`pcpsim`
MODEL FOR HOMOGENEOUS PRECIPITATION KINETICS in `GNU OCTAVE`

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1 Introduction

The model for homogeneous isothermal precipitation is partly based on the model by Langer and Schwartz, as modified by Kampmann and Wagner (MLS model) and describes the nucleation and growth of precipitates from a solid solution.

2 Theoretical background

2.1 Nucleation

As a first step we need to define the driving force for precipitation at any given time of the aging process:

$$\Delta g = -\frac{kT}{V_{at}} \cdot S \tag{1}$$

with

$$S = X_p \ln \frac{X}{X_{eq}} + (1 - X_p) \ln \frac{1 - X}{1 - X_{eq}} \tag{2}$$

where V_{at} is the atomic volume (considered as constant for all species, $V_{at} = a^3/2$ for a bcc structure with lattice parameter a), S is a thermodynamical function giving the driving force for nucleation (based on the hypothesis of a diluted and regular solid solution), X_{eq} is the equilibrium solute mole fraction in the matrix, X_p the solute mole fraction in the precipitate, and X the current solute mole fraction of the matrix. The above relation has been derived by Aaronson et al. (1970).

The nucleation rate is:

$$J_s = \frac{dN}{dt} = Z\beta^* \exp(-\frac{\Delta G^*}{kT}) \exp(-\frac{t_i}{t}) \tag{3}$$

where N is the number of nuclei per atomic site, Z is the Zeldovich factor ($\approx 1/20$) and

t_i is the incubation time. The other parameters of equation are expressed as follows:

$$\beta^* = \frac{4\pi R^{*2} D X}{a^4} \tag{4a}$$

$$R^* = \frac{2\gamma V_{at}}{S\, kT} \tag{4b}$$

$$\Delta G^* = \frac{4}{3}\pi R^{*2}\gamma \tag{4c}$$

$$t_i = \frac{1}{2\beta^* Z} \tag{4d}$$

where R^* and ΔG^* are the critical nucleation radius and free energy, respectively, γ is the matrix/precipitate interfacial energy and D is the diffusion coefficient of solute atoms in the matrix.

2.2 Growth

A precipitate with $R > R^*$ grows by incorporating solute atoms from the surrounding matrix. Thus there is a flow of solute atoms from the matrix towards the precipitate surface. It is assumed that a steady-state is reached where there is a constant gradient of the solute concentration around the precipitate $X(r)$ that supports the solute flow $J = -D\, dX/dr|_{r=R}$, where D is the diffusion constant of solute atoms in the matrix.

By solving the steady-state diffusion equation $\nabla^2 X(r) = 0$ in the region around the precipitate the following equation is obtained

$$\frac{dR}{dt} = \frac{D}{R}\,\frac{X - X_R}{X_p - X_R} \tag{5}$$

where X_R is the solute concentration at the matrix/precipitate interface. X_R should be equal to the equilibrium concentration as modified by the Gibbs-Thomson effect (surface tension). In the *ideal solution* approximation X_R is given by (Calderon et al., 1994):

$$X_R = X_{eq} \cdot \exp\left(\frac{2\gamma V_{at}}{kT\, R}\frac{1 - X_{eq}}{X_p - X_{eq}}\right) \tag{6}$$

2.3 Coarsening

When the system reaches the coarsening region the average precipitate radius grows as

$$R^3(t) = K \cdot t \tag{7}$$

where K is given in the *ideal solution* approximation by (Calderon et al., 1994)

$$K \approx K_{\mathrm{IS}} = \frac{8}{9}\frac{D\gamma V_{at}}{kT}\,\frac{X_{eq}\,(1 - X_{eq})}{(X_p - X_{eq})^2} \tag{8}$$

Thus the time differential of R is given by

$$\frac{dR}{dt} = \frac{8}{27}\,\frac{D\gamma V_{at}}{kT\, R^2}\,\frac{X_{eq}\,(1 - X_{eq})}{(X_p - X_{eq})^2} \tag{9}$$

3 Nucleation & Growth equations for the mean precipitate radius

In many cases we may ignore the precipitate size distribution and consider only the mean radius $\bar{R}$.

