# Simulation of the Nucleation of the Precipitate $Al_3Sc$ in an Aluminum Scandium Alloy using the kinetic Monte Carlo Method

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***Abstract*— This paper describes the simulation of the phenomenon of nucleation of the precipitate $Al_3Sc$ in an Aluminum Scandium alloy using the kinetic Monte Carlo (kMC) method and the density-based clustering with noise (DBSCAN) method to filter the simulation data. To conduct this task, kMC and DBSCAN algorithms were implemented in C language. The study covers a range of temperatures, concentrations, and dimensions, going from 573K to 873K, 0.25% to 5%, and 50x50x50 to 100x100x100. The $Al_3Sc$ precipitation was successfully simulated at the atomistic scale. DBSCAN revealed to be a valorous aid to identify the precipitates. The achieved results are in good agreement with those reported in the literature, but we went deeper in the evaluation of the influence of all the simulation and analysis parameters.**

## I. Introduction

Precipitate structures play a fundamental role in the material science due to the capacity of representing strong obstacles for dislocations movements within the material structure. This paper focuses on the elaboration and application of mechanical statistics knowledge, namely a kinetic Monte Carlo (kMC) method, on the study and prediction of the phenomenon of precipitation in the aluminum scandium alloy [1]. The work tackles subjects such as computational mechanics, mechanical statistics, material science, precipitation phenomenon, diffusion phenomenon, what influences this phenomenon and how to control it and also predict it, as well as data mining the vital information.

The outcome of the work undertaken is a set of software applications that allows (i) to perform Monte Carlo (MC) simulations, (ii) to analyze the results using the Density Based Spatial Clustering of Applications with Noise (DBSCAN) technique [2], and (iii) to compare the simulation results with the classical nucleation theory (CNT).

## II. Related Work

As computation extends its capacities increasingly, so has the scientific field of nucleation and precipitation modeling. The process of modeling nucleation and precipitation has been achieved at different scales, each one having its own advantages and disadvantages. It has increased the number of publications and studies related with the subject of modeling the precipitation kinetics at the atomistic level [3]. The main materials subjected to such studies are alloy materials such as Fe-Cu, Fe-P-C, Fe-Cu-Ni-Si, Al-Cu. Aluminum alloys have also their share of studies by which we would like to outline and focus on the Al-Sc alloy. Binkele and Schmauder have published studies about precipitation in binary systems using atomistic Monte Carlo simulations [4] [5]. Clouet and co-workers also published studies of atomistic MC simulations, not just based on binary systems but also on ternary systems [6] [7]. MC simulations have also been used on the study of other phenomena. Grain growth, abnormal grain growth, thin film deposition and growth, sintering for nuclear fuel aging, bubble formation in nuclear fuels are just some of them [8].

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## III. Theoretical background for kMC Simulation

This section present the model of $Al_3Sc$ precipitation applied in the kMC simulations. The transition rate for a Al atom is calculated by (1).

$$\Gamma_{AlV} = v_{Al} \exp\left(-\frac{\Delta E_{AlV}}{kT}\right) \tag{1}$$

Equation (2) describes the transition rate for a Sc atom.

$$\Gamma_{ScV} = v_{Sc} \exp\left(-\frac{\Delta E_{ScV}}{kT}\right) \tag{2}$$

The aluminum activation energy is obtained by (3).

$$\begin{aligned}\Delta E_{AlV} = {} & E_{spAl} - n^{(1)}_{AlAl}\varepsilon^{(1)}_{AlAl} - n^{(1)}_{AlSc}\varepsilon^{(1)}_{AlSc} \\ & - n^{(2)}_{AlAl}\varepsilon^{(2)}_{AlAl} - n^{(2)}_{AlSc}\varepsilon^{(2)}_{AlSc} \\ & - n^{(1)}_{AlV}\varepsilon^{(1)}_{AlV} - n^{(1)}_{ScV}\varepsilon^{(1)}_{ScV}\end{aligned} \tag{3}$$

