Precipitation Module (TC-PRISMA) User Guide

Version 2016a

Thermo-Calc Software

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Contents

Introduction to the Precipitation Module (TC-PRISMA)

In this section:

About the Precipitation Module (TC-PRISMA)

✎ As of Thermo-Calc version 2016a, 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 only 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 multi-phase 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
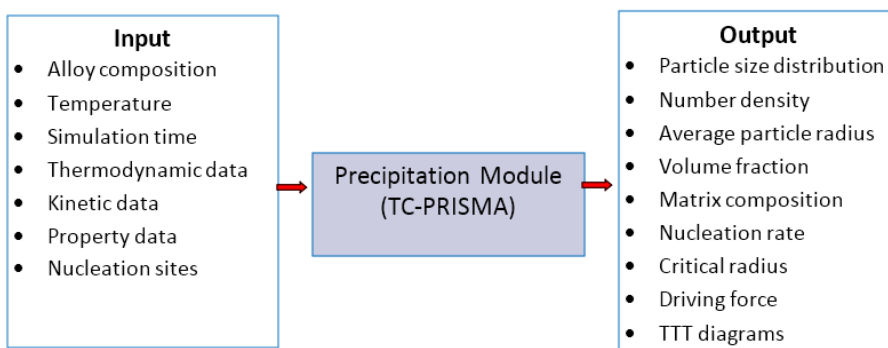
The Precipitation Module relies on CALPHAD-based software tools and databases to provide the necessary bulk thermodynamic and kinetic data for phases in multicomponent systems. The CALPHAD approach has been developed for more than 50 years and is routinely applied to design new alloys and optimize existing 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 within Thermo-Calc or the PDF called *Precipitation Module (TC-PRISMA) Documentation Set* to navigate all the content. See *Help Resources below* to learn how to access this information if you have not already done so.

Help Resources

Online and Context Help

Online Help

To access online help in a browser, open Thermo-Calc and select **Help →Online Help**. The content opens in a browser but uses local content so you don't need an internet connection.

Context Help

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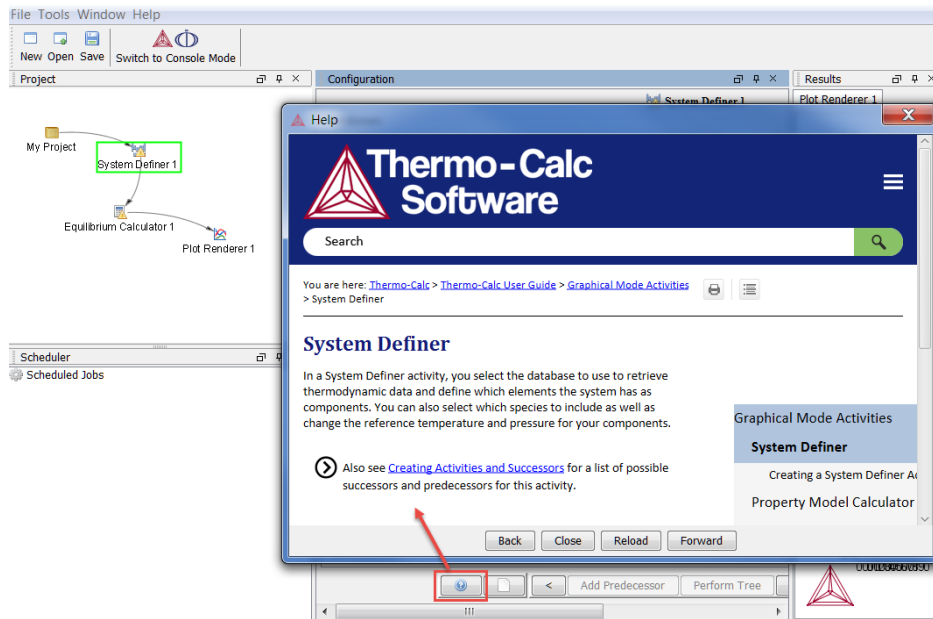
The window that opens has the same content as the help you access in the browser. There are these extra navigation buttons in this view.

- 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 to load pages and create a history), to **Close** the window, and **Reload** the original content.

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.

Precipitation Module (TC-PRISMA) Options

The Precipitation Module, previously only 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 two components. Without it you are able to use the module in *Demo Mode*. See *Demonstration (Demo) Mode* on page 9 to learn more.

Precipitation Simulation Template

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

☑   If you are using the Precipitation Module in Demo Mode, see *Demonstration (Demo) Mode on page 9* 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 this button to add these nodes to the Project.
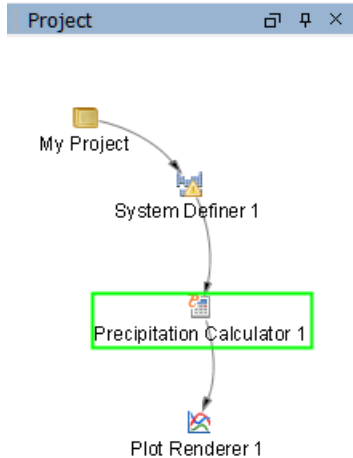
⊙ "Creating a "Project from a Template" in the *Thermo-Calc User Guide* or search the Online Help.

Precipitation Calculator

A Precipitation Calculator allows you to set the conditions for, and perform, a precipitation calculation. Details about this activity are described in *Precipitation Calculator* on page 24.

Demo Database Packages for the Examples Collection

Both a thermodynamic and mobility database is 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.

⊙ For more information see *Precipitation Module Examples* on page 10 and "Creating a Database Package" in the *Thermo-Calc User Guide*.

✎ If you are using the Precipitation Module in Demo Mode, see *Demonstration (Demo) Mode* on the next page to learn more.
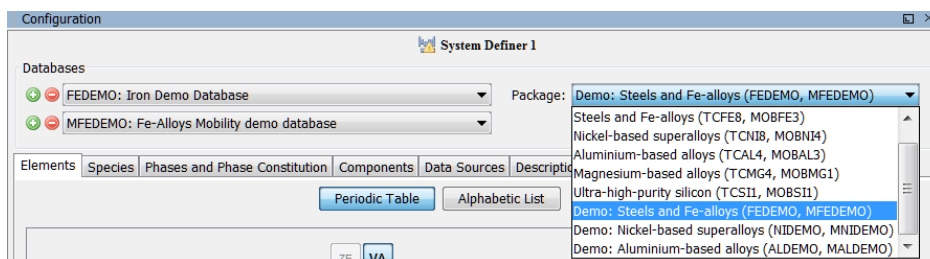
Demonstration (Demo) Mode

The Precipitation Module, and two examples (see *Precipitation Module Examples* on the next page), are available to all Thermo-Calc users but only for simulations with two components. 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.

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 two components for a demo simulation.

If you define more than two components 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.
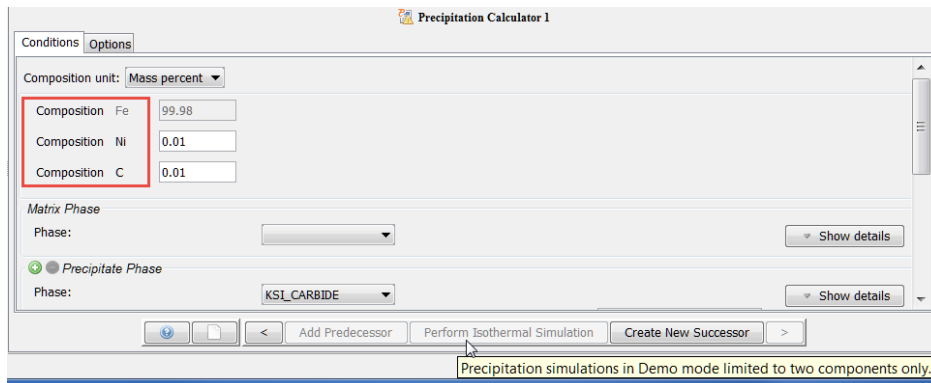
Selecting the Disordered Phase as a Matrix Phase

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

- TCAL and MOBAL (Al-based alloys)

- TCCU and MOBCU (Cu-based alloys)

- TCNI and MOBNI (Ni-based alloys)

In the TCNI/MOBNI, TCAL/MOBAL, 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 Al and 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**.

Precipitation Module Examples

The Precipitation Module examples are included with the *Graphical Mode Example Collection*, which you can find by searching the Online Help. Below are the descriptions of the examples specific to using the *Precipitation Calculator*.

> (!) Examples 13 and 16 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.

Example 13: Isothermal Precipitation of Al$_3$Sc

This example simulates the kinetics of precipitation of Al$_3$Sc from an FCC_A1 solution phase. The simulation results can be compared with experimental data collected from Marquis and Seidman[1] and Novotny and Ardell[2].

Details and Plot Example

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[1]E. Marquis, D.. Seidman, Nanoscale structural evolution of Al3Sc precipitates in Al(Sc) alloys, Acta Mater. 49 (2001) 1909–1919.

[2]G.M. Novotny, A.J. Ardell, Precipitation of Al3Sc in binary Al–Sc alloys, Mater. Sci. Eng. A Struct. Mater. Prop. Microstruct. Process. 318 (2001) 144–154.

