Precipitation Module (TC-PRISMA) User Guide

Thermo-Calc Version 2019a

Contents

Introduction to the Precipitation Module (TC-PRISMA)

In this section:

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

Input

- Alloy composition
- Temperature
- Simulation time
- Thermodynamic data
- Kinetic data
- Property data
- Nucleation sites
- Grain size
- Dislocation density

Precipitation Module (TC-PRISMA)

Output

- Particle size distribution
- Number density
- Average particle size
- Volume fraction
- Matrix composition
- Nucleation rate
- Critical radius
- Driving force
- TTT/CCT diagrams
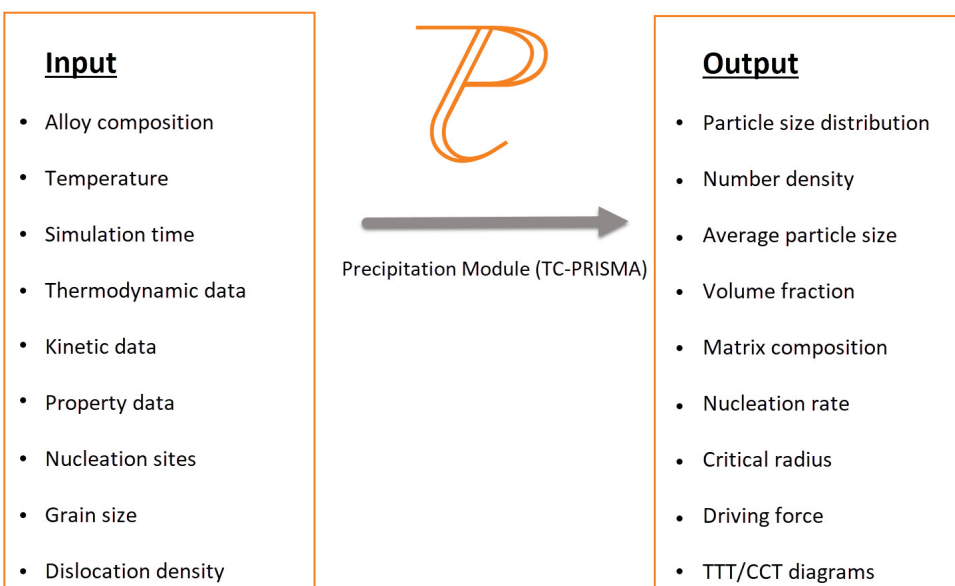
The Precipitation Module relies on CALPHAD-based software tools and databases to provide the necessary bulk thermodynamic and kinetic data for phases in multicomponent systems. The CALPHAD approach has been developed for more than 50 years and is routinely applied to design new alloys and optimize existing 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.

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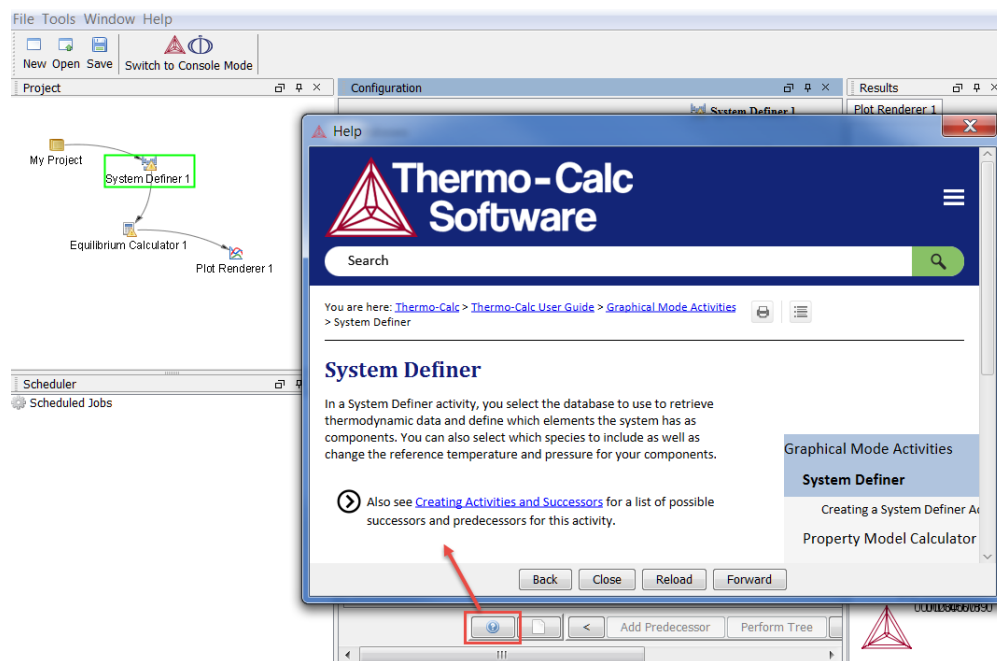
The window that opens has the same content as the help you access in the browser. There are these extra navigation buttons in this view.

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

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.
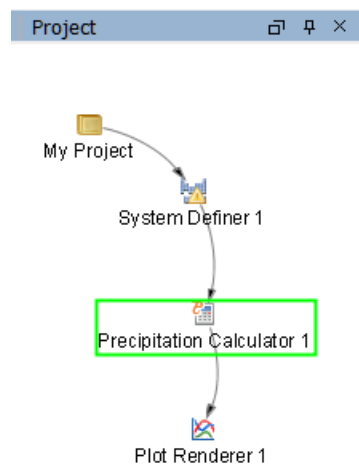
▶ "Creating a "Project from a Template" in the *Thermo-Calc User Guide* or search the Online Help.

Precipitation Calculator

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

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.
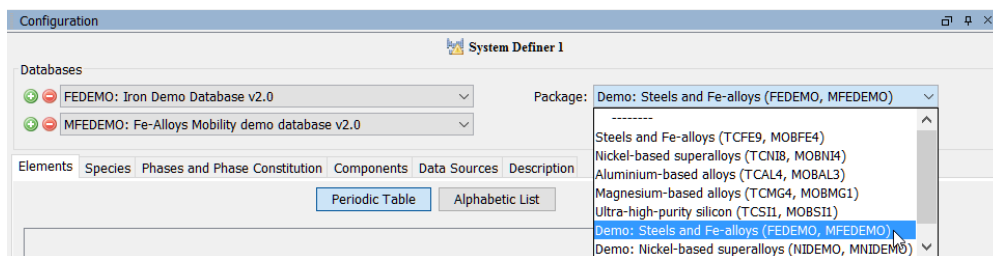
Demonstration (Demo) Mode

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.

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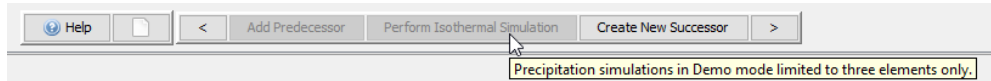
Even if you have more than three elements, the Plot Renderer or Table Renderer **Perform** button is still available. However, if you click the button and try to run the simulation the Event Log displays an error message.

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**.

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.

P_01: 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 (2001)[2].

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

System (System Definer)	
Database package	Demo: Aluminum-based alloys (ALDEMO, MALDEMO)
Elements	Al, Sc
Conditions (Precipitation Calculator)	
Composition	Al-0.18Sc Mole percent
Matrix phase	FCC_A1

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[1] Marquis, E.A, and D.N Seidman. 2001. "Nanoscale Structural Evolution of Al3Sc Precipitates in Al(Sc) Alloys." Acta Materialia 49 (11): 1909–19.

[2] Novotny, Gabriel M., and Alan J. Ardell. 2001. "Precipitation of Al3Sc in Binary Al–Sc Alloys." Materials Science & Engineering, A: Structural Materials: Properties, Microstructure and Processing 318 (1–2): 144–54.

Precipitate phase	AL3SC
Precipitate Phase Data Parameters (Precipitation Calculator)	
Nucleation sites	Bulk
Interfacial energy	Calculated
Calculation Type (Precipitation Calculator)	
Calculation type	Isothermal
Temperature	350° C
Simulation time	1.0E7 seconds
Other	
File name and location	Folder: Precipitation Module - TC-PRISMA File name: P_01_Precipitation_Al-Sc_AL3SC.tcu

Plot Results

Mean radius
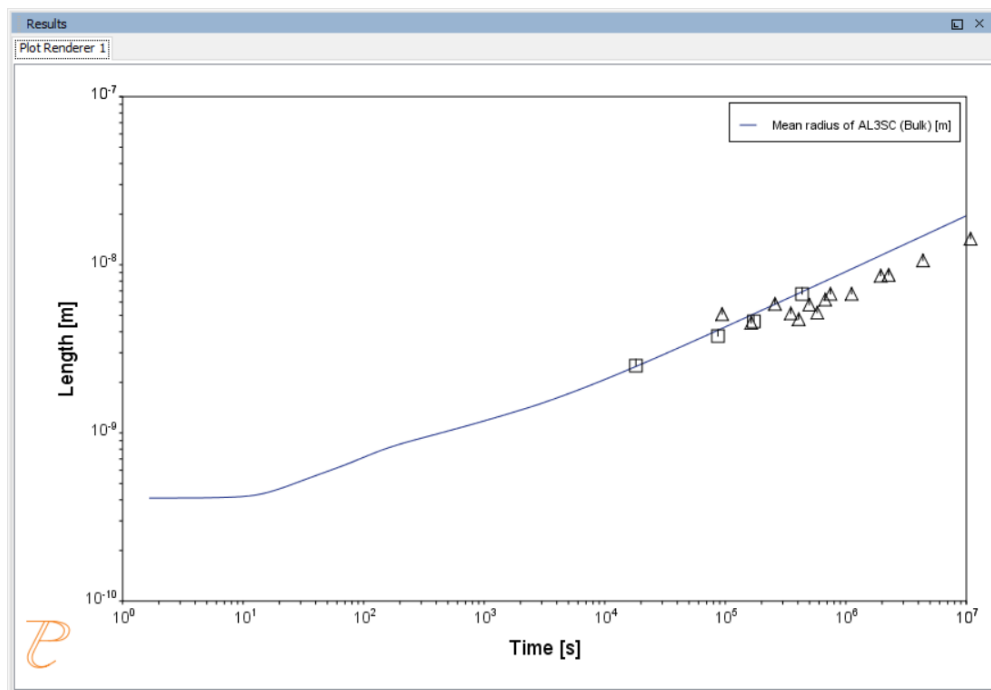
P_02: Stable and Metastable Carbides - Isothermal

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 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 (System Definer)	
Database package	Demo: Steels and Fe-alloys (FEDEMO,MFEDEMO)
Elements	Fe, C, Cr
Conditions (Precipitation Calculator)	
Composition	Fe-0.1C-12Cr Mass percent
Matrix phase	BCC_A2
Precipitate phases	Cementite, M23C6 and M7C3
Matrix Phase Data Parameters (Precipitation Calculator)	
Grain size (click **Show details** to display this setting)	1.0E-4 m
Precipitate Phase Data Parameters (Precipitation Calculator)	
Nucleation sites	Grain boundaries
Interfacial energy	Cementite 0.167 J/m^2, M23C6 0.252 J/m^2, M7C3 0.282 J/m^2
Calculation Type (Precipitation Calculator)	
Calculation type	Isothermal
Temperature	1053 K

Simulation time	400 000 seconds
Other	
File name and location	Folder: Precipitation Module - TC-PRISMA File name: P_02_Precipitation_Fe-C-Cr_Cementite-M7C3-M23C6.tcu

Plot Results

Equilibrium Calculator: How the phases change with temperature
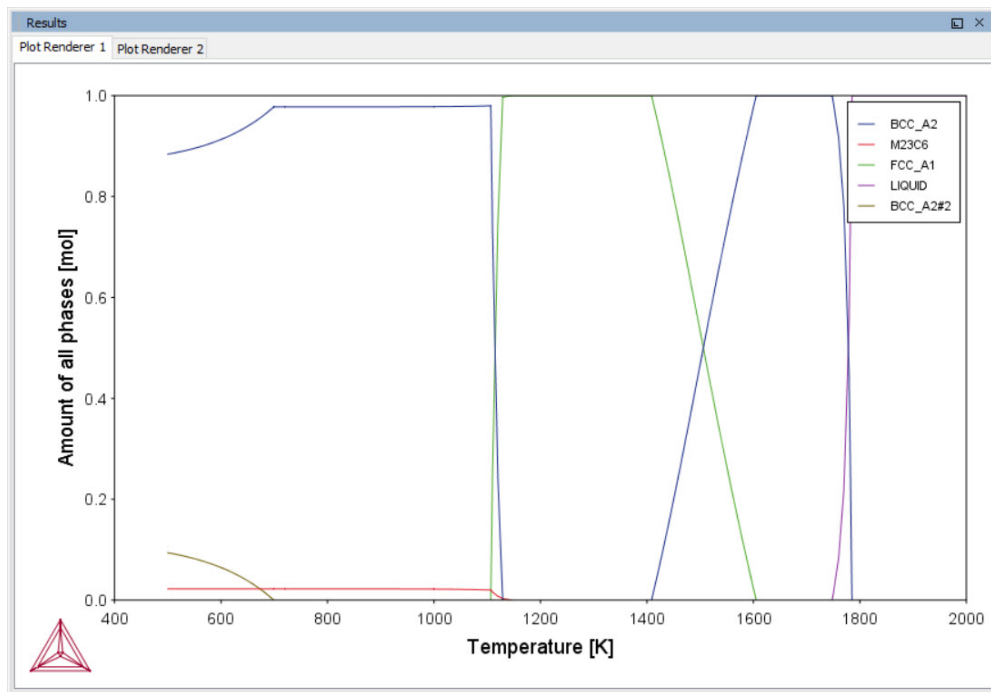
Precipitation Calculator: Volume fractions
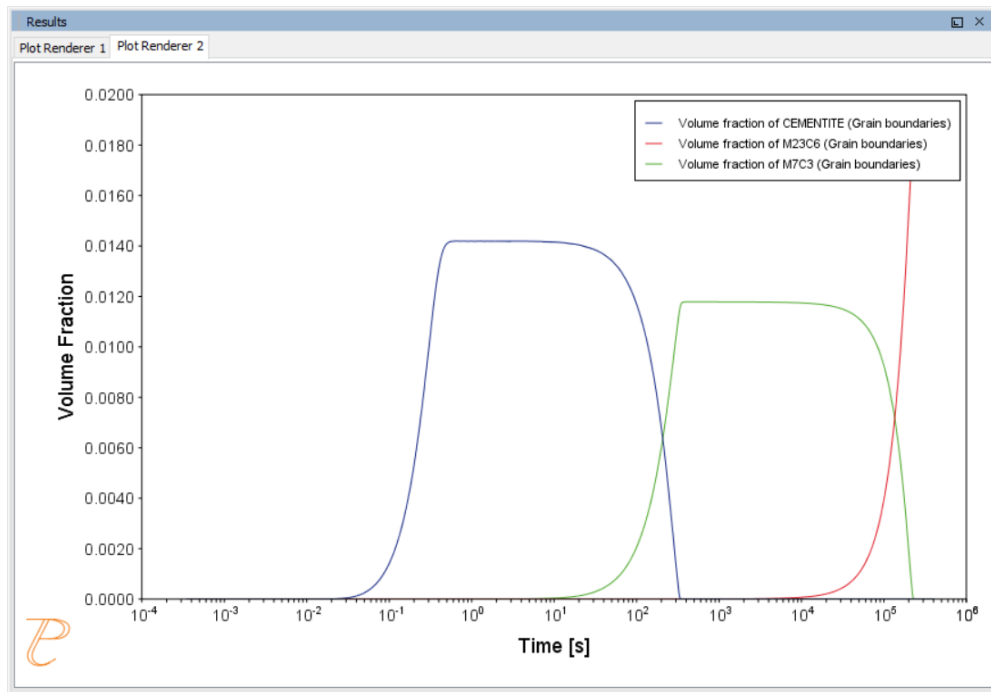
P_03: Stable and Metastable Carbides - TTT Diagram

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 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.

