TC–PRISMA
User Guide

Version 2015a

Contents

Version history

- TC-PRISMA 2015a now uses the same version as Thermo-Calc software.
- TC-PRISMA version 2.0 enables arbitrary temperature-time profiles, especially continuous cooling conditions. For the convenience of users, interfacial energy between matrix and precipitate phases can be estimated in this version by using an approximation model based on Becker's bond energy approach.
- TC-PRISMA version 1.0 and 1.1 treat isothermal precipitation process.

1. Introduction

The TC-PRISMA software is a general computational tool for simulating kinetics of diffusion controlled multi-particle precipitation process in multicomponent and multi-phase alloy systems. Precipitation, formation of particles of a second phase or second phases from a supersaturated solid solution matrix phase, is a solid state phase transformation process that has been exploited to improve the strength and toughness of various structural alloys for centuries. 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, they could happen also at the same time. With TC-PRISMA, 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 TC-PRISMA is shown in Figure 1.

Input		Output
• Alloy composition • Temperature • Simulation time • Thermodynamic data • Kinetic data • Property data • Nucleation sites • Initial microstructure	→ TC-PRISMA →	• Particle size distribution • Number density • Average particle radius • Volume fraction • Matrix composition • Precipitate composition • Nucleation rate
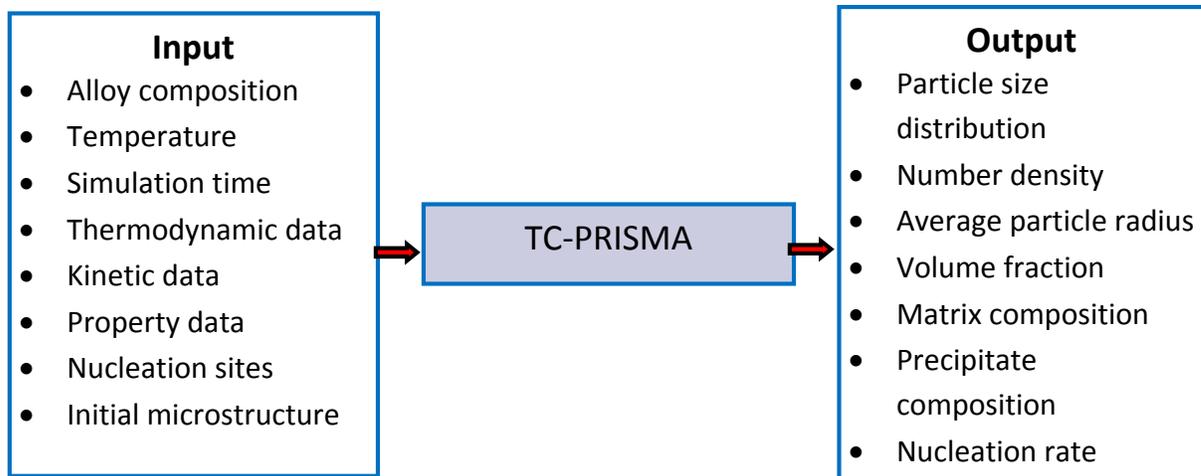
Figure 1: Input and output of TC-PRISMA.

TC-PRISMA relies on CALPHAD based software tools and databases to provide necessary bulk thermodynamic and kinetic data for phases in multicomponent systems. The CALPHAD approach has been developed for more than 50 years and is now 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. TC-PRISMA is directly integrated with Thermo-Calc and DICTRA, which are CALPHAD based computer programs for calculating phase equilibrium and diffusion controlled phase transformation in multicomponent systems and have a wide spectrum of accompanying thermodynamic and kinetic

databases. With Thermo-Calc and DICTRA and accompanying databases, almost all fundamental phase equilibrium and phase transformation information, such as driving forces for nucleation and growth, operating tie-line under local equilibrium or para-equilibrium condition, deviation from local equilibrium at interface due to interface friction, atomic mobilities or diffusivities in the matrix phase etc., can be calculated without unnecessary and inaccurate approximations.

In addition to bulk thermodynamic and kinetic data, a few other physical properties, such as interfacial energy and volume, are needed in precipitation models implemented in TC-PRISMA. These additional physical parameters can be obtained by experiments or other estimation models or first principles calculations. As a matter of fact, volume data for steels and nickel-based alloys has already been assessed and included in TCFE6, TCNI5, and TCAL2 databases. It is hoped that in future interfacial energy can also be modeled in the spirit of CALPHAD method and the model parameters can be assessed by considering various kinds of experimental data with help of TC-PRISMA.

In this document, learn how to use the TC-PRISMA software and describe various theoretical models and numerical algorithms. Section 2 is a short instruction about where to find example files and how to perform a TC-PRISMA simulation. The Graphic User Interface (GUI) is described in section 3 and there is an overview of the windows used in a fresh simulation. Section 4 covers the precipitation models and numerical method. Detailed description of physical and numerical parameters are in this section. There is also a list of references in Section 5.

2. Quick start

Once TC-PRISMA is installed, it is recommended you start by running a few examples to confirm that the installation is successful. Afterwards, you can try to perform simulations for specific alloys of interest.

2.1 Open and save script files
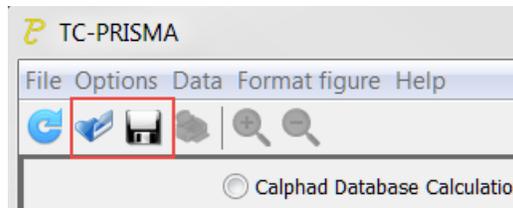
TC-PRISMA comes with sample scripts found under:

My Documents\Thermo-Calc*<version>*\TC-PRISMA\examples

where *<version>* is the current version of Thermo-Calc. Opening a script file, with extension **PRM**, gives a complete setup of a simulation.
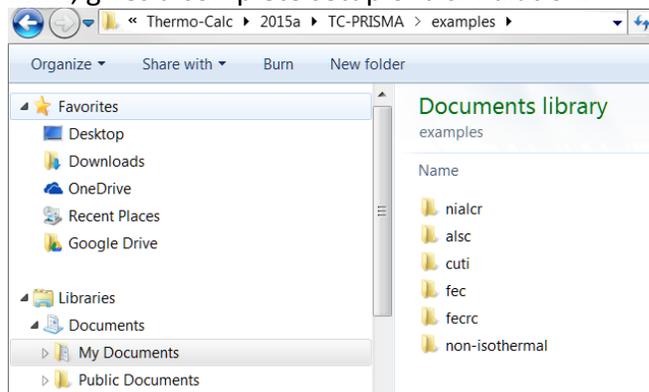
Click the **Save** button 💾 (or select **File>Save** or press Ctrl+S) to keep any user-defined simulation. Click **Reinitiate** 🔄 (or select **File>Reinitiate** or press Ctrl+N) before opening a new script.