In this approximation the mean radius grows according to (5) while new precipitates of radius R^* nucleate at a rate given by (3). Thus the mean radius evolves as

$$\frac{d\bar{R}}{dt} = \frac{D}{\bar{R}} \cdot \frac{X - X_R}{X_p - X_R} - \frac{1}{N}\frac{dN}{dt} \cdot (\bar{R} - \alpha R^*) \tag{10}$$

where the 2nd term expresses the reduction rate of $\bar{R}$ due to the nucleation of new critical nuclei. α is a value just above 1 (e.g. 1.05) which results from the fact that new precipitates only grow if their size is slightly larger than the nucleation size.

As precipitates grow they consume solute atoms and thus the matrix concentration X will be reduced from the initial X_0. The solute balance can be expressed as:

$$X_0 = X\,(1 - F) + X_p\,F \tag{11}$$

where $F = \frac{4}{3}\pi R^3 N$ is the precipitate volume fraction. The derivative of X can be obtained from the last equation:

$$\frac{dX}{dt} = -(X_p - X)\,\frac{F}{1-F}\left[3\frac{\dot{R}}{R} + \frac{\dot{N}}{N}\right] \tag{12}$$

3.1 Dimensionless formulation

Now the following dimensionless variables are defined that are easier to use for programming:

$$t' = \frac{D \cdot t}{r_{at}^2} \tag{13a}$$

$$R' = R/r_{at} \tag{13b}$$

where $r_{at} = (3V_{at}/4\pi)^{1/3}$ is the atomic radius.

The equations (3), (10) plus the differential of the solute balance constitute a system of ordinary differential equations (ODEs) for N, R' and X, which is rewritten here in terms of dimensionless variables:

$$\frac{dN}{dt'} = \frac{\beta_0 X}{S^2}\exp\left(-\frac{\Delta G_0}{S^2}\right)\exp\left(-\frac{S^2}{2\beta_0 X t'}\right) \tag{14a}$$

$$\frac{dR'}{dt'} = \frac{X - X_R}{X_p - X_R}\,\frac{1}{R'} + \frac{1}{N}\frac{dN}{dt'}\left(\frac{\alpha R_0}{S} - R'\right) \tag{14b}$$

$$\frac{dX}{dt'} = -(X_p - X)\,\frac{F}{1-F}\left[3\frac{\dot{R}'}{R'} + \frac{\dot{N}}{N}\right] \tag{14c}$$

where the following definitions have been made

$$R_0 = \frac{2\gamma V_{at}}{r_{at} kT} \tag{15a}$$

$$\beta_0 = 4\pi R_0^2 Z r_{at}^4/a^4 \tag{15b}$$

$$\Delta G_0 = R_0^3/2 \tag{15c}$$

Additionally the following hold

$$X_R = X_{eq} \exp\left(\frac{R_0}{R'} \frac{1 - X_{eq}}{X_p - X_{eq}}\right) \tag{16a}$$

$$F = R'^3 N \tag{16b}$$

In the following we will omit the prime from t' and R'.

3.2 Implementation in OCTAVE

The function file `mean_radius/mean_radius_ng.m` defines the ODE system of (14) so that it can be used in `MATLAB/OCTAVE` ODE solvers. The solver that showed the best results is `ode23`.