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

System (System Definer)	
Database package	Demo: Steels and Fe-alloys (FEDEMO and MFEDEMO)

Elements	Fe, C, Cr
Conditions (Precipitation Calculator)	
Composition	Fe-0.1C-12Cr Mass percent
Matrix phase	BCC_A2
Precipitate phases	Cementite, M23C6 and M7C3
Matrix Phase Data Parameters (Precipitation Calculator)	
Grain size (click **Show details** to display this setting)	1.0E-4 m
Precipitate Phase Data Parameters	
Nucleation sites	Grain boundaries
Interfacial energy	Cementite 0.167 J/m^2, M23C6 0.252 J/m^2, M7C3 0.282 J/m^2
Calculation Type (Precipitation Calculator)	
Calculation type	TTT diagram
Temperature	500° to 800° C with 25° C steps
Max. annealing time	1.0E8 seconds
Stop criteria	Volume fraction of phase is set to 0.0001
Options > Numerical Parameters	
No. of grid points over one order of magnitude in radius	150
Max no. of grid points over one order of magnitude in radius	200
Min no. of grid points over one order of magnitude in radius	100
Other	
File name and location	Folder: Precipitation Module - TC-PRISMA

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.

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

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

Precipitate phase	Cementite
Matrix Phase Data Parameters (Precipitation Calculator)	
Grain aspect ratio (click **Show details** to display this setting)	1.0
Dislocation density (click **Show details** to display this setting)	$1.5e11m^{-3}$
Precipitate Phase Parameters (Precipitation Calculator)	
Nucleation sites	Dislocations
Interfacial energy	0.24 J/m^2
Growth rate model (click **Show details**)	Advanced
Calculation Type (Precipitation Calculator)	
Calculation type	Isothermal
Temperature	102° C
Simulation time	600 000 seconds
Other	
File name and location	Folder: Precipitation Module - TC-PRISMA File name: P_04_Precipitation_Fe-C_Cemetite.tcu

Plot Results

Volume Fraction
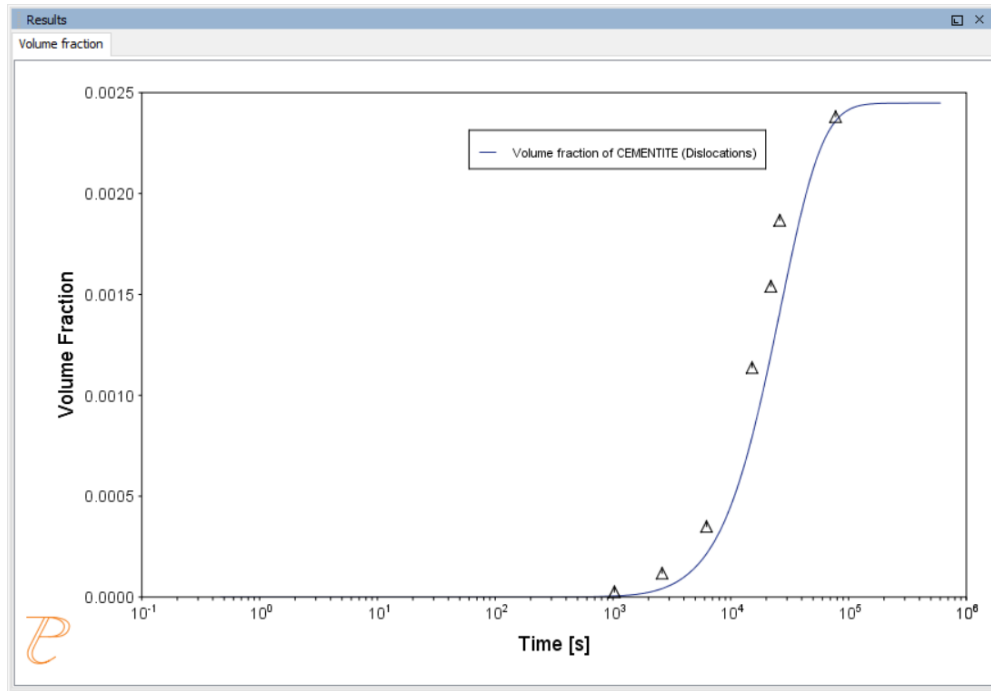
P_05: Precipitation of γ' in Ni Superalloys - Isothermal

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.

System (System Definer)	
Database package	Demo: Nickel-based Super Alloys (NIDEMO and MNIDEMO)

[1] Sudbrack, Chantal K., Tiffany D. Ziebell, Ronald D. Noebe, and David N. Seidman. 2008. "Effects of a Tungsten Addition on the Morphological Evolution, Spatial Correlations and Temporal Evolution of a Model Ni–Al–Cr Superalloy." Acta Materialia 56 (3): 448–63.

Elements	Ni, Al Cr
Conditions (Precipitation Calculator)	
Composition	Ni-9.8Al-8.3Cr Mole percent
Matrix phase	DIS-FCC_A1 (see note above about how to select this phase)
Precipitate phase	FCC_L12#2
Precipitate Phase Data Parameters (Precipitation Calculator)	
Nucleation sites	Bulk
Interfacial energy	0.012 J/m^2
Calculation Type (Precipitation Calculator)	
Calculation type	Isothermal
Temperature	800° C
Simulation time	1 000 000 seconds
Other	
File name and location	Folder: Precipitation Module - TC-PRISMA File name: P_05_Precipitation_Ni-Al-Cr_Isothermal_Gamma-Gamma_prime.tcu

Plot Results

Volume Fraction
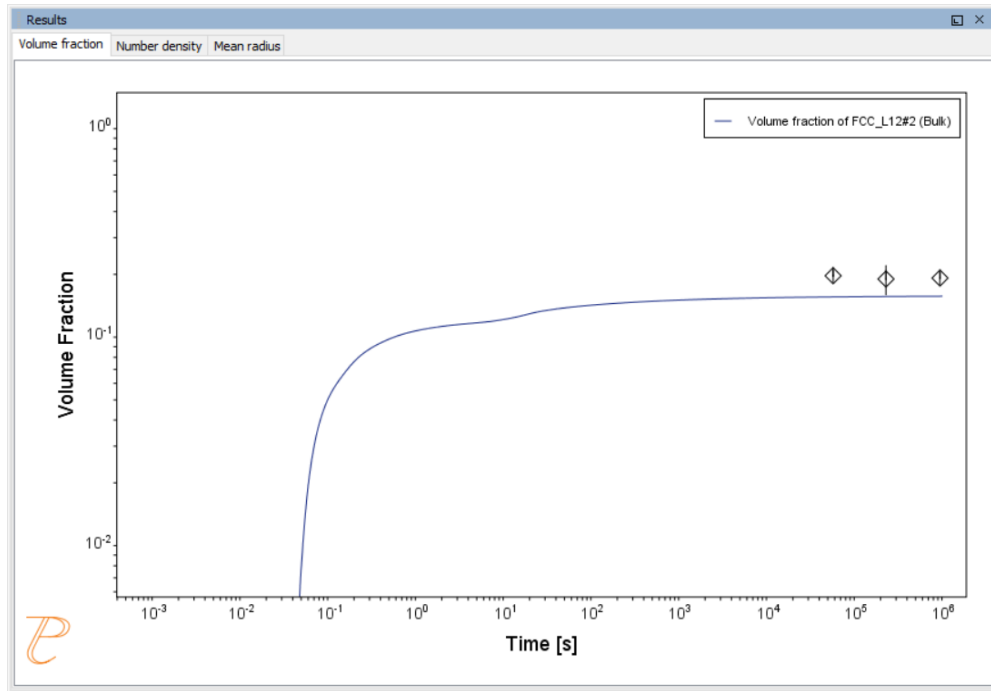
Number Density
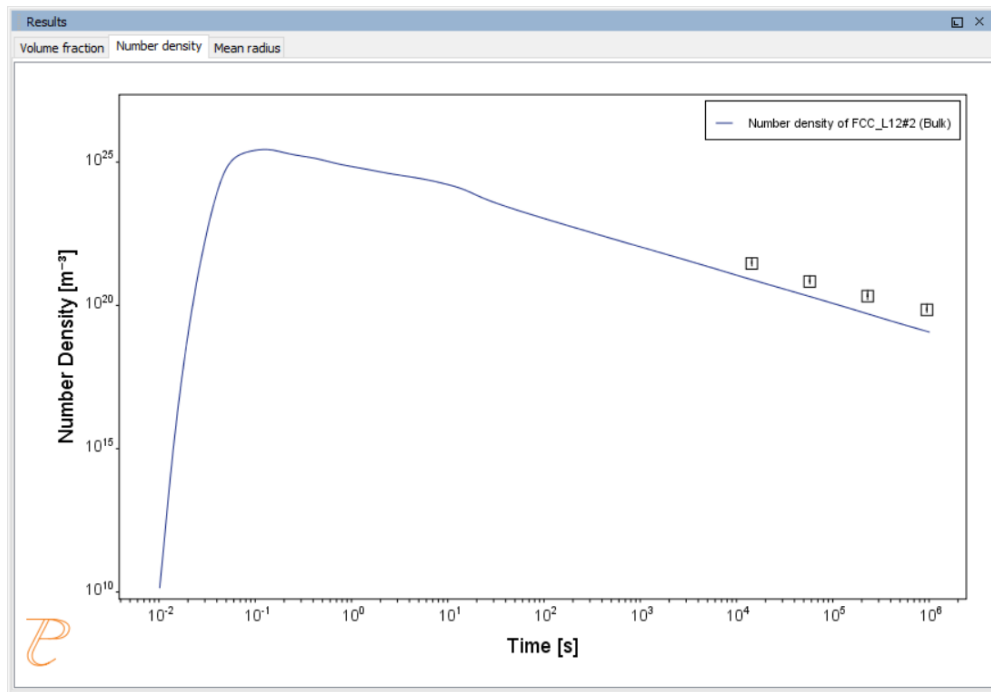
Mean Radius
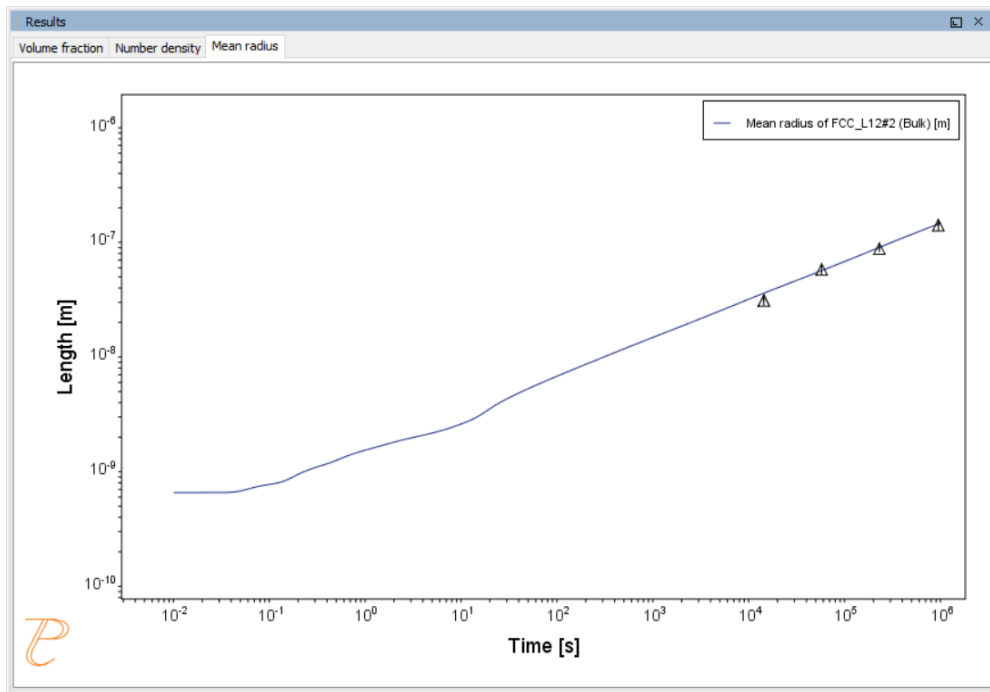
P_06: Precipitation of γ' in Ni Superalloys - Non-isothermal

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. (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

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[1] Rojhirunsakool, Tanaporn, S. Meher, J. Y. Hwang, S. Nag, J. Tiley, and Rajarshi Banerjee. 2013. "Influence of Composition on Monomodal versus Multimodal Γ' Precipitation in Ni–Al–Cr Alloys." *Journal of Materials Science* 48 (2): 825–31.

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.

System (System Definer)	
Database package	Demo: Nickel-based Super Alloys (NIDEMO and MNIDEMO)
Elements	Ni, Al, Cr
Conditions (Precipitation Calculator)	
Composition (Ni-8Al-8Cr)	Ni-8Al-8Cr Mole percent
Composition (Ni-10Al-10Cr)	Ni-10Al-10Cr Mole percent
Matrix phase	DIS_FCC_A1 (see note above about how to select this phase)
Precipitate phase	FCC_L12#2
Matrix Phase Data Parameters (Precipitation Calculator)	
Mobility enhancement prefactor (click **Show details** to display this setting)	5.0
Precipitate Phase Data Parameters (Precipitation Calculator)	
Nucleation sites	Bulk

|	
Interfacial energy	0.023 J/m^2
Calculation Type (Precipitation Calculator)	
Calculation type	Non-isothermal
Temperature unit	Celsius
Time unit	Seconds
Simulation time (Ni-8Al-8Cr)	1470 s
Simulation time (Ni-10Al-10Cr)	3300 s
Multimodal PSD (Plot Renderer)	
Separate multimodal PSD for 8Al-8Cr	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	The **Valley depth ratio** is set to 0.18 for both plots.
Other	
File name and location	Folder: Precipitation Module - TC-PRISMA File name: P_06_Precipitation_Ni-Al-Cr_Non-isothermal_Gamma-Gamma_prime.tcu