Equations (4), (5), and (6) describe relations among the number of Al-Al bonds, Al-Sc bonds, Al-vacancy bonds and Sc-vacancy bonds, regarding the first and second neighborhood. For an FCC structure, the first neighborhood is composed of twelve atoms ($Z_1$=12) and the second neighborhood is composed of six atoms ($Z_2$=6).

$$n^{(1)}_{AlAl} + n^{(1)}_{AlSc} = Z_1 - 1 \tag{4}$$

$$n^{(2)}_{AlAl} + n^{(2)}_{AlSc} = Z_2 \tag{5}$$

$$n^{(1)}_{AlV} + n^{(1)}_{ScV} = Z_1 \tag{6}$$

The scandium activation energy is obtained by (7).

$$\begin{aligned}\Delta E_{ScV} = {} & E_{spSc} - n^{(1)}_{AlSc}\varepsilon^{(1)}_{AlSc} - n^{(1)}_{ScSc}\varepsilon^{(1)}_{ScSc} \\ & - n^{(2)}_{AlSc}\varepsilon^{(2)}_{AlSc} - n^{(2)}_{ScSc}\varepsilon^{(2)}_{ScSc} \\ & - n^{(1)}_{AlV}\varepsilon^{(1)}_{AlV} - n^{(1)}_{ScV}\varepsilon^{(1)}_{ScV}\end{aligned} \tag{7}$$

Analogously, (8), (9), and (10) describe the number of Sc-Sc bonds, Al-Sc bonds, Al-vacancy bonds, Sc-vacancy bonds, regarding the first and second neighborhoods.

$$n_{ScSc}^{(1)} + n_{AlSc}^{(1)} = Z_1 - 1 \quad (8)$$

$$n_{ScSc}^{(2)} + n_{AlSc}^{(2)} = Z_2 \quad (9)$$

$$n_{AlV}^{(1)} + n_{ScV}^{(1)} = Z_1 \quad (10)$$

As a vacancy site is surrounded by 12 nearest neighbors, 12 jump frequencies are calculated: $\Gamma_1$, $\Gamma_2$, until, $\Gamma_{12}$. In the next step of a kMC algorithm one of these 12 frequencies is selected, based on their values and on a random number: the vacancy will jump to the position of atom *n* that verifies (11).

$$\sum_{i=1}^{n} \Gamma_i \leq random_number \leq \sum_{i=1}^{n+1} \Gamma_i \quad (11)$$

Equation (12) describes the computation of the kMC real time. It is composed by the averaged residence time, multiplied by a factor that takes into account the difference between the simulated and the real vacancy concentrations. Equation (13) expresses analytically the real vacancy concentration vs. temperature obtained experimentally in [9].

$$t_{MC}^{real} = \left(\frac{C_V^{sim}}{C_V^{real}}\right) \times \left(\sum_{i=1}^{12} \Gamma_i\right)^{-1} = \left(\frac{C_V^{sim}}{C_V^{real}}\right) \times t_{MC}^{sim} \quad (12)$$

$$\begin{aligned} C_{Vreal} &= -0.005792301654 + 5.281432466e^{-5} \times T \\ &-1.916781695e^{-7} \times T^2 + 3.466630615e^{-10} \times T^3 \\ &-3.132467044e^{-13} \times T^4 + 1.135950846e^{-16} \times T^5 \end{aligned} \quad (13)$$

## IV. Implementation of Simulation and Analysis

kMC algorithm was implemented in C, compiled with `gcc` and the simulations run on 64-bit Linux. Simulations were submitted to the SeARCH cluster. By using a cluster it is possible to accelerate simulations in 3 ways: (i) running multiple sequential simulations at same time, with different parameters, (ii) running parallel simulations on a multicore machine via OpenMP, or (iii) running parallel simulations on several machines via MPI. More details can be found in [1].

