, shown in Figure 1 (b), is performed by using the Gibbs energy difference corresponding to the equilibrium composition in the precipitate phase. It can be used when the standard calculation fails, mostly within a miscibility gap. Additionally, the standard calculation is also used for driving force under paraequilibrium conditions, while the approximate calculation is used for driving force under NPLE (Non-Partitioning Local Equilibrium) conditions.
Figure 1: Methods to calculate the nucleation driving force $\Delta G_m^{\alpha \rightarrow \beta}$ and the critical composition $X_i^\beta$. The left-hand side figure (a) is a standard calculation and the right-hand side (b) an approximate calculation.
Nucleation is a stochastic process and can be considered formally as a diffusion process or Brownian movement in the particle size space. Supercritical nuclei with radius slightly larger than the critical radius have a probability of passing back across the free energy barrier and dissolve in the matrix. The Zeldovich factor \( Z \) is a measure of such probability and is related solely to the thermodynamics of the nucleation process in

\[
Z = \frac{V_m^\beta}{2\pi N_A r^* \sqrt{\frac{\sigma}{kt}}}
\]

[Eq. 4]

where \( N_A \) is the Avogadro number and \( r^* \), the critical radius, is given by

\[
r^* = -\frac{2\sigma V_m^\beta}{\Delta G_m^{\alpha-\beta}}
\]

[Eq. 5]

The atomic or molecular attachment rate \( \beta^* \) reflects the kinetics of mass transport in the nucleation process and is given by Svoboda et. al (2004)\(^1\).

\[
\beta^* = \frac{4\pi r^* \alpha^4}{\sum_{i=1}^{k} \left( \frac{X_i^{\beta/\alpha} - X_i^{\alpha/\beta}}{X_i^{\alpha/\beta} D_i} \right)^2}^{-1}
\]

[Eq. 6]

where

- \( \alpha \) is the lattice parameter,
- \( X_i^{\beta/\alpha} \) and \( X_i^{\alpha/\beta} \) are the mole fractions of element \( i \) at the interface in the precipitate and matrix, respectively.
- \( D_i \) is the corresponding diffusion coefficient in the matrix.

The incubation time for an isothermal reaction is

\[
\tau = \frac{1}{\theta Z^2 \beta^*}
\]

[Eq. 7]

where \( \theta \) differs from one derivation to another. The value 2 from Feder et al. (1966)\(^2\) is adopted.

---


**Elastic Strain Energy**

Elastic strain energy, $E_{el}$, reduces the nucleation driving force, $\Delta G_{m}^{\alpha \rightarrow \beta}$ in Eq. 3, hence affecting nucleation rate and nuclei size. It also changes the shape of the particle by competing with interfacial energy.

**Cuboid Particle**

**Precipitation Morphology**

The numerical simulations by Onaka et al. (2003)\(^1\) indicate that the elastic strain energy is reduced almost linearly with increasing cubic factor $\eta$. Since the numerical simulations are computationally expensive, we assume that the elastic strain energy follows the linear relationship with $\eta$, and the elastic strain energy for spherical ($\eta = 1$) and cubic ($\eta = \sqrt{2}$) are calculated based on Khachaturyan’s approximation (1983, 2008)\(^2\):

\[ E_{el} = \frac{1}{2} (c_{11} + 2c_{12})c_{0}^{2}V[A_{1} + A_{2}] \]

where

- $c_{0}$ is the lattice misfit strain.
- $c_{11}, c_{12}, c_{44}$ are elastic constants in a cubic system.
- $V$ is particle volume
- $A_{1}$ and $A_{2}$ are expressed as

\[
A_{1} = 2 \frac{c_{11} - c_{12}}{c_{11}} - 12 \frac{c_{11} + 2c_{12}}{c_{11}} \frac{c_{11} - c_{12} - 2c_{44}}{c_{11} + c_{12} + 2c_{44}} I_{1}
\]

\[
A_{2} = -54 \frac{c_{11} + 2c_{12}}{c_{11}} \frac{(c_{11} - c_{12} - 2c_{44})^{2}}{(c_{11} + c_{12} + 2c_{44})(c_{11} + 2c_{12} + 4c_{44})} I_{2}
\]

with

**Sphere**

$\ I_{1} = \frac{1}{15} \quad I_{2} = \frac{1}{105}$

**Cubic**

$\ I_{1} = 0.006931 \quad I_{2} = 0.000959$

---


Ellipsoidal Particle (Plate and Needle)

Precipitation Morphology

Since they are ellipsoidal shape, it is convenient to use Eshelby’s theory (1957)\(^1\) and (1959)\(^2\) with a reasonable computational cost. The Eshelby’s tensor can be calculated by simply performing a surface integral over a unit sphere

\[
D_{ijkl} = -\frac{abc}{4\pi} \int_0^\pi \int_0^{2\pi} \Omega_{ij} n_k n_l \frac{\sin \theta}{\beta^3} \, d\phi d\theta
\]

where

- \(a, b, c\) are ellipsoid axes.
- \(n_i (i = 1, 2, 3)\) are unit directional vector normal to the spherical surface and \(\beta = \sqrt{(a^2 \cos^2 \phi + b^2 \sin^2 \phi) \sin^2 \theta + c^2 \cos^2 \theta}\)

For matrix phase with cubic crystal symmetry, we have for \(\Omega_{ij} (i, j = 1, 2, 3)\) See A. G. Khachaturyan (1983)\(^6\).

\[
\Omega_{ii} (\vec{n}) = \frac{c_{44} + (c_{11} - c_{12})(n_1^2 + n_2^2 + n_3^2))}{c_{44} D(\vec{n})}
\]

\[
\Omega_{ij} (\vec{n}) = -\frac{(c_{11} + c_{12})(1 + \xi n_i^n j)}{c_{44} D(\vec{n})} n_i n_j
\]

where

\[
\xi = \frac{c_{11} - c_{12} - 2c_{44}}{c_{44}}
\]

\[
D(\vec{n}) = c_{11} + \xi (c_{11} + c_{12})(n_1^2 n_2^2 + n_2^2 n_3^2 + n_3^2 n_1^2) + \xi^2 (c_{11} + 2c_{12} + c_{44}) n_1^2 n_2^2 n_3^2
\]

The Eshelby S tensor can then be calculated as

\[
S_{ijmn} = -\frac{1}{2} C_{lkmn} (D_{iklj} + D_{jkl})
\]

The total strain \(\epsilon^{ij}\) at each location inside the particle is related to its transformation strain (eigenstrain) \(\epsilon^*_{ij}\) as

---

\[ \epsilon_{ij} = S_{ijkl} \epsilon_{kl}^* \]

Combined with elastic stress calculated as
\[ \sigma_{ij} = C_{ijkl} (\epsilon_{kl} - \epsilon_{kl}^*) \]

The elastic strain energy can be then obtained
\[ E^{el} = -\frac{1}{2} \sigma_{ij} \epsilon_{ij}^* V \]

with \( V \) the particle volume.

**Spherical Approximation for Nuclei**

In the Precipitation Module, the user-input or calculated interfacial energy is assumed to be the coherent interfacial energy that applies to the habit plane, \( \sigma^\text{coh} \), consistent with the approximation made by the embedded interfacial energy model. When calculating the critical nuclei, the interfacial energy in Eq. 3 is assumed to be that of a spherical particle with constant specific interfacial energy \( \sigma^\text{sph} \). This is consistent with the fact that the nuclei tend to be spherical due to dominant interfacial energy. Interfacial energy penalty assuming a nucleus with pre-defined, and most likely large, aspect ratio is thus over-estimated, and has been found to shut down nucleation event abnormally.

Under spherical approximation, the elastic strain energy is calculated using spherical expression in Eq. 8 for spherical and cuboidal particles, or by setting \( a = b = c \) in Eq. 9 for ellipsoidal particles.

**Heterogeneous Nucleation**

All equations remain the same for the calculation of heterogeneous nucleation rate within the framework of classic nucleation theory (CNT), but the nucleation energy and available nucleation site are different.

To a first approximation, the nucleation energy may be calculated by assuming an effective interfacial energy for each heterogeneous nucleation site.

For a rigorous treatment of heterogeneous nucleation the effect of wetting angles need to be considered.

**Non-Spherical Particles and the Effect of Wetting Angle**

Precipitation Module (TC-PRISMA) References
Non-spherical particles have been considered for grain boundary (GB) precipitation. Three morphologies are implemented for grain boundary, grain edge and grain corner precipitation, respectively, as shown in Figure 1. The parameter that defines the deviation from spherical shape is wetting angle (or dihedral angle), $\theta$, as described in Figure 2 and taken from Clemm and Fisher (1955)$^1$.

![Figure 1: Non-spherical particles ($\beta$) that precipitate at grain boundaries of matrix phase ($\alpha$) (a) grain boundary (two-grain junction) (b) grain edge (three-grain junction) (c) grain corners (four-grain junction). Images taken from Zang (2004)$^2$.](image)

Some physical parameters, mainly in nucleation models, have to be modified for the effect of the wetting angle. The following discussions contribute to this effect.

---

**Shape Factors**

Following Clemm and Fisher, the eliminated grain boundary area between $\alpha - \alpha$ grains due to the formation of nucleus of a new phase $\beta$ is:

\[ A_{\alpha\alpha} = \pi r^2 \]

Where $r$ is the radius of curvature of the nucleus. The surface area of the nucleus is:

\[ A_{\alpha\beta} = 2\pi br^2 \]

and the volume of the nucleus is

\[ V = 4\pi cr^3 \]

The expression of $a$, $b$, $c$ in Eq. 1 and Eq. 3 for grain boundary (two-grain junction), grain edge (three-grain junction) and grain corner (four-grain junction) can be found in the paper by Clemm and Fisher (1955).\(^1\)

**Critical Radius and Activation Energy**

The energy change due to the formation of the new particle is thus

\[ \Delta F = \frac{\Delta G_{m}^{\alpha\beta}}{V_m} \cdot c\pi r^3 \cdot b\pi r^2 \sigma_{\alpha\beta} - a\pi r^2 \sigma_{\alpha\alpha} \]

where $\sigma_{\alpha\beta}$ and $\sigma_{\alpha\alpha}$ are the interfacial energy and grain boundary energy, respectively.

Then the critical radius should be

\[ r^* = \frac{-2(b\sigma_{\alpha\beta} - a\sigma_{\alpha\alpha})V_m}{3c\Delta G_{m}^{\alpha\beta}} \]

And the activation energy barrier for nucleation is

\[ W = \frac{4}{27} \left( \frac{b\sigma_{\alpha\beta} - a\sigma_{\alpha\alpha}}{c^2 (\Delta G_{m}^{\alpha\beta})^2} \right)^3 V_m^2 \]

The interfacial energy, grain boundary energy and wetting angle can be related as

\[ k = \cos \theta = \frac{\sigma_{\alpha\alpha}}{2\sigma_{\alpha\beta}} \]

i.e.
\[
\sigma_{\alpha\alpha} = 2k\sigma_{\alpha\beta}
\]

Which can be replaced into Eq. 5 and Eq. 6.

\[
r^* = -\frac{2(b - 2ak)\sigma_{\alpha\beta} V_m}{3c\Delta G_m^{\alpha\rightarrow\beta}}
\]

\[
W = \frac{4}{27} \frac{\sigma_{\alpha\beta}^3 V_m^2}{(\Delta G_m^{\alpha\rightarrow\beta})^2} \frac{(b - 2ak)^3}{c^2}
\]

The bulk, spherical precipitation equation is recovered by:

\[
a = 0, \quad b = 4\pi, \quad c = \frac{4\pi}{3}
\]

so that

\[
r^* = -\frac{2\sigma_{\alpha\beta} V_m}{\Delta G_m^{\alpha\rightarrow\beta}}
\]

\[
W = \frac{16\pi}{3} \frac{\sigma_{\alpha\beta}^3 V_m^2}{(\Delta G_m^{\alpha\rightarrow\beta})^2}
\]

And also the grain boundary precipitation with spherical shape (with weighting angle 90°) follows Eq. 12 and Eq. 13 by \(k = \cos \theta = 0\).