Plot Results

Mean Radius Ni-8Al-8Cr
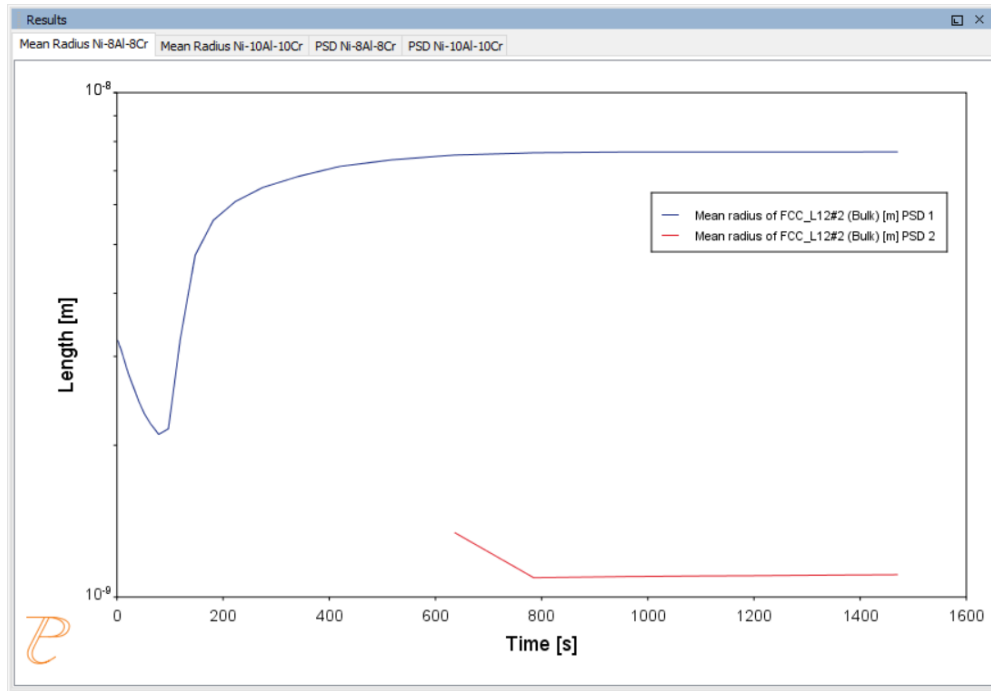
Mean Radius Ni-10Al-10CR
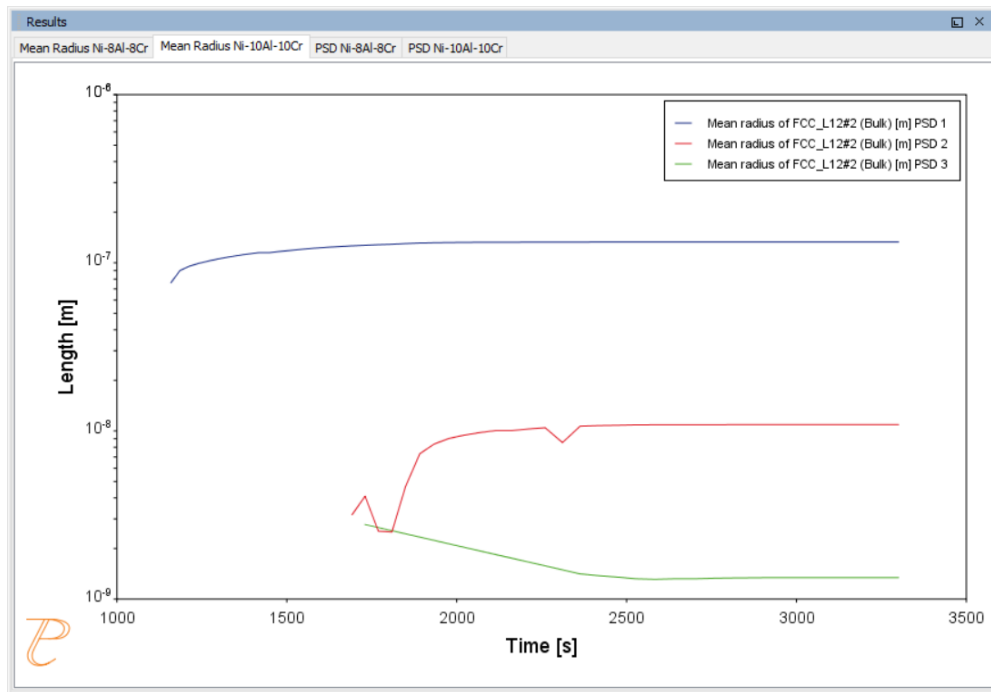
Size Distribution (PSD) Ni-8Al-8Cr
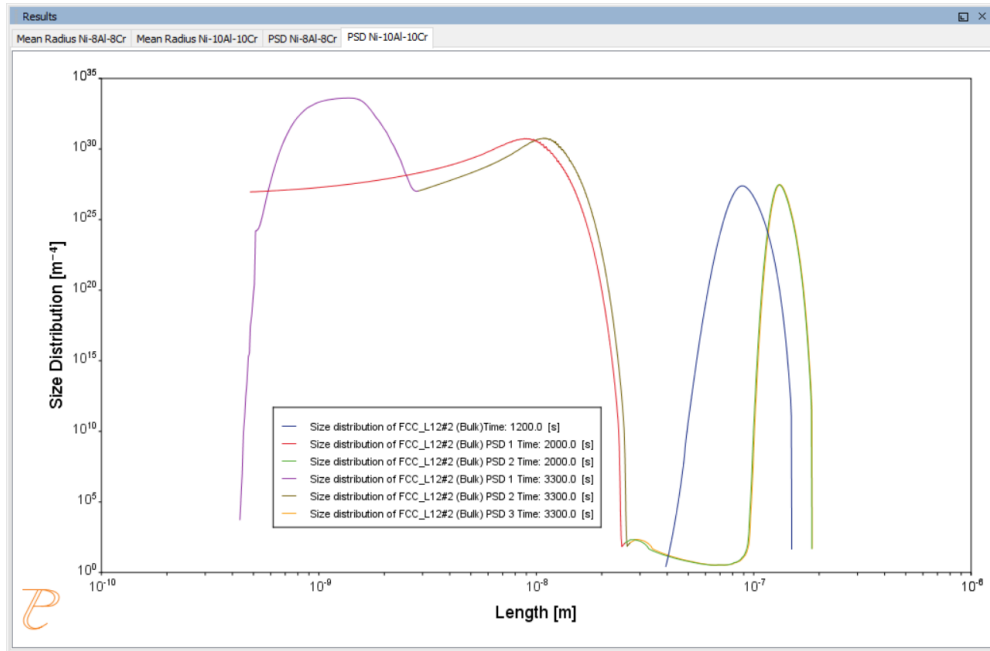
Size Distribution (PSD) Ni-10Al-10Cr
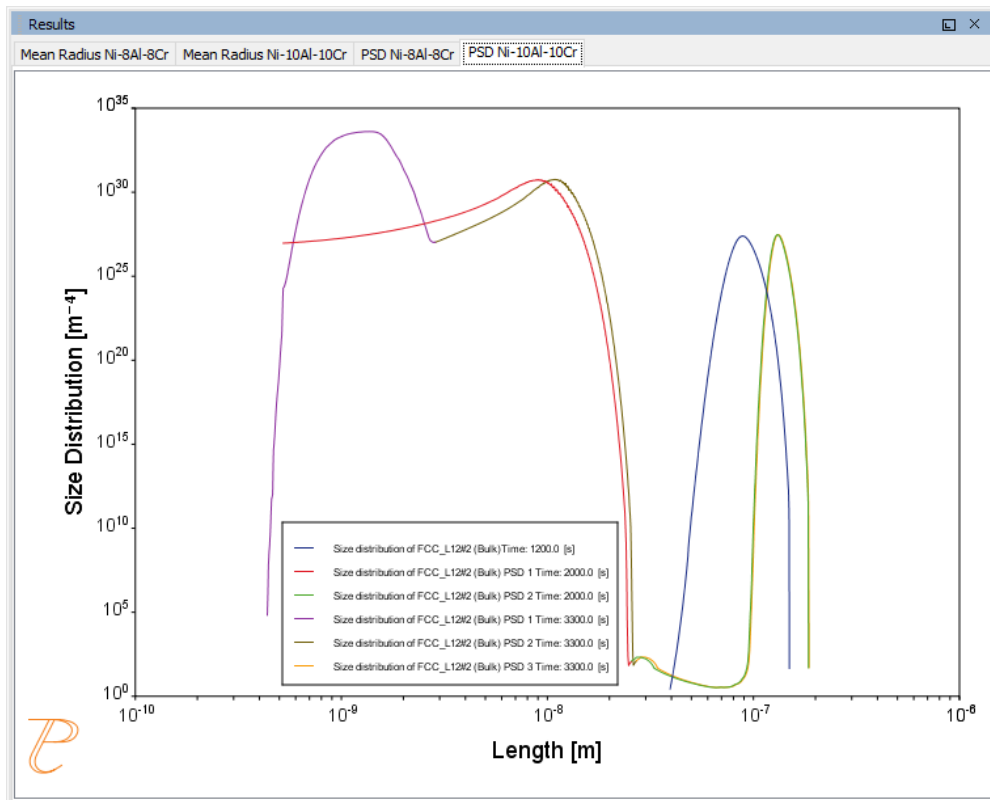
P_07: Continuous Cooling Transformation (CCT) Diagram of Ni-Al-Cr γ-γ′

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.

This example is available as a video tutorial on [our website](#) and [YouTube channel](#).

System (System Definer)	
Database package	Demo: Nickel-based Super Alloys (NIDEMO and MNIDEMO)
Elements	Ni, Al, Cr
Conditions (Precipitation Calculator)	
Composition	Ni-10Al-10Cr Mole percent
Matrix phase	DIS_FCC_A1
Precipitate phase	FCC_L12#2
Precipitate Phase Data Parameters (Precipitation Calculator)	
Nucleation sites	Bulk
Interfacial energy	0.023 J/m^2
Calculation Type (Precipitation Calculator)	
Calculation type	CCT Diagram
Temperature Min to Max	500 to 1200 Kelvin
Cooling rate(s)	.01 .1 1 10 100 K/s
Stop criteria	Volume fraction of phase 1.0E-4
Other	
File name and location	Folder: Precipitation Module - TC-PRISMA File name: P_07_Precipitation_Ni-Al-Cr_CCT_Gamma-Gamma_prime.tcu

Plot and Table Results
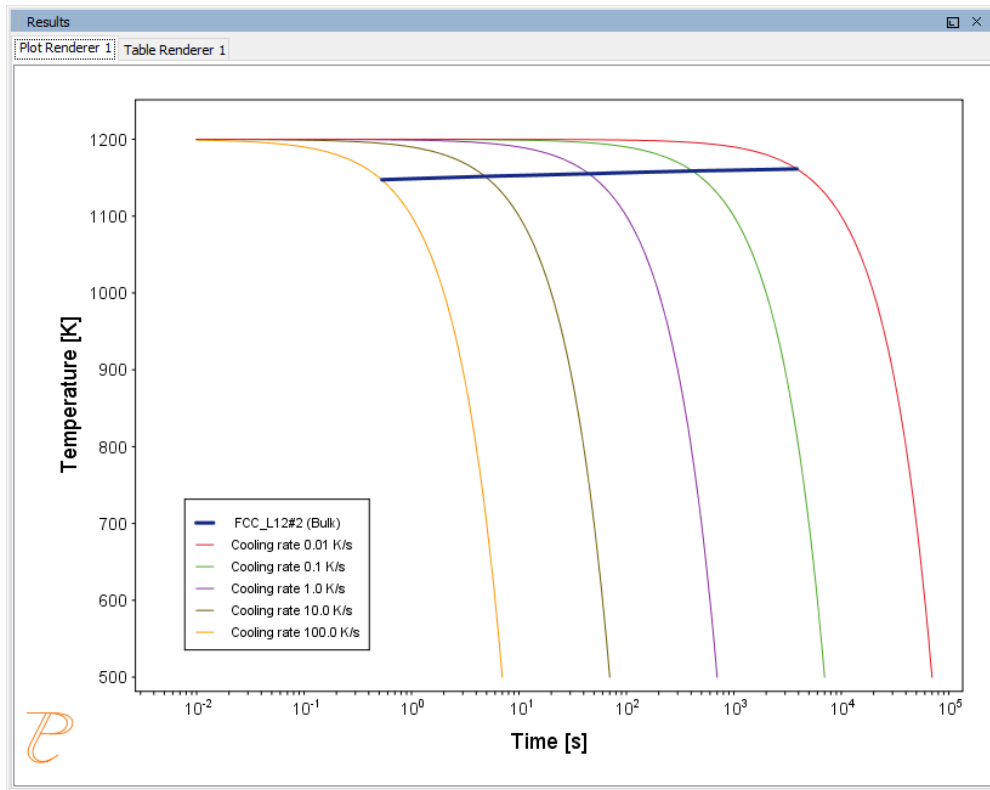
P_08: Precipitation of Cu-Ti CU4TI with Assumptions of Sphere and Needle Morphologies

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
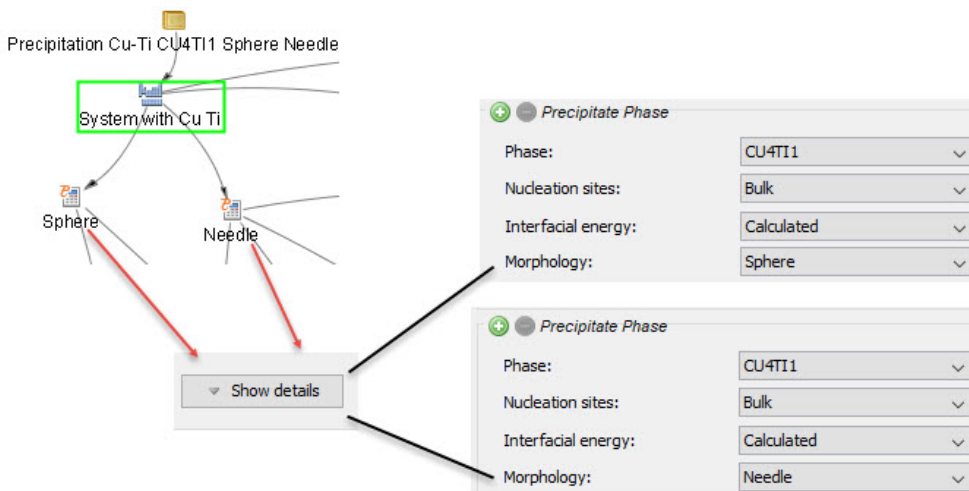
System (System Definer)	
Database package	Demo: Copper-based alloys (CUDEMO and MCUDEMO)
Elements	Cu, Ti
Sphere and Needle Conditions (Precipitation Calculator)	
Composition	Cu-1.9Ti Mole percent
Matrix phase	FCC_L12

---

[1] Borchers C. 1999. "Catastrophic Nucleation during Decomposition of Cu-0.9at.%Ti." Phil. Mag. A 79(3):537-547

[2] Kampmann R., Eckerlebe H., and Wagner R. 1987. "Precipitation Kinetics in Metastab le Solid Solutions - Theoretical Considerations and Application to Cu-Ti Alloys." Mat. Res. Soc. Symp. Proc. 57: 525-542.

Precipitate phase	CU4TI1

Matrix Phase Data Parameters (Precipitation Calculator)

Mobility enhancement prefactor (click **Show details** to display this setting)	100

Precipitate Phase Data Parameters (Precipitation Calculator)

Nucleation sites	Bulk
Interfacial energy	The default
Morphology (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), **Needle** is selected.
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: • ε11 and ε22 are set to **0.022** • ε33 is set to **0.003**

Calculation Type (Precipitation Calculator)

Calculation type	Isothermal
Temperature	350° C
Simulation time	10,000 seconds

Datasets (Experimental File Reader)

Borchers Mean radius vs Time and Borchers Number density vs Time	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.