The main goal of clustering analysis is dividing data into groups, or clusters, which share certain characteristics. Clustering is used in the present work to identify $Al_3Sc$ precipitates in a 3D matrix, containing the position of all Sc atoms, generated by the kMC simulation. The implemented clustering algorithm is designated by DBSCAN [2]. To store the atoms of each cluster it was used a data structure that varies dynamically, because the clusters are of variable and unknown size. The used data structure was inspired by the Java *ArrayList* class. After applying DBSCAN, the clusters that are split in several parts are merged in a single spatial region per cluster. This is possible because we use PBC and aims to improve the 3D visualization of clusters [1].

To allow a posterior visualization and analysis, the lattice configurations generated by kMC and DBSCAN are saved to files in a format that can be read and rendered by freely available visualization tools. The developed code allows us to save data in PDB, XYZ, and VTK formats. All these formats can be visualized with `ParaView`.

The main inputs necessary to undergo a simulation and posterior cluster analysis are: Al lattice constant (Angstrom), number of unit cells in the x, y, z direction, Sc percentage, number of MC steps, simulated temperature (Kelvin), material parameters, the radius that defines the neighborhood of an atom (***eps*** in DBSCAN) and the minimum number of neighbors that makes an atom to be core of a cluster (***minPts*** in DBSCAN). Additionally, the material parameters that support the previous equations, and therefore the simulations, are the first and second nearest-neighbor pair effective energies, saddle point energies and attempt frequencies [6]: $\varepsilon_{AlAl}^{(1)}$ = -0.56 eV; $\varepsilon_{ScSc}^{(1)}$ = -0.65 eV; $\varepsilon_{AlSc}^{(1)}$ = -0.759+21.0x10$^{-6}$T eV; $\varepsilon_{VV}^{(1)}$ = -0.084 eV; $\varepsilon_{AlSc}^{(2)}$ = 0.113 -33.4x 10$^{-6}$T eV; $\varepsilon_{AlV}^{(1)}$ =-0.222 eV; $\varepsilon_{ScV}^{(1)}$ = -0.757 eV; $e_{Al}^{sp}$ =-8.219 eV; $e_{Sc}^{sp}$ = -9.434 eV; $\nu_{Al}$ = 1.36x10$^{14}$ Hz; $\nu_{Sc}$ = 4x10$^{15}$ Hz.

## V. Results

kMC simulations produce a large volume of data, in the form of a VTK file for each snapshot and a simulation report. Fig. 1 illustrates the time evolution of the precipitation phenomenon (Sc atoms only). The reported simulation run under the conditions of 873K, 1%Sc, and over 5x10$^{11}$ MCS in a 50x50x50 lattice box. The raw configurations produced by the simulation are presented in the left part of each figure. The right configuration of each figure demonstrates the application of the DBSCAN algorithm, where the Sc atoms that do not belong to precipitate structures are labeled as noise and do not appear. From VTK and report files we can extract other metrics for each snapshot: the simulation time, the number of precipitates, the average precipitates dimension, in atoms and angstroms, the percentage of Sc in the solid Al, the percentage of Sc in precipitates, the relation between precipitates and lattice sites.

The sequence of graphics in Fig. 2 resumes the analysis undertaken over the simulation output. Fig. 2 a) represents the evolution of precipitates dimension in terms of radius measure. Fig. 2 b) acknowledges the evolution of the presence of Sc atoms distributed in the Al solid solution. As with Fig. 2 c), it is possible to acknowledge the evolution of the presentage of Sc atoms in precipitates. Fig. 2 d) is one of the most important interpretations that is conducted regarding simulation of the nucleation of precipitates.