**Zeldovich factor**

The Zeldovich factor is modified as

\[
Z = Z_b \sqrt{f}
\]

with \(Z_b\) the original value, and \(f\) the volume factor that is the ratio of the \(c\) in Eq. 3 to the spherical shape factor \(4\pi/3\).

\[
f = \frac{3c}{4\pi}
\]

**Impingement rate**

The surface area factor in impingement rate calculation is changed from \(4\pi(r^*)^2\) to \(b(r^*)^2\).
**Nucleation site density**

In each time step, the occupied grain boundary area

\[ A_{\text{red}} = a \cdot n r^{-2} \]  

is deducted when calculating available nucleation site density.

**Growth rate**

The radius \( r \) defined in previous equations is the curvature of the precipitate surface (the Big radius) as shown in Figure 2. It is exactly the definition in the growth rate whose coarsening consideration relates to the curvature effect. Therefore, the growth rate equation can be directly used with \( r \) being defined here. Again, for bulk, spherical precipitation it automatically corresponds to the particle radius.

**Output**

The volume of the precipitate should be calculated appropriately as \( cr^3 \) with \( r \) being the curvature of the particle surface as defined above. For output of the particle size (mean radius, critical radius and particle size distribution) in the user interface, it seems better to use the radius of the eliminated grain boundary area, i.e.

\[ r' = \sqrt{\frac{\alpha}{\pi}} \cdot r \]  

[Eq. 17]

With \( \alpha \) defined in Eq. 1.

For example, the size of the precipitate at grain boundary (two-grain junction) is the radius of the lens shown in Figure 2.

\[ r' = r \sin \theta = r \sqrt{1 - k^2} \]

**The Number of Available Heterogeneous Nucleation Sites**

Figure 3: An example of tetrakaidecahedron approximation of grains
The number of different nucleation sites is dependent on the shape and size of grains in the matrix. Assuming all grains are equally large tetrakaidecahedra with the distance between one pair of square faces as $H$, and that between the other two pairs as $D$ we obtain the densities $\rho_2$, $\rho_1$, and $\rho_0$ for the grain boundary area, edge length, and grain corner number respectively in

\[ \rho_2 = \frac{6\sqrt{1 + 2A^2} + 1 + 2A}{4A} D^{-1} \]

\[ \rho_1 = \frac{2\sqrt{2} + 2\sqrt{1 + A^2}}{A} D^{-2} \]

\[ \rho_0 = \frac{12}{A} D^{-3} \]

where $A = H/D$ is the aspect ratio, defining the degree of elongation of the grains.

By default, the aspect ratio is set to 1 and the densities are then the same as obtained by Cahn (1956)\(^1\). Once the densities are known, if taking boundary thickness as one atomic layer, the available nucleation sites can be calculated by

\[ N_i = \rho_i \left( \frac{N_A}{V_m} \right)^{i/3} i = 2, 1, 0 \]

where $V_m$ is the molar volume of the matrix phase and $N_A$ is the Avogadro number.

For a crystalline material, given a dislocation density $\rho_d$, the number of nucleation sites at the dislocations $N_d$ can be calculated with the same form as in

\[ N_d = \rho_d \left( \frac{N_A}{V_m} \right)^{1/3} \]

**Nucleation During a Non-isothermal Process**

Under non-isothermal conditions, temperature dependency of key parameters such as nucleation driving force, solute diffusivities and solute concentrations, etc., have been taken into account, and are updated automatically during a simulation.

Another important parameter that depends on thermal history is the incubation time, defined by

---

for an isothermal condition. In a non-isothermal process, the exact calculation of the incubation time requires a solution to the Fokker-Planck equation. In the Precipitation Module, an approximation approach has been employed to deal with the transient nucleation, which gives the incubation time as an integral form of past thermal history\(^1\) as in

\[
\int_0^\tau \beta^*(t') dt' = \frac{1}{\theta Z^2(\tau)}
\]

where

\(\tau\) is the incubation time, \(\beta^*\) is the impingement rate for solute atoms to the critical cluster as defined in

\[
\beta^* = \frac{4\pi r^2 \alpha^4}{\sigma} \left[ \sum_{i=1}^{k} \left( X_i^{\beta/\alpha} - X_i^{\alpha/\beta} \right)^2 \right]^{-1}
\]

and \(Z\) is the Zeldovich factor, previously defined in

\[
Z = \frac{V_m^\beta}{2\pi N_A r^*^2} \sqrt{\frac{\sigma}{kT}}
\]

but now as a function of \(\tau\) derived from temperature change.

The starting point of the integral \(t' = 0\) is either the starting time if there is an initial nucleation driving force, or the latest time when the nucleation driving force is vanished.

**Growth**

**Spherical Particles**

The growth rate models implemented in the Precipitation Module are called Advanced, Simplified and General. All models treat a spherical particle (precipitate) of stoichiometric composition or with negligible atomic diffusivity. Local equilibrium at the precipitate-matrix interface is assumed.

---

Advanced Growth Rate Model

The Advanced model is proposed by Chen, Jeppsson, and Ågren (CJA) (2008)\(^1\). In this model, the velocity of a moving phase interface and the operating tie-line are solved together from flux-balance equations. This model can treat both high supersaturation and cross diffusion rigorously. It can also capture the transition between NPLE (non-partitioning local equilibrium) and PLE (partitioning local equilibrium) without any *ad hoc* treatment.

According to the CJA model, the interface velocity \( v \) can be obtained together with interface concentrations by numerically solving \( 2n - 1 \) equations, comprising of the flux balance equations for \( n - 1 \) independent components and the local equilibrium conditions for all \( n \) components as in

\[
v(c_i^{\beta/\alpha} - c_i^{\alpha/\beta}) = c_i^{\alpha/\beta} M_i \frac{\mu_i^\alpha - \mu_i^{\alpha/\beta}}{\xi_i r}
\]

*Eq. 1*

\[
\mu_i^{\alpha/\beta} = \mu_i^{\beta/\alpha} + \frac{2\sigma V_m^\beta}{r}
\]

*Eq. 2*

where

- \( c_i^{\beta/\alpha} \) and \( c_i^{\alpha/\beta} \) are the volume concentrations of component \( i \) at the interface in the precipitate and matrix, respectively,
- \( M_i \) is the corresponding atomic mobility in the matrix,
- \( \mu_i^\alpha \) and \( \mu_i^{\alpha/\beta} \) are the chemical potentials in the matrix of the mean-field concentration and at the interface, respectively.
- \( \mu_i^{\beta/\alpha} \) is the chemical potential at the interface in the precipitate.

In the above local equilibrium condition, the multicomponent Gibbs-Thomson effect has been taken into account by adding a curvature induced pressure term to the Gibbs energy of the precipitate phase.

The introduced effective diffusion distance factor, \( \xi_i \), for each independent component is given by

\[
\xi_i = \frac{\Omega_i}{2\lambda_i^2}
\]

*Eq. 3*

where

$$
\Omega_i = \frac{c_i^\alpha - c_i^{\alpha/\beta}}{c_i^{\beta/\alpha} - c_i^{\alpha/\beta}}
$$

is the so-called dimensionless supersaturation for an individual component, and $\lambda_i$ is obtained via

$$
[\text{Eq. 4}] \quad 2\lambda_i^2 - 2\lambda_i^3 \sqrt{\pi} \exp(\lambda_i^3) \text{erfc}(\lambda_i) = \Omega_i
$$

**Simplified Growth Rate Model**

In some cases, the Advanced model fails to find the solution to flux-balance equations. Even when it does, the calculation can be time consuming. Therefore, a simple and efficient, albeit less rigorous, model is preferred in many applications. The Simplified model, in a pseudo-steady state approximation, is developed by solving Laplace equation along radial direction, and is expressed as

$$
[\text{Eq. 5}] \quad v = \frac{K}{r} \left[ \Delta G_m - \frac{2\sigma V_m^\beta}{r} \right] = \frac{2\sigma V_m^\beta K}{r} \left[ \frac{1}{r^*} - \frac{1}{r} \right]
$$

where $\Delta G_m$ is the nucleation driving force and $r^*$ is the radius of critical nuclei. $K$ is the kinetic parameter that is related to solute composition and mobility. Neglecting cross diffusion, it is expressed as

$$
K = K_{\text{simplified}}^{\text{sphere}} = \left[ \sum_i \left( \frac{X_i^{\beta/\alpha}(r) - X_i^{\alpha/\beta}(r)}{X_i^{\alpha/\beta}(r) M_i} \right)^2 \xi_i \right]^{-1}
$$

[\text{Eq. 6}]

The interface compositions (mole fractions) $X_i^{\beta/\alpha}(r)$ and $X_i^{\alpha/\beta}(r)$ for precipitate and matrix phase, respectively, are tie line compositions across the matrix composition. To avoid time-consuming equilibrium calculations and also realizing that precipitate composition $X_i^{\beta/\alpha}(r)$ only appears in the difference term $\left( X_i^{\beta/\alpha}(r) - X_i^{\alpha/\beta}(r) \right)$, Equation 6 is further simplified by replacing $X_i^{\beta/\alpha}(r)$ with nuclei composition from nucleation driving force calculation, and $X_i^{\alpha/\beta}(r)$ with matrix composition.

The $K$ constant defined here relates growth rate to driving force in

$$
v = \frac{K}{r} \left[ \Delta G_m - \frac{2\sigma V_m^\beta}{r} \right]
$$

which is not to be confused with coarsening rate constant relating mean particle radius cubed to time.
For the *Precipitation Calculator* > *Precipitate Phase* settings, **Phase energy addition** $G_m^a$ and **Phase boundary mobility** $M^B$ shifts the Gibbs energy of the precipitate $\beta$ phase by $G_m^a + \nu V_m^\beta / M^B$. As a result, the driving force $\Delta G_m$ is reduced by $G_m^a + \nu V_m^\beta / M^B$, and the equilibrium compositions $c_i^{\beta e}$ and $c_i^{\alpha e}$ are shifted.

**Figure 1: Effects of “Phase energy addition” $G_m^a$ and “Phase boundary mobility” $M^B$.**

**General Growth Rate Model**

The **General** model is based on the Morral-Purdy model\(^1\), which follows the same quasi-steady state approximation as the **Simplified** model, but improves by taking into account the cross diffusion. The growth rate equation has thus the same format as that in the Simplified model, i.e., Eq. 5, with the kinetic parameter $K$ defined as

\[
K = K_{\text{sphere}}^{\text{general}} = \frac{1}{(\Delta X^{\alpha \beta})[\bar{G}][D]^{-1}[\Delta X^{\alpha \beta}]}
\]

where $(\Delta X^{\alpha \beta})$ and $[\Delta X^{\alpha \beta}]$ are $n - 1$ row and column vector, respectively, whose $i$th element is the composition difference $(X_{i/\alpha}^{\beta}(\tau) - X_{i/\alpha}^{\beta}(\tau))$ as described in Eq. 6. $[\bar{G}]$, a $(n - 1) \times (n - 1)$ matrix, is based on thermodynamic factor matrix $[G^a]$ with a correction factor

where thermodynamic factor matrix is defined as the secondary derivative of free energy with respect to composition in the matrix phase

$$[G^\alpha]_{ij} = \frac{\partial^2 G_m}{\partial X_i^\alpha \partial X_j^\beta}$$

$[G^\alpha]$ is evaluated at the far-field matrix composition to consider the multicomponent Gibbs-Thomson effect. For a particle with critical nuclei size $r^*$, the Gibbs-Thomson equation is

$$[\text{Eq. 9}] \quad (\Delta X^{\alpha \beta}) [G^\alpha] [\Delta X^\alpha] \approx \frac{2 \sigma V_m}{r^*} = \Delta G_m$$

where $[\Delta X^\alpha]$ is a $n-1$ column vector representing the difference between the far-field matrix composition $[X^\alpha]$ and the equilibrium(tie-line) composition of the matrix phase $[X^{\alpha/\beta}]$. It has been found that Eq. 9 is not numerically accurate and sometimes the deviation can be quite significant. Therefore, a correction factor is introduced as

$$f = \frac{\Delta G_m}{(\Delta X^{\alpha \beta}) [G^\alpha] [\Delta X^\alpha]}$$

which then appears in Eq. 8.

$[D]^{-1}$ in Eq. 7 is the inverse of the chemical diffusivity matrix $[D]$. In some alloy systems, diffusivity is strongly composition dependent, so that an effective diffusivity is necessary. A series of numerical simulations in comparison with DICTRA calculations indicates that a good approximation can be achieved if $[D]$ is the arithmetic mean of the diffusivity with far-field matrix composition and diffusivity with equilibrium (tie-line) composition

$$[D] = \frac{1}{2} \left\{ [D](X^\alpha) + [D](X^{\alpha/\beta}) \right\}$$

### Paraequilibrium Growth Rate Model

The paraequilibrium growth rate model is only available for alloy systems where Fe is the major element and C is the only interstitial element, which also partitions into the precipitate phase.