System	
Database package	Demo: Aluminum-based alloys (ALDEMO, MALDEMO)
Elements	Al, Sc
Matrix phase	FCC_A1
Precipitate phases	AL3SC
Conditions	
Composition	Al-0.18Sc Mole percent
Temperature	350° C
Simulation time	1.0E7 seconds
Nucleation sites	Bulk
Precipitate Phase Data Parameters	
Interfacial energy	Calculated
Other	
Calculation type	Isothermal
File name	Ex_13_Precipitation_Al-Sc_AL3SC.tcu

Plot Results
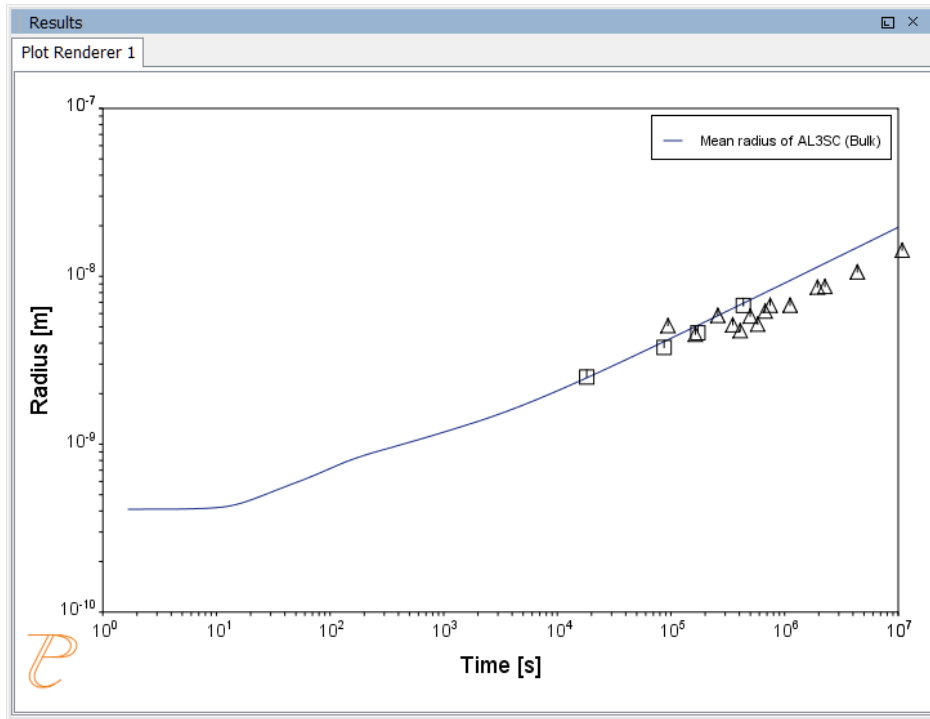
Example 14: Stable and Metastable Carbides - Isothermal

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.

Details and Plot Example

This example uses the Equilibrium Calculator and a property diagram 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.

System	
Database package	Demo: Steels and Fe-alloys (FEDEMO,MFEDEMO)
Elements	Fe, C, Cr
Matrix phase	BCC_A2

Precipitate phases	Cementite, M23C6 and M7C3
Conditions	
Composition	Fe-0.1C-12Cr Mass percent
Temperature	1053 K
Simulation time	400 000 seconds
Nucleation sites	Grain boundaries
Matrix Phase Data Parameters	
Grain radius	1.0E-4 m
Precipitate Phase Data Parameters	
Interfacial energy	Cementite 0.174 J/m^2, M23C6 0.26 J/m^2, M7C3 0.3 J/m^2
Other	
Calculation type	Isothermal
File name	Ex_14_Precipitation_Fe-C-Cr_Cementite-M7C3-M23C6

Plot Results
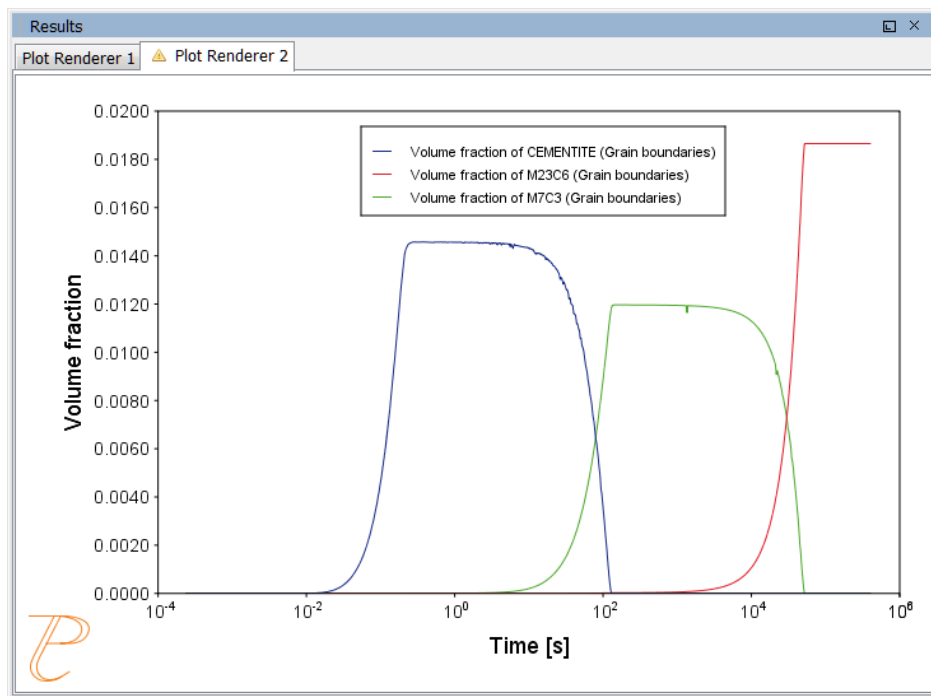
Example 15: Stable and Metastable Carbides - TTT Diagram

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.

Details and Plot Example

This example uses the Equilibrium Calculator and a property diagram 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.

System	
Database package	Demo: Steels and Fe-alloys (FEDEMO,MFEDEMO)
Elements	Fe, C, Cr
Matrix phase	BCC_A2
Precipitate phases	Cementite, M23C6 and M7C3
Conditions	
Composition	Fe-0.1C-12Cr Mass percent
Temperature	500° to 800° C with 25°C steps
Max. simulation time	1.0E8 seconds
Nucleation sites	Grain boundaries
Matrix Phase Data Parameters	
Grain radius	1.0E-4 m
Precipitate Phase Data Parameters	
Interfacial energy	Cementite 0.174 J/m^2, M23C6 0.26 J/m^2, M7C3 0.3 J/m^2
Other	
Calculation type	TTT diagram
Stop criterium	Volume fraction of phase is set to 0.0001
File name	Ex_15_Precipitation_Fe-C-Cr_TTT_Cementite-M7C3-M23C6

Plot Results
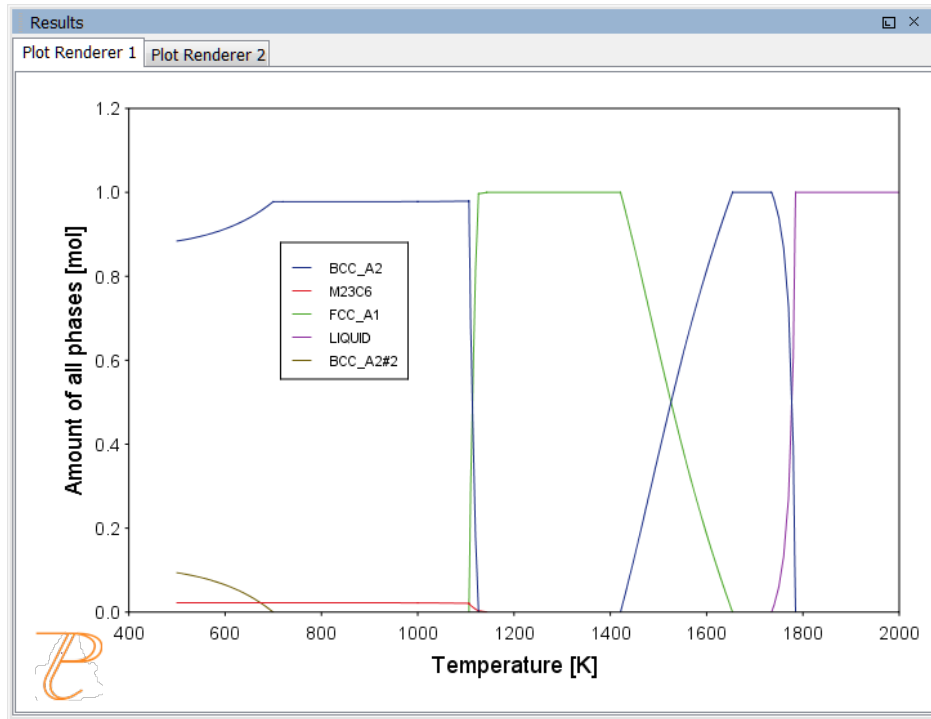
Example 16: Precipitation of Iron Carbon Cementite

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

Details and Plot Example

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.

System	
Database package	Demo: Steels and Fe-alloys (FEDEMO,MFEDEMO)
Elements	Fe, C
Matrix phase	BCC_A2
Precipitate phase	Cementite
Conditions	
Composition	Fe-0.016C mass percent

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[1]Wert, C. A. (1949). Precipitation from Solid Solutions of C and N in α-Iron. Journal of Applied Physics, 20(10), 943.