2.2 Run examples

Open the pre-installed examples from the main menu (select **File > Open Script**) or click the **Open** button and navigate to **My Documents\Thermo-Calc*<version>*\TC-PRISMA\examples**. A macro file (with extension PRM) for each example in the corresponding folder can be loaded to set up the simulation task. When the **Simulate** button is available click it to start the simulation.

📝Some pre-installed examples require a valid license to various commercial databases. Examples 5.1, 5.2.1, 5.3.1, 5.3.2, 5.5, and 5.6 need no commercial databases and should always be possible to run.

For some examples, experimental data is collected from publications and can be compared against the simulation results: click **Format figure > Add experiments**. To make comparisons, time and length units can be changed: click **Format figure > Time units** and **Format figure > length units**, respectively.

A brief description of the examples is given below. Some titles are self-explanatory.

- Ni-Al-Cr (**nialcr** folder): This example simulates the kinetics of precipitation of γ′ phase from γ phase. The simulation results can be compared with experimental data collected from C.K. Sudbrack et al., *Acta Mater.* 56 (2008) 448-463. The measurements are in hours and nanometers, respectively.

- Al-Sc (**alsc** folder): This example simulates the kinetics of precipitation of Al3Sc from an Fcc Al solution phase. The simulation results can be compared with experimental data collected from E.A. Marquis and D.N. Seidman, *Acta Mater.* 49 (2001) 1909-1919 and G.M. Novotny and A.J. Ardell, *Mater. Sci. & Eng*. A318 (2001) 144-154. The measurements are in seconds and nanometers, respectively.

- Cu-Ti (**cuti** folder with subfolders): These examples simulate the kinetics of precipitation of Cu4Ti from an Fcc Cu solution phase. Simulation results can be compared with experimental data collected from R. Wagner and R. Kampmann, Homogeneous second phase precipitation, in P. Haasen, editor, *Materials Science and Technology: A comprehensive treatment*, Weinheim, Wiley-VCH, 1991, pp. 213-303. The measurements are in minutes and nanometers, respectively. You can use a binary dilute solution model, a database package, and use a database pack and calculate TTT.

- Fe-C (**fec** folder with subfolders): These examples simulate the kinetics of precipitation of carbides from a Bcc Fe solution phase. You can use a binary dilute solution model – two carbides, binary dilute solution model – TTT calculation, or a database package.

- Fe-Cr-C (**fecrc** folder): This example simulates the kinetics of precipitation of both stable and metastable carbides from ferrite phase. It demonstrates that metastable carbides may first emerge and then disappears and the stable phase prevails.

- Non-isothermal (**ninon-isothermal** folder): The two examples simulate 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 T. Rojhirunsakool et al., *J. Mater. Sci.* 48 (2013) 825-831.

2.3 Make a new simulation

To perform a simulation for your own alloy, you can try by copying an example script file to a new folder and making necessary modifications to the script or alternatively by starting from scratch and going through the following steps (see Figure 2). When starting from scratch, it is advised to save your setup to a script file and, during the **save script** operation, select always a different folder or if necessary, make a new folder in order to avoid existing files being overwritten or output files being mixed up when running several simulations at the same time.

- **Define System:** Choose a database package, select elements, select matrix phase, and select precipitate phase(s).
- **Set Simulation Conditions:** Activate the CONDITIONS panel, enter thermal profile, and enter matrix composition.
- **Set Nucleation Properties:** Click *Properties* button to get the *Nucleation* window, select nucleation site and enter necessary microstructure information in the case a heterogeneous nucleation site is selected.
- **Set Parameters:** Enter interfacial energy, volume data, etc. if they are not available from the databases used. The *Set Parameters* window can be accessed by clicking **Data > Set Parameters**.
- Simulate
- Plot results
-
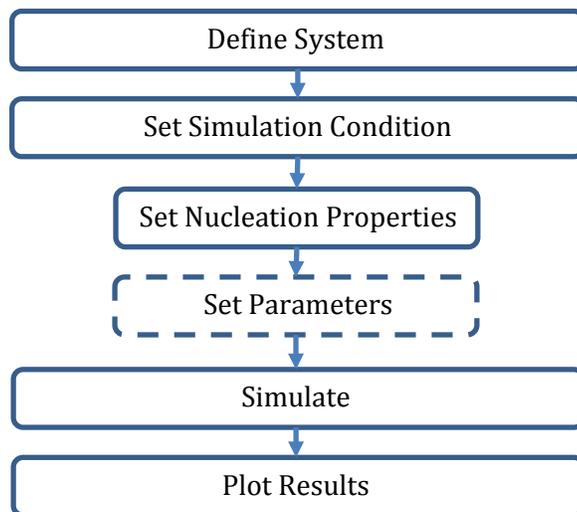
Figure 2: Starting a simulation from scratch.

2.4 File types

TC-PRISMA has the following types of files:

- **PRP file –** Database list file or database package configuration file. Be careful when trying to modify these files. Make sure that added databases are actually available on your computer. Corrupted PRP file may cause the TC-PRISMA software not able to start.

- **PRM file –** Macro file.

- **PRI file –** Workspace file. A binary file storing everything. It can be loaded for reviewing simulation results.

- **PRD file –** Result data file.

3. Graphic user interface

TC-PRISMA is a user friendly and intuitive Java-based Graphic User Interface (GUI). With only a few clicks and inputs, a simulation can be setup and performed. After the simulation is completed the results can directly be plotted and compared with pre-compiled experimental data. The figures can be edited, printed, and saved into different graphic formats.

The following is an overview of the GUI.

