

# Simulation studies on vapor phase condensation of magnesium and computations of nucleation rates using Discrete-Section model

A. K. Tak

Laser and Plasma Technology Division  
Bhabha Atomic Research Centre, Mumbai-400085, INDIA  
*Electronic mail:* aktak@rediffmail.com

(Received 10 June 2014, Published 28 July 2014)

## Abstract

Capacity of discrete section models as a reliable tool to analyze and predict the data in particle nucleation and growth experiments has been demonstrated through comparisons of simulated and experimental data. A computer code based on this model is developed and homogenous nucleation of particles and growth is simulated. The results have been benchmarked against the published data on nucleation and growth in iron vapors. The published experimental results of condensation of magnesium vapors through homogenous nucleation are then analyzed using the results of simulations. The predicted values of magnesium vapors super saturation ratio and temperature at the point of nucleation are in excellent agreement with the experimental data. The code is used to compute the particle nucleation rate and computed values are compared with the values predicted by analytical expressions based on different theories. It is demonstrated that the model is able to predict values which are close to experimental values and thus can be used to predict nucleation rate. ©2014 Science Front Publishers

**Keywords:** Particle nucleation, Discrete section models, Condensation of vapor

## 1. Introduction

Formation of particles through homogenous nucleation and their growth due to coagulation is a process which is relevant to several areas of research such as controlled production of nanoparticle in thermal plasma reactors, environmental aerosol formation and pollution control and dust formation in universe. Homogenous nucleation is basically a process of formation of liquid phase from pure vapors. Continuous collision between atoms/molecules in vapor phase results in formation of clusters. Size of some of these clusters is larger than size of critical clusters. Critical clusters are clusters which are energetically favored to grow further and it is these clusters that act as the nuclei for formation of stable particles. Formation of sufficient number of these critical clusters in the vapors, leads to rapid condensation. Nucleation results in formation of stable particle which further grow by condensation of vapor molecules on them and by coagulation among themselves. Both the nucleation and the growth of particles are a result of collisions among vapor molecules, clusters and particles. In reality both nucleation and growth are a part of one single continuous process but as there is a large difference in the time scales at which these two processes occur, they are treated as two different processes in classical modeling of vapor phase condensation. While the nucleation is treated analytically, except for very simple cases, particle growth process is solved numerically.

The general dynamic equation (GDE) describing particle growth where nucleation is treated analytically is given by Friedlander [1]. This equation treats particle size as a variable which vary continuously and uses an analytical expression to compute nucleation rate. There have been several efforts to obtain the solution of this equation either analytically or numerically. Gelbard et al. [2] have tried numerically solving this equation using method of collocation on finite elements.

They could solve it only for very simple cases of particle coagulation and nucleation rate. Analytical solution for simple functional form of particle coagulation and nucleation has been obtained Peterson [3] and Gelbard [4]. The most widely used method to obtain numerical solution of these equations when more realistic coagulation and nucleation rates are used has been methods of moments. Many authors [5-8] have used this method to obtain numerical solution of the GDE including the effect of three dimensional particle transport processes such as diffusion, thermophoresis and convection. The major shortcoming of this method is that it needs a reliable expression to compute nucleation rate for different experimental conditions. It also pre-assumes a shape for particle size distribution that limits its applicability.

Methods based on discrete representation of particle size avoid the shortcoming faced in moment based methods. Though these methods are computationally expensive making it difficult to incorporate the effects of three dimensional transport processes, predictions using these methods are more accurate so far as nucleation and particle size distribution are concerned. Under discrete representation, the GDE can be written as given by Girshick et al [9]. Simulation based on pure discrete model results in high computational load as one equation has to be written for every particle size. Gelbard et al. [10] suggested sectional representation of particle size to reduce the number of equation to be solved. Discrete-Section (DS) model which uses pure discrete representation of particle size for smaller particles and sectional representation for larger particle is employed by Girshick [9,11] and Biswas [12] for simulating particle nucleation and growth process in systems which can be modeled as one dimensional.