Other

File name and location	Folder: Precipitation Module - TC-PRISMA

File name: P_08_Precipitation_Cu-Ti_CU4TI1_Sphere_Needle.tcu

Plot Results

Mean Aspect Ratio
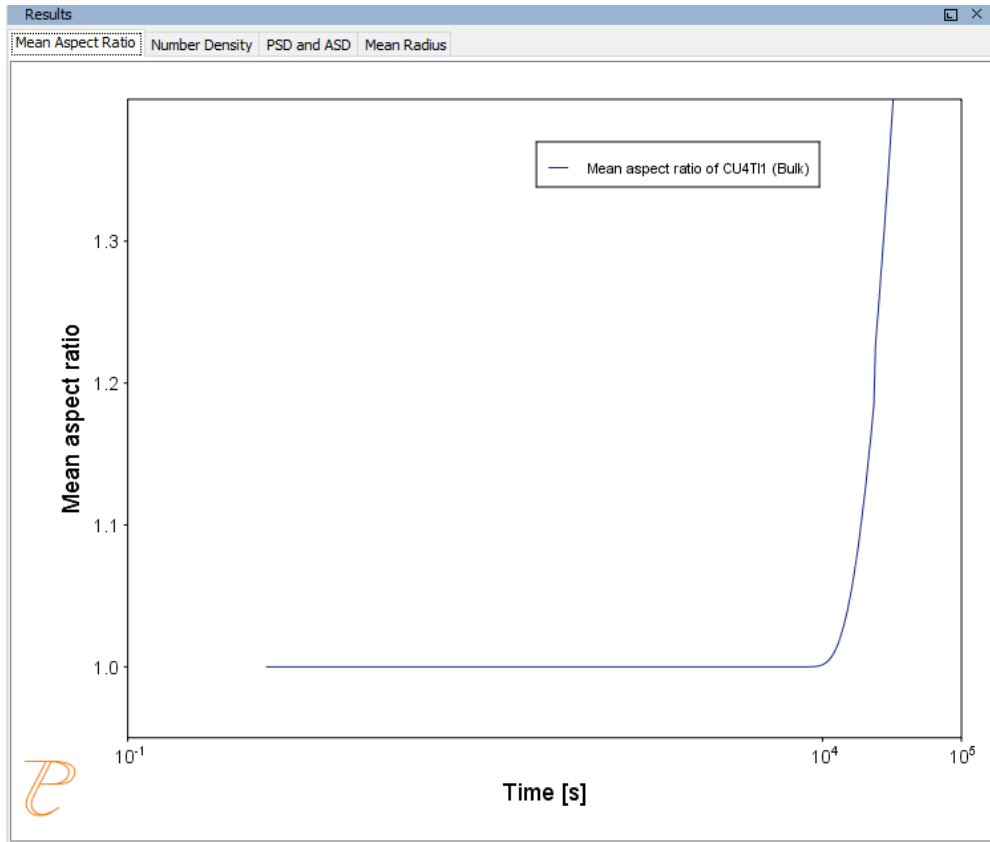
Number Density
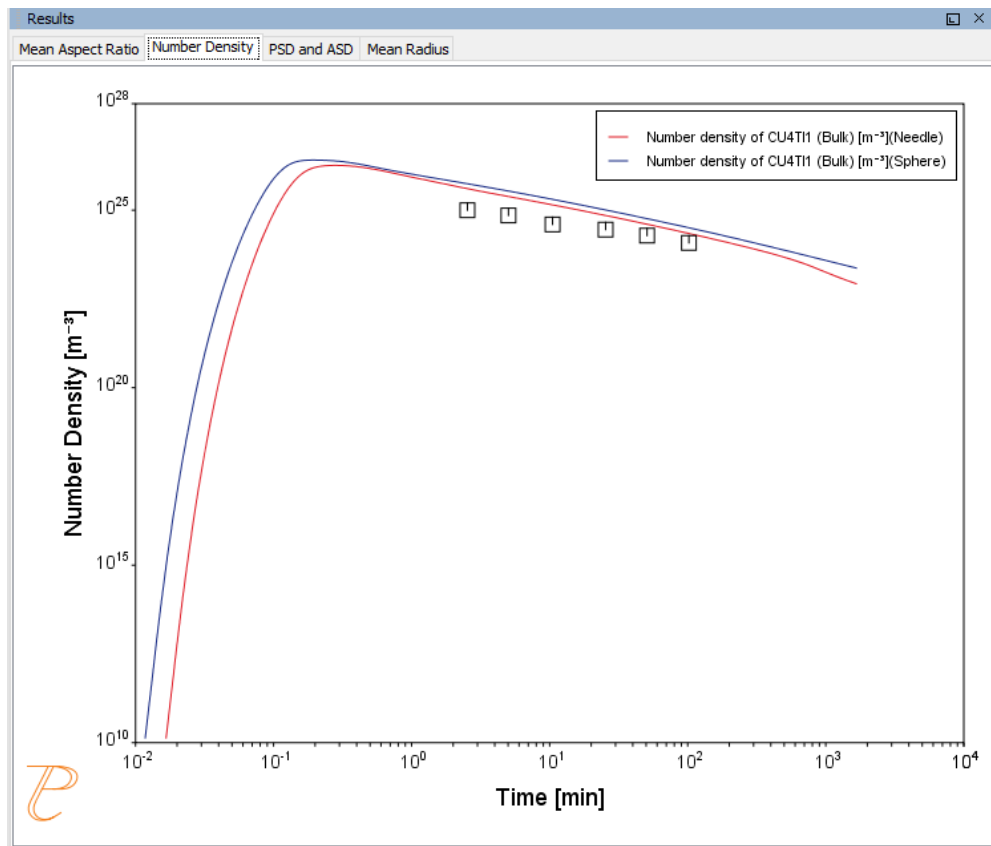
PSD and ASD
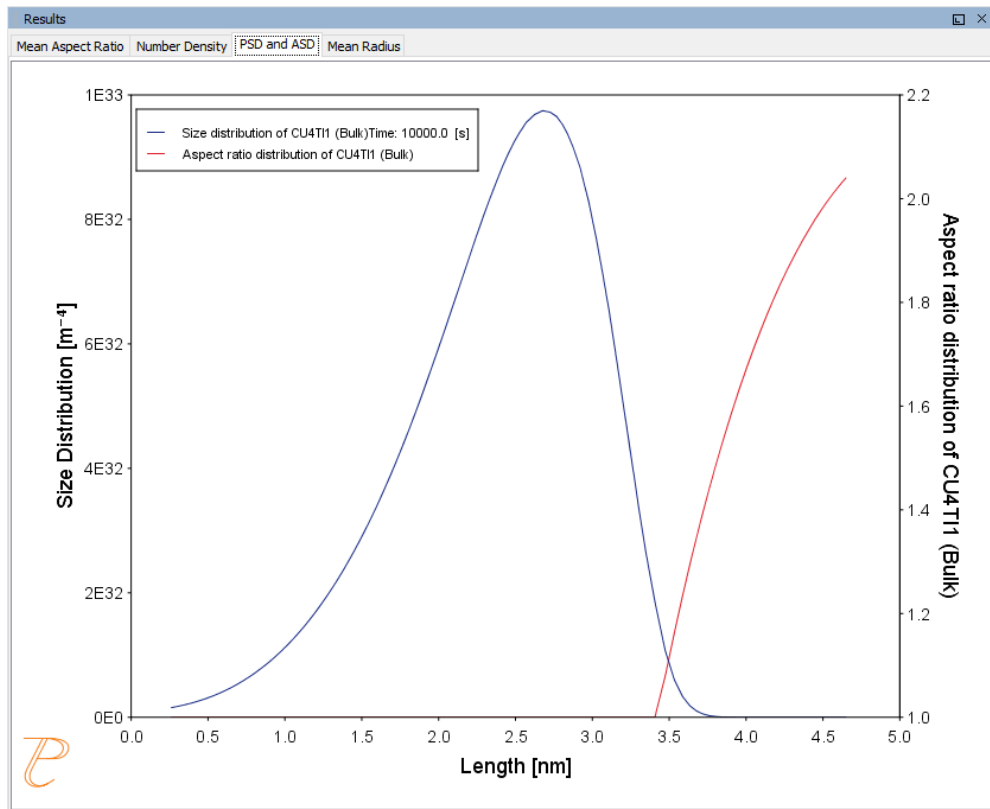
Mean Radius
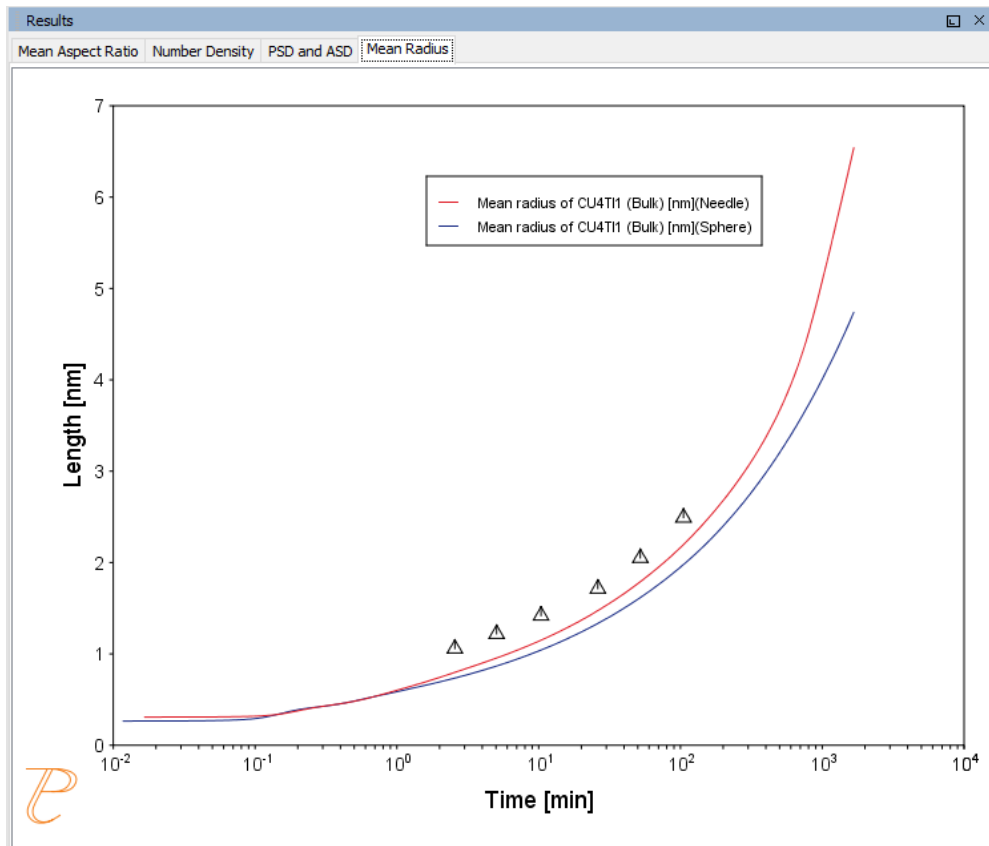
P_09: Precipitation of Al-Sc AL3SC with Assumption of Sphere and Cuboid Morphologies

In this isothermal calculation example, the precipitation of Al_3Sc 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 Seidman[1] 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.

---

[1] Marquis, E.A, and D.N Seidman. 2001. "Nanoscale Structural Evolution of Al3Sc Precipitates in Al(Sc) Alloys." Acta Materialia 49 (11): 1909–19.

[2] Novotny, Gabriel M., and Alan J. Ardell. 2001. "Precipitation of Al3Sc in Binary Al–Sc Alloys." Materials Science & Engineering, A: Structural Materials: Properties, Microstructure and Processing 318 (1–2): 144–54.

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.

This example is available as a video tutorial on [our website](#) and [YouTube channel](#).

▶ Precipitation Morphology

System (System Definer)	
Database package	Demo: Aluminum-based alloys (ALDEMO, MALDEMO)
Elements	Al, Sc
Sphere and Cuboid Conditions (Precipitation Calculator)	
Composition	Al-0.18Sc Mole percent
Matrix phase	FCC_A1
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 • c11 is **108.2** GPa • c12 is **61.3** GPa • c44 is **28.5** GPa
Precipitate Phase Data Parameters (Precipitation Calculator)	
Nucleation sites	Bulk
Interfacial energy	The default
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)	
Calculation type	Isothermal
Temperature	350° C
Simulation time	1.0E9 seconds

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.

Other	
File name and location	Folder: Precipitation Module - TC-PRISMA
	File name: P_09_Precipitation_Al-Sc_AL3SC_Sphere_Cuboid.tcu

Plot Results

Mean Radius
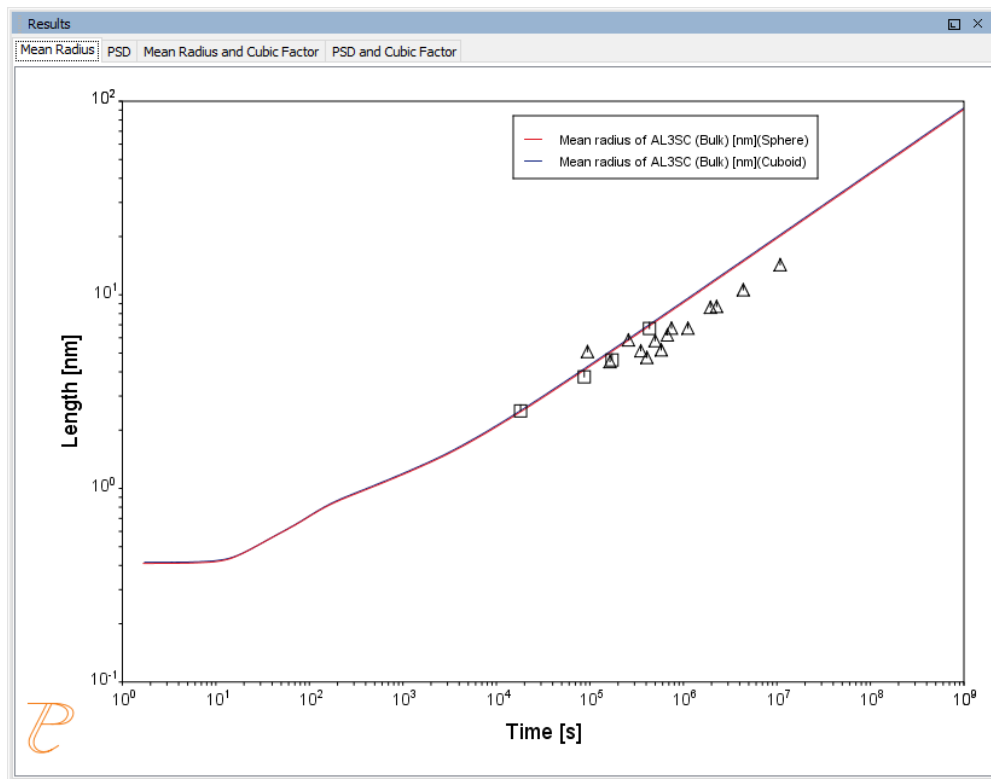
PSD
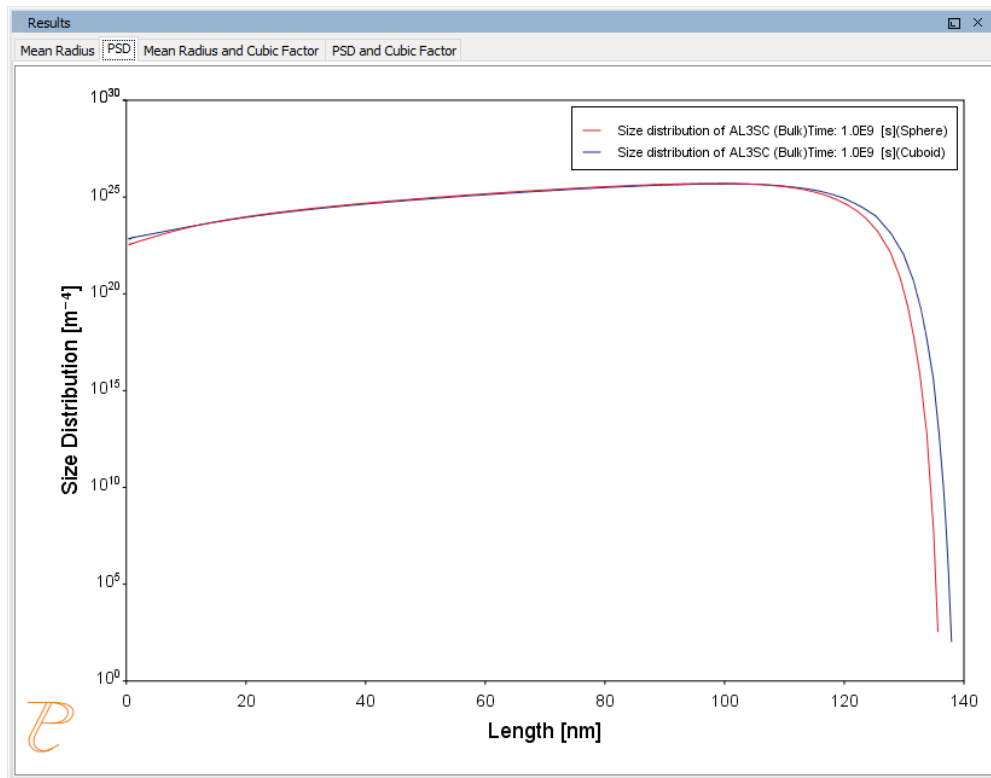
Mean Radius and Cubic Factor
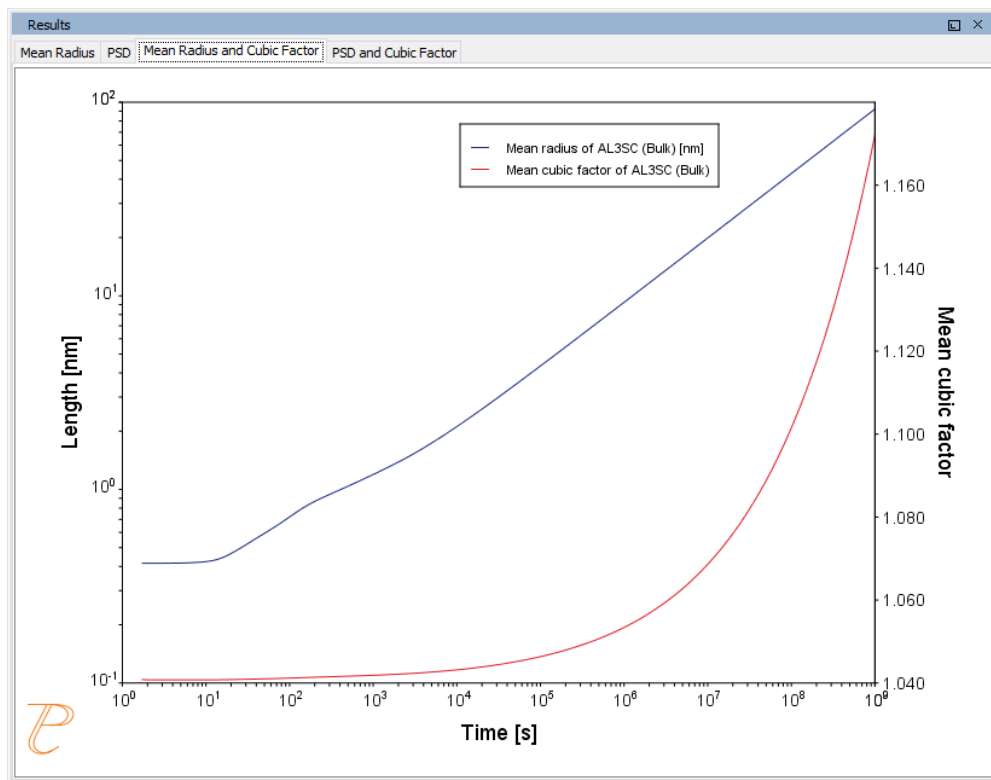
PSD and Cubic Factor
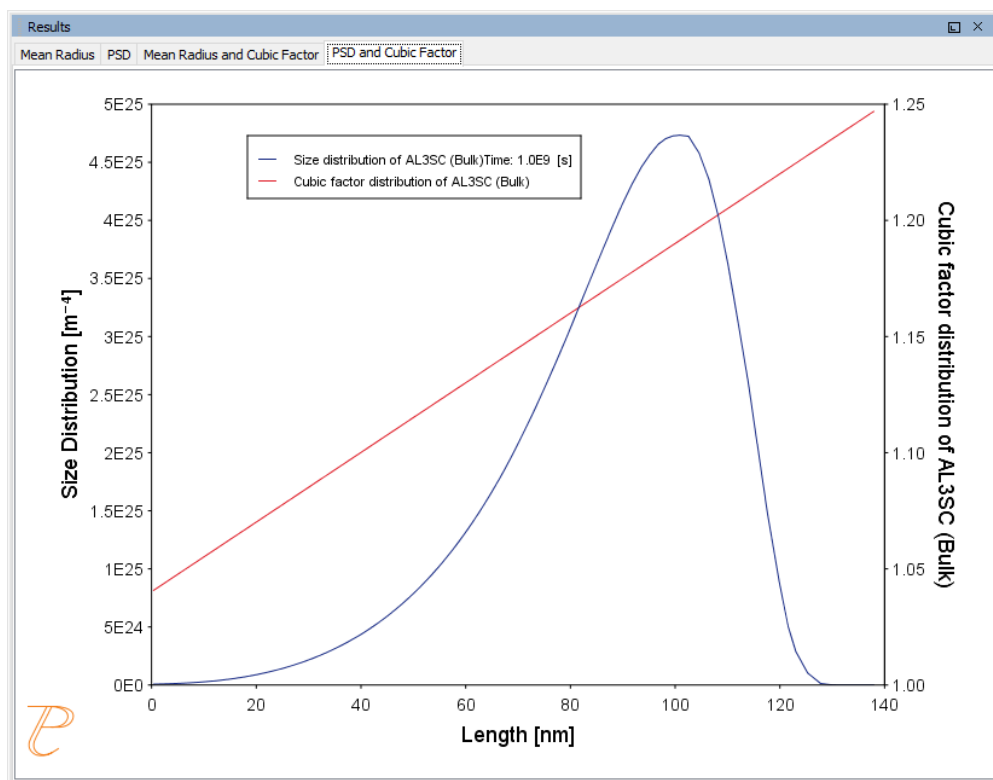
P_10: Initial Particle Size Distribution of Fe-Cr-C