3.1 Define the system

When you first open TC-PRISMA you can choose a simulation with **CALPHAD Database Calculation** input (the default) or a **User-Defined Binary Calculation** input.

3.1.1 CALPHAD database calculation
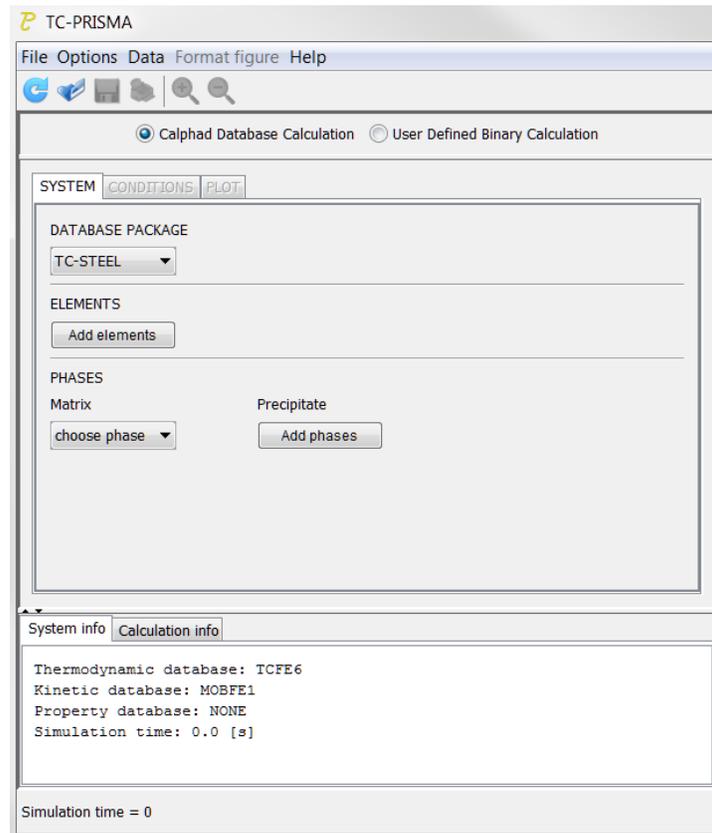
For **CALPHAD Database Calculation** use the **SYSTEM** tab to make these settings:

- Select a pre-defined **Database Package** from the list—**TC-STEEL**, **CUTI**, **ALSC**, or **NIALCR**. A package consists of three compatible databases, one for thermodynamic data, one for kinetic data, and the other for properties, such as interfacial energy. You can also define another set of database packages (see Section 3.7).

- Add **Elements**.
- Choose a **Matrix Phase**.
- Add **Precipitate Phase(s)**, where a maximum of five phases are allowed.

3.1.2   User-defined binary calculation
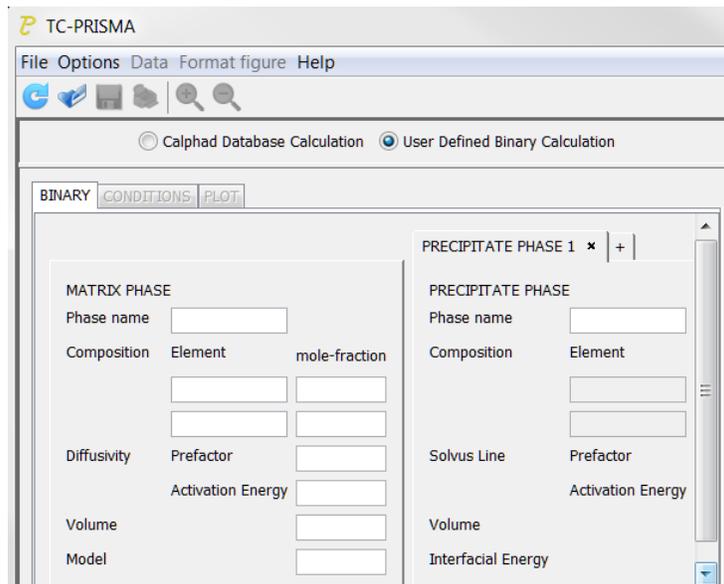
For **User-Defined Binary Calculation** use the **BINARY** tab to make a variety of settings including element, phase name (any name can be used), phase diagram (solvus line), kinetics (diffusivity), volume of different phases, interfacial energy, etc. More than one tab for precipitate phases can be added by clicking **+** next to the **Precipitate Phase** tab.