---

The interstitial elements, e.g. C, N, etc., usually have remarkably faster diffusion rate than the substitutional elements. Meanwhile, they are assumed to have negligible volume contribution, and as a result the composition variables in Eq. 6 to Eq. 9 are replaced by \( u \)-fractions when interstitial elements are included in the system. The paraequilibrium growth rate model is designed specifically to address the fast diffusion of C in Fe alloys. Based on the \textit{Simplified} growth rate model, it holds a paraequilibrium condition\textsuperscript{1} at the migrating interface, in that, instead of assuming that all alloying elements are in equilibrium at the interface as the regular ortho-equilibrium condition states, only C assumes equilibrium state, while the substitutional elements are immobile and thus have the same compositions (\( u \)-fractions) across the interface. Therefore, only composition of C and its mobility appear in Eq. 6.

\textbf{NPLE Growth Rate Model}

The Non-Partioning Local Equilibrium (NPLE) growth rate model is only available for alloy systems where Fe is the major element and at least one interstitial element partitions into the precipitate phase.

The NPLE growth model is designed specially to deal with the fast diffusion of interstitial element (C, N, etc.) in Fe alloys. Based on the \textit{Simplified} growth model, it still holds a local equilibrium condition at the migrating interface, but chooses a tie-line under NPLE condition\textsuperscript{2} that the \( u \)-fractions of all substitutional elements and minor interstitial elements in the precipitate phase are the same as those in the far-field matrix phase (i.e. the overall instantaneous matrix composition).

\textbf{Model Selections}

The most efficient model is the \textit{Simplified} model, which is the default and applicable to most alloy systems under conditions that either the supersaturation is small, or the alloying elements have comparable diffusivity. If all alloying elements are substitutional but they have remarkable diffusivity difference, e.g. in Al-Zr system, or the diffusivity is strongly composition dependent, the \textit{General} model is preferred. If the supersaturation is high, and meanwhile there are fast-diffusing interstitial elements such as C, the \textit{Advanced} model is more appropriate to capture the NPLE mechanism.

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\textsuperscript{1} Hillert, M. 1953. "Paraequilibrium." Internal Report, Swedish Institute for Metals Research.

In some cases with the **General** model, you may need to switch to another model if the matrix composition passes through a spinodal composition space where the thermodynamic factor becomes negative, thus leading to an abnormal growth rate. When this happens, Thermo-Calc alerts you that the *Matrix Composition in Spinodal Zone*. It is then recommended to switch to other models.

**Non-Zero Volume Correction**

The non-zero volume correction to the velocity according to Chen and Voorhees (1993)\(^1\) is taken into account and it follows as

\[
\nu' = \nu \left(1 + r \sqrt{4\pi N_V \langle r \rangle}\right)
\]

where

- \(\nu'\) is the corrected velocity,
- \(\langle r \rangle\) is the mean radius and
- \(N_V\) is the number density.

**Non-Spherical Particles**


**Particle Shape Determination**

The shape of the cuboid particles, the cubic factor, is determined by the minimization of combined interfacial energy and elastic strain energy. If you choose **Calculated from molar volume** for the **Transformation strain** as the **Precipitation Calculator>Precipitate Phase** settings, the lattice misfit is then calculated from difference in molar volume between matrix and precipitate phase, and the elastic strain energy is calculated accordingly. If you disregard the transformation strain, the elastic strain energy is neglected and hence the particles remain spherical in shape.

---

If you select the **Calculated aspect ratio from elastic energy** check box for either a plate or needle **Morphology** on the **Precipitation Calculator>Precipitate Phase** settings, the particle shape is determined by the minimization of combined interfacial energy and elastic strain energy. Otherwise, if you enter a value for aspect ratio, the particle shape is fixed except for nucleation calculation in which a spherical particle is always assumed.

### Homogeneous Nucleation

#### Interfacial Energy Anisotropy

**Precipitation Morphology**

Isotropic interfacial energy is always assumed for spherical and cuboidal particles. For plate and needle, when the aspect ratio becomes larger than 1, the interfacial energy anisotropy occurs, so that the interfacial energy at the edge is larger than that at the broad face (habit plane). This increases the overall interfacial energy which is given as

**Plate**

\[ E_{\text{int}} = 4\pi \sqrt{\alpha^2} \sigma_0^{\text{ph}} r^2 \]

**Needle**

\[ E_{\text{int}} = 4\pi \sqrt{\alpha} \sigma_0^{\text{ph}} r^2 \]

Where

- \( \alpha \) is the aspect ratio
- \( \sigma_0^{\text{ph}} \) is the interfacial energy of the habit plane, i.e., the plane normal to the shorter axis
- \( r \) is the radius of a sphere with equivalent volume

#### Growth Rate Adjustment

**Precipitation Morphology**

For non-spherical particles, the growth rate equations for spherical particles are still applicable, but adjustment parameters are introduced to take into account the shape effect. The cuboid particles arise from "symmetry preserving" transformation, e.g., FCC_A1 to L1_2, and are thus highly isotropic and assumed growth rate equal to that of spherical particles. The plate and needle particles, on the other hand, arise from "symmetry breaking" transformations, e.g., cubic to tetragonal transformation, and are thus anisotropic leading to a significant increase of growth rate.
We define $r$ as the radius of a sphere with equivalent volume of the non-spherical particle, so that the format of Eq. 5 keeps unchanged. In our current model, two effects are considered contributing to the growth rate for plate and needle particles, from interfacial energy anisotropy and particle shape effect. The kinetic parameter $K$ defined in Eq. 5 is thus given as

$$[\text{Eq. 11}] \quad K = K_{\sigma} \cdot K_{\text{shp}} \cdot K_{\text{sphere}}$$

with $K_{\text{sphere}}$ defined in Eq. 6 and Eq. 7. The interfacial energy $\sigma$ in Eq. 5 is that of habit plane, i.e., the plane that is normal to the shorter axis of the particle. $K_{\sigma}$ is the parameter that takes into account the Gibbs-Thomson effect due to interfacial energy anisotropy, based on Johnson (1965)$^1$

\textit{Plate}

$K_{\sigma} = \sqrt[3]{\alpha^3}$

\textit{Needle}

$K_{\sigma} = \sqrt[3]{\alpha}$

where $\alpha$ is the aspect ratio of the ellipsoidal particle. $K_{\text{shp}}$ is the parameter that takes into account the non-spherical concentration field around the particle. Assuming a shape-conserving concentration field and thus following the derivation by Ham (1958)$^2$ and Ham (1959)$^3$, it is given as

\textit{Plate}

$$K_{\text{shp}} = \frac{e^{\frac{1}{2} \sqrt[3]{\alpha}}}{\arccos(0)-\arccos(e)}$$

\textit{Needle}

$$K_{\text{shp}} = \frac{2^{\frac{1}{2}} \alpha^2 e}{\ln(1+e)-\ln(1-e)}$$

where $e$ is the eccentricity of the ellipsoidal particle.

$$e = \sqrt{1 - \frac{1}{\alpha^2}}$$

---

**Coarsening**

Physically speaking, coarsening or Ostwald ripening where big particles grow and small particles shrink is a process driven by lowering the total surface energy of the system. From a thermodynamic point of view, the Gibbs-Thomson effect leads to inhomogeneous chemical potentials in the system if the particle sizes are not uniform. Solutes at the interface in the matrix near a particle of a radius smaller than critical radius have a higher chemical potential than that corresponding to the mean concentration of the matrix. As a result, the solutes diffuse from the precipitate/matrix interface to the inside of the matrix and cause dissolution of the particle. Conversely, particles with a radius larger than the critical size have lower interface potentials, and the solutes diffuse to the interface and cause growth of the particles.

Since it is not possible to find a closed form analytic solution for the problem of diffusion-controlled spherical particle dissolution (Aaron, 1970)\(^1\), we simply apply the Growth equations 1 to 5 with the absolute value of \( \Omega_i \) to calculate the interface velocity for particles of all sizes.

As can be easily seen, if \( r < r^* \), then the Gibbs-Thomson Equation 1 gives \( \mu_i^{\alpha/\beta} > \mu_i^{\alpha} \), and a negative velocity results from Equation 2 for particles having \( r < r^* \), which means that they shrink.

Results for particles having \( r > r^* \) are obtained vice versa. In all situations, when the absolute values of \( \Omega_i \) are very small, the steady-state solution for either growth or dissolution are recovered. In conclusion, the dissolution is treated as the reverse of growth (Aaron, 1970, Ibid.), and the coarsening comes out naturally either together with nucleation and growth or as a dominant process finally in the course of the evolution of the PSD.

**Continuity Equation**

Let \( f(r) \) be the PSD of a precipitate phase, \( N \) the number of particles per unit volume, \( \langle r \rangle \) the mean radius and \( \phi \) - the particle volume fraction, is expressed as

\[
[Eq. 1] \quad N = \int_0^\infty f(x) \, dx
\]

\[
[Eq. 2] \quad \langle r \rangle = \int_0^\infty r f(r) \, dr
\]

The time evolution of \( f(r) \) follows the continuity as in Langer and Schwartz (1980)\(^2\).

\[
[Eq. 3] \quad \frac{\partial f}{\partial t} = -\frac{\partial}{\partial r} [v(r)f(r)] + j(r)
\]

---


Where \(v(r)\) is the growth rate of a particle of size \(r\), and \(j(r)\) is the distributed nucleation rate, which is defined by

\[
[\text{Eq. 4}] \quad J = \int_{r^*}^{\infty} j(r)dr
\]

where \(J\) is the nucleation rate.

**Mass Conservation**

The matrix concentration is updated at each time step according to the law of mass conservation. If the alloy concentration, i.e. initial mole fraction of component \(i\) in the matrix phase is \(X_i^0\), the new concentration \(X_i\) can be obtained from the following mass balance shown in

\[
X_i^0 = \left(1 - \sum_p \int_{r^*}^{\infty} \frac{4\pi r^2 f(r_p)}{3V_m} dr_p \right) X_i + \sum_p \int_{r^*}^{t_j} \int_{r_p}^{t_j} \frac{4\pi r^2 f(r_p, t) v(r_p, t)}{V_m^p} X_i^p(r_p, t) dt dr_p
\]

where

- \(X_i^p(r_p, t)\) is the mole fraction of element \(i\) at the interface in the precipitate phase \(p\) of particle size \(r_p\) at time \(t\). \(f(r_p, t)\), \(v(r_p, t)\) and \(V_m^p\) are the PSD function, growth rate, and molar volume of the precipitate phase \(p\), respectively.
- \(t_j\) is the time at time step \(j\).

Apparently, the new matrix concentration, and thus the updated supersaturation, nucleation rate, and interface velocity are all functions of the PSD function. This inevitably leads to the complex non-linear behavior of and great difficulty in solving the continuity equation.

**Numerical Method**

Since it is impossible to have a general close form solution, the complex non-linear continuity equation (see Continuity Equation) of the particle size distribution (PSD) function has to be solved numerically. Different numerical methods can be found in the literature to solve this equation, such as finite difference and method of characteristics. In all approaches, the continuous PSD is discretized into a sufficiently large number of size classes, and then integrated discretely in the time space. The Precipitation Module utilizes the method of characteristics, where the number of particles in each size class is kept constant unless particles of the same size have been nucleated.

An adaptive geometric grid allocation method has been used for particle size discretization since from nucleation to coarsening the particle size can span several orders of magnitude. In this approach, the new size grids are allocated evenly in a logarithmic scale and the number of
grid points over one order of magnitude is kept almost constant during the whole process by class merging and splitting. The time step is controlled by several adjustable numerical parameters based on mechanistic quantities.

Summarized below are all numerical parameters used in this approach to control either the size grid distribution or time steps.

**MAXIMUM TIME STEP FRACTION**

\[ \frac{P_{\text{maz}}}{dt} \]

Maximum time step allowed for time integration as fraction of the simulation time.

**NUMBER OF GRID POINTS OVER ONE ORDER OF MAGNITUDE IN R**

\[ P_{N_{r}} \]

Default number of grid points for every order of magnitude in size space. The number determines a default ratio between two adjacent grid points. When there is a need to create new grid points, such as nucleating at a new radius not covered by the current range of PSD, this default ratio is used to add these new radius grid points. A larger value of this parameter enforces a finer grid to allow better numerical accuracy. However, this also comes with performance penalty, since finer grid in the size space often requires smaller time step to resolve the calculations.