Temperature	102° C
Simulation time	600 000 seconds
Nucleation sites	Dislocations
Matrix Phase Data Parameters	
Grain aspect ratio	1.0
Precipitate Phase Parameters	
Interfacial energy	0.24 J/m^2
Dislocation density	1.5e11m^{-3}
Other	
Calculation type	Isothermal
Growth rate model	Advanced (on the Options tab)
File name	Ex_16_Precipitation_Fe-C_Cemetite

Volume Fraction
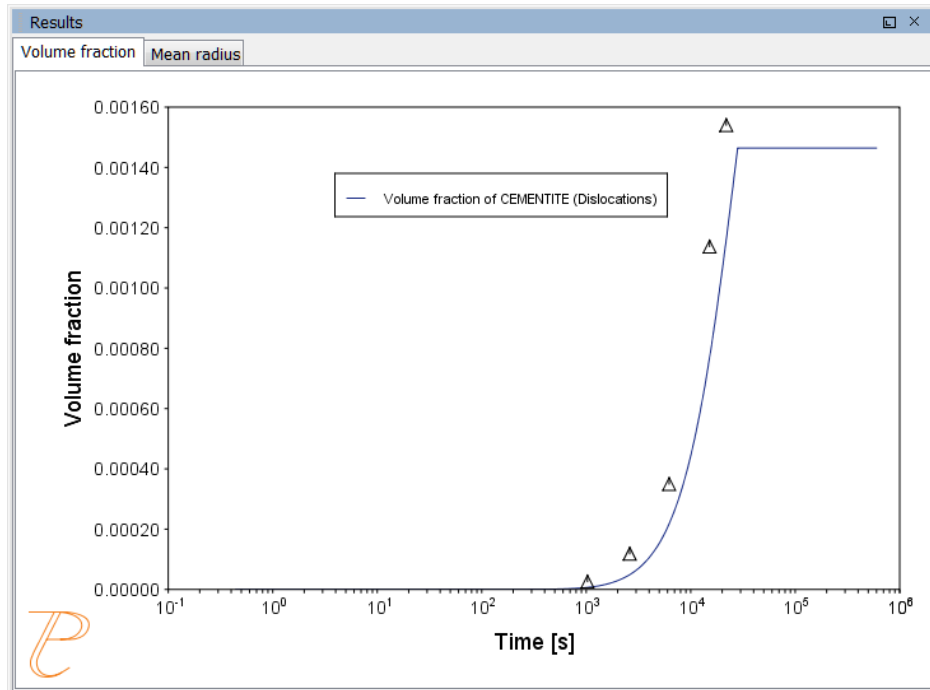
Example 17: Precipitation of γ′ in Ni Superalloys - Isothermal

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.[1].

Details and Plot Examples

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. Search the online help for **About Ordered Phases** in the *Precipitation Module (TC-PRISMA) User Guide* for details.

System	
Database package	Demo: Nickel-based Super Alloys (NIDEMO and MNIDEMO)
Elements	Ni, Al Cr
Matrix phase	DIS-FCC_A1 (see note above about how to select this phase)
Precipitate phase	FCC_L12#2
Conditions	
Composition	Ni-9.8Al-8.3Cr Mole percent
Temperature	800° C
Simulation time	1 000 000 seconds
Nucleation sites	Bulk
Precipitate Phase Data Parameters	
Interfacial energy	0.023 J/m^2
Other	
Calculation type	Isothermal
File name	Ex_17_Precipitation_Ni-Al-Cr_Isothermal_Gamma-Gamma_prime

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[1]C.K. Sudbrack, T.D. Ziebell, R.D. Noebe, D.N. Seidman, Effects of a tungsten addition on the morphological evolution, spatial correlations and temporal evolution of a model Ni–Al–Cr superalloy, Acta Mater. 56 (2008) 448–463.

Volume Fraction
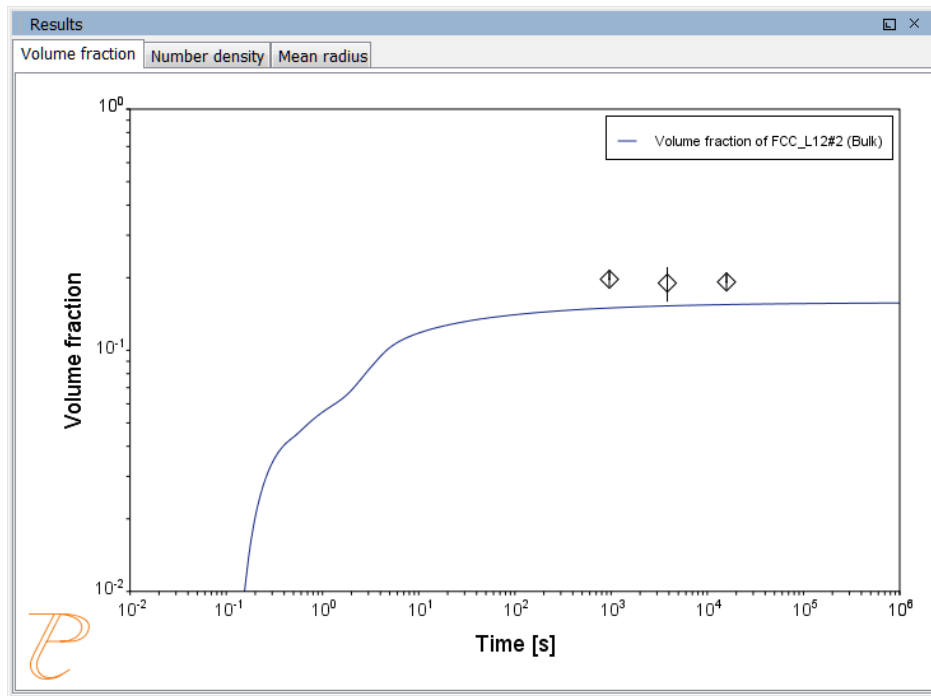
Number Density
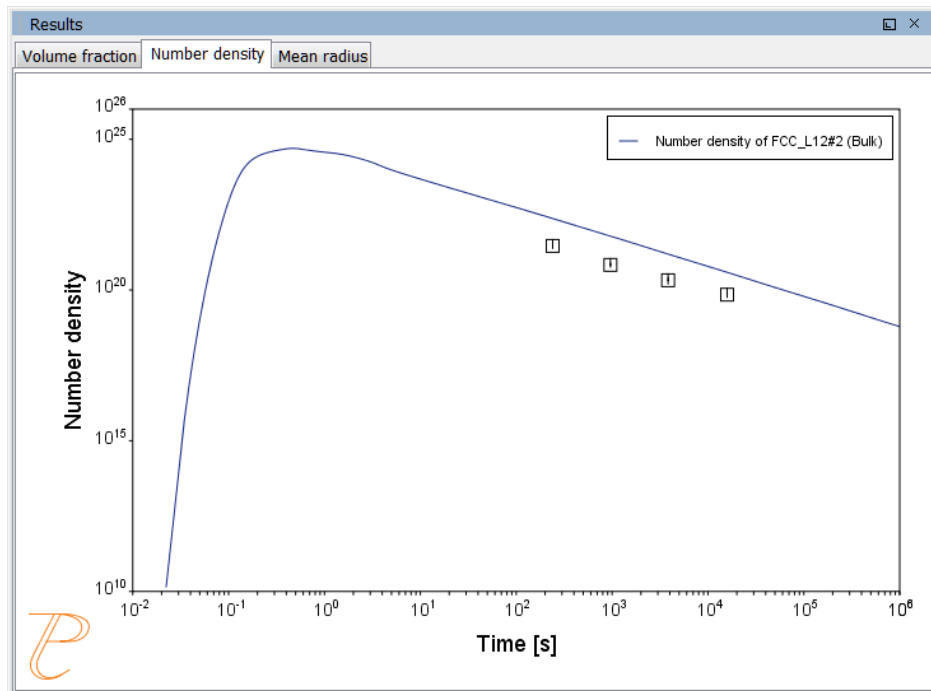
Mean Radius
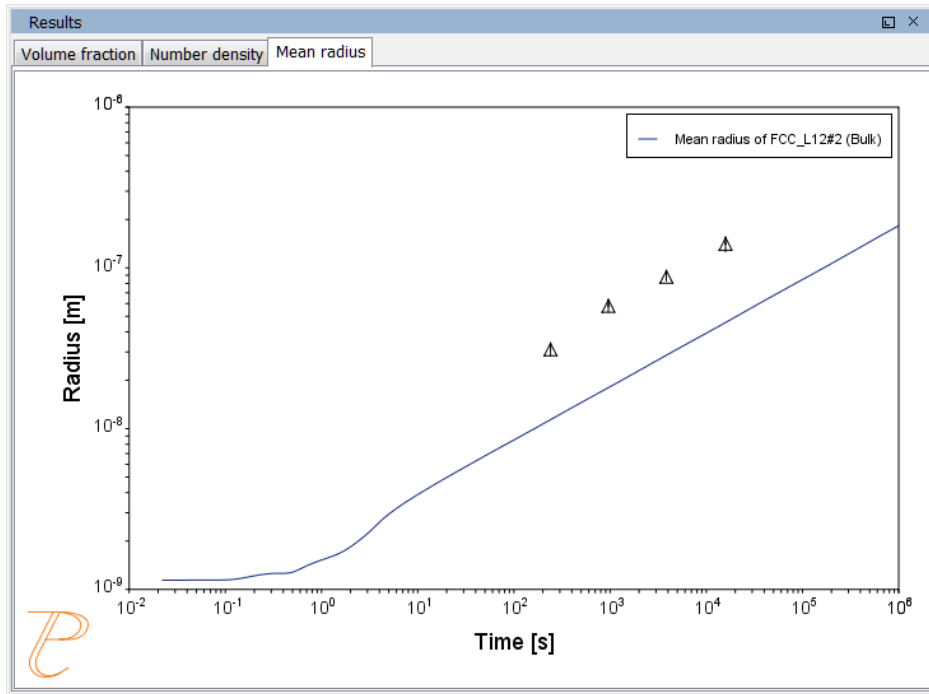
Example 18: Precipitation of γ′ in Ni Superalloys - Non-isothermal

This example simulates the kinetics of precipitation of γ′ phase from γ 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.[1] .