The content is listed below:

```
function [xdot, F, S] = mean_radius_ng(t,x,Xp,Xeq,b0,dG0,R0,incub,dbg)
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% [xdot, F, S] = mean_radius_ng(t,x,Xp,Xeq,b0,dG0,R0,incub,dbg)
%
% Define the ODEs describing mean precipitate radius during nucleation and
% growth
%
% Input:
%  t          : time (D*t/rat^2)
%  x(1,3)     : ODE variables,
%               x(1): precipitate atomic concentration,
%               x(2): mean radius (in units of rat),
%               x(3): atomic concentration of solute in matrix
%  Xp, Xeq : solute conc. in the precipitate and in the matrix at equilibrium
%  R0,dG0,b0 : nucleation & growth physical parameters
%  incub     : if 1 then incubation time is calculated
%  dbg       : if 1 turn on debugging
%
% Output
%   xdot     : dx/dt
%   F        : precipitate volume fraction
%   S        : nucleation entropy
%
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

  N = x(1); R = x(2); X = x(3);
  if N<0,
    error(['Negative N value, N=' num2str(N)]);
  endif
  if X<0,
    error(['Negative X value, X=' num2str(X)]);
  endif

  xdot = zeros(size(x));
  y=0;

  S = Xp*log(X/Xeq) +(1-Xp).*log((1-X)/(1-Xeq));
```

```
  F = R^3 * N;
  Xr = Xeq*exp(R0./R*(1-Xeq)/(Xp-Xeq));
  Xr=min(0.9*Xp,Xr);

  if S>0, % nucleation & growth
    if R<0,
      error(['Negative R in nucleation, R=' num2str(R)]);
    endif
    S2 = S^2;
    b = X * b0 / S2;
    xdot(1) = b .*exp(-dG0./S2);
    if incub,
      if t>0,
        xdot(1) = xdot(1) .*exp(-1./2/b/t);
        if N>1e-23,
          y = xdot(1,:)/N;
        else
          y = 0;
        endif
      else
        xdot(1) = 0;
      end
    else
      if N>0,
        y=xdot(1)/N;
      endif
    endif

    xdot(2) = (X-Xr) / (Xp-Xr) / R + y*(1.05*R0./S - R);
    if xdot(2)<0, xdot(2)=0; end
    xdot(3) = (X - Xp) * F / (1-F) * (3*xdot(2)/R + y );
  else % dissolution
    if R>0,

      xdot(2) = (X-Xr) / (Xp-Xr) / R;
      xdot(3) = (X - Xp) * F / (1-F) * 3 * xdot(2) / R;
    endif
  endif


  if dbg, disp(num2str([t x' xdot' y])); end

endfunction
```