Though Discrete Section model has been used to understand the nucleation and growth process qualitatively, it has not been applied to analyze actual experimental data. We have used Discrete-section model and developed a computer code based

on this model to simulate particle nucleation and growth process, benchmarked the data against published simulated results on iron vapors and analyzed the published experimental data on magnesium nucleation. Thus we demonstrate that this model can be used to predict the experimental data.

In classical nucleation theory, calculation of nucleation rates is based on Becker-Doring formula. Girshick [9] has suggested modification to nucleation theory. Though there have been different approaches, discrepancy exist in predicted values of nucleation rates. Theory which predicts correct nucleation rates for one experimental condition is not able to do so in a different experimental condition. In the paper we have used computation based on Discrete-Section model to compute the particle nucleation rates and demonstrated that it can be effectively used for predicting nucleation rates in the system where the vapor flow can be approximated to one dimensional flow.

## 2. Mathematical model

The particle general dynamic equations have been solved by employing discrete section model. Under discrete models particle size is treated as a discrete variable. It is assumed that all the particles are spherical. Particles grow via collision among vapor molecules, clusters and particles and it is assumed that all collisions are effective. Reduction in particle size takes place only through monomer evaporation. Size of the particle is defined as the number of vapor molecules/atoms it contains. With these assumptions the particle GDE under the discrete representation of particle size can be written as given by Girshick [9].

For density of condensable vapors (atom/molecule)

$$\frac{Dn_1}{Dt} = -n_1 \sum_{j=1}^{\infty} \beta_{ij} n_j + \sum_{j=2}^{\infty} (1 + \delta_{2j}) E_j n_j \quad (1)$$

and for cluster of size larger than 1

$$\frac{Dn_k}{Dt} = \frac{1}{2} \sum_{i+j=k} \beta_{ij} n_i n_j - n_k \sum_{i+j=k} \beta_{ij} n_j + E_{k+1} n_{k+1} - E_k n_k \quad k > 1 \quad (2)$$

Where  $n_k$  is number density of particles of size  $k$ .  $\beta_{ij}$  is collision frequency function for collision between particles of size  $i$  and  $j$ ,  $t$  is time and  $E_k$  is monomer evaporation coefficient defined as rate of evaporation of monomers from a particle of size  $k$ . For the case where Knudsen number is sufficiently large, the collision frequency function from the gas kinetic theory may be applied.  $\beta_{ij}$  is given by Eq. (3)

$$\beta_{ij} = \left[ \frac{8 \pi k_B T}{m_l} \left( \frac{1}{i} + \frac{1}{j} \right) \right]^{1/2} (i^{1/3} + j^{1/3})^2 \quad (3)$$

and evaporation coefficient,  $E_k$  is given by Eq. (4)

$$E_k = \beta_{1,k-1} n_z \exp[\Theta(k^{2/3} - (k-1)^{2/3})] \quad (4)$$

Where  $m_l$  is mass of the monomer,  $T$  is temperature,  $k_B$  is Boltzman constant,  $n_z$  is the equilibrium monomer concentration for the saturated vapors and  $\Theta$  is dimension less surface tension defined by Eq. (5)

$$\Theta = \frac{\sigma}{k_B T} \frac{s_1}{k} \quad (5)$$

Here  $\sigma$  is surface tension of bulk liquid,  $S_1$  is surface area of vapor molecule/atom. For a system containing a micrometer size particle,  $k$  in Eq. (2) may run up to  $10^6$ , making it impossible to solve such a large set of equations. Discrete-Section model is employed to reduce the number of equations. Under discrete-section model particle size is divided into sections. An integrated quantity for each section is defined in following manner,

$$Q_m(t) = \sum_{i=J_{m-1}+1}^{J_m} x i^y n_i(t) \quad (6)$$

$$m = 1, 2, 3, \dots, z$$

Particle number density for a particle of size  $i$  which lies in the section  $m$ , is assumed to be related to the sectional property  $Q_m$  by following relation.