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.
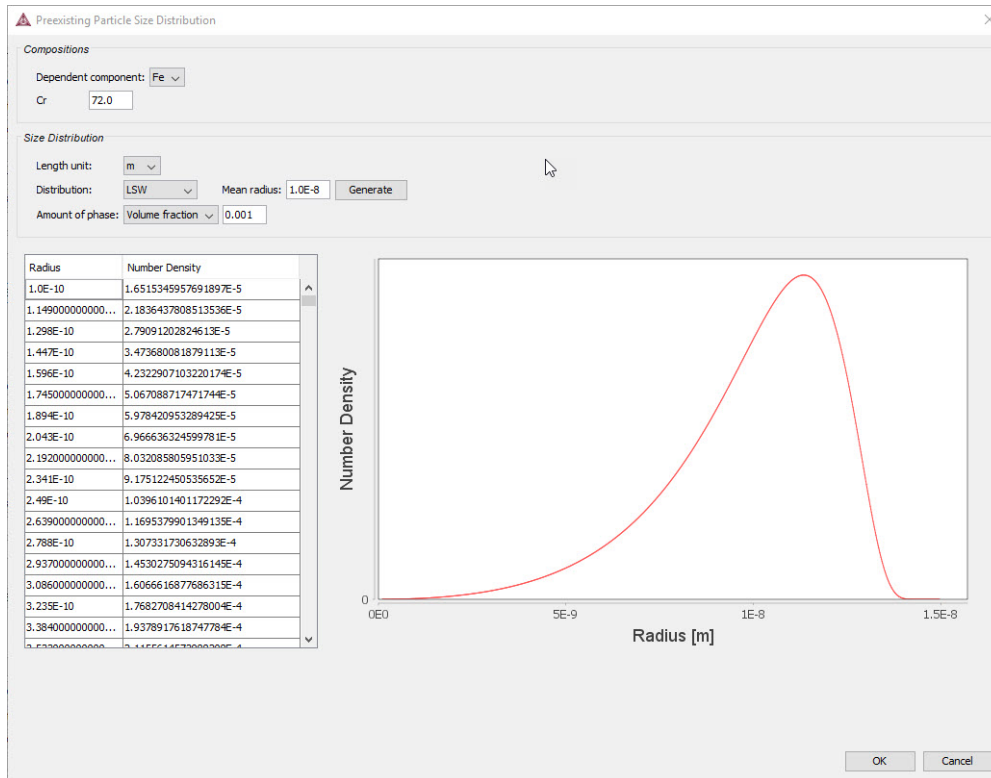
System (System Definer)	
Database package	Demo: Steels and Fe-alloys (FEDEMO and MFEDEMO)
Elements	Fe, C, Cr
Conditions (Precipitation Calculator)	
Composition	Fe-0.1C-12Cr Mass percent
Matrix phase	BCC_A2 All other defaults are kept.
Precipitate phases	CEMENTITE, M23C6 and M7C3
Precipitate Phase Data Parameters (Precipitation Calculator)	
Nucleation sites	Grain boundaries (all calculations): Calculated from the matrix settings with a wetting angle of 90°
Interfacial energy	User-defined function f(r,T) (all calculations): • CEMENTITE: 0.167 J/m^2

	- M23C6 0.252 J/m^2 - M7C3 0.282 J/m^2
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.

Calculation Type (Precipitation Calculator)

Calculation type	Isothermal
Temperature	1053 K
Simulation time	400 000 seconds

Other

File name and location	Folder: Precipitation Module - TC-PRISMA File name: P_10_Precipitation_Initial_PSD_FeCrC.tcu

Plot Results

Volume Fraction with Initial Particle Size Distribution
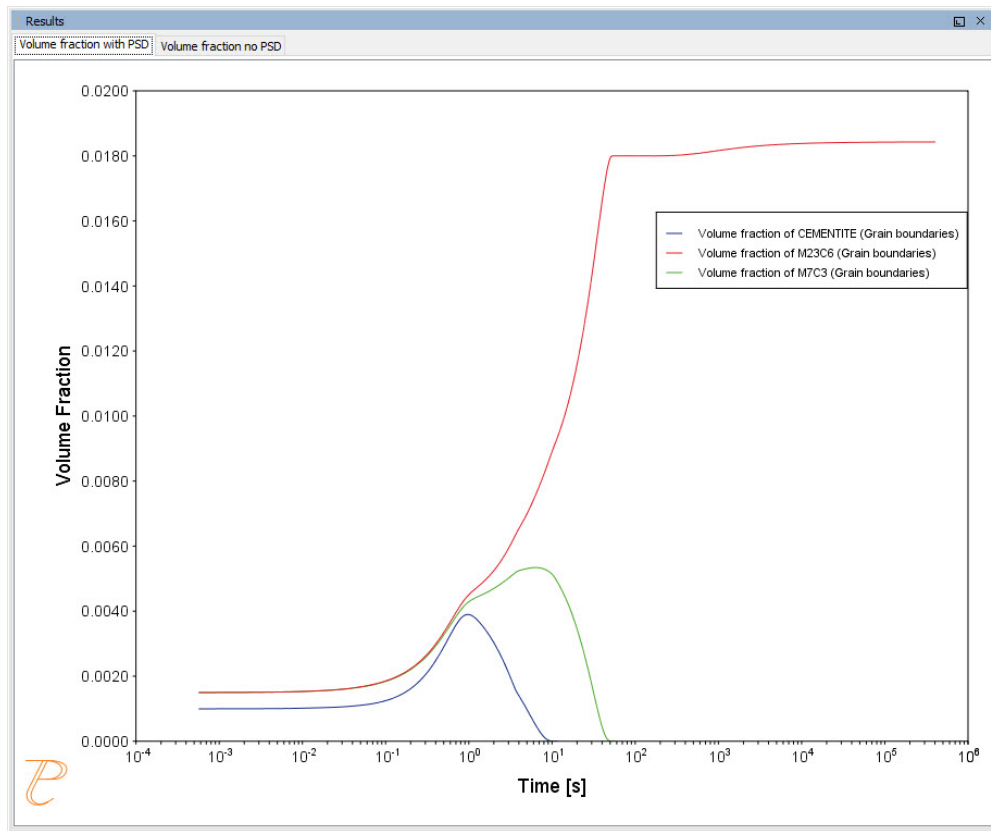
Volume Fraction with No Initial Particle Size Distribution
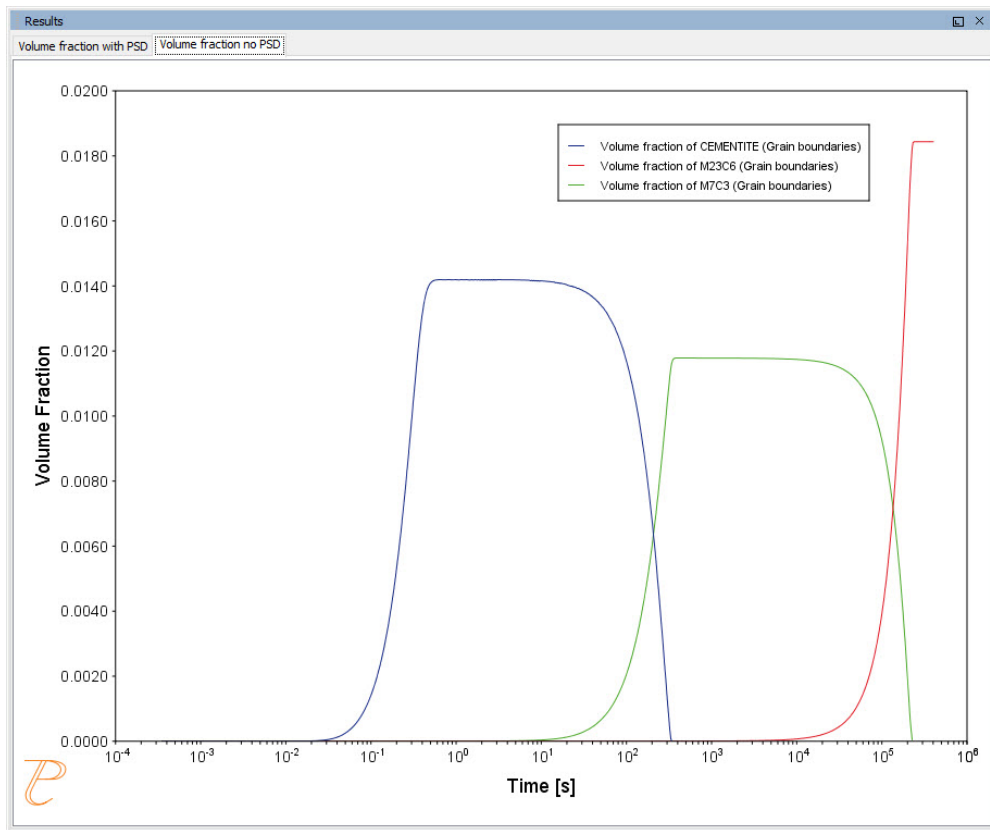
P_11: Interfacial Energy Function

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/m^2 to 0.085 J/m^2 for particle radii below and above 1e^{-8}m and 5e^{-8}m, respectively.

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

System (System Definer)	
Database package	Demo: Aluminum-based Alloys (ALDEMO, MALDEMO)

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[1] Iwamura, S, and Y Miura. 2004. "Loss in Coherency and Coarsening Behavior of Al3Sc Precipitates." *Acta Materialia* 52 (3): 591–600.

Elements	Al, Sc

Conditions (Precipitation Calculator)

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

Calculation Type (Precipitation Calculator)

Calculation type	Isothermal (all calculations)
Temperature	Four temperature points in 30 K increments: 673 K, 703 K, 733 K, and 763 K.
Simulation time	1 000 000 seconds (all calculations)

Datasets (Experimental File Reader)

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

Other

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

Plot Results

Mean Radius
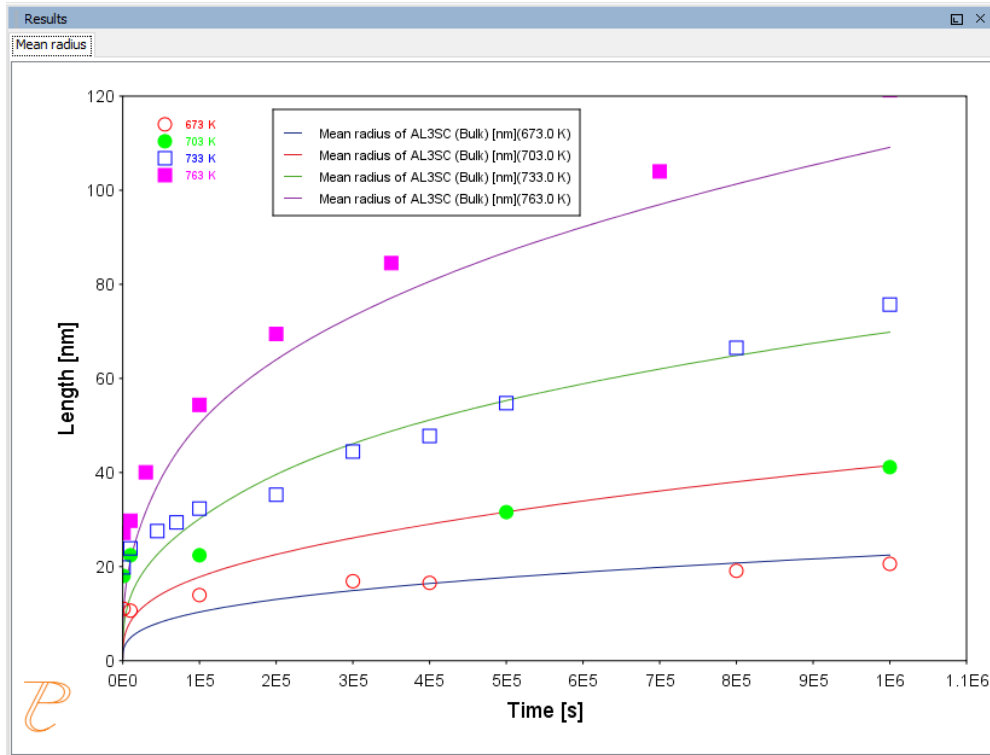
P_12: Comparing Growth Rate Models for an Al-Zr System

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.