3.2 Set simulation conditions

After a system is defined you can click to open the **CONDITIONS** tab. Here materials chemistry, thermal profile (temperature and time), and nucleation properties are specified. Two types of calculations are allowed, one for a single thermal profile simulation (**Multi particle**), and the other for a **TTT diagram** calculation. When ready, click **Simulate** to start the simulation.
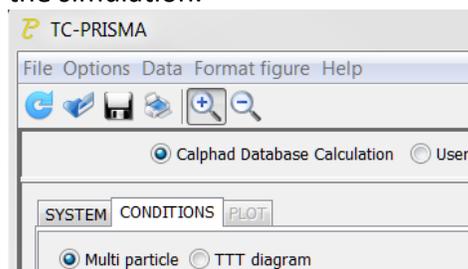
3.2.1   Single thermal profile
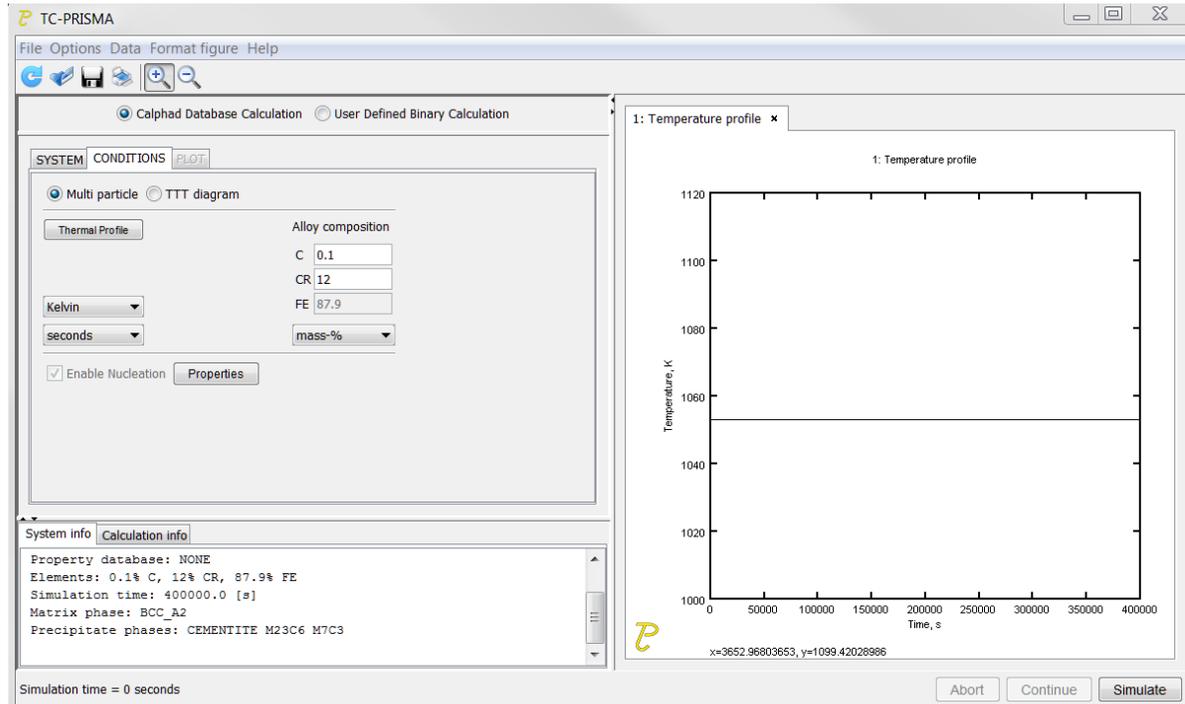
Here you specify the heat treatment schedule (the **Thermal Profile**) and **Alloy composition**.
Click **Properties** to **Enable Nucleation** (see Section 3.3) then add some physical parameters
(see Section 3.4) if, for example, there is no interfacial energy or volume data available in
the database package.

Click **Thermal Profile** to define the heat treatment schedule. Here the **Temperature** and
Time coordinates of thermal profile points are entered. A minimum of two points is
required.
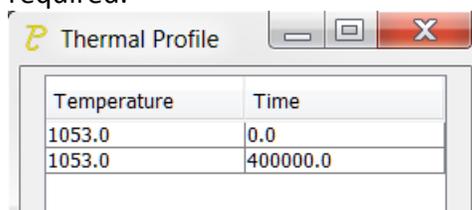
3.2.2 TTT diagram
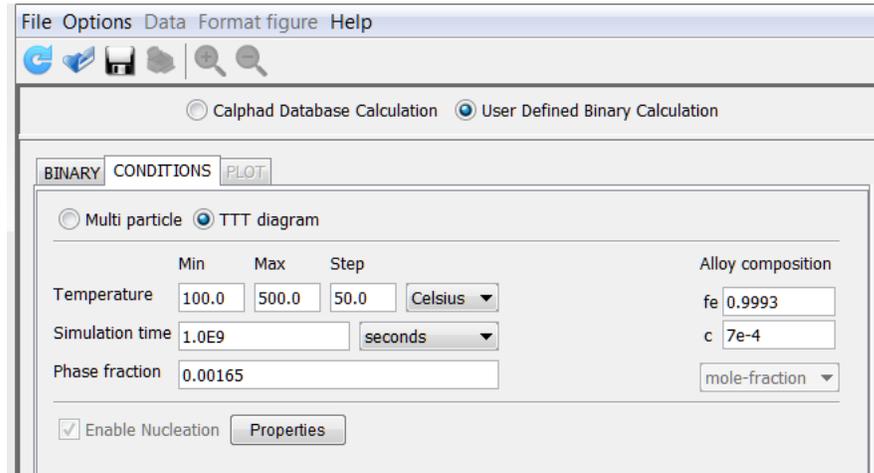
The TTT diagram is the same as for the single thermal profile calculation except that a **Temperature** range and a **Phase fraction** for the precipitate phase is required.

3.3 Set nucleation properties
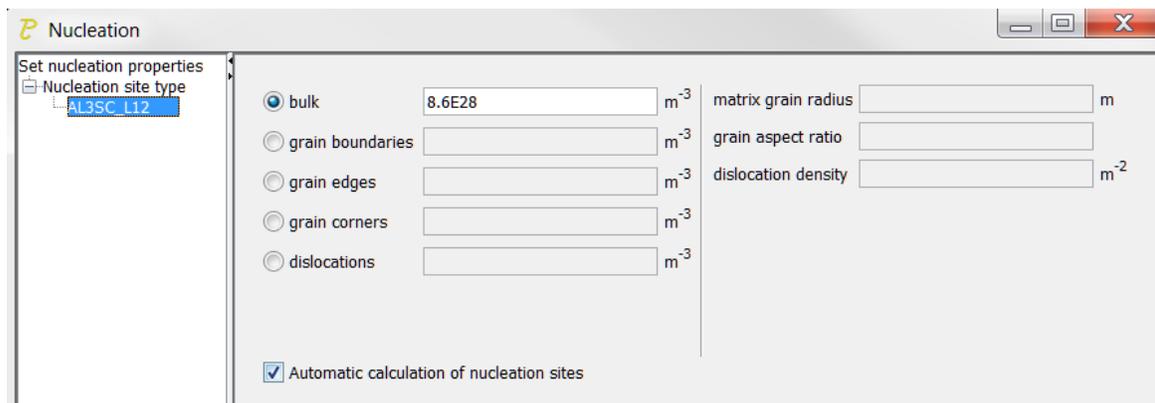
On the **CONDITIONS** tab click **Properties** to open the **Nucleation** window. In this window you can specify the type of nucleation site and its available number. For grain boundaries, edges, and corners, the grain size and aspect ratio of the matrix phase are required. For dislocations, the dislocation density is required. To enter a specific value for the number of nucleation site instead of accepting the automatically calculated value, click to clear the **Automatic calculation of nucleation sites** check box.