$$n_i(t) = \frac{Q_m(t)}{x i^y (k_m - k_{m-1})} \quad (7)$$

Here  $K_m$  is the size of largest particle in section  $m$ . If  $Q_m$  is a quantity which remains conserved during collision of particles, using Eq. (2) and (7) can be rewritten as conservation equations for  $Q_m$

$$\frac{dQ_l}{dt} = \frac{1}{2} \sum_{r=1}^{l-1} \sum_{p=1}^{l-1} \gamma_{r,p,l} Q_r Q_p - Q_l \sum_{r=1}^{l-1} \gamma_{r,l} Q_r - \frac{\gamma_{l,l} Q_l^2}{2} - Q_l \sum_{r=l+1}^z \gamma_{r,l} Q_r \quad (8)$$

Where coefficient  $\gamma$  are given by

$$^1 \gamma_{r,p,l} = \sum_{i=k_{r-1}+1}^{k_r} \sum_{j=k_{p-1}+1}^{k_p} \frac{\theta(k_{l-1} < (i+j) < k_l) (i+j)^y \beta_{i,j}}{x j^y i^y (k_r - k_{r-1}) (k_p - k_{p-1})}$$

(for  $2 \leq l \leq z, r < l, p < l$ )

$$^2 \gamma_{r,l} = \sum_{i=k_{r-1}+1}^{k_r} \sum_{j=k_{l-1}+1}^{k_l} \frac{\{\theta((i+j) < k_l) j^y - \theta((i+j) \leq k_l) [(i+j)^y - j^y]\} \beta_{i,j}}{x j^y i^y (k_r - k_{r-1}) (k_p - k_{p-1})}$$

(for  $2 \leq l \leq z, r < l$ )

$$^3 \gamma_{l,l} = \sum_{i=k_{l-1}+1}^{k_l} \sum_{j=k_{l-1}+1}^{k_l} \frac{\{\theta((i+j) > k_l) (i+j)^y + \theta((i+j) \leq k_l) [i^y + j^y - (i+j)^y]\} \beta_{i,j}}{x j^y i^y (k_r - k_{r-1})^2}$$

(for  $1 \leq l \leq z$ )

$$^4 \gamma_{r,l} = \sum_{i=k_{r-1}+1}^{k_r} \sum_{j=k_{l-1}+1}^{k_l} \frac{j^y \beta_{i,j}}{x j^y i^y (k_r - k_{r-1}) (k_p - k_{p-1})}$$

(for  $2 \leq l \leq z, r < l$ )

$\theta = 1$  (if  $x < y < z$ ) and  $\theta = 0$  (otherwise)

By assuming logarithmically increasing section sizes, the complete particle size spectrum can be covered by much less number of equations. Solution in terms of  $Q_l$  can be obtained and can be used to get the particle size distribution at any instant of time by using Eq. (7). We have used  $x=y=1$  for which  $Q_m$  is simply total number of monomers in section  $m$ .

Nucleation rate is defined as the rate at which critical cluster are formed during the period when phase transition from vapor to gas phase starts. In the discrete section model it is possible to keep track of size of critical cluster and also the number density of the critical cluster. Thus, by computing the rate of change of critical cluster number density, it is possible to compute the nucleation rate using the model. Prediction of nucleation rates can be made exact by ensuring that size of critical cluster at the time of nucleation falls in the discrete part of the particle size spectrum. The method has advantage over other method because it can handle the variation in material properties with temperature.

### 3. Results and discussions

Results are presented in three subsections. To benchmark our code, we have presented the data related to nucleation and growth in iron vapor in section 3.1. After benchmarking we have applied our code to analyze the experimental data on nucleation in magnesium vapors reported by Ferguson [13]. These data are presented in section 3.2. Results related to the application of our code for computing nucleation rate are presented in section 3.3.