System (System Definer)	
Database package	Demo: Aluminum-based Alloys (ALDEMO, MALDEMO)
Elements	Al, Zr
Conditions (Precipitation Calculator)	
Composition	Al-0.2Zr Mole percent
Matrix phase	FCC_A1 All other defaults are kept.
Precipitate phase	AL3ZR_D023 Click **Show details** to select the **Growth rate model** (**Simplified**, **Advanced** and **General**). All other defaults are kept.
Calculation Type (Precipitation Calculator)	
Calculation type	Isothermal
Temperature	425 Celsius
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
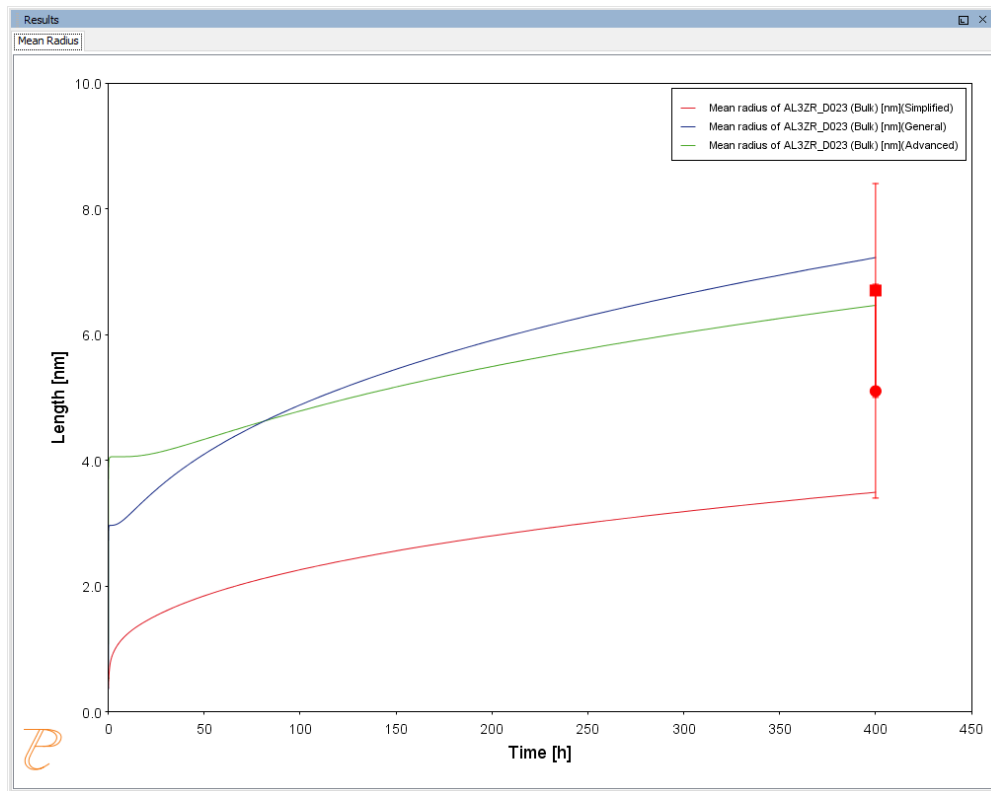
Using the Precipitation Calculator

In this section:

Precipitation Calculator

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 where you define the settings:

- **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.

Configuration Settings

Below are details about the settings available from the **Conditions** and **Options** tabs.

📝 You can edit the defaults for some of these settings by going to **Tools → Options → Graphical Mode → 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.

Conditions Tab

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 make sure that both thermodynamic and kinetic databases are selected and defined.

▶ In Thermo-Calc press F1 and search for "System Definer".

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.

Elastic properties

Choose the default **Disregard** to ignore the elastic properties. Otherwise choose **Isotropic** or **Cubic** and enter the elastic constants accordingly. Default elastic constants are given based on the major element of your alloy system. The elastic properties can affect nucleation rate, nucleation size, and particle shape.

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 size

Enter a numerical value and choose a unit from the list. The default is 1.0E-4 m. The value entered for grain size 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 options.

Grain aspect ratio

Enter a numerical value. The default is 1.0. The value entered for grain aspect ratio 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 options.

Dislocation density

Enter a numerical value. The default is 5.0E12 m^{-3}. The value entered for dislocation density changes the available nucleation sites when Dislocations is selected along with "Calculate from matrix settings" in the Precipitate Phase options.

Mobility enhancement prefactor

A parameter that multiplies to the mobility data from 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 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 make sure that both types of databases are selected and defined.

▶ In Thermo-Calc press F1 and search for "System Definer".

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

Nucleation sites

▶ Heterogeneous Nucleation

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** in

addition to the matrix settings.

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

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.

Growth rate model

Select **Simplified**, **General** or **Advanced**.

▶ Growth

Morphology

▶   Precipitation Morphology

Choose the particle shape from the list: **Sphere** (default), **Cuboid**, **Plate** and **Needle**.

Cuboid is available only when **Cubic** is chosen in **Elastic properties** in the Matrix Phase section.

When **Plate** or **Needle** is chosen, a check box is provided to **Calculate aspect ratio from elastic energy**, which is available when **Isotropic** or **Cubic** is chosen in **Elastic properties** in the Matrix Phase section. Alternatively, a value can be entered in the **Grain aspect ratio** field to provide a constant aspect ratio.
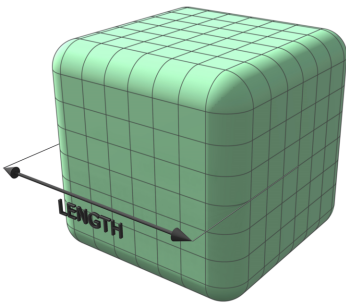
Figure 1: The cuboid shape is described by a supersphere. Cuboids have six faces, which form a convex polyhedron.
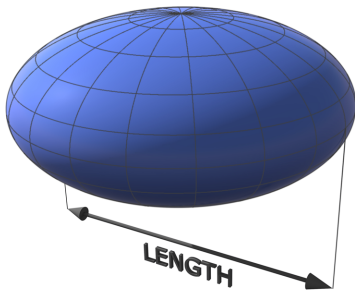
Figure 2: The plate is described as oblate spheroid. Oblate spheroids have rotational symmetry around an axis from pole to pole.
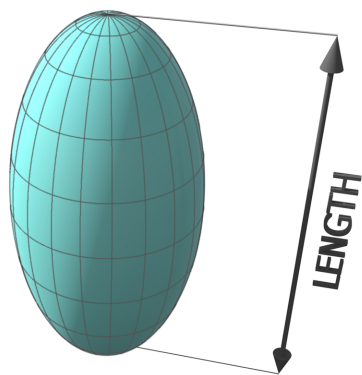
Figure 3: The needle shape is described as prolate spheroid. A prolate spheroid is a surface of revolution obtained by rotating an ellipse about its major axis.

Transformation strain

▶   Precipitation Morphology

Choose the default, **Disregard**, to ignore the transformation strain. Otherwise choose **Calculated from molar volume** to obtain a purely dilatational strain, or **User defined** to enter the values.

These options are available only when **Isotropic** or **Cubic** is chosen in **Elastic properties** in Matrix Phase. In addition, if **Cuboid** is chosen as **Morphology**, only **Calculated from molar volume** is available.

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

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.

Phase energy addition

An energy value that adds to the Gibbs free energy of the precipitate phase from database.

Approximate driving force

▶   Nucleation Theory

Select the check box to include this if simulations with several compositions sets of the same phase create problems.

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.

> See Particle Size Distribution (PSD) for detailed instructions.

See example P_10 and P_11.

Calculation Type

Isothermal

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

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**. 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.
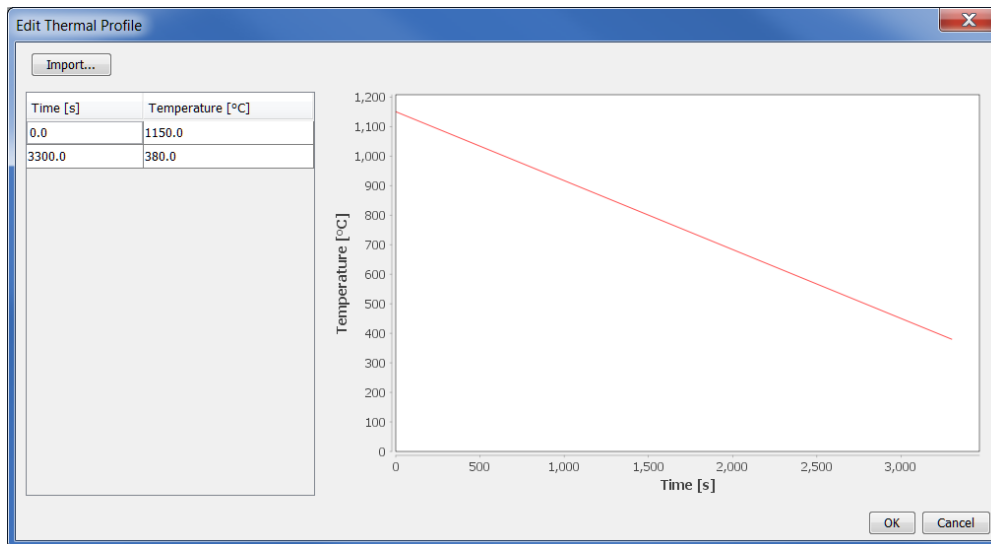
See example P_06.

TTT diagram

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

Temperature: Enter **Min**, **Max**, and **Step** values and choose a **Unit** (**Kelvin**, **Celsius**, or **Fahrenheit**).

Max annealing time: Enter a numerical value and choose a **Unit** (**Seconds**, **Minutes**, **Hours**, or **Days**).

Stop criteria: 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 criteria is fulfilled or if the maximum simulation time is reached, whichever happens first.

See example P_03.

CCT diagram

Use a **CCT-diagram** calculation type to calculate the continuous-cooling-transformation (CCT) curve for precipitation.

Temperature: Enter **Min** and **Max** values and choose a **Unit** (**Kelvin**, **Celsius**, or **Fahrenheit**).

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 **Unit** selected above.

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.

Options Tab

Numerical Parameters

▶ Numerical Method

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

Max time step fraction

The maximum time step 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 isothermal stage. The default is 0.01.

Particle Size Distribution (PSD)

See example P_10 and P_11 .

On the Precipitation Calculator you can set the pre-exisiting 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.
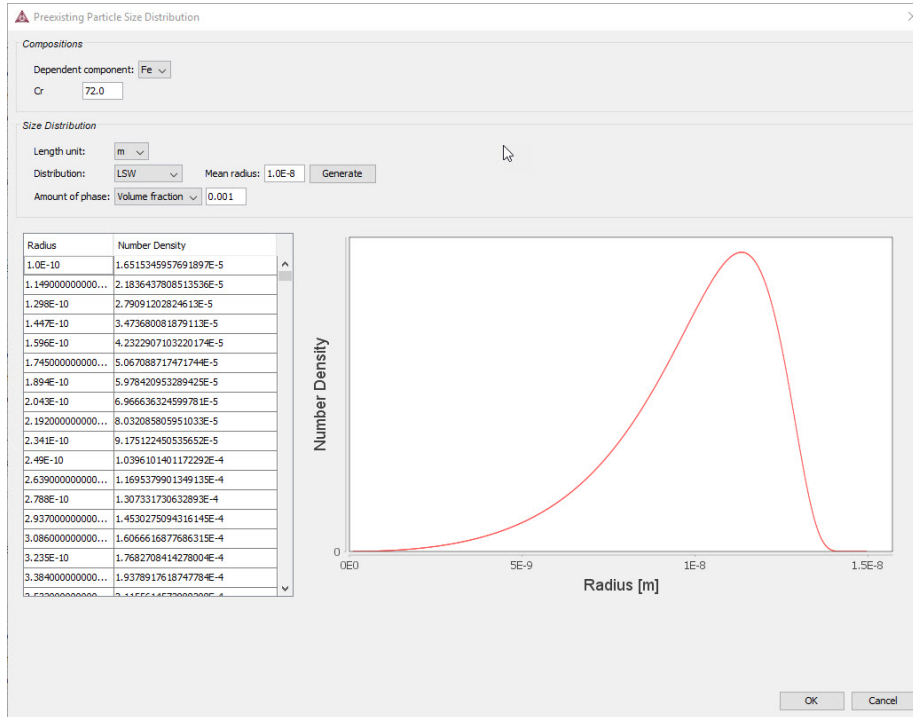
Defining the Preexisting size distribution

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.

   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**.

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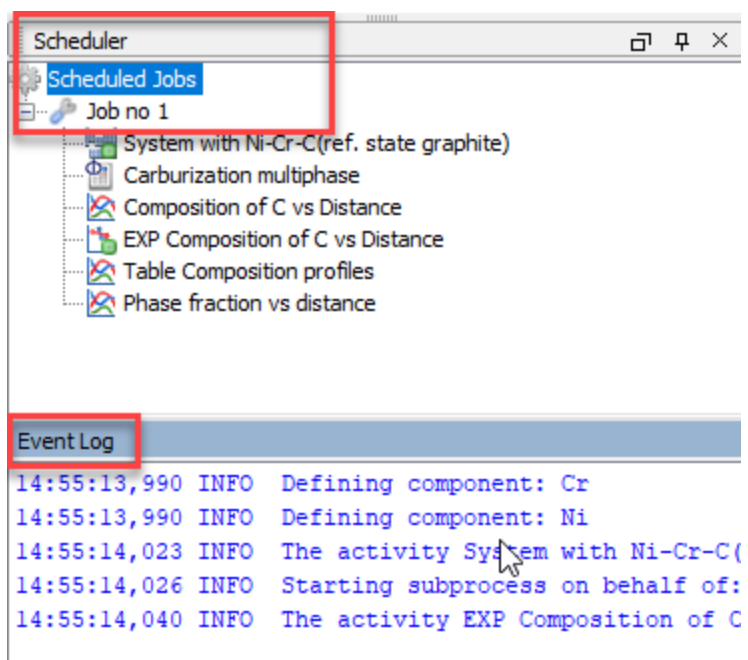
2. In the **Project** window, click the **Precipitation Calculator** node.