Two parameters were used to compare the kMC simulations results with the classical nucleation theory (CNT) calculations: the steady state nucleation rate ($J^{st}$) and the cluster concentration ($C_{nSc}$). To carry out this comparison it was necessary to execute a small clusters analysis, beyond the stable precipitates analysis. The steady-state nucleation rate ($J^{st}$) is the number of supercritical nuclei that form per unit of time in a unit of volume. Based on CNT, to obtain $J^{st}$ it is necessary to calculate the equilibrium concentration, the impurity diffusion, the average interface free energy, the

nucleation free energy, the nucleation barrier, the condensation rate, and the Zeldovitch factor.

Fig. 3 compares the kMC simulation with CNT for temperatures of 723K and 773K. The kMC values for $J^{st}$ were approximated by the initial gradient of the time evolution of stable precipitates (*Nsp*) vs. the number of lattice sites (*Ns*) (Fig. 2 d)). To capture the initial phase of precipitates nucleation, shorter simulations were performed but with a higher sampling frequency. It is possible to observe that $J^{st}$ values calculated by kMC, for 0.5 and 0.75 Sc percentages, are quite bigger than those obtained by CNT. For the other Sc percentages, kMC results are in accordance with CNT.

Cluster size distribution ($C_{nSc}$) defines the probability to encounter a cluster with a dimension of *n* atoms in a solid solution and also being characterized by a $L1_2$ structure. Fig. 4 compares the cluster concentration predictions obtained by CNT and kMC. We can conclude that cluster concentration obtained by kMC is in accordance with CNT for small cluster sizes (up to 7/8 Sc atoms). For larger cluster sizes, and higher Sc concentrations, there are significant differences between both methods predictions, as occurs in related work.

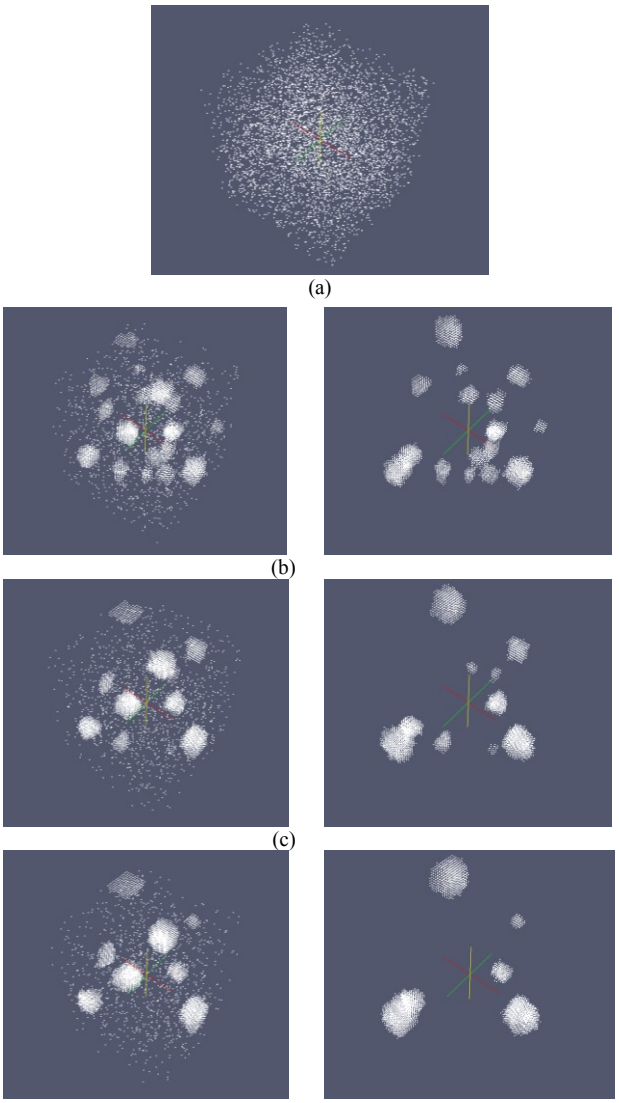



Figure 1. Evolution of simulation: (a) initial configuration; (b) t=1.55ms; (c) t=3.03ms; (d) t=4.945ms (left/right ⇔ before/after applying DBSCAN).