#### 3.1 Nucleation behavior in iron vapors

We have simulated nucleation and growth in iron vapors mixed with argon gas and cooling at a constant given rate. The system is similar to as described by Girshick [11]. Iron vapors mixed with argon gas exist at stagnation temperature of 2500 K. At this temperature partial pressure of argon gas is  $10^{-3}$  atmosphere. Vapor mixture cools at a rate of 10000 to 30000 K/S. Particles of size less than 50 were treated similar to pure discrete case by taking only one particle per section. Larger particles are treated in sections.

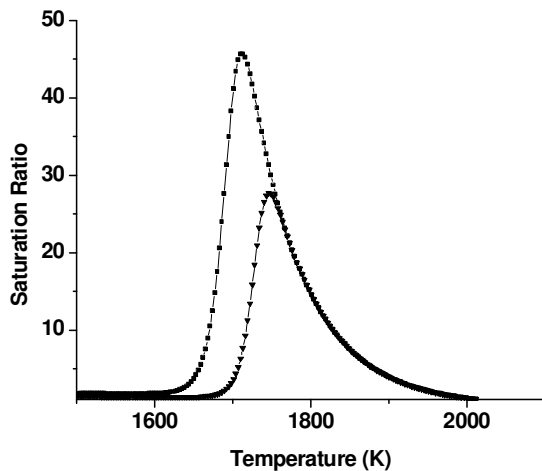


Fig. 1 supersaturation ratio of iron vapors for two different cooling rates.

- ▼ Vapor cooling rate 10000 K/sec.
- Vapor cooling rate 30000 K/sec

Size of a section is larger by a factor of 2 compared to size of its previous section. Total 25 sections were used to represent the particle size, thus covering particle containing up to  $50 \times 225$  monomers. Fig. 1 shows the variation in super saturation

ratio as the iron vapors cools at the rate of 10000 K/S and 30000 K/S. The super saturation ratio increases rapidly, peaks around 1750 K and then decreases. The peak in saturation ratio marks the onset of nucleation. For faster cooling rate, saturation ratio peaks at a higher value. This is because at faster cooling rate the vapors cools to a lower temperature before the nucleation is completed, thereby resulting in increased value of saturation ratio. The Fig. 2 shows the effect of initial iron vapor concentration on the peak value of supersaturation ratio. For a lower initial concentration, the peak value of supersaturation ratio reaches to a higher value. The reason for this is that at lower vapor concentration, the formation of critical clusters is delayed because of reduced number of collisions. Results of our simulations are in excellent agreement with the published results of Girshick [11].

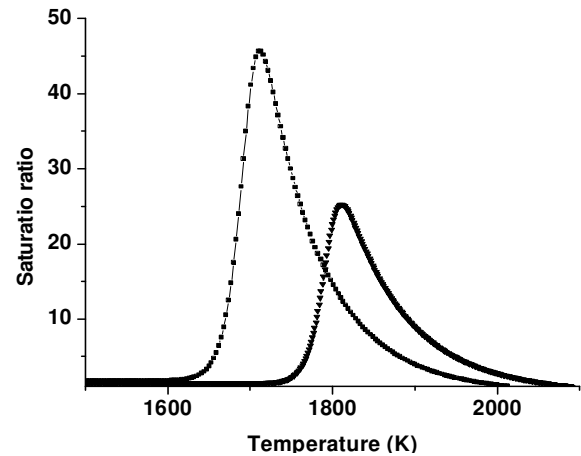


Fig. 2 Supersaturation ratio of iron vapors for two different initial vapor mass fractions. ▼ Iron vapor mass fraction  $1.0 \times 10^{-3}$ . ■ Iron vapor mass fraction  $4.4 \times 10^{-4}$