**MAXIMUM NUMBER OF GRID POINTS OVER ONE ORDER OF MAGNITUDE IN R**

\[ P_{\text{maz}}^{N_{r}} \]

The maximum allowed number of grid points in size space. This parameter determines a lower bound limitation for the ratio of every two next nearest grid points in order to maintain adequate computational efficiency. When a ratio of two next nearest grid points is less than this limit, the middle grid point is removed and the corresponding size class merged with the two neighbouring ones.

**MINIMUM NUMBER OF GRID POINTS OVER ONE ORDER OF MAGNITUDE IN R**

\[ P_{\text{min}}^{N_{r}} \]
The minimum allowed number of grid points in size space. This parameter determines an upper bound limitation for the ratio of every two adjacent grid points in order to maintain proper numerical accuracy. When a ratio of two adjacent grid points exceeds this limit, a new grid point is then inserted between the two adjacent grids to keep the required resolution.

**Maximum relative radius change**

$P_r$

The maximum value allowed for relative radius change in one time step. This parameter limits the time step according to the following relation, which is controlled by the particle growth:

$$\Delta t \leq P_r \times r/|dr/dt| \text{ for } r > r_{dt}$$

where $r_{dt}$ is a cut-off subcritical size defined by the next parameter. The growth rates of supercritical particles (with $r > r_c$) are always bounded, and there is a size class and the corresponding growth rate that controls the time step. The subcritical particles (with $r < r_c$), however, has a mathematical singularity (negative infinity) in growth rate as $r$ approaches 0. This means that the time step can become extremely small if applying the above criterion to very small subcritical particles. In open literature, several researchers have tried mathematical transformation to avoid this singularity. Unfortunately, the transformation also complicates the formulation of the models. The Precipitation Module implementation uses a simple approach to deal with this issue by defining a cut-off size $r_{dt}$. All the particles with $r < r_{dt}$ may disappear within one time step. $r_{dt}$ is determined by the next input parameter.

**Maximum relative volume fraction of subcritical particles allowed to dissolve in one time step**

$P_{r_{dt}}$

This parameter represents the portion of the volume fraction that can be ignored when determining the time step. It is used to calculate the cut-off subcritical size, $r_{dt}$, for the above time step control that allows a maximum relative radius changes for all particles:

$$\left(\int_{0}^{r_{dt}} r^3 \, dr\right)/\left(\int_{0}^{\infty} r^3 \, dr\right) = P_{r_{dt}}$$

**Relative radius change for avoiding class collision**

$P_{rc}$
For the supercritical particles, the growth rate is non-linear – usually, it first increases with \( r \) and then decreases after a certain size. In the region(s) with growth rate decreasing with \( r \), it is possible that the smaller size grid point can catch up with the larger size grid, if the time step is not controlled. To prevent this from happening, an additional parameter, \( P_{\infty} \), can be used to set a limit on time step according to the following relation:

\[
\Delta t \leq P_{\infty} \times (r_{i+1} - r_i)/(dr_i/dt - dr_{i+1}/dt)
\]

for

\[ r_{i+1} > r_{i+1} \]

and

\[ dr_{i+1}/dt < dr_i/dt \]

**MAXIMUM OVERALL VOLUME CHANGE**

\( P_V \)

This parameter defines the maximum absolute (not ratio) change of the volume fraction allowed during one time step. This parameter is also used in controlling allowable variation in volume fraction due to the newly created particles within one time step. That is

\[
\Delta t \leq P_V/10/(4\pi r_{\text{eff}}^3 J/3)
\]

where \( r_{\text{eff}} \) and \( J \) are effective radius and nucleation rate, respectively.

**MAXIMUM RELATIVE CHANGE OF NUCLEATION RATE IN LOGARITHMIC SCALE**

\( P_{\log J} \)

This parameter ensures accuracy for the evolution of effective nucleation rate. It sets a limit on time step so that the relative change of nucleation rate does not exceed the specified value, based on the information of previous step. That is

\[
\Delta t \leq P_{\log J} \times \Delta t_{\text{previous}}/(|\log(J_1/J_2)|)
\]

where nucleation rate \( J_1 \) and \( J_2 \) occurs at the beginning and end of \( \Delta t_{\text{previous}} \).

**MAXIMUM RELATIVE CHANGE OF CRITICAL RADIUS**

\( P_{rc} \)
During the nucleation under high supersaturation, the critical radius can vary dramatically. Hence, this parameter can be used to place a constraint on how fast the critical radius can vary, and thus put a limit on time step:

$$\Delta t \leq P_{rc} \times \Delta t_{previous} /[|r_{c1} - r_{c2}/r_{c1}|]$$

**MINIMUM RADIUS FOR A NUCLEUS TO BE CONSIDERED AS A PARTICLE**

$P_{r_{min}}$

The cut-off lower limit of precipitate radius. Particles with radius smaller than the value specified for this parameter are discarded. In reality, the particle cannot be smaller than an atom; hence, there is no reason to keep track of particles of unphysical sizes.

**MAXIMUM TIME STEP DURING HEATING STAGES**

$P_{t_{max}}$

The upper limit of the time step that has been enforced in the heating stages. The current algorithm may over-estimate the subsequent time increment when temperature is increased. It is thus required to reduce this value when the calculation terminates unexpectedly during or after a heating stage.

**NUMERICAL CONTROL PARAMETERS DEFAULT VALUES**

Default value for numerical parameters that controls the size grid distribution and time step.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Default value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P_{t_{max}}$</td>
<td>0.1</td>
</tr>
<tr>
<td>$P_{N_{r}}$</td>
<td>200</td>
</tr>
<tr>
<td>$P_{r_{max}}^{N_{r}}$</td>
<td>300</td>
</tr>
<tr>
<td>$P_{r_{min}}^{N_{r}}$</td>
<td>100</td>
</tr>
<tr>
<td>$P_{r}$</td>
<td>0.01</td>
</tr>
</tbody>
</table>
Parameter | Default value
--- | ---
$P_{rdt}$ | 0.01
$P_{cc}$ | 0.5
$P_{v}$ | 0.001
$P_{logJ}$ | 0.5
$P_{rc}$ | 0.1
$P_{min}$ | 5e-10m
$P_{htmax}$ | 1.0s

**Estimation of Coherent Interfacial Energy**

Interfacial energy is an important parameter used in precipitation simulations to calculate the rates of nucleation, growth/dissolution, and coarsening. The value of interfacial energy can vary dramatically (usually between 0.01 to 2.0 J/m$^2$).

The extended Becker’s model functions to estimate coherent interfacial energy by using thermodynamic data from existing CALPHAD thermodynamic databases:

$$\sigma_c = \frac{n_s z_s \Delta E_s}{N_A z_l}$$

where $\sigma_c$ is the coherent interfacial energy, $n_s$ is the number of atoms per unit area at the interface, $z_s$ is the number of cross bonds per atom at the interface, $z_l$ is the coordination number of an atom within the bulk crystal lattice, and $\Delta E_s$ is the energy of solution in a multicomponent system involving the two phases being considered [Becker, 1938]$^1$.

**Precipitation Morphology**

As the spherical particle is the default morphology, for precipitations within the grain, three non-spherical shapes are considered: *cuboid, plate and needle*.

- Growth
- Homogeneous Nucleation

---

Figure 1: Cuboids have six faces, which form a convex polyhedron.

The cuboid shape is described by a supersphere

\[ x_1^p + x_2^p + x_3^p = R^p \quad (p \geq 2) \]

with \( p=2 \) being spherical shape. The larger the \( p \), the more cubic the shape. Sometimes it is useful to define the cubical character as

\[ \eta = \sqrt{2} \cdot 2^{-1/p} \]

Which gives a spherical shape when \( \eta = 1 \), and a cubic shape when \( \eta = \sqrt{2} \).

Plate

Figure 2: Oblate spheroids have rotational symmetry around an axis from pole to pole.

The plate is described as oblate spheroid

\[ \frac{x_1^2}{l^2} + \frac{x_2^2}{l^2} + \frac{x_3^2}{r^2} \leq 1 \quad l > r \]

with aspect ratio

\[ \alpha = \frac{l}{r} > 1 \]
Needle

![Figure 3: A prolate spheroid is a surface of revolution obtained by rotating an ellipse about its major axis.](image)

The needle shape is described as prolate spheroid

$$\frac{x^2}{r^2} + \frac{y^2}{r^2} + \frac{z^2}{l^2} \leq 1 \quad l > r$$

with aspect ratio

$$\alpha = \frac{l}{r} > 1$$

Precipitations at a Grain Boundary, Edge or Corner

For precipitations at a grain boundary, grain edge or grain corner, non-spherical particles are considered based on wetting angle.

- Heterogeneous Nucleation
- Conditions Tab Settings

Precipitation Module (TC-PRISMA) References


Precipitation Module Examples

Examples that use up to three elements are available to all users. The other examples require a Precipitation Module (TC-PRISMA) license to calculate and plot results.

All examples use demonstration database packages included with your installation. You can open the examples from the main menu: File → or Help → Examples Files.

Unless specified in tables for each example, all the numerical parameters are assumed default values.

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P_12: Comparing Growth Rate Models for an Al-Zr System ............................... 126
P_13: Paraequilibrium Precipitation of Cementite Fe-Cr ................................. 128
P_01: Isothermal Precipitation of Al₃Sc

This example simulates the kinetics of precipitation of Al₃Sc from an FCC_A1 solution phase. The simulation results can be compared with experimental data collected from Marquis and Seidman¹ and Novotny and Ardell (2001)².

**PROJECT FILE, STEP-BY STEP INSTRUCTIONS AND VIDEO INFORMATION**

- Folder: Precipitation Module - TC-PRISMA
- File name: P_01_Precipitation_Al-Sc_AL3SC.tcu

This example is available as a video tutorial on our website and YouTube channel.

You can also use the step-by-step instructions included in a PDF to follow the video or compare to the project file in Thermo-Calc.

<table>
<thead>
<tr>
<th>System (System Definer)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Database package</td>
<td>Demo: Aluminum-based alloys (ALDEMO, MALDEMO)</td>
</tr>
<tr>
<td>Elements</td>
<td>Al, Sc</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Conditions (Precipitation Calculator)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition</td>
<td>Al-0.18Sc Mole percent</td>
</tr>
<tr>
<td>Matrix phase</td>
<td>FCC_A1</td>
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<tr>
<td>Precipitate phase</td>
<td>AL3SC</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Precipitate Phase Data Parameters (Precipitation Calculator)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Nucleation sites</td>
<td>Bulk</td>
</tr>
</tbody>
</table>

Precipitation Module (TC-PRISMA) User Guide

<table>
<thead>
<tr>
<th>Interfacial energy</th>
<th>Calculated</th>
</tr>
</thead>
</table>

**Calculation Type (Precipitation Calculator)**

<table>
<thead>
<tr>
<th>Calculation type</th>
<th>Isothermal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>350° C</td>
</tr>
<tr>
<td>Simulation time</td>
<td>1.0E7 seconds</td>
</tr>
</tbody>
</table>

**Plot Results**

*Mean radius*

![Plot of mean radius over time](image)
Isothermal Precipitation Calculation: Example P_01 – Precipitation Al-Sc AL3SC

This example shows you how to set up an isothermal precipitation calculation for the formation of AL3SC in an aluminium-scandium alloy at 350° using the Precipitation module (TC-PRISMA).

This is one of the most basic calculations using the Precipitation module (TC-PRISMA), so it is a good place to start if you are new to this simulation type.

HELPFUL INFORMATION

- All users can run this calculation, even those who do not have a license for the Precipitation module (TC-PRISMA).
- A companion video is available for this example, which can be watched here: https://www.youtube.com/playlist?list=PLfv6McToaTGSpqYuLoY3b_UV-8xpgLUkJ
- This calculation is based on Precipitation module example P_01 – Precipitation Al-Sc AL3SC, which is included in your installation. To run the example file, open Thermo-Calc and select Help > Examples Files. Open the Precipitation module (TC-PRISMA) folder. Double-click the example file and click Perform at the bottom centre of the Configuration window in Thermo-Calc.