3. In the **Configuration** window at the bottom, click **Pause**. If there are intermediate results available these will be listed in the **Event Log**.
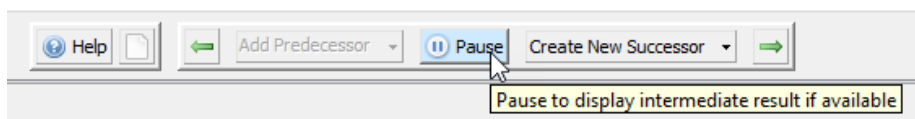
4. When ready, click **Continue** to resume your calculations from the last time step or click

Discard to discard the calculation (then click **Yes** or **No** on the window that opens).
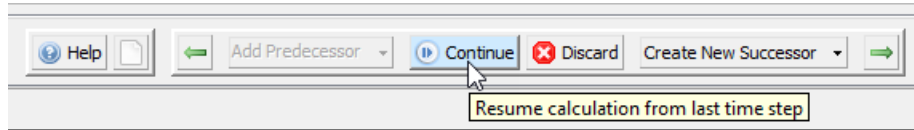
To Cancel a Job

- In the **Scheduler** window, right-click the job you want to cancel and select **Cancel Job**.
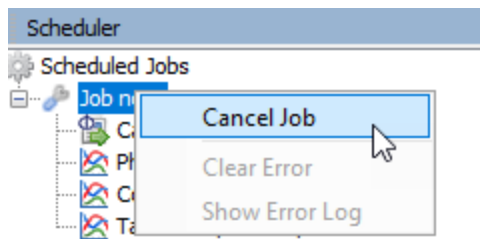
Plot Renderer

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 **Solutes** 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 area 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.
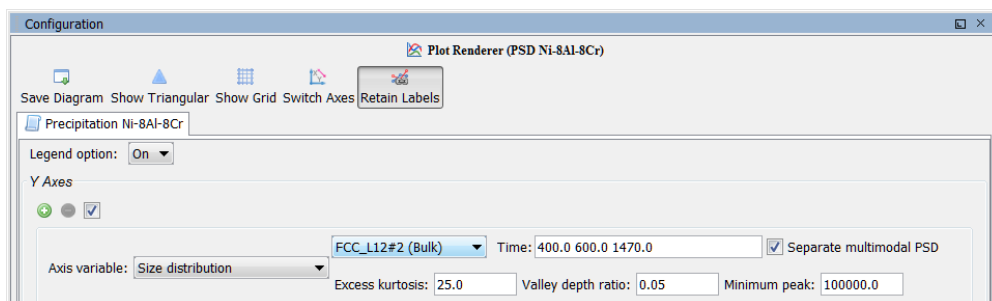
It can be applied on the following plot properties:

- Mean radius

- Size distribution

- Number density

- Volume fraction

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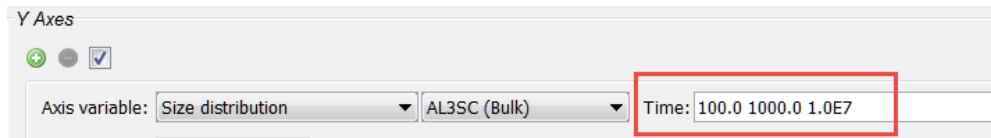
This field is available when **Mean radius**, **Number density** or **Volume fraction** is selected as the **Axis variable**. Since the evaluation of multi-modality at each time step is costly, you can specify how many evaluation **Points** to use. The points are geometrically distributed over the

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:

When you click **Perform** the times are plotted:
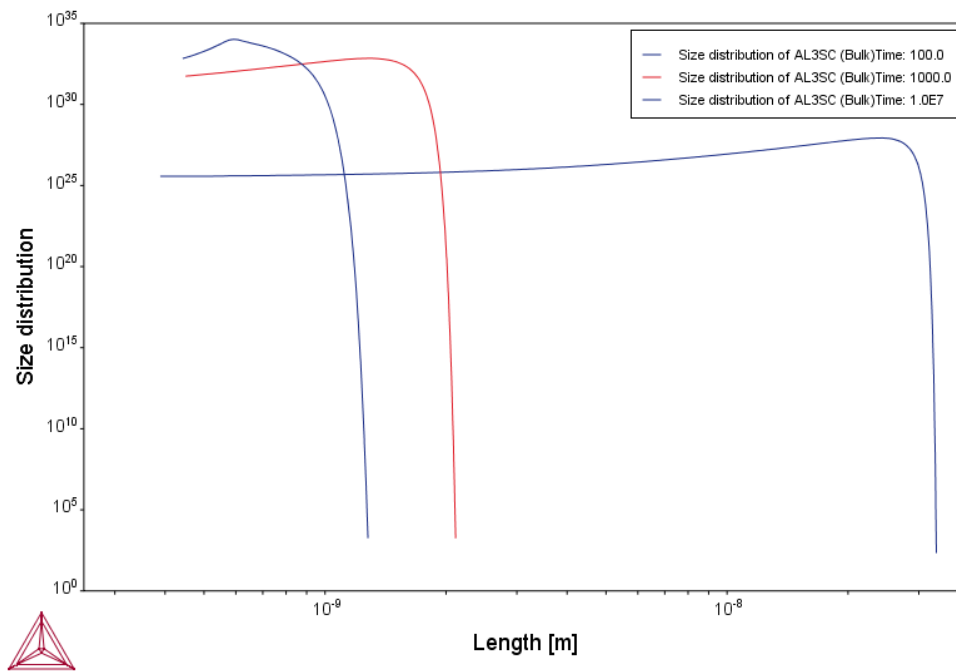
Excess Kurtosis

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. 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:

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 nth moment (*0*: number density; *1*st: mean radius; *3*rd: 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).
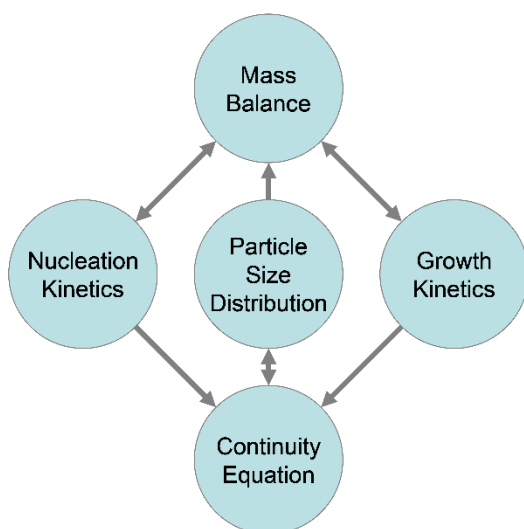
[1] Langer, J. S., and Schwartz, A. J. (1980). "Kinetics of nucleation in near-critical fluids, " *Physical Review A*, 21(3), 948–958.

[2] '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: 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. 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,
- τ 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

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

[*Eq. 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. In the case of homogeneous nucleation, each atom in the mother phase is a potential nucleation site.
- ΔG^* 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

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

[*Eq. 3*]

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[1] Kashchiev, Dimo. 2000. Nucleation. Butterworth-Heinemann.

[2] Russell, Kenneth C. 1980. "Nucleation in Solids: The Induction and Steady State Effects." Advances in Colloid and Interface Science 13 (3–4): 205–318.

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.

If elastic strain energy is excluded, $\Delta G_m^{\alpha \to \beta}$ is the chemical driving force for nucleation. 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}. The first figure is a standard calculation and the second an approximate calculation.
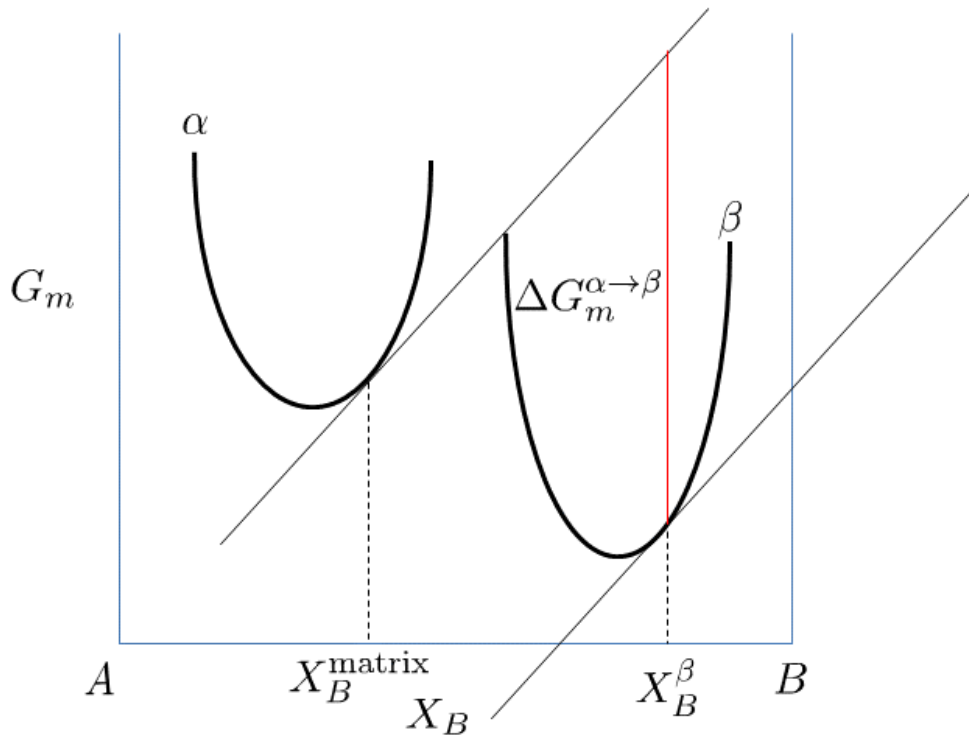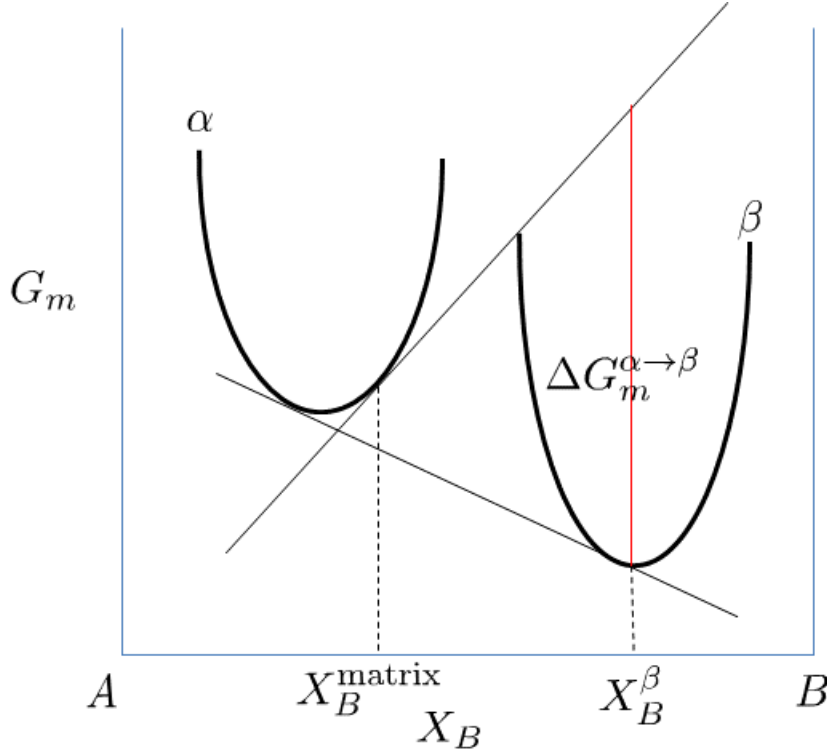
Nucleation is a stochastic process and can be considered formally as a diffusion process or Brownian movement in the particle size space. Supercritical nuclei with radius slightly larger than the critical radius have a probability of passing back across the free energy barrier and dissolve in the matrix. The Zeldovich factor Z is a measure of such probability and is related solely to the thermodynamics of the nucleation process in

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

[Eq. 4]

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

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

[Eq. 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 (2004)[1] .

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[1] Svoboda, J., F.D. Fischer, P. Fratzl, and Ernst Kozeschnik. 2004. "Modelling of Kinetics in Multi-Component Multi-Phase Systems with Spherical Precipitates." Materials Science and Engineering: A 385 (1–2): 166–74.

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

[*Eq. 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

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

[*Eq. 7*]

where θ differs from one derivation to another. The value 2 from Feder et al. (1966)[1] is adopted.

Elastic Strain Energy

Elastic strain energy, E_{el}, reduces the nucleation driving force, $\Delta G_m^{\alpha \to \beta}$ in [Equation 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)[2] indicate that the elastic strain energy is reduced almost linearly with increasing cubic factor η. Since the numerical simulations are computationally expensive, we assume that the elastic strain energy follows the linear relationship with η, and the elastic strain energy for spherical ($\eta = 1$) and cubic ($\eta = \sqrt{2}$) are calculated based on Khachaturyan's approximation (1983, 2008)[3].

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[1] Feder, J., K.C. Russell, J. Lothe, and G.M. Pound. 1966. "Homogeneous Nucleation and Growth of Droplets in Vapours." Advances in Physics 15 (57). Taylor & Francis Group: 111–78.

[2] Onaka, Susumu, Noriko Kobayashi, Toshiyuki Fujii, and Masaharu Kato. 2003. "Energy Analysis with a Superspherical Shape Approximation on the Spherical to Cubical Shape Transitions of Coherent Precipitates in Cubic Materials." Materials Science and Engineering: A 347 (1–2): 42–49.

[3] Khachaturyan, Armen G. 2013. "Habit Plane and Orientation Relations in Precipitates: Comparison with Experimental Data." In Theory of Structural Transformations in Solids, 299–305. Mineola, New York: Dover Publications, Inc.

[Eq. 8]

$$E_{\text{el}} = \tfrac{1}{2}(c_{11} + 2c_{12})\epsilon_0^2 V[A_1 + A_2]$$

where

- ϵ_0 is the lattice misfit strain.
- c_{11}, c_{12}, c_{44} are elastic constants in 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

$$I_1 = \tfrac{1}{15} \qquad I_2 = \tfrac{1}{105}$$

Cubic

$$I_1 = 0.006931 \qquad I_2 = 0.000959$$

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

[Eq. 9]

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

where

a, b, c are ellipsoid axes.

$n_i (i = 1, 2, 3)$ are unit directional vector normal to the spherical surface and

[1] Eshelby, J. D. 1957. "The Determination of the Elastic Field of an Ellipsoidal Inclusion, and Related Problems." Proceedings of the Royal Society A: Mathematical, Physical and Engineering Sciences 241 (1226): 376–96.
[2] Eshelby, J. D. 1959. "The Elastic Field Outside an Ellipsoidal Inclusion." Proceedings of the Royal Society A: Mathematical, Physical and Engineering Sciences 252 (1271): 561–69.

$$\beta = \sqrt{(a^2 \cos^2 \phi + b^2 \sin^2 \phi) \sin^2 \theta + c^2 \cos^2 \theta}$$

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

$$\Omega_{ii}(\vec{n}) = \frac{c_{44} + (c_{11} - c_{44})(n_j^2 + n_k^2) + \xi(c_{11} + c_{12})n_j^2 n_k^2}{c_{44} D(\vec{n})}$$

$$\Omega_{ij}(\vec{n}) = -\frac{(c_{12} + c_{44})(1 + \xi n_k^2)}{c_{44} D(\vec{n})} n_i n_j$$

where

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

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

The Eshelby S tensor can then be calculated as

[Eq. 10]
$$S_{ijmn} = -\frac{1}{2} C_{lkmn} \left(D_{iklj} + D_{jkli} \right)$$

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

[Eq. 11]
$$\epsilon_{ij} = S_{ijkl} \epsilon_{kl}^*$$

Combined with elastic stress calculated as

$$\sigma_{ij} = C_{ijkl} \left(\epsilon_{kl} - \epsilon_{kl}^* \right)$$

The elastic strain energy can be then obtained

[Eq. 12]
$$E^{el} = -\frac{1}{2} \sigma_{ij} \epsilon_{ij}^* V$$

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, σ_{coh}^{sph}, consistent with the approximation made by the embedded interfacial energy model. When calculating the critical nuclei, the interfacial energy in Equation 3 is assumed to be that of a spherical particle with constant specific interfacial energy σ_{coh}^{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 Equation 8 for spherical and cuboidal particles, or by setting $a = b = c$ in Equation 9 for ellipsoidal particles.