Details and Plot Examples

In these examples the Separate multimodal PSD check box is selected on the Plot Render to plot the mean radius and size distributions of the two compositions.

Plotting the size distribution from the final simulation time of 1470 seconds, you can see there are several peaks, although these are not completely separated. Use the 'Separate multimodal PSD' check box on the Plot Renderer to separate the peaks. Then 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 1470'.

    ✎   DIS_FCC_A1 needs to be selected on the System Definer. Search the online help for **About Ordered Phases** in the *Precipitation Module (TC-PRISMA) User Guide* for details.

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[1]T. Rojhirunsakool, S. Meher, J.Y. Hwang, S. Nag, J. Tiley, R. Banerjee, Influence of composition on monomodal versus multimodal γ′ precipitation in Ni–Al–Cr alloys, J. Mater. Sci. 48 (2013) 825–831.

System	
Database package	Demo: Nickel-based Super Alloys (NIDEMO and MNIDEMO)
Elements	Ni, Al, Cr
Matrix phase	DIS_FCC_A1 (see note above about how to select this phase)
Precipitate phase	FCC_L12#2
Conditions	
Composition (Ni-8Al-8Cr)	Ni-8Al-8Cr Mole percent
Composition (Ni-10Al-10Cr)	Ni-10Al-10Cr Mole percent
Temperature	0.23 K/s cooling rate
Simulation time	1470 s (Ni-8Al-8Cr), 3300 s (Ni-10Al-10Cr)
Nucleation sites	Bulk
Matrix Phase Data Parameters	
Mobility enhancement prefactor	5.0
Precipitate Phase Data Parameters	
Interfacial energy	0.023 J/m^2
Other	
Calculation type	Non-isothermal
Separate multimodal PSD for 8Al-8Cr	On the Plot Renderer, 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.
Separate multimodal PSD for 10Al-10Cr	On the Plot Renderer, the Valley depth ratio is set to 0.18 for both plots.
File name	Ex_18_Precipitation_Ni-Al-Cr_Non-isothermal_Gamma-Gamma_ prime

Mean Radius Ni-8Al-8Cr
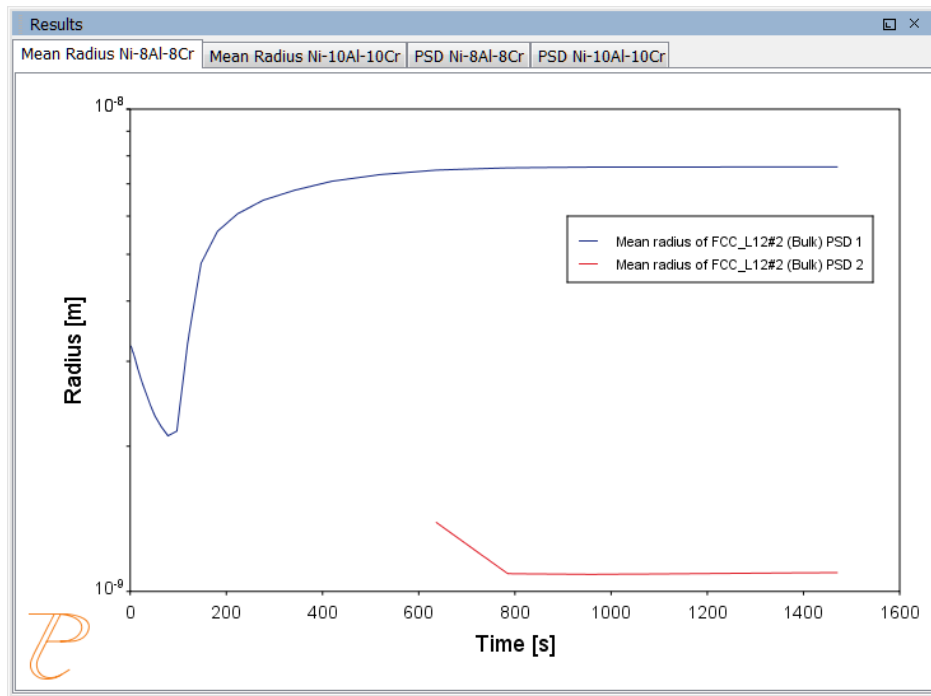
Mean Radius Ni-10Al-10CR
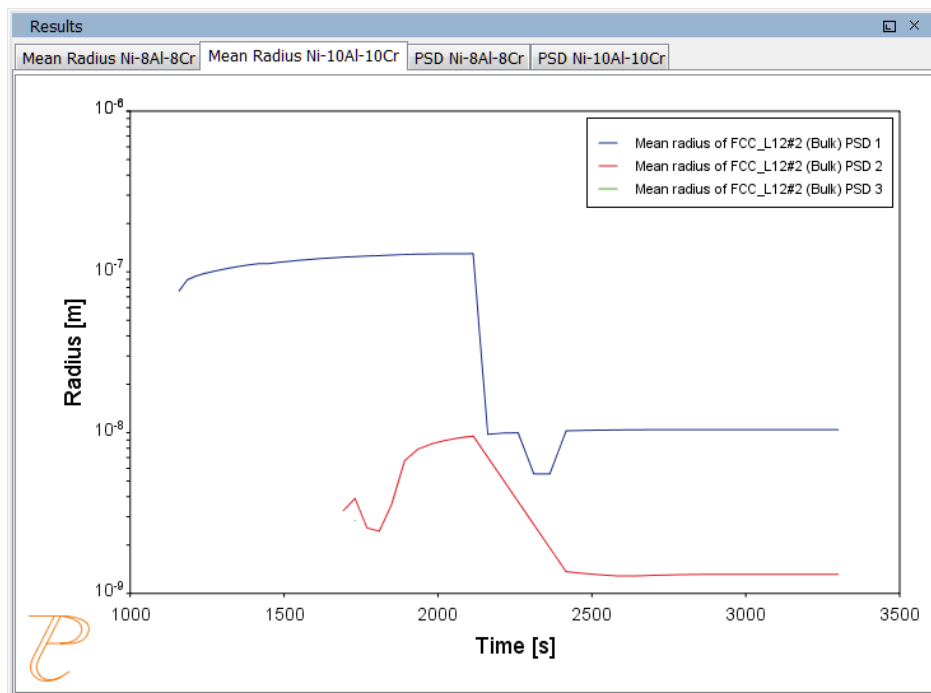
Size Distribution (PSD) Ni-8Al-8Cr
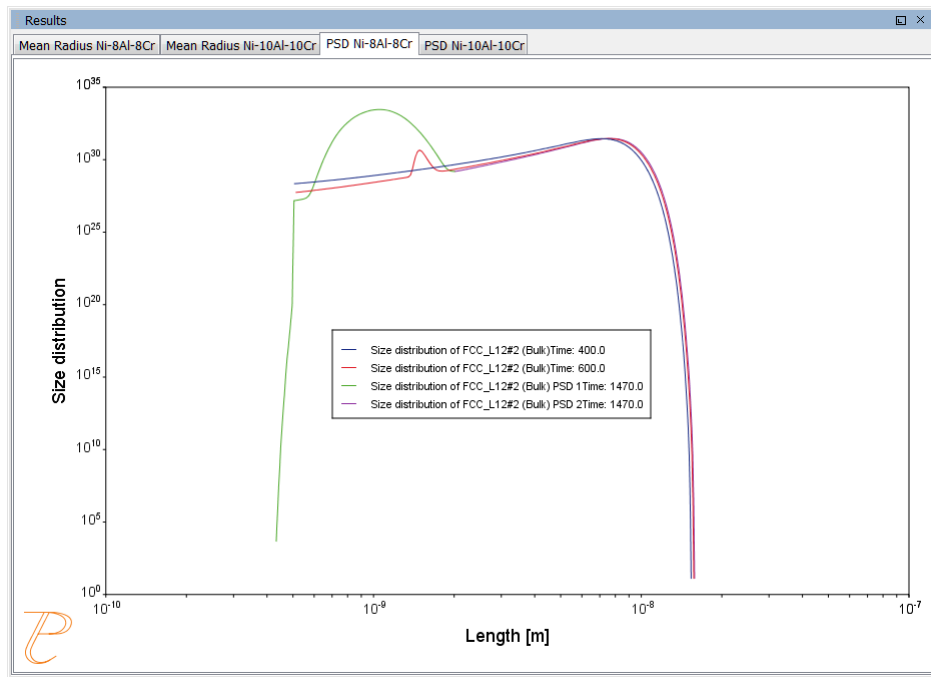
Size Distribution (PSD) Ni-10Al-10Cr
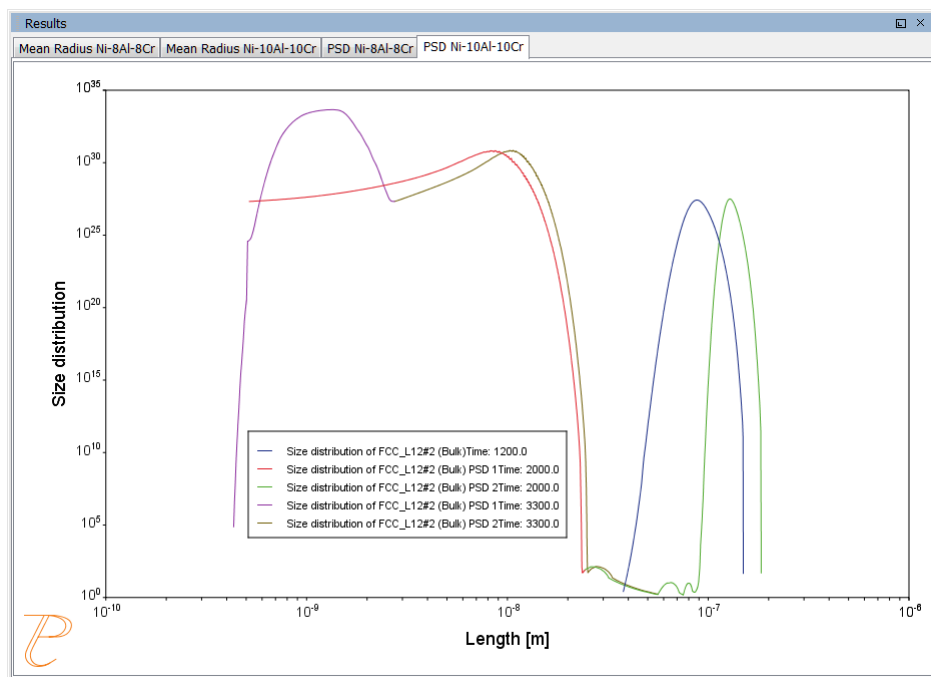
Using the Precipitation Calculator

In this section:

Precipitation Calculator

> ⚠ The Precipitation Calculator is available with two components if you do not have the additional Precipitation Module (TC-PRISMA) license. With the add-on module you can use all available components.