3.3 Example calculations

3.3.1 Nucleation of Fe_3C carbide

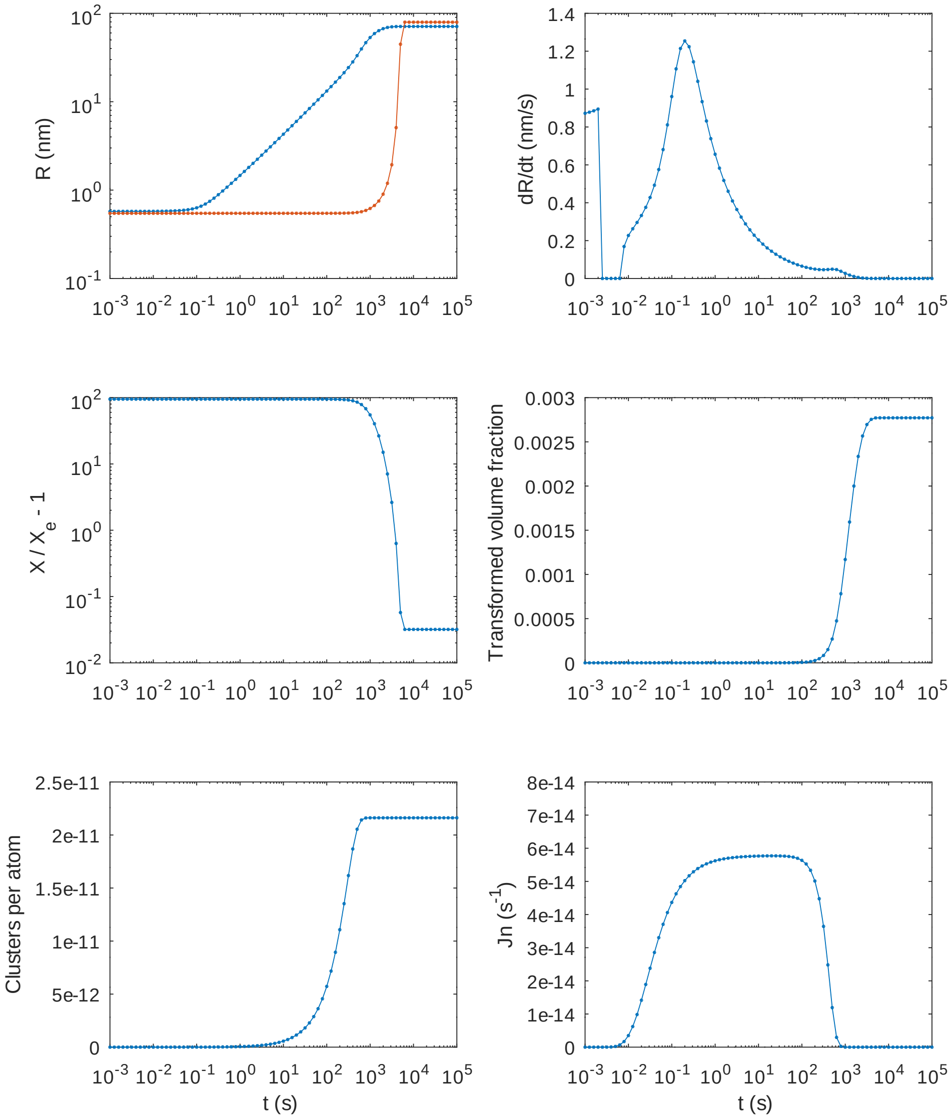

Figure 1: `mean_radius/FeC_meanR_nucl.m` Nucleation of Fe_3C carbide in a Fe - 0.07 at.% C alloy at 487 K calculated with the mean radius ODEs. Model parameter: $\gamma = 0.174$ J/m^2. Compare to Perez and Deschamps (2003)

3.3.2 Nucleation of α'' nitride at 373 K

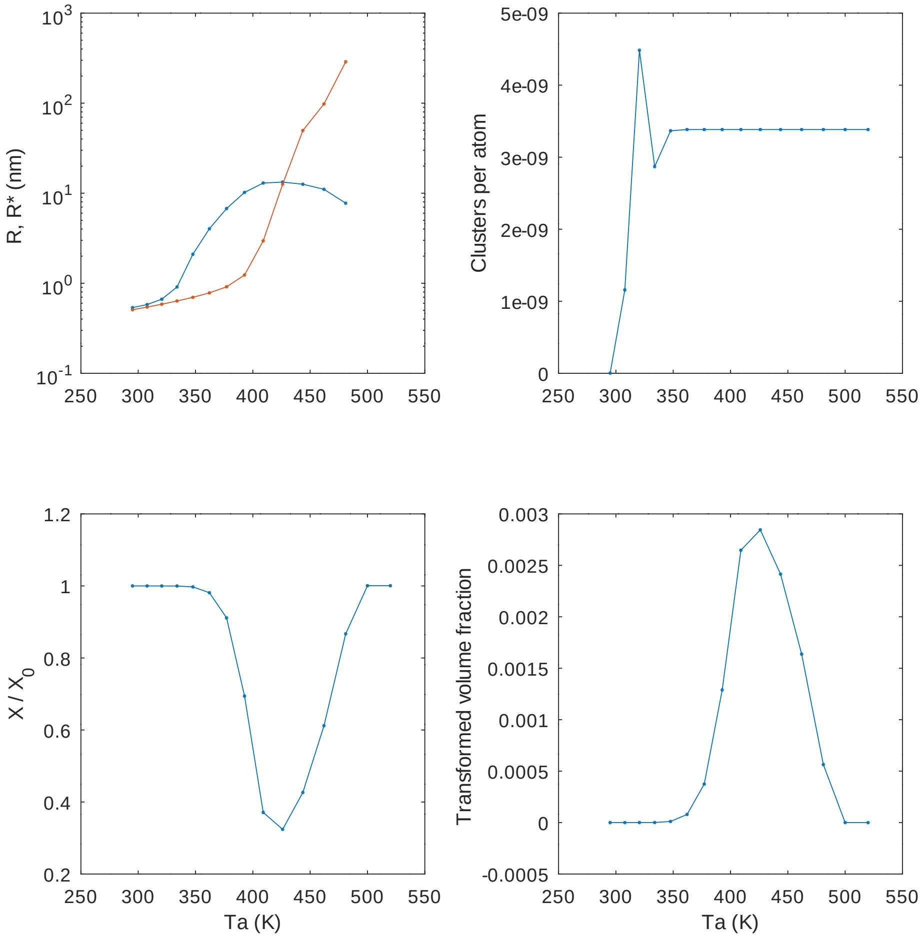

Figure 2: `mean_radius/FeC_meanR_nucl.m` Nucleation of α'' nitride in a Fe - 0.088 at.% N alloy at 373 K calculated with the mean radius ODEs. Model parameter: $\gamma = 0.062$ J/m^2. Compare to Abiko & Ymai 1977

3.3.3 Nucleation/Dissolution of α'' nitride during isochronal annealing

The mean radius ODEs are not suitable for modelling dynamic/transient processes like isochronal annealing.