#### 3.2 Analysis of magnesium nucleation data

Ferguson et al. [13] experimentally studied nucleation of magnesium. They used an electrically heated crucible to melt and evaporate magnesium. The crucible was located in a vacuum chamber filled with hydrogen at controlled pressure. As the magnesium vapors moves through the chamber, it cools and at some point nucleation takes place resulting in cloud formation. They observed the location of vapor–cloud interface and measured the temperature at the interface using a thermocouple. Temperature of molten magnesium was also measured using a thermocouple. Measurements were done for different pressure of hydrogen gas and at several values of crucible temperatures at each pressure. They argued that in the region of interest convective flow of the buoyant plume arising due to temperature gradient is very strong making the flow essentially one dimensional. In their paper they have presented data of condensation point temperatures corresponding to various source temperatures. This data is given in the form of a fitted function given by Eq. (9).

$$T_{\text{source}} = 0.977 T_{\text{condensation}} + 139.4 \quad (9)$$

If thermal equilibrium is assumed, number density of magnesium atoms at the surface of the crucible can be calculated using vapor pressure values of magnesium. Vapor

pressure of magnesium used by above author is given by Eq. (10).

$$\log(P) = -\frac{A}{T} + B + C \log(T) \quad (10)$$

Where A = 7780, B = 11.41 and C = -.855 if 923 K > T > 300 K  
And A = 7550, B = 12.79 and C = -1.41 if 1363 K > T > 923 K

Number density can also be calculated by experimentally data on weight loss measurement. The difficulty in this approach is determination of correct velocity of the vapor front near the crucible surface. A value of between 10-50 m/sec is expected and the average value of 30 m/sec has been used by the author to compute the number density. They found disagreement in the values calculated by two methods. Other details of their experiment can be found in Ferguson et al [13].

We applied our simulations to their experiment in order to analyze their experimental data and predict Eq. (9). Cooling rate of the vapor is an important factor for computing particle nucleation and growth. We calculated the cooling rate using the Eq. (11).

$$\text{Cooling rate} = \frac{(T_{\text{source}} - T_{\text{condensation}}) * V}{x} \quad (11)$$

Here V is the velocity of the vapor front and x is the distance of vapor-cloud interface from the crucible surface.

Fig. 3 shows the variation in vapor saturation ratio as the vapor flows away from the crucible and cools. The temperature at which the saturation ratio peaks is the temperature at which nucleation takes place and the temperature at that point is taken as computed value of condensation temperature. Values of condensation temperature for different values of source temperature are plotted in Fig. 4. This was done for the two different methods of calculating source number density. The values predicted assuming thermal equilibrium near the crucible top surface consistently underestimates the value of condensation temperature indicating that assumption of thermal equilibrium does not hold. As the reduced number density results in delayed nucleation we conclude that the number density predicted assuming thermal equilibrium is higher compared to the experimental value. This is in agreement with the observation of Ferguson et al. [13].

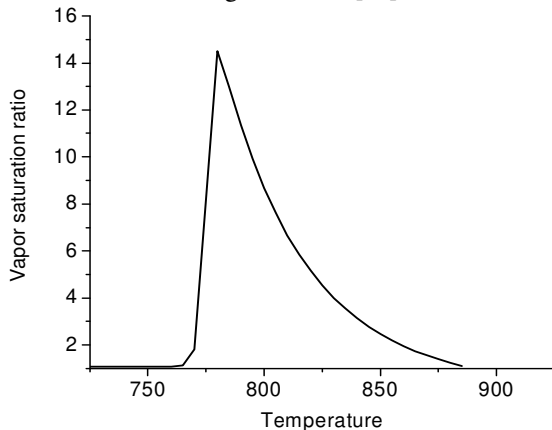


Fig. 3 supersaturation ratio of magnesium vapors with vapor temperature.

Values of condensation temperature for two different values of vapor front velocities are plotted in Fig. 5. A lower value of vapor front velocity predicts the closer value of condensation point temperature. By looking at our data we expect that vapor front velocity would be closer to 25 m/sec in lower part of the temperature range and increase slowly with temperature to values which will be smaller than 30 m/sec.