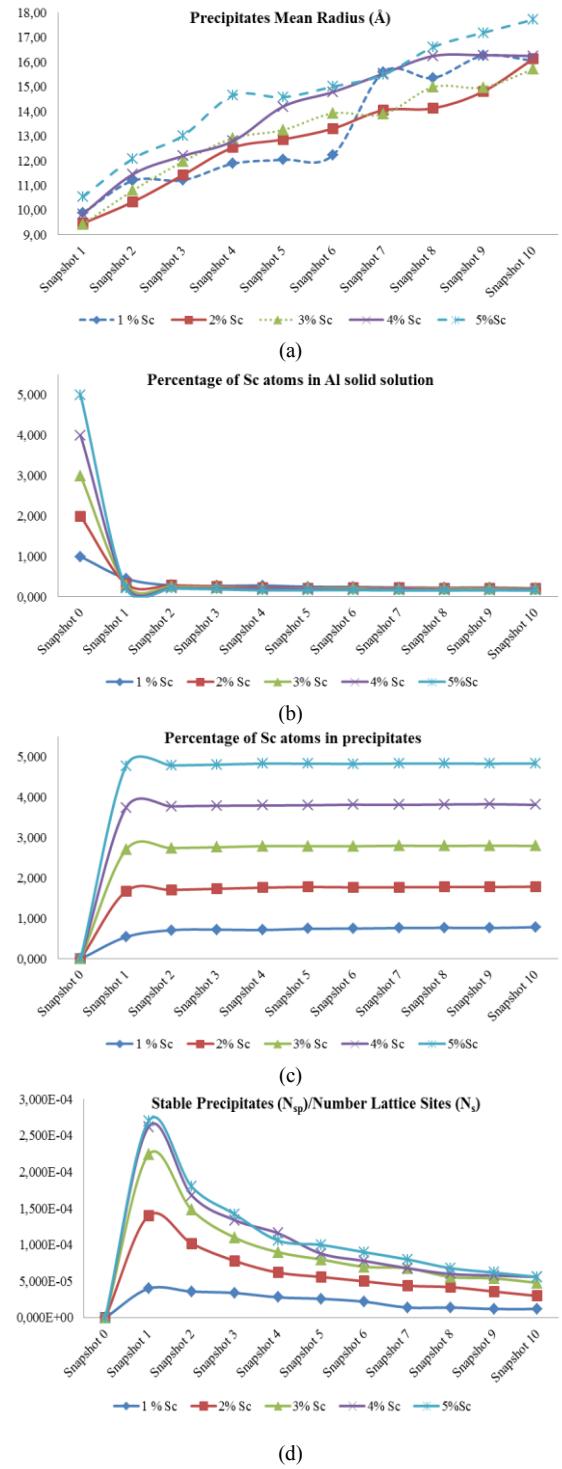
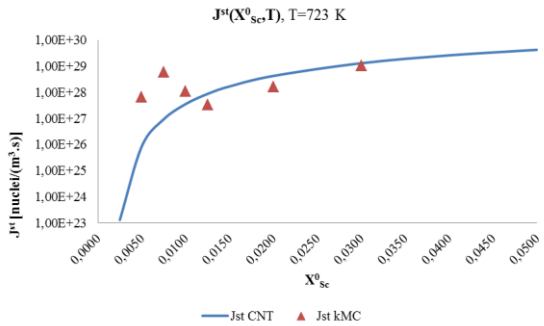
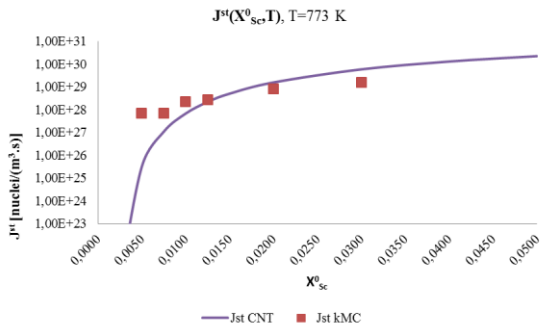



Figure 2. Simulation metrics.