For example, if some particles have nucleated at some temperature T_1 with radius $R \sim R_1^*$ and then we go to a higher temperature $T_2 > T_1$ where $R < R_2^*$ then the particles are unstable and will dissolve. However, this cannot be properly described by the mean radius ODEs.

Here we make the following approximation in order to model nitride nucleation/dissolution by the mean radius ODEs. If at some temperature the existing particles are below R^*, they are immediately "dissolved" and the nucleation process starts again from scratch. The results are shown below in comparison to experiment.The value of γ can be adjusted so that the minimum coincides with the experimentally observed at 430 K. The optimum value is $\gamma = 0.056$ J/m^2.

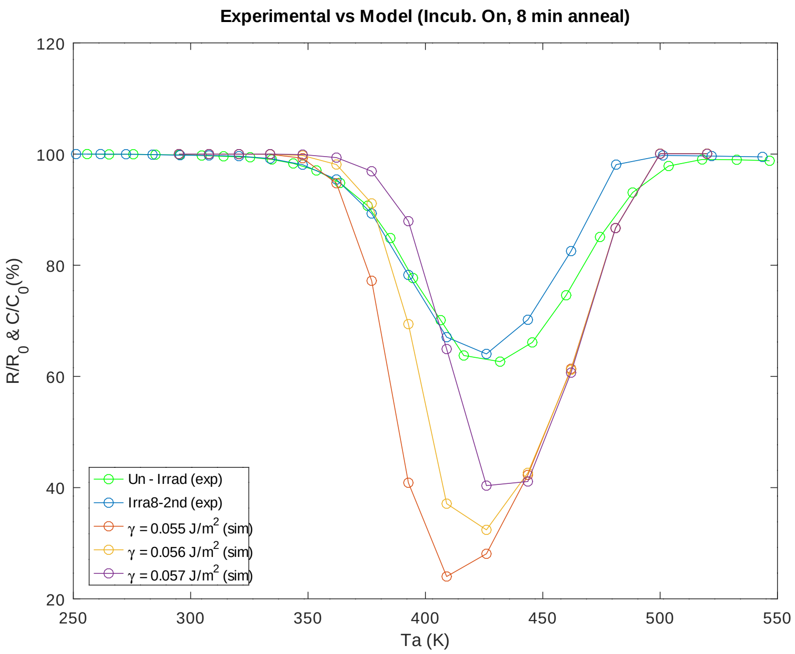

Figure 3: `mean_radius/FeN_exp_vs_sim.m` Nucleation and dissolution of α'' nitride in a Fe - 0.047 at.% N alloy during isochronal (8 or 5 min) annealing. Our experimental resistivity data. Simulation with the mean radius ODEs with different values for γ.

The question arises whether it is correct to consider here an incubation period or not. The simulation can be done also without incubation and the minimum is obtained with slightly different γ (0.059). However, the simulation result is much more sensitive then to the value of Δt whereas in the experiment we had very similar results using 5 and 8 min anneals.

The simulation details of particle radius, density, volume fraction are shown in the following figure for $\gamma = 0.056$