3.4 Set physical parameters
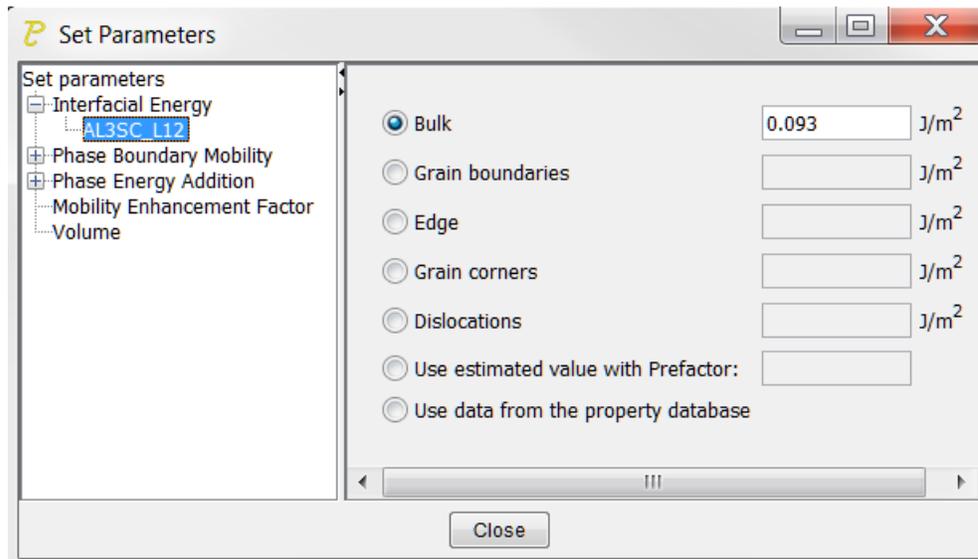
From the menu, select **Data> Set Parameters** to open the **Set Parameters** window. In this window you can set the interfacial energy, volume, interface mobility (to consider deviation from local equilibrium due to interface friction), mobility enhancement factor (to consider grain boundary diffusion etc.), or phase energy addition to the precipitate phase(s) (to alter the phase diagram).

3.5 Open and save workspace file

The TC-PRISMA scripts only contain setup for a simulation. The simulation data is saved in TC-PRISMA workspaces. These are files with the file extension **PRI**. As a default, all the current simulation data is saved in a workspace called **TKDATA.PRI**. From the **File** menu you can open and save workspaces.

- **Open Workspace.** This opens an old workspace and loads the data stored in this workspace. Click **Reinitiate** ⟳ before opening a new workspace.

- **Save Workspace**. This enables you to rename the workspace. Very important: This **RESETS** the workspace and clears all data from it. **Save Workspace** must be performed **BEFORE** doing any simulations.

3.6 Reinitiate

At the top left of the GUI is the **Reinitiate** button ⟳. This action is also available from the **File** menu. Clicking this button terminates the current simulation and restarts the program. It is necessary to do this before continuing a new simulation.

3.7 Add a new database package

To add a new database package, from the **Data** menu select **Edit Database Package**. Click the arrow ▾ at the right side of any box to confirm if the database to be included in the new package is available for each corresponding category. If not, close this window, and then from the **Data** menu select **Edit Database List**. In the **Edit Database List** window, click **Apply** to select a database and add it to the list of either thermodynamic, kinetic, or property databases. Close this window, and reopen the **Edit Database Package** window, where now you can enter a new package name in the field, and then in the same row choose the right database from each category of databases. Make sure that everything is correct before clicking **Apply**. A new database package is then generated and stored, available for future use.
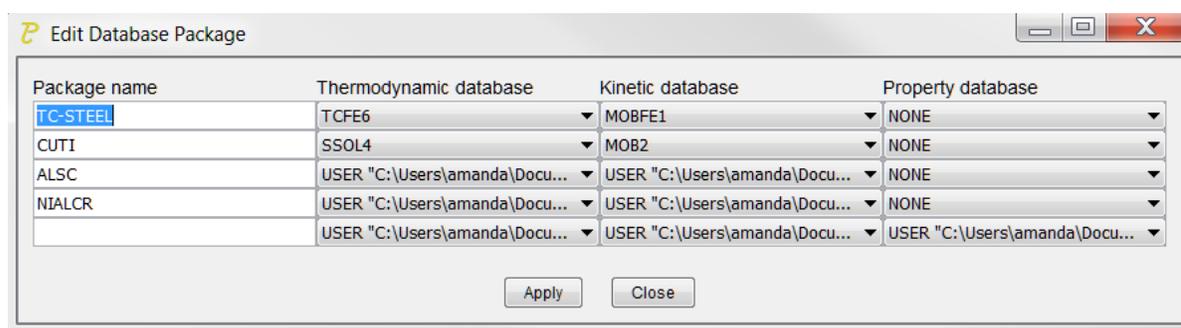
You can also add a new database package by directly editing the TKDBPACK.PRP file. You must make sure that each database in the new package is available in the TKDBLIST.PRP file. If not, add it to the corresponding category in this file. Be careful that the specified databases should be actually available on your computer. It is always a good idea to keep a copy of the original files.

3.8 Postprocessing of multi-modal size distributions

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 can separate the peaks of multi-modal distributions into separate functions.

This functionality is activated when checking **Separate multi-modal size distributions**. When turned on, 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:

- Size Distribution
- Mean Radius
- Volume Fraction
- Number Density

3.8.1   Input fields

Number of Evaluation Points.

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.

Excess Kurtosis for Binomial Split.

This 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.

Minimum Separation Limit.

This is a rough method to prevent that noise or wiggles are interpreted as different distributions. If a local minima is encountered above this absolute value the following peak is not interpreted as a new distribution.

Minimum Distribution Peak.

Any separated peak below this value is removed.