The simulations were run on the SeARCH cluster, located at the University of Minho. We observed that the computation time mainly depends on the number of MC steps. Simulations duration is also influenced by the technical specifications of the machines where the simulations were run. For example, the duration of a simulation with $5x10^{11}$ MCS ranged from 8 to 12 days. Computation time does not depend significantly on the Sc percentage, the lattice size, or any other parameter.




(a)




(b)

Figure 3. Comparison between $J^{st}$ computed by CNT and kMC, for the temperature of 723K (a) and 773K (b).

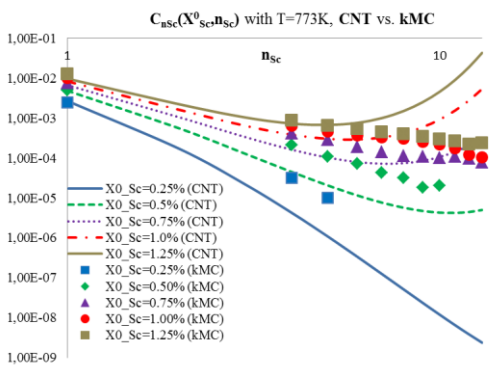



Figure 4. Cluster size distribution comparison: kMC vs. CNT.

## VI. Conclusions and Future Work

kMC simulation of $Al_3Sc$ precipitation on a supersaturated Al solid solution was successfully achieved. This proves that the equations used to model $Al_3Sc$ precipitation are correct. The results from kMC simulations were further improved by the application of DBSCAN, which proved to be a valorous aid to identify the $Al_3Sc$ precipitates, by eliminating the unclustered Sc atoms and improving visualization. By simulating with various Sc percentages, as well as temperatures, the capacity of clustering $Al_3Sc$ precipitates maintains accurate.

The number of stable precipitates strongly increases in the initial phase. After that, the number of precipitates reduces, as predicted by the theory of nucleation. Consequently the surviving precipitates increase in size, either in number of atoms or in radius. The mean precipitates radius increases almost linearly over time. The number of precipitates normalized by the number of lattice sites increases rapidly in the initial phase of the simulation and then decreases slightly during the rest of the simulation. Temperature has a profound influence on the evolution of the precipitation simulation. As the classical nucleation states, and the simulation graphics do prove, the steady state nucleation rate rises with the temperature increase.

The achieved results are very much in good agreement with those reported by Clouet [6]: the increase of the precipitates average size and the reduction of the Sc concentration in the Al solid solution during the simulation follow the same tendency. The comparison between kMC and CNT are very much similar. Although we have used the same model for $Al_3Sc$ precipitation as [6], it was possible to go deeper in the evaluation of the influence of all the parameters involved in simulation: lattice size, temperature, Sc concentration, number of MC steps, and the technique used in cluster identification and measuring. We also tried strategies to accelerate the simulation, although with same lack of success.

A field for future research is the exploration of parallelization techniques for the kMC simulation. Due to the sequential nature of the precipitation problem, a hypothesis is to use multiple vacancies and run multiple simulations in parallel, each one with a vacancy and a sub-lattice. Examples of algorithms that follow this strategy are the optimistic synchronous relaxation (OSR) and the semi-rigorous synchronous sub-lattice (SL) [10]. These approaches have to deal with two critical issues: correct the excessive vacancy concentration and synchronize the parallel instances of the asynchronous kMC simulation. Another future research topic would be extending Monte Carlo method to simulate ternary alloys, such as Al-Mg-Sc, Al-Sc-Si or Al-Sc-Zr.

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