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 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 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)[1] .

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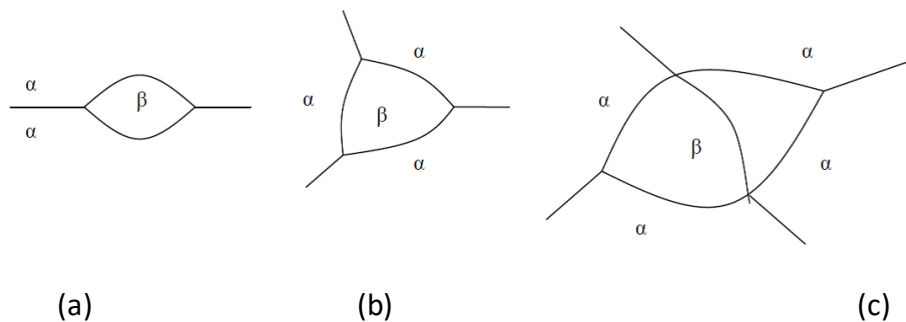
Figure 1: Non-spherical particles (β) that precipitate at grain boundaries of matrix phase(α) (a) grain boundary (two-grain junction) (b) grain edge (three-grain junction) (c) grain corners (four-grain junction). Images taken from Zang (2004)[2] .

[1] Clemm, P J, and J C Fisher. 1955. "The Influence of Grain Boundaries on the Nucleation of Secondary Phases." Acta Metallurgica 3 (1): 70–73.

[2] Zang. 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
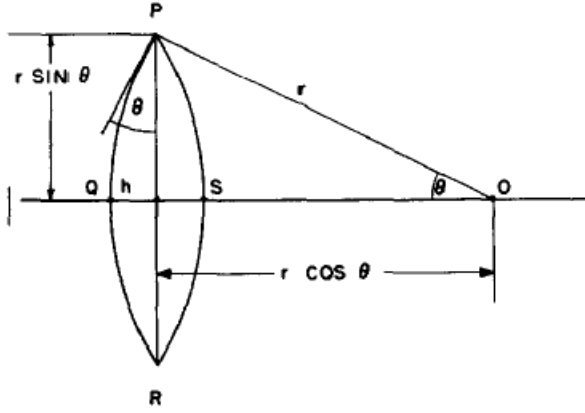
Figure 2: The nucleus at the grain boundary. Image from Clemm and Fisher, 1955.

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:

[Eq. 1]
$$A_{\alpha\alpha} = ar^2$$

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

[Eq. 2]
$$A_{\alpha\beta} = br^2$$

and the volume of the nucleus is

[Eq. 3]
$$V = cr^3$$

The expression of a, b, c in Equation 1, and 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

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

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

Then the critical radius should be

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

[Eq. 5]

And the activation energy barrier for nucleation is

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

[Eq. 6]

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

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

[Eq. 7]

i.e.

[Eq. 8] $$\sigma_{\alpha\alpha} = 2k\sigma_{\alpha\beta}$$

Which can be replaced into Equation 5 and 6.

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

[Eq. 9]

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

[Eq. 10]

The bulk, spherical precipitation equation is recovered by:

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

[Eq. 11]

so that

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

[Eq. 12]

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

[Eq. 13]

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

Zeldovich factor

The Zeldovich factor is modified as

[Eq. 14]
$$Z = Z_b \sqrt{f}$$

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 $4\pi/3$.

[Eq. 15]
$$f = \frac{3c}{4\pi}$$

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

[Eq. 16]
$$A_{\mathrm{red}} = a \cdot nr^{-2}$$

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.

[Eq. 17]
$$r' = \sqrt{\frac{a}{\pi}} \cdot r$$

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.

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

The Number of Available Heterogeneous Nucleation Sites
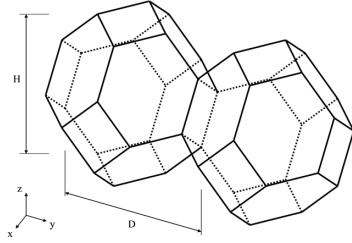
Figure 3: An example of tetrakaidecahedron approximation of grains

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

[Eq. 18]
$$\rho_2 = \frac{6\sqrt{1+2A^2}+1+2A}{4A}D^{-1}$$

[Eq. 19]
$$\rho_1 = 2\frac{\sqrt{2}+2\sqrt{1+A^2}}{A}D^{-2}$$

[Eq. 20]
$$\rho_0 = \frac{12}{A}D^{-3}$$

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

[Eq. 21]
$$N_i = \rho_i \left(\frac{N_A}{V_m^\alpha}\right)^{i/3} \quad i = 2, 1, 0$$

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

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[1] Cahn, John W. 1956. "Transformation Kinetics during Continuous Cooling." Acta Metallurgica 4 (6): 572–75.

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

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

[*Eq. 22*]

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

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

[*Eq. 1*]

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

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

[*Eq. 2*]

where

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

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

[*Eq. 3*]

and *Z* is the Zeldovich factor, previously defined in

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

[*Eq. 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.

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

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

[Eq. 1]
$$v(c_i^{\beta/\alpha} - c_i^{\alpha/\beta}) = c_i^{\alpha/\beta} M_i \frac{\mu_i^\alpha - \mu_i^{\alpha/\beta}}{\xi_i r}$$

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

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.

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[1] Chen, Qing, Johan Jeppsson, and John Ågren. 2008. "Analytical Treatment of Diffusion during Precipitate Growth in Multicomponent Systems." Acta Materialia 56 (8): 1890–96.

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

[Eq. 3]
$$\xi_i = \frac{\Omega_i}{2\lambda_i^2}$$

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

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

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

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

where ΔG_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

[Eq. 6]
$$K = K_{\text{sphere}}^{\text{simplified}} = \left[\sum_i \frac{\left(X_i^{\beta/\alpha}(r) - X_i^{\alpha/\beta}(r)\right)^2 \xi_i}{X_i^{\alpha/\beta}(r) M_i}\right]^{-1}$$

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.

Phase energy addition G_m^a and *Phase boundary mobility* M^B shifts the Gibbs energy of the precipitate β phase by $G_m^a + vV_m^\beta/M^B$. As a result, the driving force ΔG_m is reduced by $G_m^a + vV_m^\beta/M^B$, and the equilibrium compositions $c_i^{\beta e}$ and $c_i^{\alpha e}$ are shifted.
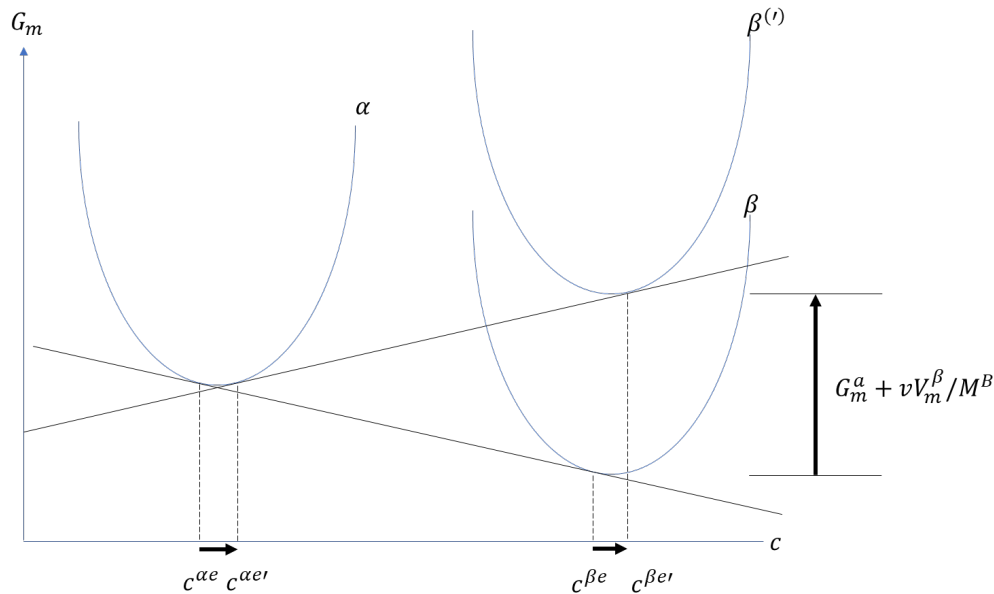
Effects of "Phase energy addition" G_m^a and "Phase boundary mobility" M^B.

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., Equation 5, with the kinetic parameter K defined as

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[1] Morral, J.E. and Purdy, G.R. 1994. "Particle Coarsening in Binary and Multicomponent Alloys." Scripta Metallurgica et Materialia 30(7): 905-908

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

[Eq. 7]

where $(\Delta X^{\alpha\beta}]$ and $[\Delta X^{\alpha\beta})$ are $n-1$ row and column vector, respectively, whose ith element is the composition difference $\left(X_i^{\beta/\alpha}(r) - X_i^{\alpha/\beta}(r)\right)$ as described in Equation 6. $[\ddot{G}]$, a $(n-1) \times (n-1)$ matrix, is based on thermodynamic factor matrix $[G^{\alpha}]$ with a correction factor

[Eq. 8] $$[\ddot{G}] = f[G^{\alpha}]$$

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

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

$[G^{\alpha}]$ is evaluated at the far-field matrix composition to consider the multicomponent Gibbs-Thomson effect[1]. For a particle with critical nuclei size r^*, the Gibbs-Thomson equation is

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

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 Equation 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 Equation 8.

$[D]^{-1}$ in Equation 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

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

[1.] Morral, J.E. and Purdy, G.R. 1995. "Thermodynamics of Particle Coarsening." J. Alloys and Compounds 220(1-2): 132-135

Model Selections

The most efficient model is the *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 *General* model is preferred. If the supersaturation is high, and meanwhile there are fast-diffusing interstitial elements such as C, the *Advanced* model is more appropriate to capture the NPLE mechanism.

> 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

[*Eq. 10*]
$$v' = v\left(1 + r\sqrt{4\pi N_V \langle r \rangle}\right)$$

where

- v' is the corrected velocity,
- $\langle r \rangle$ is the mean radius and
- N_V is the number density.

Non-Spherical Particles

> A reference for this section can be found in Wu, Kaisheng, Qing Chen, and Paul Mason. 2018. "Simulation of Precipitation Kinetics with Non-Spherical Particles." *Journal of Phase Equilibria and Diffusion*, 39 (5): 571–83.

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[1] Chen, M K, and P W Voorhees. 1993. "The Dynamics of Transient Ostwald Ripening." Modelling and Simulation in Materials Science and Engineering 1 (5): 591–612.

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 users choose transformation strain as **calculated from molar volume**, 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 users disregard the transformation strain, the elastic strain energy is neglected and hence the particles remain spherical shape.

If you choose **calculated aspect ratio from elastic energy** for plate and needle, 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

$$E_{\mathrm{int}} = 4\pi \sqrt[3]{\alpha^2} \sigma_0^{\mathrm{sph}} r^2$$

Needle

$$E_{\mathrm{int}} = 4\pi \sqrt[3]{\alpha} \sigma_0^{\mathrm{sph}} r^2$$

Where

- α is the aspect ratio

- σ_0^{sph} 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 Equation 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 Equation 5 is thus given as

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

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

Plate

$$K_\sigma = \sqrt[3]{\alpha^2}$$

Needle

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

where α is the aspect ratio of the ellipsoidal particle. K_{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

Plate

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

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[1]. Johnson, Charles A. 1965. "Generalization of the Gibbs-Thomson Equation." Surface Science 3 (5): 429–44.

[2]. Ham, Frank S. 1958. "Theory of Diffusion-Limited Precipitation." Journal of Physics and Chemistry of Solids 6 (4): 335–51.

[3]. Ham, Frank S. 1959. "Shape-Preserving Solutions of the Time-Dependent Diffusion Equation." Quarterly of Applied Mathematics 17 (2): 137–45.

Needle

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

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 Ω_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 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 (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.

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[1] Aaron, Howard B. 1970. "Diffusion-Limited Phase Transformations: A Comparison and Critical Evaluation of the Mathematical Approximations." Journal of Applied Physics 41 (11). AIP Publishing: 4404.

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 ϕ - the particle volume fraction, is expressed as

[Eq. 1] $$N = \int_0^\infty f(x)dr$$

[Eq. 2] $$\langle r \rangle = \int_0^\infty rf(r)dr$$

The time evolution of $f(r)$ follows the continuity as in Langer and Schwartz (1980)[1].

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

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

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

where J is the nucleation rate.

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[1] Langer, J. S., and A. J. Schwartz. 1980. "Kinetics of Nucleation in near-Critical Fluids." Physical Review A 21 (3): 948–58.

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

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

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 X_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 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 rr 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:

$$(\int_0^{r_{dt}} fr^3 dr)/(\int_0^\infty fr^3 dr) = P_{rdt}$$

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:

$$\Delta t \le P_{cc} \times (r_{i+1} - r_i)/(dr_i/dt - dr_{i+1}/dt)$$

for

$$r_{i+1} > r_{i+1}$$

and

$$dr_{i+1}/dt < dr_i/dt$$

MAXIMUM OVERALL VOLUME CHANGE

P_ν

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

$$\Delta t \le P_V/10/(4\pi r_{eff}^3 J/3)$$

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:

$$\Delta t \leq P_{rc} \times \Delta t_{previous} / (|r_{c1} - r_{c2}/r_{rc1}|)$$

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.

Parameter	Default value
P_{dt}^{max}	0.1
P_{Nr}	200
P_{Nr}^{max}	300
P_{Nr}^{min}	100
P_r	0.01
P_{rdt}	0.01
P_{cc}	0.5
P_ν	0.001
P_{logJ}	0.5
P_{rc}	0.1
P_{rmin}	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:

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

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 [Becker, 1938][1].

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[1] Becker, 1938. 'Die Keimbildung bei der Ausscheidung in metallischen Mischkristallen', *Ann. Phys.* 424, 128–140.

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
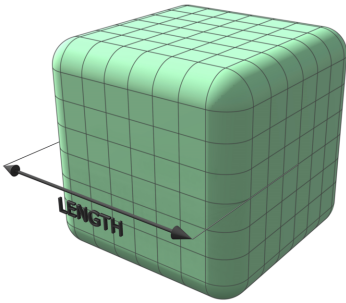
▶   Configuration Settings

Cuboid

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

The cuboid shape is described by a supersphere

$$x_1^p + x_2^p + x_3^p = R^p \qquad (p \geq 2)$$

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 $\eta = \sqrt{2}$.
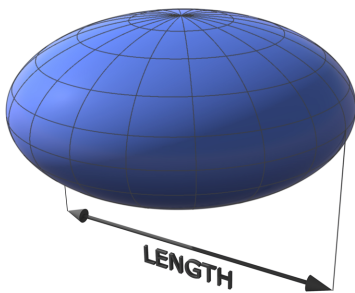
Plate

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

The plate is described as oblate spheroid

$$\frac{x_1^2}{l^2} + \frac{x_2^2}{l^2} + \frac{x_3^2}{r^2} \leq 1 \qquad l > r$$

with aspect ratio
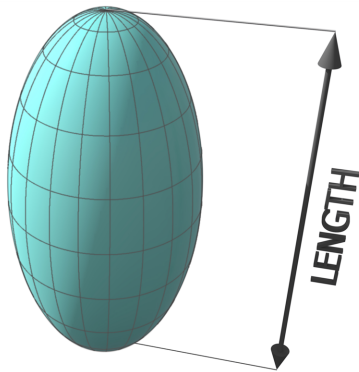
$$\alpha = \frac{l}{r} > 1$$

Needle

Figure 3: A prolate spheroid is a surface of revolution obtained by rotating an ellipse about its major axis.

The needle shape is described as prolate spheroid

$$\frac{x_1^2}{r^2} + \frac{x_2^2}{r^2} + \frac{x_3^2}{l^2} \leq 1 \qquad l > r$$

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

▶   Configuration Settings

Precipitation Module (TC-PRISMA) References

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