A Precipitation Calculator allows you to set the conditions for, and perform, a precipitation calculation. The Configuration window for a Precipitation Calculator has these 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 viewed in Simplified or Advanced mode.

Configuration Window

Example

Conditions Tab Settings

These are the settings on the Precipitation Calculator Conditions tab.

Setting or Condition	Options
Composition unit	Choose from **Mass percent**, **Mole percent**, **Mass fraction** or **Mole fraction**.
Matrix Phase	Specify the **Phase**. Click **Show Details** for more settings.
Precipitate Phase	Specify the **Phase**, **Nucleation Sites**, and **Interfacial energy**. Click **Show Details** for more settings.
Calculation Type	Choose **Isothermal**, **Non-isothermal** or **TTT diagram**.

Matrix Phase

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

> Only phases with kinetic data can be selected as the matrix phase. If the list is empty, go to the System Definer to make sure that both types of databases are selected and defined. See "System Definer" in the *Thermo-Calc User Guide* or search the Online Help.

> Click **Show details** to view these additional settings:

- **Molar volume**: Choose the default to take the value from the **Database** or **User-defined** to enter another value. **Database** is available in the list when the molar volume for the phase is defined in the thermodynamic database.

- **Grain radius**: Enter a numerical value and choose a unit from the list.

- **Grain aspect ratio**: Enter a numerical value.

- **Dislocation density**: Enter a numerical value.

- **Mobility enhancement prefactor**: Enter a numerical value.

- **Mobility enhancement activation energy**: Enter a numerical value.

Precipitate Phase

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

> The phases available to choose have both thermodynamic and kinetic data. If the list is empty, go to the System Definer to make sure that both types of databases are selected and defined. See "System Definer" in the *Thermo-Calc User Guide* or search the Online Help.

Nucleation sites: Choose one of the following from the list.

- **Bulk**, **Grain boundaries**, **Grain edges**, **Grain corners**, or **Dislocations**. Click to select the **Calculate from matrix settings** check box if you want to calculate the number density of sites.

- For Grain boundaries, Grain edges and Grain corners, enter the **Wetting angle** in addition to the matrix settings.

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

Interfacial energy: Choose **Calculated** to use the estimated value and then enter a different **prefactor** value if you want to adjust the estimated value. You can also choose **User defined** to enter a value in J/m^2.

☑ Click **Show details** to view these additional settings:

- **Molar volume**: Choose the default to take the value from the **Database** or **User-defined** to enter another value. **Database** is available in the list when the molar volume for the phase is defined in the thermodynamic database.

- **Phase boundary mobility**: Enter a numerical value.

- **Phase energy addition**: Enter a numerical value.

- **Approximate driving force**: Select the check box to include this if simulations with several compositions sets of the same phase create problems. See the theory for .

Calculation Type

Isothermal

Use an **Isothermal** calculation type to do a precipitation simulation at constant temperature.

For the **Isothermal** calculation type, enter a **Temperature** and **Simulation time**.

Non-Isothermal

For the **Non-isothermal** calculation type, select a **Temperature unit** and **Time unit** from the lists. Enter a value for the **Simulation time**.

Click **Thermal Profile** to define the heat treatment schedule. Here the **Temperature** and **Time** coordinates of thermal profile points are entered. A minimum of two points is required. You can also click **Import** to add your own thermal profile from an Excel spreadsheet.

Edit Thermal Profile Window
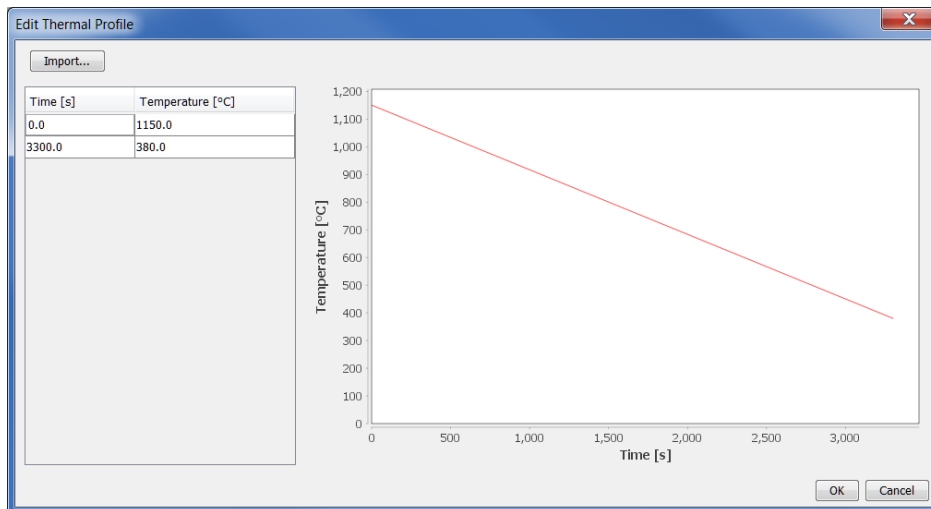
TTT-Diagram

Use a **TTT-diagram** calculation type to do a a precipitation simulation of the time-temperature-transformation (TTT).

For the **TTT diagram** calculation type , enter **Min**, **Max**, and **Step** values for the **Temperature** and choose a **Unit** from the list.

Max simulation time: Enter a numerical value and choose a **Unit** from the list.

Stop criterium: Choose **Volume fraction of phase** or **% of equilibrium fraction** and then enter a numerical value in the field. For each temperature, the simulation stops when the stop criterium is fulfilled or if the maximum simulation time is reached, whichever happens first.

Options Tab Settings

See *Numerical Method* on page 48 for details and equations about each of these settings.

These are the settings on the Precipitation Calculator Options tab.

Settings

Growth Rate Model

Choose from **Simplified** (the default) or **Advanced**.

Numerical Parameters

Enter numerical values for the following as required.

- **Max time step fraction**: The maximum time step allowed for time integration as fraction of the simulation time.

- **No. of grid points over one order of magnitude in radius**: Default number of grid points for every order of magnitude in size space.

- **Max no. of grid points over one order of magnitude in radius**: The maximum allowed number of grid points in size space.

- **Min no. of grid points over one order of magnitude in radius**: The minimum allowed number of grid points in size space.

- **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.

- **Max relative radius change**: The maximum value allowed for relative radius change in one time step.

- **Relative radius change for avoiding class collision**: Set a limit on the time step.

- **Max overall volume change**: This defines the maximum absolute (not ratio) change of the volume fraction allowed during one time step.

- **Max relative change of nucleation rate in logarithmic scale**: This parameter ensures accuracy for the evolution of effective nucleation rate.

- **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

- **Min radius for a nucleus to be considered as a particle**: The cut-off lower limit of precipitate radius.

- **Max time step during heating stages**: The upper limit of the time step that has been enforced in the heating stages.

Plot Renderer for the Precipitation Calculator

The Plot Renderer for the *Precipitation Calculator* has additional functionality when using the non-isothermal calculation type. This is described in this section. For standard information, see "Plot Renderer" in the *Thermo-Calc User Guide* or search for it in the Online Help.

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.

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.
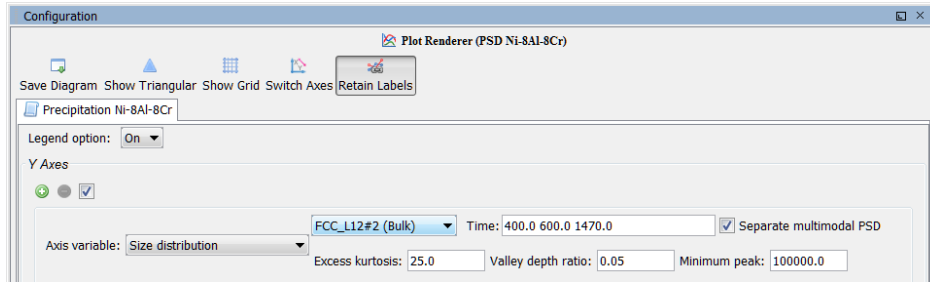
It can be applied on the following plot properties:

- 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** is selected as the **Axis variable**. Enter one or a series of numbers in the field, separated by a space, colon (:), semicolon (;) or comma (,).