4. Theoretical Models and Numerical Methods

4.1 Overview

Based on Langer-Schwartz theory [1], TC-PRISIMA adopts Kampmann-Wagner numerical (KWN) method [2] to simulate the concomitant nucleation, growth, and coarsening of precipitates in multicomponent and multiphase alloy systems. The KWN method is an extension of the original Langer-Schwartz (LS) approach [1] and its modified (MLS) form [2], where the temporal evolution of the mean radius and particle density over the whole course of precipitation are predicted by solving a set of rate equations derived with certain assumptions for the rates of nucleation and growth, as well as the function of particle size distribution (PSD). The MLS approach differs from the LS with respect to the Gibbs-Thomson equations used for calculating equilibrium solubilities of small particles. The former applies the exact exponential form, whereas the latter takes the convenient linearized version. Instead of assuming a PSD function *a priori* and working with rate equations for determining only mean radius and particle density, the KWN method extends the LS and MLS approaches by discretizing the PSD and solving the continuity equation of the PSD directly. Therefore, the time evolution of the PSD and its *n*-th moment (*0*-th: number density; *1*-th: mean radius; *3*-th: 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 (Figure 3). Coarsening comes out naturally without any *ad hoc* treatment.
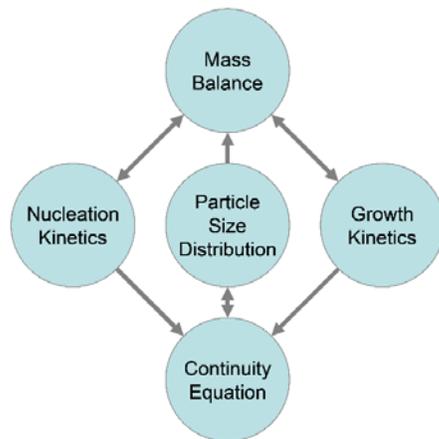
Figure 3: The key elements of the KWN method and their relations as implemented in TC-PRISMA.

TC-PRSIMA is integrated with Thermo-Calc and DICTRA in order to obtain directly all necessary thermodynamic and kinetic information required in the KWN method, which has mostly so far been applied for binary or pseudo-binary systems where the nucleation and growth rates can be approximated quite easily. 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 or para-equilibrium condition, the Gibbs-Thomson effect, and the deviation from local equilibrium due to interface friction etc. With Thermo-Calc and DICTRA and accompanying databases, all these properties and effects can be calculated without unnecessary and inaccurate approximations.

In the following sections, various models and numerical methods implemented in TC-PRISMA are introduced.

4.2 Nucleation

Precipitation process 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, edges, and 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.

4.2.1   Homogeneous Nucleation

The classic nucleation theory (CNT) [3][4] has been extended for the purpose of modeling nucleation in multicomponent alloy systems. The time dependent nucleation rate $J(t)$ is given by

$$J(t) = J_S \exp\left(-\frac{\tau}{t}\right), \tag{1}$$

where J_S is the steady state nucleation rate, τ is the incubation time for establishing steady state nucleation conditions, and t is the isothermal reaction time. The steady state nucleation rate J_S can be expressed by

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

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

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

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

where σ is the interfacial energy, $\Delta G_m^{\alpha\to\beta}$ is the molar Gibbs energy change for the formation of the β precipitate of the critical composition X_i^β from the α matrix, i.e. the maximum driving force for the $\alpha\to\beta$ phase transformation. V_m^β is the molar volume of the β precipitate phase. The maximum driving force $\Delta G_m^{\alpha\to\beta}$ and the critical composition X_i^β can be obtained by finding the parallel tangent lines or surfaces passing through the alloy composition of the α matrix, which is a routine calculation in Thermo-Calc.

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:

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

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

$$r^* = -\frac{2\sigma V_m^\beta}{\Delta G_m^{\alpha\to\beta}} .$$ (5)

The atomic or molecular attachment rate β^* reflects the kinetics of mass transport in the nucleation process and is given by [5]

$$\beta^* = \frac{4\pi r^{*2}}{a^4}\left[\sum_{i=1}^{k}\frac{\left(X_i^{\beta/\alpha}-X_i^{\alpha/\beta}\right)^2}{X_i^{\alpha/\beta}D_i}\right]^{-1} ,$$ (6)

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

The incubation time for an isothermal reaction is

$$\tau = \frac{1}{\theta Z^2\beta^*} ,$$ (7)

where θ differs from one derivation to another. The value 2 from Feder et al. [6] is adopted.

4.2.2   Heterogeneous nucleation

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

To a first approximation, the nucleation energy is calculated by assuming an effective interfacial energy for each heterogeneous nucleation site.
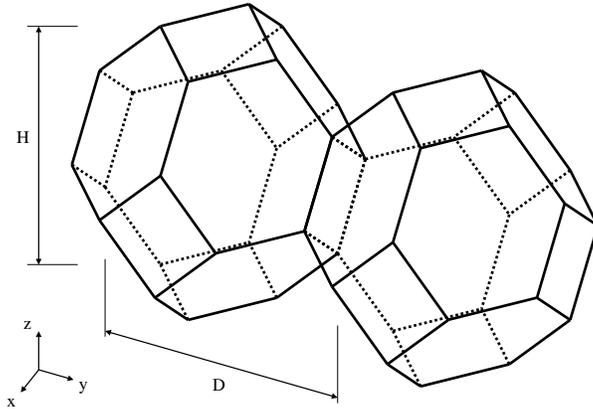
Figure 4: Tetrakaidecahedron approximation of grains.

The number of different nucleation site 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 (see Figure 4), we obtain the densities ρ_2, ρ_1, and ρ_0 for the grain boundary area, edge length, and grain corner number respectively:

$$\rho_2 = \frac{6\sqrt{1+2A^2}+1+2A}{4A}D^{-1},$$ (8.1)

$$\rho_1 = 2\frac{\sqrt{2}+2\sqrt{1+A^2}}{A}D^{-2},$$ (8.2)

$$\rho_0 = \frac{12}{A}D^{-3},$$ (8.3)

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 [7]. Once the densities are known, if taking boundary thickness as one atomic layer, the available nucleation sites can be calculated by

$$N_i = \rho_i \left(\frac{N_A}{V_m^\alpha}\right)^{i/3} \quad (i = 2,1,0)$$ (9.1)

where V_m^α is the molar volume of the matrix phase and N_A is the Avogadro number. For a crystalline material, given a dislocation density ρ_d, the number of nucleation sites at the dislocations N_d can be calculated with the same form,

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

(9.2)

4.2.3   Nucleation during a non-isothermal process

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

Another important parameter that depends on thermal history is the incubation time, defined by Eq. (7) for an isothermal condition. In a non-isothermal process, the exact calculation of the incubation time requires a solution to the Fokker-Plank equation. In TC-PRISMA, 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 [8]

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

(10)

where τ is the incubation time, β^* is the impingement rate for solute atoms to the critical cluster as defined in Eq. (6), and Z is the Zeldovich factor, previously defined in 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.