ABOUT THE EXAMPLE

This example simulates the kinetics of precipitation of Al3Sc from an FCC_A1 solution phase.

SETTING UP THE SYSTEM

1. Open Thermo-Calc in Graphical Mode.
2. Under templates, click Precipitation Simulation.
3. All the nodes for a precipitation calculation are added to the Project window:
4. Click the **System Definer 1** node.
5. Set the database package to **DEMO: Aluminium based alloys**, which loads both thermodynamic and kinetic demonstration aluminium databases.
6. From the periodic table, select the elements **Al** (aluminium) then **Sc** (scandium). Be sure to select **Al** first so that it is the dependant element.
7. Just to the right of the periodic table, select **Mole Percent** as the **Amount**.
8. Enter 0.18 for **Sc**. This automatically sets **Al** to 99.82.
Our system is now defined, but before we start the precipitation calculation, we will do a quick one axis calculation to find the phases present around 350°.

**ONE AXIS CALCULATION**

*Why We Do This*

In order to set up an isothermal precipitation calculation, we need to know which phases are present at 350°. A one axis calculation gives us this information.

**Setting up a One Axis Calculation**

1. In the Project window, right-click the **System Definer 1** node, and from the Create New Successor menu select **Equilibrium Calculator**.
2. In the Configuration window, select a Temperature in Celsius and enter 300.
3. Under Calculation Type, select **One axis**.
4. We are looking for the phases present around 350 degrees, so under Axis Definitions enter the Temperature range from Min 300 to Max 700 to capture the temperature wanted.
5. Keep the default values for everything else.
6. Our system is now defined.

7. Right-click the **Equilibrium Calculator** node and select Create New Successor>Plot Renderer.
8. In the Project window, right-click the **Plot Renderer 2** node you just created and select Perform Now.

**Interpreting the Results of the One Axis Calculation**

Once the calculation is complete, a plot is displayed in the Results window. This plot shows you which phases are present at each temperature between 300° and 700° and the amount of that phase at each temperature.
If you hover your cursor over any of the lines on the plot, a label gives you the name of the phase, the temperature and the amount of the phase at that temperature.

We can see that there are two phases present at 350°. FCC_A1 is at the very top of the plot and makes up more than 99% of the system. The remainder of the system is made up of AL3SC, which is near the very bottom of the plot and is the precipitate phase in the alloy we are considering.

Remember these two phases because we will use them in our precipitation calculation.
PRECIPITATION CALCULATION

Setting up the Precipitation Calculation

1. In the Project window, click the Precipitation Calculator 1 node.
2. Notice that the composition we set in the System Definer auto-populated here.
3. Under Matrix Phase, select FCC_A1, which is the primary phase we saw present in the one axis calculation.

NOTE: If you do not see any phases listed here it is probably because you do not have a kinetic database selected. If so, simply go back to the System Definer and add a kinetic (mobility) database.

4. Under Precipitate Phase select AL3SC from the Phase menu because that is the other phase present around 350°, as shown in the one axis calculation.
5. Accept the default settings in the Precipitate Phase section. You could choose to define your own interfacial energy settings if you have them.
6. Under Calculation Type, make sure Isothermal is selected.
7. Enter 350 as the Temperature and select Celsius.
8. Enter 1.0E7 as the Simulation time and select Seconds, which is ten million seconds.

9. In the Project window, click the Plot Renderer 1 node.
10. Under Y-axes, from the Axis type menu select Logarithmic 10 for a better view of the plot.
11. Click Perform at the bottom, centre of the Configuration window.
Interpreting the Results of the Precipitation Calculation

Once the calculation is complete, your plot is shown in the Results window.

This plot shows the Mean radius of the AL3SC precipitate as a function of time.

At the beginning, which is the left-most side of the plot, the mean radius is quite small and then grows rapidly over time, which is represented by moving rightward on the plot.
**Setting Other Variables in the Precipitation module (TC-PRISMA)**

The Precipitation module (TC-PRISMA) offers many variables that you can plot for the same calculation.

1. Click the **Plot Renderer 1** node.
2. In the Y-axes section, select the **Axis variable** menu to see what other options are available.
3. Once you have made your selection, click **Perform** at the bottom, centre of the **Configuration** window to create a new plot.
P_02: Stable and Metastable Carbides - Isothermal

This example simulates the kinetics of precipitation of both stable and metastable carbides from ferrite phase. It demonstrates that metastable carbides (cementite, M7C3) may first emerge and then disappear and the stable phase (M23C6) prevails.

This example uses the Equilibrium Calculator and a One axis calculation to determine how the phases change with temperature. We are interested in the carbide precipitation at 1053K where only the carbide M23C6 is stable according to the equilibrium calculation. The Precipitation Calculator is used to do an isothermal calculation of the three phases (cementite, M23C6 and M7C3) where cementite and M7C3 are metastable phases.

**PROJECT FILE INFORMATION**

- Folder: Precipitation Module - TC-PRISMA
- File name: P_02_Precipitation_Fe-C-Cr_Cementite-M7C3-M23C6.tcu

<table>
<thead>
<tr>
<th><strong>System (System Definer)</strong></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Database package</td>
<td>Demo: Steels and Fe-alloys (FEDEMO,MFEDEMO)</td>
</tr>
<tr>
<td>Elements</td>
<td>Fe, C, Cr</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>Conditions (Precipitation Calculator)</strong></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition</td>
<td>Fe-0.1C-12Cr Mass percent</td>
</tr>
<tr>
<td>Matrix phase</td>
<td>BCC_A2</td>
</tr>
<tr>
<td>Precipitate phases</td>
<td>Cementite, M23C6 and M7C3</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>Matrix Phase Data Parameters (Precipitation Calculator)</strong></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Grain size (click Show details to display this setting)</td>
<td>1.0E-4 m</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>Precipitate Phase Data Parameters (Precipitation Calculator)</strong></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Nucleation sites</td>
<td>Grain boundaries</td>
</tr>
</tbody>
</table>
Interfacial energy

|                | Cementite 0.167 J/m², M23C6 0.252 J/m², M7C3 0.282 J/m² |

Calculation Type (Precipitation Calculator)

<table>
<thead>
<tr>
<th>Calculation type</th>
<th>Isothermal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>1053 K</td>
</tr>
<tr>
<td>Simulation time</td>
<td>400 000 seconds</td>
</tr>
</tbody>
</table>

Plot Results

Equilibrium Calculator: How the phases change with temperature
Precipitation Calculator: Volume fractions

![Image of graph showing volume fractions over time]

**P_03: Stable and Metastable Carbides - TTT Diagram**

In this example, the kinetics of precipitation of both stable and metastable carbides is calculated from the ferrite phase. It demonstrates that metastable carbides may first emerge and then disappear and the stable phase prevails.

This example uses the Equilibrium Calculator and a *One axis* calculation type to determine how the phases change with temperature. Using this result, the Precipitation Calculator is used to do a TTT (Time-Temperature-Transformation) diagram calculation of the three phases (cementite, M23C6 and M7C3) at the grain boundaries.

For a TTT diagram calculation, select **TTT diagram** in **Calculation Type**, then enter **Min**, **Max**, and **Step of Temperature**, as well as **Max annealing time**. In **Stop criterion**, choose **Volume fraction of phase** and enter the value.

**PROJECT FILE INFORMATION**

- Folder: Precipitation Module - TC-PRISMA
- File name: *P_03_Precipitation_Fe-Cr_TTT_Cementite-M7C3-M23C6.tcu*
### System (System Definer)

<table>
<thead>
<tr>
<th>Database package</th>
<th>Demo: Steels and Fe-alloys (FEDEMO and MFDEMO)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Elements</td>
<td>Fe, C, Cr</td>
</tr>
</tbody>
</table>

### Conditions (Precipitation Calculator)

<table>
<thead>
<tr>
<th>Composition</th>
<th>Fe-0.1C-12Cr Mass percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Matrix phase</td>
<td>BCC_A2</td>
</tr>
<tr>
<td>Precipitate phases</td>
<td>Cementite, M23C6 and M7C3</td>
</tr>
</tbody>
</table>

### Matrix Phase Data Parameters (Precipitation Calculator)

| Grain size (click Show details to display this setting) | 1.0E-4 m                        |

### Precipitate Phase Data Parameters

<table>
<thead>
<tr>
<th>Nucleation sites</th>
<th>Grain boundaries</th>
</tr>
</thead>
<tbody>
<tr>
<td>Interfacial energy</td>
<td>Cementite 0.167 J/m², M23C6 0.252 J/m², M7C3 0.282 J/m²</td>
</tr>
</tbody>
</table>

### Calculation Type (Precipitation Calculator)

<table>
<thead>
<tr>
<th>Calculation type</th>
<th>TTT diagram</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>500° to 800° C with 25° C steps</td>
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<tr>
<td>Max. annealing time</td>
<td>1.0E8 seconds</td>
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<tr>
<td>Stop criteria</td>
<td>Volume fraction of phase is set to 0.0001</td>
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</table>

### Options > Numerical Parameters

<table>
<thead>
<tr>
<th>No. of grid points over one order of magnitude in radius</th>
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</tr>
</thead>
<tbody>
<tr>
<td>Max no. of grid points over one order of magnitude in radius</td>
<td>200</td>
</tr>
<tr>
<td>Min no. of grid points over one order of magnitude in radius</td>
<td>100</td>
</tr>
</tbody>
</table>
Plot Results

Equilibrium Calculator: How the phases change with temperature

Precipitation Calculator: TTT diagram
P_04: Precipitation of Iron Carbon Cementite

Simulate the kinetics of precipitation of carbides from a BCC Fe solution phase. This example is based on Wert (1949)\(^1\).

This example uses two Experimental File Reader activities with the Precipitation Calculator and an isothermal calculation, to plot the volume fraction of the cementite phase.

**PROJECT FILE INFORMATION**

- Folder: Precipitation Module - TC-PRISMA
- File name: P_04_Precipitation_Fe-C_Cementite.tcu

### System (System Definer)

<table>
<thead>
<tr>
<th>Database package</th>
<th>Demo: Steels and Fe-alloys (FEDEMO and MFEDEMO)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Elements</td>
<td>Fe, C</td>
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</table>

### Conditions (Precipitation Calculator)

<table>
<thead>
<tr>
<th>Composition</th>
<th>Fe-0.016C mass percent</th>
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</thead>
<tbody>
<tr>
<td>Matrix phase</td>
<td>BCC_A2</td>
</tr>
<tr>
<td>Precipitate phase</td>
<td>Cementite</td>
</tr>
</tbody>
</table>

### Matrix Phase Data Parameters (Precipitation Calculator)

<table>
<thead>
<tr>
<th>Grain aspect ratio (click Show details to display this setting)</th>
<th>1.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dislocation density (click Show details to display this setting)</td>
<td>1.5e11m(^{-3})</td>
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</table>

### Precipitate Phase Parameters (Precipitation Calculator)

<table>
<thead>
<tr>
<th>Nucleation sites</th>
<th>Dislocations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Interfacial energy</td>
<td>0.24 J/m(^2)</td>
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</table>

---

Growth rate model (click Show details) | Advanced

**Calculation Type (Precipitation Calculator)**

<table>
<thead>
<tr>
<th>Calculation type</th>
<th>Isothermal</th>
</tr>
</thead>
<tbody>
<tr>
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<td>102°C</td>
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<td>Simulation time</td>
<td>600 000 seconds</td>
</tr>
</tbody>
</table>

**Plot Results**

**Volume Fraction**

![Graph showing volume fraction over time](image)

**P_05: Precipitation of γ’ in Ni Superalloys - Isothermal**

This example simulates the kinetics of precipitation of γ’ phase from γ phase. The simulation results can be compared with experimental data collected from Sudbrack et al. (2008)\(^1\).

---

This example uses three Experimental File Reader activities with the Precipitation Calculator. It does an isothermal calculation to plot the volume fraction, mean radius and number density of the cementite phase.

DIS_FCC_A1 needs to be selected on the System Definer. See Selecting the Disordered Phase as a Matrix Phase for details.