Example

For example, if you enter `100.0`, `1000.0` and `1.0E7` in the field:
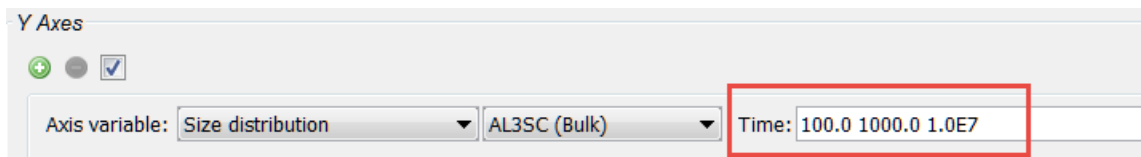
When you click **Perform** the three times are plotted:
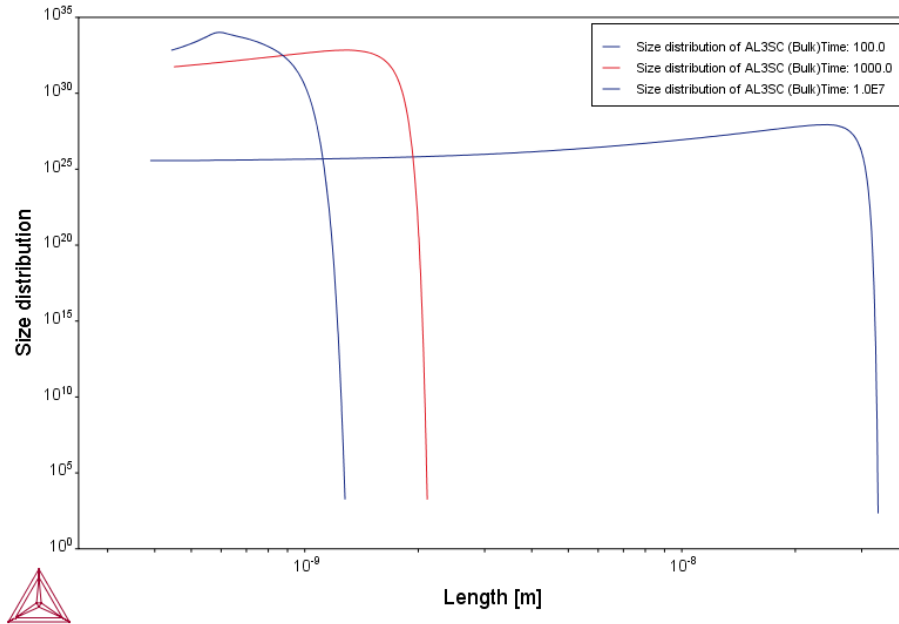
Excess Kurtosis

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. 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.

Theoretical Models

In this section:

Theory Overview

Based on Langer-Schwartz theory[1], Precipitation Module (TC-PRISMA) adopts Kampmann-Wagner numerical (KWN) method[2] 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 nth 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).

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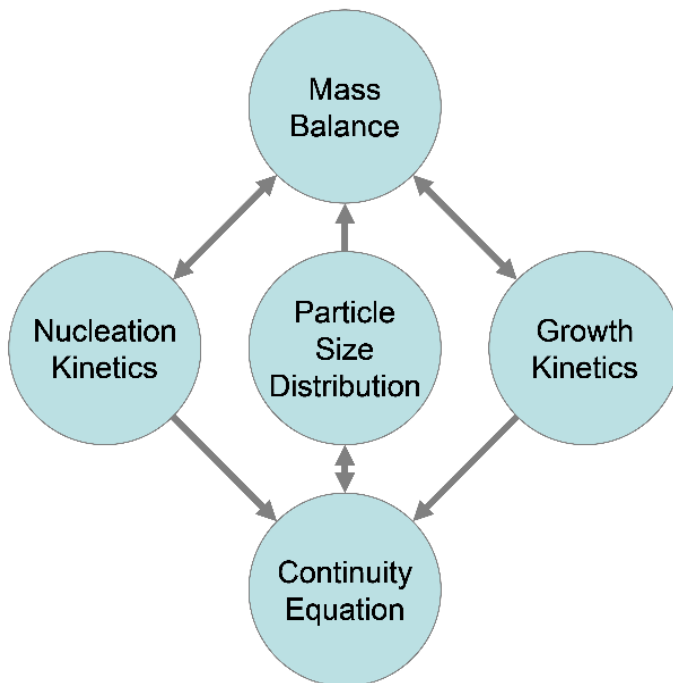
[1]J.S. Langer, A.J. Schwartz, Kinetics of nucleation in near-critical fluids, Phys. Rev. A. 21 (1980) 948–958.

[2]R. Kampmann, R. Wagner, Homogeneous second phase precipitation, in: R.W. Cahn, P. Haasen, E.J. Kramer (Eds.), Mater. Sci. Technol., Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, 1991: pp. 213–304.

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. Spherical particles are assumed in the discussion. For non-spherical and wetting angle effect, see *Homogeneous Nucleation* below.

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.

- *Homogeneous Nucleation* below

- *Heterogeneous Nucleation* on page 37

- *Nucleation During a Non-isothermal Process* on page 43

Homogeneous Nucleation

The classic nucleation theory (CNT)[1] has been extended for the purpose of modeling nucleation in multicomponent alloy systems. The time dependent nucleation rate J *(t)* is given by

$$J(t) = J_S \exp\left(-\frac{\tau}{t}\right)$$

(1)

where

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[1]D. Kashchiev, Nucleation, Butterworth-Heinemann, 2000 and K.C. Russell, Nucleation in solids: The induction and steady state effects, Adv. Colloid Interface Sci. 13 (1980) 205–318.

- J_s is the steady state nucleation rate,
- τ is the incubation time for establishing steady state nucleation conditions, and
- t is the isothermal incubation time.

The steady state nucleation rate J_s is expressed by

$$J_s = Z\beta^* N_0 \exp\left(\frac{-\Delta G^*}{kT}\right) \tag{2}$$

where

- Z is the Zeldovich factor,
- β^* 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,
- ΔG^* is the Gibbs energy of formation of a critical nucleus,
- k is Boltzmann's constant, and
- T is absolute temperature. In the case of homogeneous nucleation, each atom in the mother phase is a potential nucleation site.

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

$$\Delta G^* = \frac{16\pi\sigma^3}{3\left(\Delta G_m^{\alpha\to\beta}/V_m^{\beta}\right)^2} \tag{3}$$

where

- σ is the interfacial energy,
- $\Delta G_m^{\alpha\to\beta}$ is the molar Gibbs energy change for the formation of the β precipitate of the critical composition X_i^{β} from the α matrix, i.e. the maximum driving force for the $\alpha\to\beta$ phase transformation
- V_m^{β} is the molar volume of the β precipitate phase.

There are two ways to calculate the nucleation driving force $\Delta G_m^{\alpha\to\beta}$ and the critical composition X_i^{β}, 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 Thermo-Calc. 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.

Figure 1. Methods to calculate the nucleation driving force $\Delta G_m^{\alpha \to \beta}$ and the critical composition X_i^{β}. Figure (a) is a Standard Calculation and (b) an Approximate Calculation.

Figure 1A
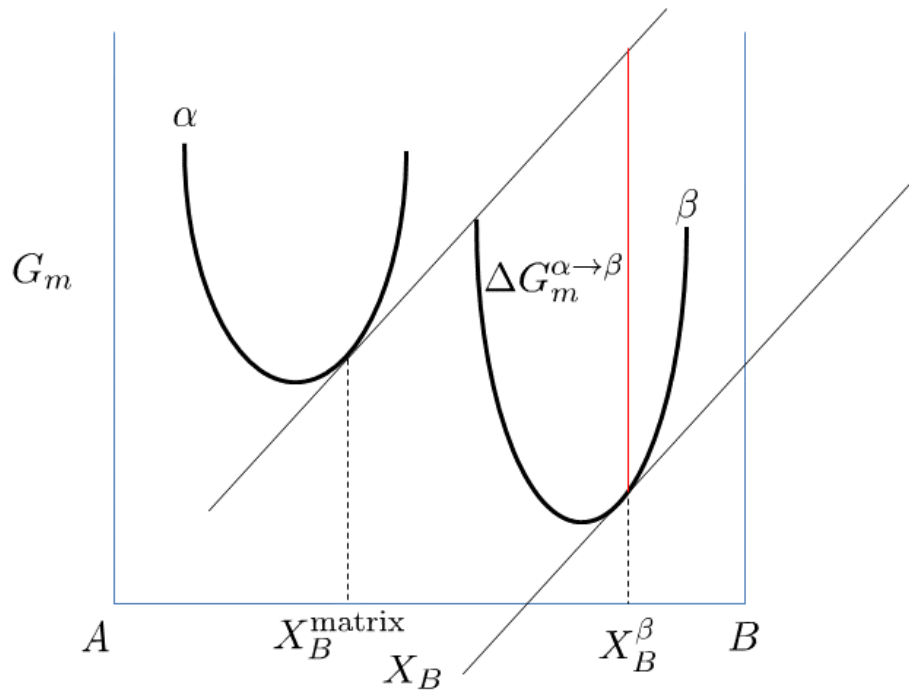
Figure 1B
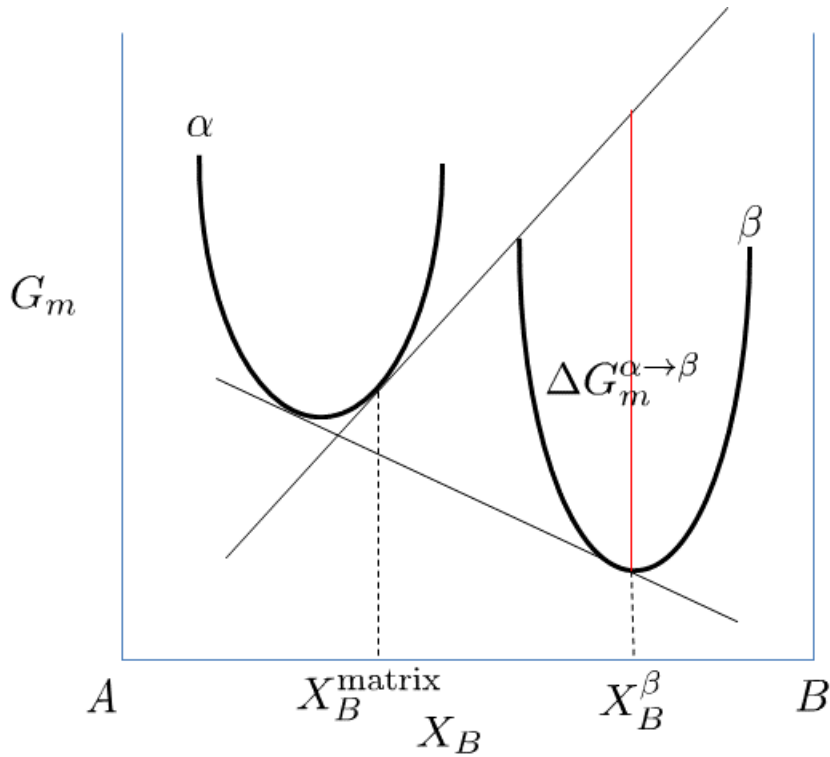
Nucleation is a stochastic process and can be considered formally as a diffusion process or Brownian movement in the particle size space. Supercritical nuclei with radius slightly larger than the critical radius have a probability of passing back across the free energy barrier and dissolve in the matrix. The Zeldovich factor Z is a measure of such probability and is related solely to the thermodynamics of the nucleation process in