4.3 Growth

Three different growth rate models have been implemented in TC-PRISMA and they are called advanced, simplified, and binary dilute solution models, respectively.

The advanced model is proposed by Chen, Jeppsson, and Agren (CJA) [9] and calculates the velocity of a moving phase interface in multicomponent systems by identifying the operating tie-line from the solution of flux-balance equations. This model can treat both high supersaturation and cross diffusion rigorously. Spontaneous transitions between different modes (LE and NPLE) of phase transformation can be captured without any *ad hoc* treatment. Since it is not always possible to solve the flux-balance equations and it takes time when possible, a less rigorous but simple and efficient model is preferred in many applications. The simplified model is based on the advanced model but avoids the difficulty to find the operating tie-line and uses simply the tie-line across the bulk composition.

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

The governing equations for the advanced and simplified models are given below. For the binary dilute solution model, please see Section 4.8.

According to the CJA model, the interface velocity υ 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:

$$\upsilon\left(c_i^{\beta/\alpha} - c_i^{\alpha/\beta}\right) = c_i^{\alpha/\beta} M_i \frac{\mu_i^\alpha - \mu_i^{\alpha/\beta}}{\xi_i r} \tag{11}$$

$$\mu_i^{\alpha/\beta} = \mu_i^{\beta/\alpha} + \frac{2\sigma V_m^\beta}{r} \tag{12}$$

where $c_i^{\beta/\alpha}$ and $c_i^{\alpha/\beta}$ are the volume concentrations of component i at the interface in the precipitate and matrix, respectively, M_i is the corresponding atomic mobility in the matrix, μ_i^α and $\mu_i^{\alpha/\beta}$ are the chemical potentials in the matrix of the mean-field concentration and at the interface, respectively. $\mu_i^{\beta/\alpha}$ is the chemical potential at the interface in the precipitate. In the above local equilibrium condition, the multicomponent Gibbs-Thomson effect has been taken into account by adding a curvature induced pressure term to the Gibbs energy of the precipitate phase. The introduced effective diffusion distance factor, ξ_i, for each independent component is given by

$$\xi_i = \frac{\Omega_i}{2\lambda_i^2} \tag{13}$$

where $\Omega_i = \dfrac{c_i^\alpha - c_i^{\alpha/\beta}}{c_i^{\beta/\alpha} - c_i^{\alpha/\beta}}$ is the so-called dimensionless supersaturation for individual component, and λ_i is obtained via the following equation:

$$2\lambda_i^2 - 2\lambda_i^3 \sqrt{\pi} \exp\left(\lambda_i^2\right) erfc\left(\lambda_i\right) = \Omega_i \tag{14}$$

Combining Eq.(11) and (12), the simplified model can be derived:

$$\upsilon = \frac{K}{r}\left[\Delta G_m - \frac{2\sigma V_m^\beta}{r}\right], \tag{15}$$

where $K = \left[\displaystyle\sum_i \frac{\left(X_i^{\beta/\alpha}(r) - X_i^{\alpha/\beta}(r)\right)^2 \xi_i}{X_i^{\alpha/\beta}(r) M_i}\right]^{-1}$ and ΔG_m is the driving force. The interface compositions $X_i^{\beta/\alpha}(r)$ and $X_i^{\alpha/\beta}(r)$ are simply taken from the tie line across the matrix composition.

The non-zero volume correction to the velocity according to Chen and Voorhees [10] has been taken into account and it follows

$$v' = v\left(1 + r\sqrt{4\pi N_v <r>}\right)$$

where v' is the corrected velocity, <r> is the mean radius and N_v is the number density.

4.4 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 [11], we simply apply Eq.11-14 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, Eq. 12, gives $\mu_i^{\alpha/\beta} > \mu_i^{\alpha}$, and a negative velocity results from Eq.11 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 [11], 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.

4.5 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,

$$N = \int_0^\infty f(r)dr, \qquad \langle r \rangle = \int_0^\infty rf(r)dr, \qquad \phi = \int_0^\infty \frac{4}{3}\pi r^3 f(r)dr. \qquad (16)$$

The time evolution of $f(r)$ follows the continuity equation [1]

$$\frac{\partial f}{\partial t} = -\frac{\partial}{\partial r}\left[v(r)f(r)\right] + j(r), \qquad (17)$$

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

$$J = \int_{r_*}^{\infty} j(r)dr \ , \tag{18}$$

where J is the nucleation rate.

4.6 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 equation:

$$X_i^0 = \left(1 - \sum_p \int_0^{\infty} \frac{4\pi r_p^3 f(r_p)}{3V_m^p} dr_p \right) X_i + \sum_p \int_0^{\infty} \int_0^{t_j} \frac{4\pi r_p^2 f(r_p,t)\upsilon(r_p,t)}{V_m^p} X_i^p(r_p,t)dtdr_p \ , \tag{19}$$

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. $f(r_p,t)$, $\upsilon(r_p,t)$, and V_m^p are the PSD function, growth rate, and molar volume of the precipitate phase p, respectively. t_j is the time at time step j.

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

4.7 Numerical method

Since it is impossible to have a general close form solution, the complex non-linear 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. TC-PRISMA 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. Summarised below are all numerical parameters used in this approach to control either the size grid distribution or time steps:

- **Maximum time step fraction (P_{dt}^{max})** – Maximum time step allowed for time integration as fraction of the simulation time.

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

- **Maximum number of grid points over one order of magnitude in r (P_{Nr}^{max})** – The maximum allowed number of grid points in size space. This parameter determines a lower bound limitation for the ratio of every two next nearest grid points in order to maintain adequate computational efficiency. When a ratio of two next nearest grid points is less than this limit, the middle grid point is removed and the corresponding size class merged with the two neighbouring ones.

- **Minimum number of grid points over one order of magnitude in r (P_{Nr}^{min})** – The minimum allowed number of grid points in size space. This parameter determines an upper bound limitation for the ratio of every two adjacent grid points in order to maintain proper numerical accuracy. When a ratio of two adjacent grid points exceeds this limit, a new grid point is then inserted between the two adjacent grids to keep the required resolution.