**PROJECT FILE INFORMATION**

- Folder: Precipitation Module - TC-PRISMA
- File name: P_05_Precipitation_Ni-Al-Cr_Isothermal_Gamma-Gamma_prime.tcu

<table>
<thead>
<tr>
<th><strong>System</strong> (System Definer)</th>
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</thead>
<tbody>
<tr>
<td>Database package</td>
<td>Demo: Nickel-based Super Alloys (NIDEMO and MNIDEMO)</td>
</tr>
<tr>
<td>Elements</td>
<td>Ni, Al Cr</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>Conditions</strong> (Precipitation Calculator)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition</td>
<td>Ni-9.8Al-8.3Cr Mole percent</td>
</tr>
<tr>
<td>Matrix phase</td>
<td>DIS-FCC_A1 (see note above about how to select this phase)</td>
</tr>
<tr>
<td>Precipitate phase</td>
<td>FCC_L12#2</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>Precipitate Phase Data Parameters</strong> (Precipitation Calculator)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Nucleation sites</td>
<td>Bulk</td>
</tr>
<tr>
<td>Interfacial energy</td>
<td>0.012 J/m²</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>Calculation Type</strong> (Precipitation Calculator)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Calculation type</td>
<td>Isothermal</td>
</tr>
<tr>
<td>Temperature</td>
<td>800° C</td>
</tr>
<tr>
<td>Simulation time</td>
<td>1 000 000 seconds</td>
</tr>
</tbody>
</table>
Plot Results

Volume Fraction

Number Density
Mean Radius

P_06: Precipitation of $\gamma'$ in Ni Superalloys - Non-isothermal

This example simulates the kinetics of precipitation of $\gamma'$ phase from $\gamma$ phase in Ni-8Al-8Cr and Ni-10Al-10Cr at.% alloys during continuous cooling. The simulation results can be compared with experimental results from Rojhirunsakool et al. (2013)\(^1\).

When you run (Perform) this example, it takes about 10 minutes for the calculations to complete.

In these examples a linear, continuously cooling condition is set up. This is done on the Precipitation Calculator settings window in the Calculation Type section:

1. Select a Non-Isothermal.
2. Select a Temperature Unit and Time Unit from the lists.
3. Click Thermal Profile, where Time-Temperature profile points are entered to describe the stepwise heat treatment schedule with linear segments. Up to 999 rows of data points can be entered.

In these examples two rows of data points are needed for starting time 0s and temperature 1150°C, as well as end time 3300s and temperature 380°C.

4. Click the **Plot Renderer** node to select the **Separate multimodal PSD** check box.

Plotting the size distribution from the final simulation time of 3300 seconds, you can see there are several peaks, although these are not completely separated. As above, select the **Separate multimodal PSD** check box to separate the peaks.

5. Adjust the **Valley depth ratio** setting to 0.05 to separate into two peaks as shown in the **Ni-10Al-10Cr plot example**. You can experiment with this setting to see how the size distribution evolves with time, for example, try entering several values as plot times 400 600 3300.

DIS_FCC_A1 needs to be selected on the System Definer. See *Selecting the Disordered Phase as a Matrix Phase* for details.

**PROJECT FILE INFORMATION**

- Folder: Precipitation Module - TC-PRISMA
- File name: *P_06_Precipitation_Ni-Al-Cr_Non-isothermal_Gamma-Gamma_prime.tcu*

<table>
<thead>
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</thead>
<tbody>
<tr>
<td>Database package</td>
<td>Demo: Nickel-based Super Alloys (NIDEMO and MNIDEMO)</td>
</tr>
<tr>
<td>Elements</td>
<td>Ni, Al, Cr</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Conditions (Precipitation Calculator)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition (Ni-8Al-8Cr)</td>
<td>Ni-8Al-8Cr Mole percent</td>
</tr>
<tr>
<td>Composition (Ni-10Al-10Cr)</td>
<td>Ni-10Al-10Cr Mole percent</td>
</tr>
<tr>
<td>Matrix phase</td>
<td>DIS_FCC_A1 (see note above about how to select this phase)</td>
</tr>
<tr>
<td>Precipitate phase</td>
<td>FCC_L12#2</td>
</tr>
<tr>
<td>------------------------</td>
<td>----------------------</td>
</tr>
</tbody>
</table>

**Matrix Phase Data Parameters (Precipitation Calculator)**

<table>
<thead>
<tr>
<th>Mobility enhancement prefactor (click Show details to display this setting)</th>
<th>5.0</th>
</tr>
</thead>
</table>

**Precipitate Phase Data Parameters (Precipitation Calculator)**

<table>
<thead>
<tr>
<th>Nucleation sites</th>
<th>Bulk</th>
</tr>
</thead>
<tbody>
<tr>
<td>Interfacial energy</td>
<td>0.023 J/m²</td>
</tr>
</tbody>
</table>

**Calculation Type (Precipitation Calculator)**

<table>
<thead>
<tr>
<th>Calculation type</th>
<th>Non-isothermal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature unit</td>
<td>Celsius</td>
</tr>
<tr>
<td>Time unit</td>
<td>Seconds</td>
</tr>
<tr>
<td>Simulation time (Ni-8Al-8Cr)</td>
<td>1470 s</td>
</tr>
<tr>
<td>Simulation time (Ni-10Al-10Cr)</td>
<td>3300 s</td>
</tr>
</tbody>
</table>

**Multimodal PSD (Plot Renderer)**

<table>
<thead>
<tr>
<th>Separate multimodal PSD for 8Al-8Cr</th>
<th>The Valley depth ratio is set to 0.05 for both plots. The number of Points is increased to 200 for an average radius plot.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Separate multimodal PSD for 10Al-10Cr</td>
<td>The Valley depth ratio is set to 0.18 for both plots.</td>
</tr>
</tbody>
</table>
Plot Results

Mean Radius Ni-8Al-8Cr

Mean Radius Ni-10Al-10Cr
Size Distribution (PSD) Ni-8Al-8Cr

Size Distribution (PSD) Ni-10Al-10Cr
**P_07: Continuous Cooling Transformation (CCT) Diagram of Ni-Al-Cr γ-γ’**

In this example, a Continuous Cooling Transformation (CCT) diagram for a Ni-10Al-10Cr γ-γ’ alloy is calculated and plotted with superimposition of the cooling rate values.

**PROJECT FILE, STEP-BY STEP INSTRUCTIONS AND VIDEO INFORMATION**

- Folder: Precipitation Module - TC-PRISMA
- File name: _P_07_Precipitation_Ni-Al-Cr_CCT_Gamma-Gamma_prime.tcu_

This example is available as a video tutorial on our website and YouTube channel.

You can also use the step-by-step instructions included in a PDF to follow the video or compare to the project file in Thermo-Calc.

<table>
<thead>
<tr>
<th>System (System Definer)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Database package</td>
</tr>
<tr>
<td>Elements</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Conditions (Precipitation Calculator)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition</td>
</tr>
<tr>
<td>Matrix phase</td>
</tr>
<tr>
<td>Precipitate phase</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Precipitate Phase Data Parameters (Precipitation Calculator)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nucleation sites</td>
</tr>
<tr>
<td>Interfacial energy</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Calculation Type (Precipitation Calculator)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calculation type</td>
</tr>
<tr>
<td>Temperature Min to Max</td>
</tr>
</tbody>
</table>
Precipitation Module (TC-PRISMA) User Guide

Plot and Table Results

<table>
<thead>
<tr>
<th>Cooling rate(s)</th>
<th>.01 .1 1 10 100 K/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stop criteria</td>
<td>Volume fraction of phase 1.0E-4</td>
</tr>
</tbody>
</table>

![Graph showing Temperature vs. Time for different cooling rates.]

### Results

<table>
<thead>
<tr>
<th>Temperature [K]</th>
<th>FCC_112#2 (Bulk)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1147.52034</td>
<td>0.53291</td>
</tr>
<tr>
<td>1151.74192</td>
<td>4.83553</td>
</tr>
<tr>
<td>1155.24636</td>
<td>44.76534</td>
</tr>
<tr>
<td>1158.85368</td>
<td>411.49173</td>
</tr>
<tr>
<td>1161.48750</td>
<td>3851.47779</td>
</tr>
</tbody>
</table>

Precipitation Module Examples | 93 of 130
Continuous Cooling Transformation (CCT) Diagram of Ni-Al-Cr γ-γ': Precipitation Example P_07

HELPFUL INFORMATION

- All users can run this calculation, even those who do not have a license for the Precipitation module (TC-PRISMA).
- A companion video is available for this example, which can be watched here: [https://www.youtube.com/playlist?list=PLfv6McToaTGSpqvuLoY3b_UV-8xpGLUkI](https://www.youtube.com/playlist?list=PLfv6McToaTGSpqvuLoY3b_UV-8xpGLUkI)
- This calculation is based on Precipitation module example P_07 – Precipitation Ni-Al-Cr_CCT_Gamma-Gamma_prime, which is included in your installation. To run the example file, open Thermo-Calc and select Help > Examples Files. Open the Precipitation module (TC-PRISMA) folder. Double-click the example file and click Perform at the bottom centre of the Configuration window in Thermo-Calc.

ABOUT THE EXAMPLE

This example shows you how to simulate a CCT diagram for gamma prime (γ') precipitation in a Ni-Cr-Al alloy using the Precipitation module known as TC-PRISMA.

CCT stands for Continuous Cooling Transformation and is a calculation that maintains the same cooling rate the entire time.

The system is a Ni-10Al-10Cr γ - γ' alloy and it is calculated and plotted with superimposition of the cooling rate values using the Precipitation module (TC-PRISMA).

SETTING UP THE SYSTEM

1. Open Thermo-Calc in Graphical Mode.
2. Under templates, click Precipitation Simulation.
3. All the nodes for a precipitation calculation are added to the Project window:
4. Click the System Definer 1 node.
5. Set the database package to DEMO: Nickel based superalloys, which loads both thermodynamic and kinetic demonstration nickel databases.
6. From the periodic table, select the elements Ni (nickel), Al (aluminium) then Cr (chromium). Be sure to select Ni first so that it is the dependant element.
7. Just to the right of the periodic table, select Mole Percent as the Amount.
8. Enter 10 for Al and 10 for Cr, which automatically sets Ni to 80 mole percent.
9. Click the Phases and Phase Constitution tab.
10. Click to select both check boxes next to the disordered FCC phase, DIS_FCC_A1.

Our system is now defined, so we will set up the precipitation calculation.

SETTING UP THE PRECIPITATION CALCULATION

1. In the Project window, click the Precipitation Calculator 1 node.
2. Notice that the composition we set in the System Definer auto-populated here.
3. Under Matrix Phase, from the Phase list select Dis_FCC_A1, which is the disordered FCC phase.
4. Under Precipitate Phase from the Phase list select FCC_L12#2.
5. Change the Interfacial energy to User-defined then enter 0.023 in the field.
6. Under Calculation Type, select CCT Diagram, which stands for Continuous-Cooling-Transformation and means that the same cooling rate is maintained throughout the calculation.
7. In the fields, set the Min (minimum) Temperature to 500 and the Max (maximum) to 1200 and choose Kelvin as the temperature unit.
8. We will enter several cooling rates for our calculation. The rates are separated by a space, so enter these values as shown: .01 .1 1 10 100.
9. Keep the default Stop criteria of 1E-4 volume fraction of the γ' phase.
10. The calculation is now set, so click Perform CCT Diagram Simulation at the bottom, centre of the Configuration window.
INTERPRETING THE RESULTS OF THE PRECIPITATION CALCULATION

In this plot, the blue, horizontal line shows the time it takes for gamma prime to transform at each of the cooling rates according to the stop criteria, which we set as $1e^{-4}$ volume fraction.

In this plot, the blue line shows the time it takes for γ′ to transform at each of the cooling rates according to the stop criteria, which we set as $1e^{-4}$ volume fraction. The cooling rates are represented by the multi-coloured curved lines.
If you hover your mouse over the intersection of the blue line and any of the vertical lines, a yellow box shows the approximate time it takes for $\gamma'$ to transform according to the stop criteria, which is a volume fraction of $1e^{-4}$, followed by the approximate temperature. In the image above, we can see a time of 0.54147 seconds and a temperature of 1147.60 Kelvin for the cooling rate of 100.0 K/s, which is represented by the yellow line.

**SHOWING THE RESULTS AS A TABLE**

You can also view these results in the form of a table, which gives you more precise results.

1. In the **Project** window, right-click the **Precipitation Calculator 1** node and select **Create New Successor>Table Renderer**.
2. Right-click the **Table Renderer 1** node and select **Perform Now**.