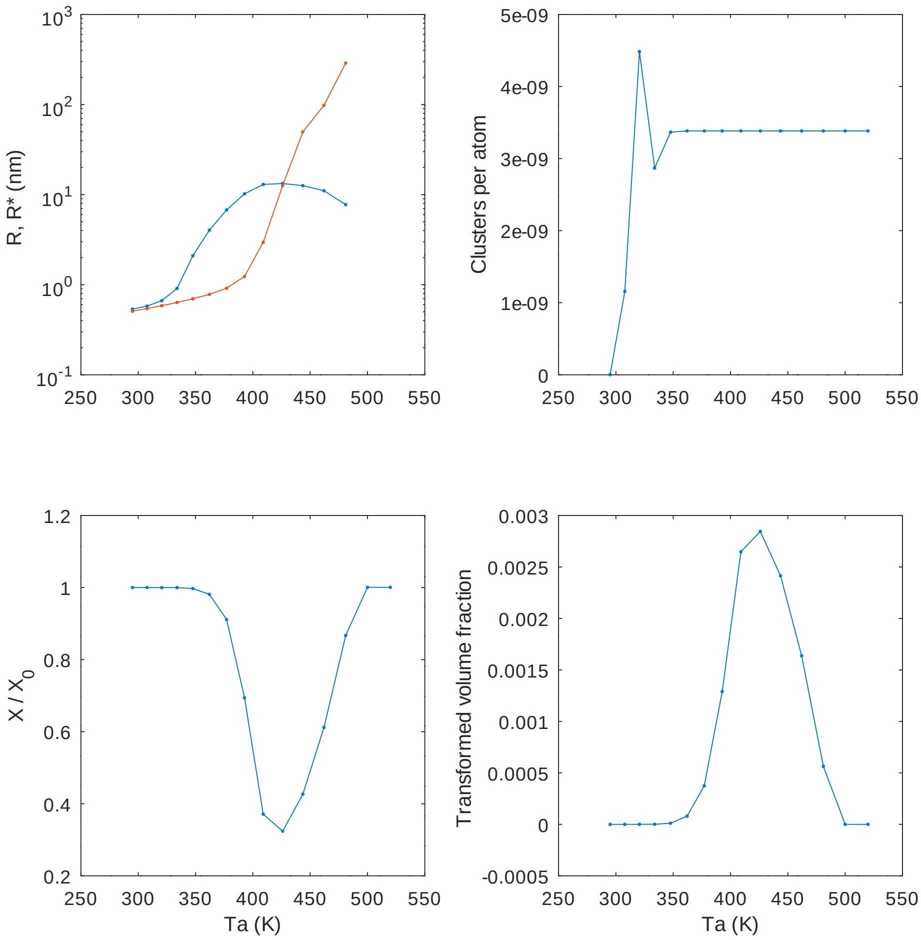

Figure 4: `mean_radius/FeN_meanR_nucl.m` Nucleation and dissolution of α'' nitride in a Fe - 0.047 at.% N alloy during isochronal annealing. Simulation parameters: $\gamma = 0.056$ J/m^2, $\Delta t = 8$ min, incubation on.

4 Numerical evolution of the precipitate size distribution (PSD)

In this type of modelling, first discussed by Kampmann & Wagner (see Wagner et al. (2005), the "N-modell",) we consider the evolution of the precipitate distribution function with respect to radius, $f(R,t)$. The PSD satisfies the equation of continuity:

$$\frac{\partial f}{\partial t} + \frac{\partial}{\partial R}(f \cdot v_R) = J_s \cdot \delta(R - \alpha R^*) \tag{17}$$

where the precipitate growth rate $v_R = dR/dt$ is given by (5). The source term on the right side of (17) describes the generation of new nuclei with radius αR^* at a rate given by J_s from eq. (3).

This PDE is solved numerically by discretizing the (t, R) space and approximating the partial derivatives by finite differences. Defining the grid points (t_i, R_k), where (i, k) are integers, the discretized distribution is defined as

$$f_{ik} = \frac{1}{\Delta R_k} \int_{R_{k-1}}^{R_k} f(R, t_i)\, dR \tag{18}$$

and the discretized PDE becomes

$$\frac{f_{i+1,k} - f_{ik}}{\Delta t_i} = -\frac{J_{ik} - J_{i,k-1}}{\Delta R_k} + \frac{J_s}{\Delta R_{k^*+1}} \delta_{k,k^*+1} \tag{19}$$

where the precipitate "current" J_{ik} is given by

$$J_{ik} = \begin{cases} f_{ik} v_k & v_k \geq 0 \\ f_{i,k+1} v_k & v_k < 0 \end{cases} \tag{20}$$

The above finite difference scheme has been introduced by Myhr and Grong (2000) for this type of calculation and corresponds to "*upwind differencing*" used in CFD (see Press et al. "Numerical Recipes", ch. 20).

The index k^* corresponds to the spatial grid point where $R_{k^*-1} \leq R^* < R_{k^*}$. The generated nuclei are added to f_{i,k^*+1} so that all of them survive and grow. [1]

The total precipitate concentration, average radius and volume fraction can be obtained from $f_{i,k}$ by the following relations:

$$N_i = \int_0^\infty f(R, t_i) dR \approx \sum_k f_{i,k} \Delta R_k \tag{21a}$$

$$\bar{R}_i = \frac{1}{N_i} \int_0^\infty f(R, t_i) R dR \approx \frac{1}{2N_i} \sum_k f_{i,k} (R_k^2 - R_{k-1}^2) \tag{21b}$$

$$F_i = \frac{4\pi}{3V_{at}} \int_0^\infty f(R, t_i) R^3 dR \approx \frac{1}{4\, r_{at}^3} \sum_k f_{i,k} (R_k^4 - R_{k-1}^4) \tag{21c}$$