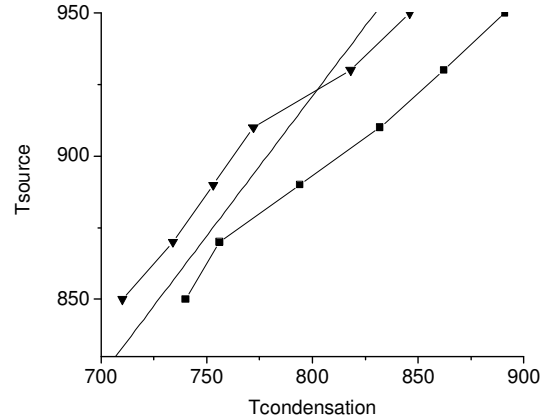


Fig. 4 Values of crucible temperature and vapor-cloud interface temperature. ▼ simulated using source number density calculated from experimental data. ■ simulated using source number density calculated based on assumption of thermal equilibrium. Graph without symbol is experimental data.

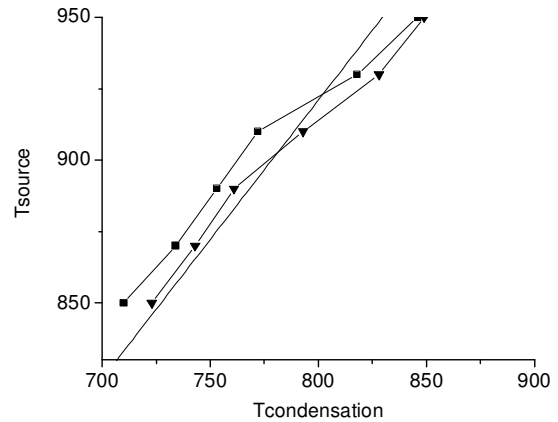


Fig. 5 Values of crucible temperature and vapor-cloud interface temperature for two different velocities of vapor front. ▼ Vapor front velocity 25 m/s. ■ Vapor front velocity 30 m/s. Graph without symbol is experimental data.

### 3.3 Computation of nucleation rates

There have been several efforts to develop an analytical expression to predict the nucleation rates

$$J_{cl} = v_1 \left( \frac{2\sigma}{\pi m_1} \right)^{1/2} n_s^2 S \exp\left( -\frac{4\Theta^3}{27 (\ln S)^2} \right) \quad (12)$$

Becker and Doring formula given by Eq. (12) is used for calculating nucleation rate in classical nucleation theory. Girshick et al. [9] have proposed modification the classical nucleation theory. They proposed a modified expression which is given by Eq. (13).



$$J_{kin} = \frac{e^{-\Theta}}{S} J_{cl} \quad (13)$$

Taking a different approach Barbara Hale proposed a nucleation theory based on scaled variable. They called it Scaled nucleation theory.

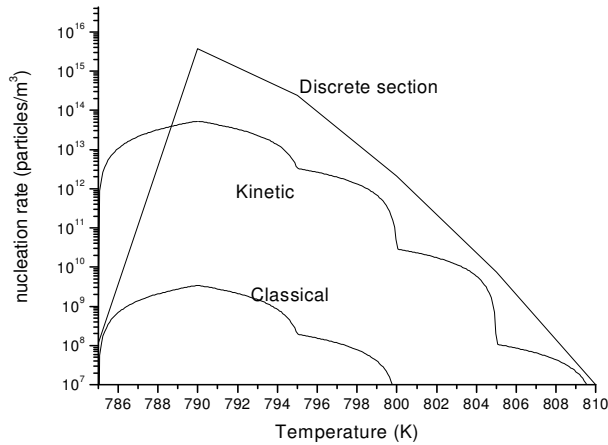


Fig. 6 Nucleation rate of magnesium vapor with vapor temperature using three different models

Though there have been different approaches and efforts, there is a large spread in nucleation rates predicted by different authors and expressions. Theory which predicts correct nucleation rates for one experimental condition is not able to do so in different experimental conditions. In Fig. 6 we have shown the comparison between nucleation rates computed by us using discrete section model and values predicted by Eq. (12) and Eq. (13). These rates are computed for the experimental conditions of Ferguson et al. Expected value of nucleation rate in their system is around  $10^{14}$  particles/  $m^3$  / second.