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

(4)

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

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

(5)

The atomic or molecular attachment rate β^* reflects the kinetics of mass transport in the nucleation process and is given by Svoboda et. al.[1]

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[1]Svoboda, J., Fischer, F. D., Fratzl, P., and Kozeschnik, E. (2004). Modelling of kinetics in multi-component multi-phase systems with spherical precipitates. Materials Science and Engineering: A, 385(1–2), 166–174.

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

(6)

where

- a 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

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

(7)

where θ differs from one derivation to another. The value 2 from Feder et al.[1] is adopted.

Heterogeneous Nucleation

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

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

Non-Spherical Particles and the Effect of Wetting Angle

⊙ *Precipitation Module (TC-PRISMA) References* on page 52

Non-spherical particles have been considered for grain boundary 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), θ, as described in Figure 2 and taken from Clemm and Fisher (1955)[2].

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[1]J. Feder, K.C. Russell, J. Lothe, G.M. Pound, Homogeneous nucleation and growth of droplets in vapours, Adv. Phys. 15 (1966) 111–178.
[2]Clemm, P. and Fisher, J. (1955). The influence of grain boundaries on the nucleation of secondary phases. Acta Metallurgica, 3(1), 70–73.
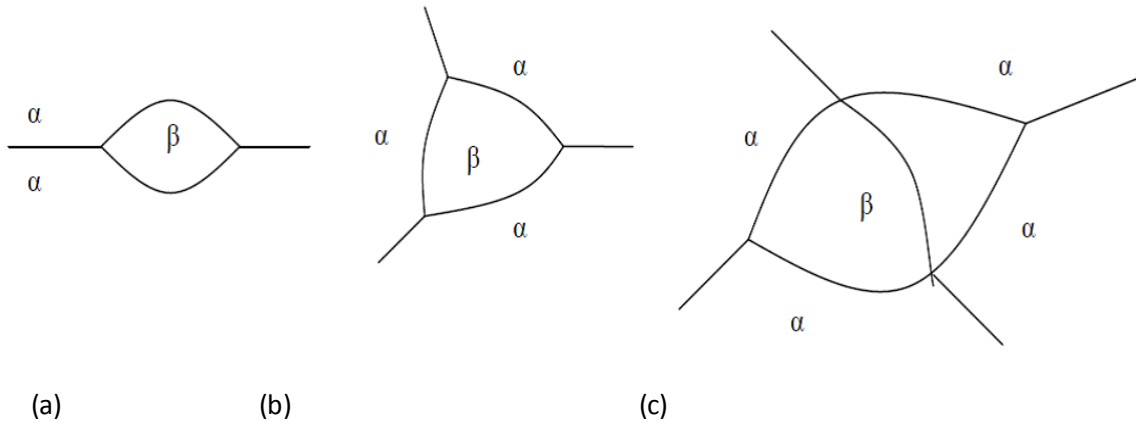
Figure 1. Non-spherical particles (β) that precipitate at grain boundaries of matrix phase(α) (a) grain boundary (two-grain junction) (b) grain edge (three-grain junction) (c) grain corners (four-grain junction). Images taken from Zang (2004)[1].
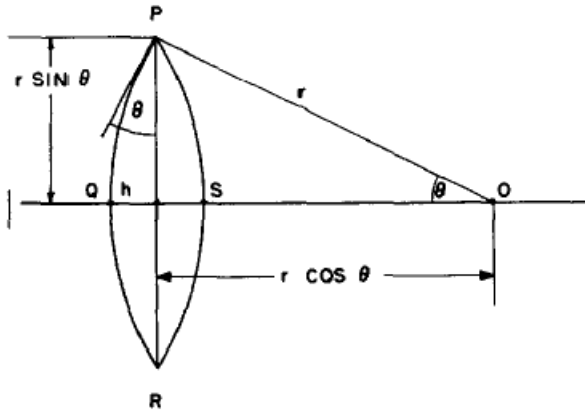
Figure 2. The nucleus at the grain boundary. Image from Clemm and Fisher, 1955.

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 GB area between $\alpha - \alpha$ grains due to the formation of nucleus of a new phase β is:

$$A_{\alpha\alpha} = ar^2 \tag{1}$$

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

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[1]Zang, L. (2004). Lecture 13: Heterogeneous Nucleation: Effects of Grain Boundaries and Surface Defects. Lecture slides, Salt Lake City, Utah: The Zang Research Group, The University of Utah. Retrieved from http://www.eng.utah.edu/~lzang/images/lecture-13.pdf

$$A_{\alpha\beta} = br^2 \tag{2}$$

and the volume of the nucleus is

$$V = cr^3 \tag{3}$$

The expression of *a*, *b*, *c* in *Equations 1 to 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

$$\Delta F = \frac{\Delta G_m^{\alpha\to\beta}}{V_m} \cdot cr^3 + br^2\sigma_{\alpha\beta} - ar^2\sigma_{\alpha\alpha} \tag{4}$$

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

Then the critical radius should be

$$r^* = -\frac{2(b\sigma_{\alpha\beta} - a\sigma_{\alpha\alpha})V_m}{3c\Delta G_m^{\alpha\to\beta}} \tag{5}$$

And the activation energy barrier for nucleation is

$$W = \frac{4}{27}\frac{(b\sigma_{\alpha\beta} - a\sigma_{\alpha\alpha})^3 V_m^2}{c^2(\Delta G_m^{\alpha\to\beta})^2} \tag{6}$$

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

$$k = \cos\theta = \frac{\sigma_{\alpha\alpha}}{2\sigma_{\alpha\beta}} \tag{7}$$

i.e.

$$\sigma_{\alpha\alpha} = 2k\sigma_{\alpha\beta} \tag{8}$$

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[1]Clemm, P. and Fisher, J. (1955). The influence of grain boundaries on the nucleation of secondary phases. Acta Metallurgica, 3(1), 70–73.

Which can be replaced into Equations 5 and 6.

$$r^* = -\frac{2(b - 2ak)\sigma_{\alpha\beta}V_m}{3c\Delta G_m^{\alpha\to\beta}} \tag{9}$$

$$W = \frac{4}{27}\frac{\sigma_{\alpha\beta}^3 V_m^2}{(\Delta G_m^{\alpha\to\beta})^2}\frac{(b - 2ak)^3}{c^2} \tag{10}$$

The bulk, spherical precipitation equation is recovered by:

$$a = 0, \quad b = 4\pi, \quad c = \frac{4\pi}{3} \tag{11}$$

so that

$$r^* = -\frac{2\sigma_{\alpha\beta}V_m}{\Delta G_m^{\alpha\to\beta}} \tag{12}$$

$$W = \frac{16\pi}{3}\frac{\sigma_{\alpha\beta}^3 V_m^2}{(\Delta G_m^{\alpha\to\beta})^2} \tag{13}$$

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

Other Parameters

Zeldovitch Factor

The Zeldovitch factor is modified as

$$Z = Z_b\sqrt{f} \tag{14}$$

with Z_b the original value, and f the volume factor that is the ratio of the *c* in *Equation 3* to the spherical shape factor 4π /3.

$$f = \frac{3c}{4\pi} \tag{15}$$

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

$$A_{\text{red}} = a \cdot n\bar{r}^2 \tag{16}$$

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.

$$r' = \sqrt{\frac{a}{\pi}} \cdot r \tag{17}$$

With *a* defined in Equation 1.