4.1 Numerical integration

A static logarithmic grid is selected for the R-space discretization with constant $\Delta R_k / R_k$ (typically ~ 0.05.) The first point is typically positioned just below R^* and the last point should be higher than the largest anticipated radius $R_{\max}$ for the simulation period. To obtain an estimate of $R_{\max}$ we define the function $\tau(R)$

$$\tau(R) = \int_{R^*}^{R} \frac{dR}{v_R}$$

where the initial solute concentration X_0 is employed in the evaluation of v_R. This function corresponds to the time needed for a precipitate to grow to radius R. Then $R_{\max}$ is found by solving numerically the equation $\tau(R_{\max}) = t_s$, where t_s the total simulation time.

The PSD is initialized either to zero or to some initial precipitation state obtained either from experiment or other simulation.

The evolution of the PSD is done iteratively with the following steps:

1. Calculate the current volume fraction F_i and matrix concentration X

[1] If the generated nuclei where added to f_{i,k^*} a fraction of them would dissolve since $v_{k^*-1} < 0$.

2. Calculate the nucleation rate J_s and the bin index k^* where the generated nuclei are to be inserted.
3. Calculate the right side of eq. (19).
4. Adaptively decide the time step Δt_i (see below)
5. Advance the PSD to $f_{i+1,k}$ and simulation time
6. Repeat until the total simulation time is reached

4.1.1 Adaptive time step selection

Δt_i is selected according to 2 criteria.

First, an upper limit is set by the following relation

$$v_k \Delta t_i < \Delta R_k, \quad \forall k \tag{22}$$

This is the well-known *Courant condition* which ensures the stability of the PDE numerical solution (again see Press et al. "Numerical Recipes", ch. 20). Essentially it means that in one time-step nuclei from one distribution bin can move only to adjacent bins and not further away. Thus the time interval is initially set by

$$\Delta t_i = \min\{|\Delta R_k / v_k|\} \tag{23}$$

A second criterion is set by the requirement that R^*, which is a critical simulation parameter, does not change appreciably during a time step. Typically we require that $\Delta R^*/R^* < 0.01$. To implement this, $f_{i+1,k}$ and the new R^* must first be calculated with the current value of Δt_i; if the change of R^* is too large the time step is halved and $f_{i+1,k}$ is recalculated. The process is repeated until the criterion is fulfilled.

4.1.2 Lower cut-off radius

A drawback of the method is that the time step is bounded by the smallest $\Delta R_k/v_k$ which occurs at the lower R bins. However, as the simulation advances and the average radius becomes larger, the concentration in the first few bins becomes very low and can be neglected. Thus we define a lower cut-off index k_c and set $f = 0$ for $R < R_{k_c}$. The grid points below k_c are not considered when selecting Δt_i and this allows for much more efficient simulation in the growth phase.

The cut-off index k_c is initially set to the 1st grid point and then it is advanced by one each time the concentration in the 1st bin above cut-off, $f_{i,k_c+1} \cdot \Delta R_{k_c+1}$, falls below a certain threshold N_{min}. A reasonable threshold could be 1 nucleus per cm^3 or, equivalently, $N_{min} \sim 10^{-23}$. This means that effectively when the concentration in the first bin above k_c falls below N_{min}, the bin is zeroed-out and becomes inactive.

When nuclei dissolution occurs the distribution will move gradually towards smaller R and we have to allow k_c to go down again, i.e., to gradually reactivate the lower bins of the distribution. For this we check the concentration δN_c of nuclei that would move from bin $k_c + 1$ towards k_c during a time-step. This is equal to

$$\delta N_c = |v_{k_c}| f_{i,k_c+1} \Delta t_i$$

If δN_c becomes larger than a threshold then the cut-off index k_c is decreased by one. This threshold is selected as

$$\delta N_c \geq N_{min} + \epsilon N \tag{24}$$

where $N = \sum_k f_{i,k} \Delta R_k$ is the total concentration of nuclei and ϵ a small number (typically 10^{-3} or 10^{-4}). Here the relative term ϵN is used to raise the threshold, otherwise the lower cut-off will extend to very small R and the simulation will become significantly slower.

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