It is observed that classical nucleation theory severely underestimate the nucleation rate by a large amount, while values predicted by both kinetic and the discrete section model are closer to realistic value. The discrete section method provides a flexibility over the other methods as it could take into account the variation of experimental conditions and material properties during an experiments. This is particularly helpful because properties such as surface tension, vapor pressures etc. are function of temperature and nucleation rates are very sensitive to their value.

#### 4. Conclusion

To simulate homogenous nucleation and growth, computer code is developed and benchmarked. We have analyzed published experimental data on nucleation in magnesium vapors. We computed the value of condensation point temperature for a given crucible temperature. Our analysis show that assumption of thermal equilibrium does not hold near crucible surface as the number density predicted under this assumption over predicts the experimental value. We also demonstrated that from our analysis it is possible to obtain experimental data such as the velocity of vapor front near the crucible surface which is otherwise difficult to measure. We

also proposed a method to use the discrete section based model to compute nucleation rate. The nucleation rate values computed using this method is in line with expected experimental values. As there is a lot of uncertainty in the values of nucleation rate predicted by existing theories, this technique could serve as an alternative method to compute nucleation rate in systems having one dimensional flow.

#### References

- [1] S. K. Friedlander, *Smoke, dust and haze*. Oxford University press, New York, (2000)
- [1] F. Gelbard, & J. H. Seinfeld, "Numerical solution of the dynamic equations for particulate systems", *Journal of computational Physics*, **28**, 357 (1978)
- [3] T. W. Peterson, F. Gelbard, & J. H. Seinfeld, "Dynamics of source-reinforced , coagulating and condensing aerosols", *Journal of colloid and interface science*, **63(3)**, 426 (1978)
- [4] F. Gelbard, & J. H. Seinfeld, "The general dynamic equation for aerosols: Theory and application to aerosol formation and growth", *Journal of colloid and interface science*, **68(2)**, 363 (1979)
- [5] Pratsinis S., "Simultaneous nucleation, condensation and coagulation in aerosol reactors", *Journal of colloid and interface science*, **124(2)**, 416 (1988)
- [6] Pratsinis S., & Kim Kyo-Seon, "Particle coagulation, diffusion and thermophoresis in laminar tube flow", *Journal aerosol science and technology*, **20(1)**, 101 (1989)
- [7] S. L. Girshick, C. P. Chiu, R. Munro, C. Y. Wu, L. Yang, S. K. Singh and P. H. McMurry, "Thermal plasma synthesis of ultrafine iron particles", *Aerosol science*, **24(3)**, 367 (1993)
- [8] B. Schwade and P. Roth, "Simulation of nano-particle formation in a wall-heated aerosol reactor including coalescence", *Aerosol science*, **34**, 339 (2003)
- [9] S. L. Girshick, C. P. Chiu and P. H. McMurry, "Homogenous nucleation rates", *Aerosol science and technology*, **13**, 465 (1990)
- [10] F. Gelbard, Y. Tambour and J. H. Seinfeld, "Sectional representations for simulating aerosol dynamics", *Journal of colloid and interface science*, **76(2)**, 541 (1980)
- [11] S. L. Girshick and C. P. Chiu, "Homogenous nucleation of particles from the vapor phase in thermal plasma synthesis", *Plasma Chem. Plasma Process*, **9(1)**, 355 (1989)
- [12] P. Biswas, C. Y. Wu, M. R. Zachariah and B. McMillan, "Characterization of iron oxide-silica nano-composites in flames: Part II. Comparison of discrete-sectional model predictions to experimental data", *Journal of Materials research*, **12(3)**, 714 (1997)
- [13] F. T. Ferguson and J. A. Nuth, "Experimental studies of the vapor phase nucleation of refractory compounds. IV. The condensation of magnesium", *Journal of Chemical Physics*, **104(9)**, 3205 (1996)