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

$$r' = r\sin\theta = r\sqrt{1 - k^2} \tag{18}$$

The Shape and Size of Grains in the Matrix
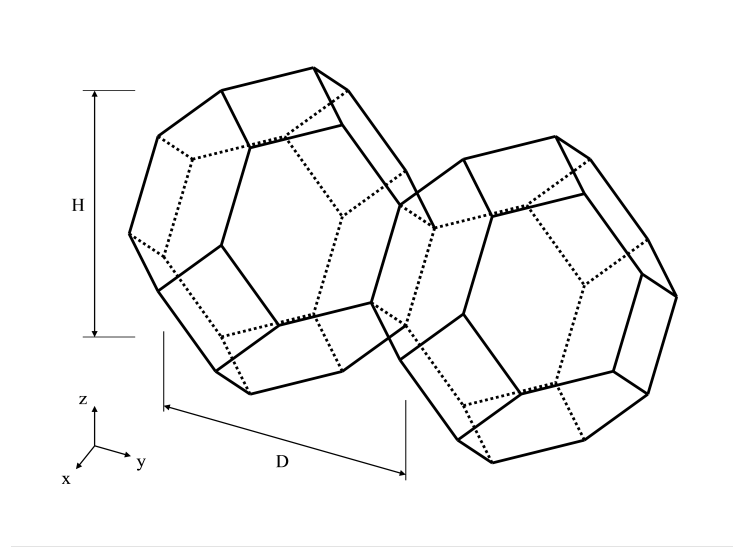
An example of tetrakaidecahedron approximation of grains

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 ρ_2, ρ_1, and ρ_0 for the grain boundary area, edge length, and grain corner number respectively in

$$\rho_2 = \frac{6\sqrt{1+2A^2}+1+2A}{4A}D^{-1} \tag{19}$$

$$\rho_1 = 2\frac{\sqrt{2}+2\sqrt{1+A^2}}{A}D^{-2} \tag{20}$$

$$\rho_0 = \frac{12}{A}D^{-3} \tag{21}$$

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

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[1]J.W. Cahn, Transformation kinetics during continuous cooling, Acta Metall. 4 (1956) 572–575.

$$N_i = \rho_i \left(\frac{N_A}{V_m^\alpha} \right)^{i/3} \quad (i = 2, 1, 0) \tag{22}$$

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

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

$$N_d = \rho_d \left(\frac{N_A}{V_m^\alpha} \right)^{1/3} \tag{23}$$

Nucleation During a Non-isothermal Process

Under a 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

$$\tau = \frac{1}{\theta Z^2 \beta^*} \tag{1}$$

for an isothermal condition. In a non-isothermal process, the exact calculation of the incubation time requires a solution to the Fokker-Plank 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

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

where

τ is the incubation time, β^* is the impingement rate for solute atoms to the critical cluster as defined in

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[1]H.-J. Jou, P. Voorhees, G.B. Olson, Computer simulations for the prediction of microstructure/property variation in aeroturbine disks, Superalloys. (2004) 877–886.

$$\beta^* = \frac{4\pi r^{*2}}{a^4} \left[\sum_{i=1}^{k} \frac{\left(X_i^{\beta/\alpha} - X_i^{\alpha/\beta} \right)^2}{X_i^{\alpha/\beta} D_i} \right]^{-1} \tag{3}$$

and Z is the Zeldovich factor, previously defined in

$$Z = \frac{V_m^{\beta}}{2\pi N_A r^{*2}} \sqrt{\frac{\sigma}{kT}} \tag{4}$$

but now as a function of τ 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

The growth rate models implemented in the Precipitation Module are called Advanced and Simplified.

The *Advanced* model is proposed by Chen, Jeppsson, and Ågren[1] (CJA) and calculates the velocity of a moving phase interface in multicomponent systems by identifying the operating tie-line from the solution of flux-balance equations. This model can treat both high supersaturation and cross diffusion rigorously. Spontaneous transitions between different modes (LE and NPLE) of phase transformation can be captured without any *ad hoc* treatment. Since it is not always possible to solve the flux-balance equations and it takes time when possible, a less rigorous but simple and efficient model is preferred in many applications. The simplified model is based on the advanced model but avoids the difficulty to find the operating tie-line and uses simply the tie-line across the bulk composition.

All models treat a spherical particle of stoichiometric composition or with negligible atomic diffusivity growing under the local equilibrium condition.

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

$$\upsilon \left(c_i^{\beta/\alpha} - c_i^{\alpha/\beta} \right) = c_i^{\alpha/\beta} M_i \frac{\mu_i^{\alpha} - \mu_i^{\alpha/\beta}}{\xi_i r} \tag{1}$$

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[1] Q. Chen, J. Jeppsson, J. Ågren, Analytical treatment of diffusion during precipitate growth in multicomponent systems, Acta Mater. 56 (2008) 1890–1896.

$$\mu_i^{\alpha/\beta} = \mu_i^{\beta/\alpha} + \frac{2\sigma V_m^{\beta}}{r} \qquad (2)$$

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, μ_i^{α} 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, ξ_i, for each independent component is given by

$$\xi_i = \frac{\Omega_i}{2\lambda_i^2} \qquad (3)$$

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 λ_i is obtained via

$$2\lambda_i^2 - 2\lambda_i^3 \sqrt{\pi} \exp\left(\lambda_i^2\right) erfc\left(\lambda_i\right) = \Omega_i \qquad (4)$$

Combining Equation 1 and Equation 2, the simplified model is derived in

$$\upsilon = \frac{K}{r}\left[\Delta G_m - \frac{2\sigma V_m^{\beta}}{r}\right] \qquad (5)$$

where

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

and ΔG_m is the driving force.

The interface compositions $X_i^{\beta/\alpha}(r)$ and $X_i^{\alpha/\beta}(r)$ are simply taken from the tie line across the matrix composition.

The non-zero volume correction to the velocity according to Chen and Voorhees[1] is taken into account and it follows as

$$\upsilon' = \upsilon \left(1 + r\sqrt{4\pi N_V <r>} \right) \qquad (6)$$

where

- υ' is the corrected velocity,
- *<r>* is the mean radius and
- N_V is the number density.

⊚ Also see *Coarsening* below for further discussion of these equations.

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)[2]], we simply apply the *Growth* on page 44 equations 1 to 5 with the absolute value of Ω_i to calculate the interface velocity for particles of all sizes.

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[1]M.K. Chen, P.W. Voorhees, The dynamics of transient Ostwald ripening, Model. Simul. Mater. Sci. Eng. 1 (1993) 591–612.

[2]H.B. Aaron, Diffusion-Limited Phase Transformations: A Comparison and Critical Evaluation of the Mathematical Approximations, J. Appl. Phys. 41 (1970) 4404.

As can be easily seen, if $r < r*$, then the Gibbs-Thomson Equation 1 (see *Growth* on page 44) gives $\mu_i^{\alpha/\beta} > \mu_i^{\alpha}$, and a negative velocity results from Equation 2 (see *Growth* on page 44) 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 Ω_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[1] , 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, $<r>$ the mean radius and ϕ - the particle volume fraction, is expressed as

$$N = \int_0^\infty f(r)dr \tag{1}$$

$$\langle r \rangle = \int_0^\infty rf(r)dr \qquad \phi = \int_0^\infty \frac{4}{3}\pi r^3 f(r)dr \tag{2}$$

,

The time evolution of *f(r)* follows the continuity as in Langer and Schwartz (1980)[2].

$$\frac{\partial f}{\partial t} = -\frac{\partial}{\partial r}\left[\upsilon(r)f(r)\right] + j(r) \tag{3}$$

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

$$J = \int_{r*}^\infty j(r)dr \tag{4}$$

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 $X^0{}_i$, the new

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[1]H.B. Aaron, Diffusion-Limited Phase Transformations: A Comparison and Critical Evaluation of the Mathematical Approximations, J. Appl. Phys. 41 (1970) 4404.
[2]J.S. Langer, A.J. Schwartz, Kinetics of nucleation in near-critical fluids, Phys. Rev. A. 21 (1980) 948–958.

concentration X_i can be obtained from the following mass balance shown in

$$X_i^0 = \left(1 - \sum_p \int_0^\infty \frac{4\pi r_p^3 f(r_p)}{3V_m^p} dr_p\right) X_i + \sum_p \int_0^\infty \int_0^{t_j} \frac{4\pi r_p^2 f(r_p,t)\upsilon(r_p,t)}{V_m^p} X_i^p\left(r_p,t\right) dt dr_p$$

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

VP_m 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* on the previous page) of the PSD function has to be solved numerically. Different numerical methods can be found in 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

P_{dt}^{max}

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_{Nr}

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_{Nr}^{max}

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_{Nr}^{min}

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:
$\Delta t \leq P_r \times r/(|dr/dt|)$ 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_{rdt}

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: $(\int_0^{r_{dt}} f r^3 dr)/(\int_0^{\infty} f r^3 dr) = P_{rdt}$.

Relative radius change for avoiding class collision

P_{cc}

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_{cc}, can be used to set a limit on time step according to the following relation: $\Delta t \leq P_{cc} \times (r_{i+1} - r_i)/(dr_i/dt - dr_{i+1}/dt)$ 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 $\Delta t \leq P_v/10/(4\pi r_{eff}^3 J/3)$, where r_{eff} and J are effective radius and nucleation rate, respectively.

Maximum relative change of nucleation rate in logarithmic scale

P_{logJ}

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 $\Delta t \leq P_{logJ} \times \Delta t_{previous}/(|\log(J_1/J_2)|)$, where nucleation rate J_1 and J_2 occurs at the beginning and end of $\Delta t_{previous}$.

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 radium 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_{rmin}

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_{htmax}

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.

	P_{dt}^{max}	P_{Nr}	P_{Nr}^{max}	P_{Nr}^{min}	P_r	P_{rdt}	P_{cc}	P_V	P_{logJ}	P_{rc}	P_{rmin}	P_{htmax}
Default value	0.1	200	300	100	0.01	0.01	0.5	0.001	0.5	0.1	5e-10m	1.0s

Interfacial Energy

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:

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

where σ_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 ΔE_s is the energy of solution in a multicomponent system involving the two phases being considered. (Reference[1]).

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