Your table is shown in the **Results** window and shows the same information as in the plot - for each cooling rate the temperature and the time it takes for $\gamma'$ to transform according to the stop criteria, which is a volume fraction of $1e^{-4}$.
**P_08: Precipitation of Cu-Ti CU4TI with Assumptions of Sphere and Needle Morphologies**

In this isothermal calculation example, the precipitation of Cu4Ti phase in a Cu-Ti binary alloy is calculated. To make a comparison, two separate simulations are performed, one assuming spherical morphology without elastic strain energy, and the other assuming needle morphology whose shape, determined by competition between interfacial energy and elastic strain energy, is changed during the simulation. The transformation strain is obtained from Borchers\(^1\). The results are compared with experiment results from Kampmann et al\(^2\).

This example takes a few minutes to run.

To ensure that the settings are done on the correct Precipitation Calculators, the **Sphere** and **Needle** nodes are renamed from **Precipitation Calculator** to match their morphology. The morphology is set in the **Precipitate Phase** section when you click **Show details**.

**Precipitation Morphology**

![Precipitation Morphology Diagram]

**PROJECT FILE INFORMATION**

Folder: Precipitation Module - TC-PRISMA
File name: P_08_Precipitation_Cu-Ti_CU4TI1_Sphere_Needle.tcu

<table>
<thead>
<tr>
<th>System (System Definer)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Database package</td>
</tr>
<tr>
<td>Elements</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sphere and Needle Conditions (Precipitation Calculator)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition</td>
</tr>
<tr>
<td>Matrix phase</td>
</tr>
<tr>
<td>Precipitate phase</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Matrix Phase Data Parameters (Precipitation Calculator)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mobility enhancement prefactor (click Show details to display this setting)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Precipitate Phase Data Parameters (Precipitation Calculator)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nucleation sites</td>
</tr>
<tr>
<td>Interfacial energy</td>
</tr>
<tr>
<td>Morphology (click Show details to display this setting)</td>
</tr>
</tbody>
</table>
| Transformation strain (click **Show details** to display this setting) | For the **Sphere** node (renamed from Precipitation Calculator), keep the default. For the **Needle** node (renamed from Precipitation Calculator), **User defined** is selected. In this example, the following settings are defined:

- $\varepsilon_{11}$ and $\varepsilon_{22}$ are set to **0.022**
- $\varepsilon_{33}$ is set to **0.003** |
| --- | --- |

**Calculation Type (Precipitation Calculator)**

<table>
<thead>
<tr>
<th>Calculation type</th>
<th>Isothermal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>350° C</td>
</tr>
<tr>
<td>Simulation time</td>
<td>10,000 seconds</td>
</tr>
</tbody>
</table>

**Datasets (Experimental File Reader)**

<table>
<thead>
<tr>
<th>Borchers Mean radius vs Time and Borchers Number density vs Time</th>
<th>Data sets included with this example and imported to two Experimental File Readers. These data sets are used for the Mean Radius and Number Density plots, respectively.</th>
</tr>
</thead>
</table>
Plot Results

Mean Aspect Ratio
Number Density

![Graph showing number density over time](image)

- Number density of CU4T1 (BuLi) (m$^{-3}$/Nanodroplet)
- Number density of CU4T1 (BuLi) (m$^{-3}$/Sphere)
PSD and ASD
Mean Radius

P_09: Precipitation of Al-Sc AL3SC with Assumption of Sphere and Cuboid Morphologies

In this isothermal calculation example, the precipitation of Al₃Sc phase from FCC_A1 matrix phase in an Al-Sc binary alloy is simulated. To make a comparison, two separate calculations are performed, one assuming spherical morphology without elastic strain energy, and the other assuming cuboid morphology whose shape is determined by competition between interfacial energy and elastic strain energy. The simulation results are compared with experimental data collected from Marquis and Seidman¹ and Novotny and Ardell (2001)². In addition, mean cubic factor and cubic factor distribution are also plotted for cuboid shape to illustrate the spherical-cuboidal transition during precipitation.

Precipitation Morphology

To ensure that the settings are done on the correct Precipitation Calculators, the **Sphere** and **Cuboid** nodes are renamed from **Precipitation Calculator** to match their morphology. The morphology is set in the **Precipitate Phase** section when you click **Show details**. See P_08 for an example of this.

**PROJECT FILE, STEP-BY STEP INSTRUCTIONS AND VIDEO INFORMATION**

- Folder: Precipitation Module - TC-PRISMA
- File name: *P_09_Precipitation_Al-Sc_AL3SC_Sphere_Cuboid.tcu*

This example is available as a video tutorial on our website and YouTube channel.

You can also use the step-by-step instructions included in a PDF to follow the video or compare to the project file in Thermo-Calc.

<table>
<thead>
<tr>
<th><strong>System (System Definer)</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>Database package</td>
</tr>
<tr>
<td>Elements</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>Sphere and Cuboid Conditions (Precipitation Calculator)</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition</td>
</tr>
<tr>
<td>Matrix phase</td>
</tr>
</tbody>
</table>
### Precipitate phase

| AL3SC |

### Matrix Phase Data Parameters (Precipitation Calculator)

| Elastic properties (click Show details to display this setting) | For the **Sphere** node (renamed from Precipitation Calculator), the default, **Disregard** is kept.  
For the **Cuboid** node (renamed from Precipitation Calculator), choose **Cubic**. Then enter the elastic constants accordingly. Default elastic constants are given based on the major element of the alloy system. In this example that is  
- $c_{11}$ is 108.2 GPa  
- $c_{12}$ is 61.3 GPa  
- $c_{44}$ is 28.5 GPa |

### Precipitate Phase Data Parameters (Precipitation Calculator)

<table>
<thead>
<tr>
<th>Nucleation sites</th>
<th>Bulk</th>
</tr>
</thead>
<tbody>
<tr>
<td>Interfacial energy</td>
<td>The default</td>
</tr>
</tbody>
</table>

**Morphology (click Show details to display this setting)**  
For the **Sphere** node (renamed from Precipitation Calculator), keep the default.  
For the **Cuboid** node (renamed from Precipitation Calculator), **Cuboid** is selected.  

**Transformation strain (click Show details to display this setting)**  
For the **Sphere** node (renamed from Precipitation Calculator), keep the default.  
For the **Cuboid** node (renamed from Precipitation Calculator), **Calculate from molar volume** is selected to obtain a purely dilatational strain.  

### Calculation Type (Precipitation Calculator)

<table>
<thead>
<tr>
<th>Calculation type</th>
<th>Isothermal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>350° C</td>
</tr>
<tr>
<td>Simulation time</td>
<td>1.0E9 seconds</td>
</tr>
</tbody>
</table>

### Datasets (Experimental File Reader)

| Dataset 1 and Dataset 2 | Data sets included with this example and imported to one Experimental File Reader. It is used for the Mean Radius plot. |
Plot Results

Mean Radius

![Graph showing mean radius over time](image-url)
PSD
Mean Radius and Cubic Factor
PSD and Cubic Factor
Precipitation of Al-Sc AL3SC with Assumption of Sphere and Cuboid Morphologies: Precipitation Example P_09

HELPFUL INFORMATION

- All users can run this calculation, even those who do not have a license for the Precipitation module (TC-PRISMA).
- A companion video is available for this example, which can be watched here: https://www.youtube.com/playlist?list=PLfv6McToaTGSpvylOy3b_UV-8xpqLukJ
- This calculation is based on Precipitation module example P_09 – Precipitation_Al-Sc_AL3SC_Sphere_Cuboid, which is included in your installation. To run the example file, open Thermo-Calc and select Help > Examples Files. Open the Precipitation module (TC-PRISMA) folder. Double-click the example file and click Perform at the bottom centre of the Configuration window in Thermo-Calc.

ABOUT THE EXAMPLE

This example shows you how to calculate the precipitation of Al3Sc phase from FCC_A1 matrix phase in an Al-Sc binary alloy using the Precipitation module (TC-PRISMA).

Two separate calculations are performed so you can make a comparison of the results, one assuming spherical morphology without elastic strain energy, and the other assuming cuboid morphology whose shape is determined by competition between interfacial energy and elastic strain energy.

In addition, mean cubic factor and cubic factor distribution are plotted for cuboid shape to illustrate the spherical-cuboidal transition during precipitation.

If you run the example file included in your software, the simulation results are compared with experimental data collected from Marquis and Seidman (2001) and Novotny and Ardell (2001).
SETTING UP THE SYSTEM

1. Open Thermo-Calc in Graphical Mode.
2. Under templates, click **Precipitation Simulation**.
3. All the nodes for a precipitation calculation are added to the **Project** window:

4. Click the **System Definer 1** node.
5. Set the database package to **DEMO: Aluminium based alloys**, which loads both thermodynamic and kinetic demonstration aluminium databases.
6. From the periodic table, select the elements **Al** (aluminium) then **Sc** (scandium). Be sure to select Al first so that it is the dependant element.
7. Just to the right of the periodic table, select **Mole Percent** as the **Amount**.
8. Enter **0.18** for Sc. This automatically sets Al to **99.82**.
Our system is now defined, so we will set up the precipitation calculations.

**SETTING UP THE PRECIPITATION CALCULATIONS**

We will have two precipitation calculations in this example, one assuming spherical morphology without elastic strain energy, and the other assuming cuboid morphology whose shape is determined by competition between interfacial energy and elastic strain energy. We will then compare the results of the two calculations.

**Setting up the Precipitation Calculation with Spherical Morphology**

1. In the **Project** window, right-click the **Precipitation Calculator 1** node and select **Rename**. Enter **Sphere**, then press enter or click **OK**.

2. Notice that the composition we set in the **System Definer** auto-populated here.

3. Under **Matrix Phase** from the **Phase** list select **FCC_A1**.

4. Under **Precipitate Phase** from the **Phase** list select **AL3SC**.

5. Under **Calculation Type**, select **Isothermal**, which means that the same temperature is maintained throughout the calculation.

6. Enter **350** as the **Temperature** and select **Celsius**.

7. Enter **1.0E9** as the **Simulation time** and select **Seconds**.

Our first calculation is set, so we will configure the plot.
Configuring the Plot

1. In the Project window, right-click Plot Renderer 1 and select Rename. Name the plot Mean radius then press enter or click OK.
2. Under Y-axes, change the units to nm (nanometres) and from the Axis type list select Logarithmic 10.

The plot is now set, but we will set up another calculation and link it to the same plot renderer before we run the simulation.

Setting up the Precipitation Calculation with Cuboid Morphology

1. In the Project window, right-click the Sphere node and select Clone.
2. Right-click the new calculator node and select Rename.
3. Name the node Cuboid and click OK.
4. On the Configuration window to the right of Matrix Phase click Show Details.
5. From the Elastic Properties list select Cubic. The program automatically suggests a good set of default values, so we will leave them as they are.
6. To the right of Precipitate Phase, click Show Details.
7. From the Morphology list select Cuboid.
8. From the Transformation strain list select Calculate from molar volume.
The second calculation is now set up, so we will link it to the Plot Renderer node.

**Linking the Plot to the Calculation with Cuboid Morphology**

1. In the **Project** window, right-click the **Mean radius** node and select **Add Predecessor > Cuboid**.
2. Notice that in the **Configuration** window there are two tabs associated with this plot, one for **Sphere** and one for **Cuboid**. We already configured the Sphere settings, so we just need to set up the Cuboid tab.
3. Click the **Cuboid** tab.
4. Under **Y-axes**, change the unit to **nm** (nanometers) and from the **Axis type** list select **Logarithmic 10**.
5. Our calculation is now ready, so right-click the **Mean radius** node and select **Perform Now**.
INTERPRETING THE RESULTS OF THE PRECIPITATION CALCULATIONS

In this plot, the blue line represents the sphere calculation and the red line represents the cuboid calculation. You can see that, in this instance, they are almost identical.

By ‘radius for non-spherical particles’ we mean the radius of equivalent spheres with the same volume.

If you run the example file that is included in your software, the plot also contains an experimental file, which you can see closely matches the calculations.

PLOTTING ADDITIONAL VARIABLES

We will now use the same calculation to set up additional plots using the many plot variables that are available in the program. The examples below include two Y-axes each.

Plotting Mean Radius and Cuboid Factor

This plot will have two Y-axes: Mean radius and Cuboid factor.