- **Maximum relative radius change (P_r)** – The maximum value allowed for relative radius change in one time step. This parameter limits the time step according to the following relation, which is controlled by the particle growth: $\Delta t \leq P_r \times r/(|dr/dt|)$ for $r > r_{dt}$, where r_{dt} is a cut-off subcritical size defined by the next parameter. The growth rates of supercritical particles (with $r > r_c$) are always bounded, and there is a size class and the corresponding growth rate that controls the time step. The subcritical particles (with $r < r_c$), however, has a mathematical singularity (negative infinity) in growth rate as r approaches 0. This means that the time step can become extremely small if applying the above criterion to very small subcritical particles. In open literature, several researchers have tried mathematical transformation to avoid this singularity. Unfortunately, the transformation also complicates the formulation of the models. TC-PRISMA 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 input 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: $(\int_0^{rdt} fr^3 dr)/(\int_0^\infty fr^3 dr) = P_{rdt}$.

- **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 user input parameter, P_{cc}, can be used to set a limit on time step according to the following relation: $\Delta t \leq P_{cc} \times (r_{i+1} - r_i)/(dr_i/dt - dr_{i+1}/dt)$ for $r_{i+1} > r_{i+1}$ and $dr_{i+1}/dt < dr_i/dt$.

- **Maximum overall volume change (P_V)** – This input parameter defines the maximum absolute (not ratio) change of the volume fraction allowed during one time step. This parameter is also used in controlling allowable variation in volume fraction due to the newly created particles within one time step. That is $\Delta t \leq P_V/10/(4\pi r_{eff}^3 J/3)$, where r_{eff} and J are effective radius and nucleation rate, respectively.

- **Maximum relative change of nucleation rate in logarithmic scale (P_{logJ})** – This input 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 input parameter can be used to place a constraint on how fast the critical radium can vary, and thus put a limit on time step: $\Delta t \leq P_{rc} \times \Delta t_{previous}/(|(r_{c1} - r_{c2})/r_{c1}|)$.

- **Minimum radius for a nucleus to be considered as a particle (P_{rmin})** – The cut-off lower limit of precipitate radius. Particles with radius smaller than the value specified for this parameter are discarded. In reality, the particle cannot be smaller than an atom; hence, there is no reason to keep track of particles of unphysical sizes.

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

The default values for the above numerical control parameters are given in Table 1.

Table 1 Default value for numerical parameters that controls the size grid distribution and time step.

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

4.8 Binary approximation

Many investigations on precipitation modeling were based on assumptions of stationary growth rate and dilute solution in matrix to calculate nucleation and growth rates in binary or pseudo-binary systems. It offers a first approximation to the precipitation problem with all necessary model parameters calculated analytically if values of the phase boundary, volume, and diffusivity are known from any sources.

With dilute solution assumption, the driving force of nucleation is given by

$$\Delta G_m^{\alpha \to \beta} = -\frac{X^\beta - X_e^\alpha}{1 - X_e^\alpha} RT \ln \frac{X^\alpha}{X_e^\alpha},$$

(20)

and the Gibbs-Thomson equation becomes

$$X^{\alpha/\beta} = X_e^\alpha \exp(\frac{1 - X_e^\alpha}{X^\beta - X_e^\alpha} \frac{2\sigma V_m^\beta}{RTr}).$$

(21)

The growth/dissolution rate of a particle in the steady-state approximation is represented by

$$\upsilon = \frac{X^\alpha - X^{\alpha/\beta}}{X^\beta - X^{\alpha/\beta}} \frac{D}{r}.$$

(22)

In addition to the formula given before for the calculation of the attachment rate and incubation time Eq. (6-7), other ways were also widely used in many publications. According to Russell [4], the attachment rate in a binary system is written as

$$\beta^* = \frac{4\pi r^{*2} X^\alpha D}{a^4}.$$

(23)

It should be noted that Eq. (6) for multicomponent systems does not reduce to this representation for binary systems. The incubation time was first approximated by Kampmann and Wagner [12] as

$$\tau = \frac{1}{2D} \frac{X^\beta - X_e^\alpha}{X^\alpha - X_e^\alpha} r^{*2} c_w^2$$

(24)

where c_w is an adjustable parameter for each particular alloy system and ranges from 1.4 to 3.5. Another formula suggested by Wagner and Kampmann [2] is

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

(25)

Although these descriptions are not consistent with more rigorous theoretical derivations, they are offered as options to choose in the specialized BINARY module due to their acceptance in many investigations.

4.9 Estimation of coherent interfacial energy

Interfacial energy is probably the most important parameter in the calculation of rates of nucleation, growth/dissolution, and coarsening. Yet, this parameter is also a physical property that is least known to everyone so far. As mentioned in the introduction, it is hoped that in future interfacial energy can also be modeled in the spirit of CALPHAD method and interfacial energy databases can be developed by considering various kinds of experimental data with help of computational tools, such as TC-PRISMA. Before this day comes, we have to provide a value for this important parameter to conduct precipitation simulations. Since the value of interfacial energy can vary dramatically (mostly between 0.01 to 2.0 J/m^2) it would be a great help to many users of TC-PRISMA to have a mean to obtain a rough number to start with. Therefore, an extended Becker's model [13] has been implemented in TC-PRISMA to estimate coherent interfacial energy by using thermodynamic data from existing thermodynamic databases:

$$\sigma_c = \frac{n_s z_s}{N_A z_l} \Delta E_s .$$
(26)

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 considered. In the actual calculation, the coefficients taken distinguish between only bcc and fcc structure for the (110) and (111) lattice plane respectively. It should be emphasized that the method is merely a simple approximation and you should consider it fortuitous if the estimated value gives excellent results for precipitation modeling. In most situations, you may need to do some adjustment and calibration work on the basis of the estimation. This can be justified by the fact that interfacial energy is dependent on so many factors, such as temperature, incoherency, orientation, and curvature etc., which have been ignored in the estimation. Since the method is taking advantage of the existing databases, the uncertainties of assessed thermodynamic data should also be kept in mind in the cautious use of the estimated value for the interfacial energy.

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