1. Right-click the Cuboid node and add a Plot Renderer.
2. Right-click the new node and rename it Mean radius and Cuboid factor.
3. Under Y-axes click the green plus sign to add another axis.
4. Leave the first axis variable as Mean radius, but change the units to nm (nanometers) and set the axis type to Logarithmic 10.
5. Set the second Axis variable to Mean cubic factor.
6. Click to clear the Automatic Scaling check box. In the fields, enter the Limits from 1 to 1.41 and the step to 0.1.
7. The plot is now set, so right-click the **Mean radius and Cuboid factor** node and select **Perform Now**.

**Interpreting the Results of Mean Radius and Cuboid Factor**

In this plot, the blue line represents the evolution of the average radius of the cubic particles as a function of time. The red line shows the average cubic factor as a function of time.

The blue line represents the evolution of the average radius of the cubic particles as a function of time. Again, for non-spherical precipitates this means the radius of equivalent spheres with the same volume.
The red line shows the average cubic factor as a function of time. A value of one represents a spherical shape. A square root of two represents a cubic shape.

The evolution of the shape when the particles grow is determined by competition between interfacial energy and elastic strain energy. In general the shape is close to spherical at small particle sizes because the interfacial energy term dominates.

At large sizes the elastic energy dominates and it is therefore more favourable with a non-spherical shape. We can see that the particles get a more cubic form at later times when they grow to larger sizes.

**Plotting Particle Size and Cubic Factor Distribution**

This final plot will show the particle size and cubic factor distribution at the end of the simulation.

This plot will also have two Y-axes, so we will clone the previous plot.

1. Right-click the **Mean radius and Cuboid factor** node and select **Clone**.
2. Right-click the new node and rename it **PSD and Cuboid factor**.
3. Under the **Y-axes**, select **Size Distribution** as the first **Axis variable**.
4. Change the **Axis type** to **Linear**.
5. Set the second Y-axis to **Cubic factor distribution** and enter a **Time** of **1e9 Seconds**.
6. Click to clear the **Automatic Scaling** check box. Enter the **Limits** from 1 to 1.45 and the **step** to 0.1.
7. Under **Size X-axis**, change the unit to **nm** (nanometers).
8. Click **Perform** at the bottom centre of the **Configuration** window.
Interpreting the Results of Particle Size Distribution and Cuboid Factor

The blue curve, which shows the particle size distribution, is close to the regular LSW size distribution that we would have expected for spherical particles.

The cubic factor distribution shows that the smallest particles are closer to spherical and that the larger ones get more and more cubic.

References

**P_10: Initial Particle Size Distribution of Fe-Cr-C**

This example demonstrates the effect of initial particle size distribution of the precipitate phases on the overall precipitation kinetics. It uses two Precipitation Calculators to simulate and compare carbide precipitations from a ferritic BCC_A2 matrix in a Fe-0.1C-12Cr alloy. Three carbides, CEMENTITE, M23C6 and M7C3, are included in the calculations for competitive precipitations, and the precipitation kinetics are compared with or without initial particle size distribution.

The example illustrates the use of the particle size distribution setting. You can import data from a spreadsheet or text file (.xls, .xlsx, .csv or .txt formats are acceptable). The Preexisting Particle Size Distribution window shown below, provides a graphical representation of the radius versus corresponding frequencies.

![Precipitation Particle Size Distribution](image)

**PROJECT FILE INFORMATION**

- Folder: Precipitation Module - TC-PRISMA
- File name: P_10_Precipitation_Initial_PSD_FeCrC.tcu
<table>
<thead>
<tr>
<th>System (System Definer)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Database package</td>
<td>Demo: Steels and Fe-alloys (FEDEMO and MFDEMO)</td>
</tr>
<tr>
<td>Elements</td>
<td>Fe, C, Cr</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Conditions (Precipitation Calculator)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition</td>
<td>Fe-0.1C-12Cr Mass percent</td>
</tr>
</tbody>
</table>
| Matrix phase                         | BCC_A2  
All other defaults are kept. |
| Precipitate phases                   | CEMENTITE, M23C6 and M7C3 |

<table>
<thead>
<tr>
<th>Precipitate Phase Data Parameters (Precipitation Calculator)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Nucleation sites</td>
<td>Grain boundaries (all calculations): Calculated from the matrix settings with a wetting angle of 90°</td>
</tr>
</tbody>
</table>
| Interfacial energy                                            | User-defined function f(r,T) (all calculations):  
  - CEMENTITE: 0.167 J/m²  
  - M23C6 0.252 J/m²  
  - M7C3 0.282 J/m² |
| Preexisting size distribution (click Show details to display this setting) | For the Precipitation Calculator including particle size distribution, and for all precipitate phases, this check box is selected.  
For each precipitate phase (CEMENTITE, M23C6 and M7C3), click Edit particle size distribution to make changes to the parameters. A window opens with a graphical representation of the radius vs number density. |

<table>
<thead>
<tr>
<th>Calculation Type (Precipitation Calculator)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Calculation type</td>
<td>Isothermal</td>
</tr>
<tr>
<td>Temperature</td>
<td>1053 K</td>
</tr>
<tr>
<td>Simulation time</td>
<td>400 000 seconds</td>
</tr>
</tbody>
</table>
**Plot Results**

*Volume Fraction with Initial Particle Size Distribution*

![Graph showing volume fraction with initial particle size distribution over time.](image-url)
Volume Fraction with No Initial Particle Size Distribution

P_11: Interfacial Energy Function

In some cases, interfacial energy may be a function of temperature and/or particle radius. This example uses four Precipitation Calculators at four temperature points in 30 K increments: 673 K, 703 K, 733 K, and 763 K. It is an isothermal calculation to examine the mean radius of an Al-0.12Sc system. It uses an FCC_A1 matrix phase and AL3SC precipitate phase with bulk nucleation sites and user-defined interfacial energy function. The user defined interfacial energy function uses an error function to set a smooth transition of the interfacial energy from 0.065 J/m² to 0.085 J/m² for particle radii below and above 1e⁻⁸m and 5e⁻⁸m, respectively.

A dataset based on Iwamura and Miura (¹) data is compared with the calculated results.

PROJECT FILE INFORMATION

- Folder: Precipitation Module - TC-PRISMA
- File name: P_11_Interfacial_energy_function.tcu

### System (System Definer)

<table>
<thead>
<tr>
<th>Database package</th>
<th>Demo: Aluminum-based Alloys (ALDEMO, MALDEMO)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Elements</td>
<td>Al, Sc</td>
</tr>
</tbody>
</table>

### Conditions (Precipitation Calculator)

<table>
<thead>
<tr>
<th>Composition</th>
<th>Al-0.12Sc Mole percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Matrix phase</td>
<td>FCC_A1</td>
</tr>
<tr>
<td></td>
<td>All other defaults are kept.</td>
</tr>
<tr>
<td>Precipitate phase</td>
<td>AL3SC</td>
</tr>
<tr>
<td></td>
<td>Nucleation sites (all calculations): Bulk (6.025E28 m(^3))</td>
</tr>
<tr>
<td></td>
<td>Interfacial energy (all calculations): User-defined function (f(r,T): 0.075+0.011*\text{erf}(\frac{r-3e-8}{1e-8}) J/m(^2))</td>
</tr>
</tbody>
</table>

### Calculation Type (Precipitation Calculator)

<table>
<thead>
<tr>
<th>Calculation type</th>
<th>Isothermal (all calculations)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>Four temperature points in 30 K increments: 673 K, 703 K, 733 K, and 763 K.</td>
</tr>
<tr>
<td>Simulation time</td>
<td>1 000 000 seconds (all calculations)</td>
</tr>
</tbody>
</table>

### Datasets (Experimental File Reader)

| Wamura 2004 (Dataset 1)   | Data set included with this example and imported to one Experimental File Reader. |
**Plot Results**

**Mean Radius**

This example compares the **Simplified, General** and **Advanced** growth rate models for an Al-Zr system. The resulting plot compares the mean radius of the spheres for each AL3ZR_D023 precipitate phase calculated for each type of growth rate model.

For more details, see the theory described in *Growth*.

The example takes several minutes to run.

All models treat a spherical particle (precipitate) of stoichiometric composition or with negligible atomic diffusivity. Local equilibrium at the precipitate-matrix interface is assumed.

When you use the **Advanced** model, the velocity of a moving phase interface and the operating tie-line are solved together from flux-balance equations. This model can treat both high supersaturation and cross diffusion rigorously. It can also capture the transition between NPLE (non-partitioning local equilibrium) and PLE (partitioning local equilibrium) without any *ad hoc* treatment.
The *Simplified* model is based on the quasi-steady state diffusion approximation, and estimates solute partitioning with matrix composition and nuclei composition instead of time-consuming stepwise tie-line calculations. It also neglects cross diffusion for simplicity.

The *General* model can be considered the same theoretical approximation as, but an improvement over, the *Simplified* model, with cross-diffusion terms taken into account, as well as adjustment of Gibbs-Thomson effect and effective diffusivity implemented.

A dataset based on Knipling et al. (1) data is compared with the calculated results.

**PROJECT FILE INFORMATION**

- Folder: Precipitation Module - TC-PRISMA
- File name: *P_12_Precipitation_Al-Zr_GrowthRateModel_comparation.tcu*

**System (System Definer)**

<table>
<thead>
<tr>
<th>Database package</th>
<th>Demo: Aluminum-based Alloys (ALDEMO, MALDEMO)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Elements</td>
<td>Al, Zr</td>
</tr>
</tbody>
</table>

**Conditions (Precipitation Calculator)**

<table>
<thead>
<tr>
<th>Composition</th>
<th>Al-0.2Zr Mole percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Matrix phase</td>
<td>FCC_A1</td>
</tr>
<tr>
<td>All other defaults are kept.</td>
<td></td>
</tr>
<tr>
<td>Precipitate phase</td>
<td>AL3ZR_0023</td>
</tr>
<tr>
<td>Click <a href="#">Show details</a> to select the <em>Growth rate model</em> (<em>Simplified</em>, <em>Advanced</em> and <em>General</em>). All other defaults are kept.</td>
<td></td>
</tr>
</tbody>
</table>

**Calculation Type (Precipitation Calculator)**

<table>
<thead>
<tr>
<th>Calculation type</th>
<th>Isothermal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>425 Celsius</td>
</tr>
</tbody>
</table>

---

Simulation time | 400 hours

Datasets (Experimental File Reader)

2008 Knipling | Data set included with this example and imported to one Experimental File Reader.

Plot Results

Mean Radius

P_13: Paraequilibrium Precipitation of Cementite Fe-C-Cr

In this example, the precipitation of cementite during tempering of a Fe-Cr-C steel is simulated considering two interface conditions: one is the usual ortho-equilibrium condition; the other is the para-equilibrium condition. The simulation results are compared with the experimental data from Sakuma et al (1980) T. Sakuma, N. Watanabe, and T. Nishizawa, "The effect of alloys element on the coarsening behavior of cementite particles in ferrite", Trans. JIM, v. 21, 1980, pp.159-168.

This example demonstrates that the early stage of the cementite precipitation can only be accounted for by a simulation applying the para-equilibrium condition, under which the precipitation kinetics are controlled by the diffusion of C. The comparison also shows a later
stage gradual transition from the para-equilibrium condition to the ortho-equilibrium condition, and if the tempering time is long enough the diffusion of Cr has a dominating effect on the coarsening of cementite.

**PROJECT FILE INFORMATION**

- Folder: Precipitation Module - TC-PRISMA
- File name: P_13_Precipitation_Fe-Cr_Paraequilibrium_Precipitation_of_Cementite.tcu

For more details, see the theory described in *Growth*.

The example may take over two hours to run.

| **System (System Definer)** |
| Database package | Demo: Steels and Fe-alloys (FEDEMO, MFDEMO) |
| Elements | Fe, Cr, C |

| **Conditions (Precipitation Calculator)** |
| Composition | Fe-0.95Cr-1.065C Mass percent |
| Matrix phase | BCC_A2 |
| | All other defaults are kept. |
| Precipitate phase | CEMENTITE |
| | Click Show details to select the Growth rate model (Simplified and Para-eq). All other defaults are kept. |

| **Calculation Type (Precipitation Calculator)** |
| Calculation type | Isothermal |
| Temperature | 773 Kelvin |
| Simulation time | 20 hours for the paraequilibrium model and 600 hours for the simplified model. |

| **Datasets (Experimental File Reader)** |
| 1980 Sakuma | Data set included with this example and imported to one Experimental File Reader. |
Plot Results

**Mean Radius**

Comparing results from Para-eq (PE) and Simplified (OE) growth models.