# A novel approach for the estimation of nanoparticle evaporation through the Method of Moments

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# A novel approach for the estimation of nanoparticle evaporation through the Method of Moments

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**Abstract:** In this article the results of the application of two numerical approaches - the Method of Moments and the nodal method - for the prediction of the evaporation phenomena in the synthesis of nanoparticles are presented and compared, in order to evaluate the limits of the moment methods and to determine the usability of the method in plasma environments (i.e. high temperatures and steep gradients). Furthermore, a new closure term is introduced in the Method of Moments, in order to consider the disappearance of the particles due to the evaporation process. The Nodal Method is used as a benchmark for the Method of Moments.

## 1. Introduction

The synthesis of nanoparticles is of high importance for the industrial production of advanced metallic and ceramic materials as well as in biomedical and environmental industry [1,2]. Numerous methods were developed in the past to achieve the goal of a fully controlled production, flame reactors and plasma reactors being among the most effective. Notably, the processes involving ICTP (Inductively Coupled Thermal Plasma) torches have been found to be particularly apt to the task, being characterised by high standards in process purity and the possibility of achieving decidedly controlled mass production, since these reactors can run continuously [3,4].

However, due to the plasma environment, the ICTP reactors are characterised by highly non-uniform and non-isothermal fields and, therefore, by extremely high heating and cooling rates (up to $\pm 10^7$ K/s) [5,6]. Whilst these characteristics can be considered as an asset for the production, they certainly have the effect of rendering the physical and computational modelling of the complete process particularly challenging: a full simulation should include models for nucleation, condensation, evaporation and coagulation of the nanoparticles and be sufficiently stable in order to be able to handle the high gradients of the plasma environment.

Several approaches were developed in the past to model nanoparticle synthesis, with the method of moments (MoM) [7,8] and the sectional method [9] being among the simplest and most used. Within the former, a distribution of the particle size is assumed as mathematical closure for solving the aerosol general dynamic equation (GDE); this model, with the assumption of a unimodal lognormal profile for the PSD (Particle Size Distribution), becomes extremely simple, computationally fast and easy to implement and, for these reasons, it has been used in the past in several works at various degrees of complexity (e.g. from 1D to 3D models of plasma reactors [5,10]). However, the assumption of a fixed distribution remains a critical drawback especially in a plasma environment, since the model is not capable of properly predict phenomena which tend to effect the distribution non-uniformly and therefore tend to change the shape of the distribution, such as recirculation or evaporation. The poor results of the MoM in simulating evaporation processes in even less severe environments than those of plasma reactors have already been studied in the past [11,12]. On the other hand, the discrete sectional method - or its simplified form used in this work, the so called nodal method (NM) - does not assume any fixed distribution and it is therefore more suited to model the whole synthesis; nonetheless the required computational effort is considerably higher than with the MoM.

In this work a comparison between the zero-dimensional form of the two is presented for the prediction of the evaporation phenomena in which, chiefly because of re-heating, the disappearing of the nanoparticles might

become relevant in order to highlight the limitations of the moment methods and to determine the limits of usability of the method in plasma environments (i.e. high temperatures and steep gradients). Furthermore, a closure term is proposed for the method of moments, in order to take into account the disappearance of the particles due to the evaporation process.

## 2. Modelling Approach

As stated above, the synthesis of nanoparticles is a process involving several complex phenomena; Friedlander [7] proposed an equation to describe the whole process, known as the aerosol general dynamic equation (GDE):

$$\frac{\partial n(v_p)}{\partial t} + \nabla \cdot [\boldsymbol{u} n(v_p)] = \nabla \cdot [D(v_p)] + I\delta_D(v_p - v_p^*) - \frac{\partial}{\partial v_p}[G n(v_p)]$$
$$+\frac{1}{2}\int_0^{v_p} \beta(v_p', v_p - v_p') n(v_p') n(v_p - v_p') dv_p' - \int_0^{\infty} \beta(v_p, v_p') n(v_p) n(v_p')\, dv_p \quad (1)$$

where $n$ is the particle size distribution function (PSDF), $v_p$ is the particle volume, $\boldsymbol{u}$ is the gas velocity, $D$ is the particle diffusion coefficient, $I$ is the nucleation rate, $\delta_D$ is the Dirac delta function, $G$ is the heterogeneous condensation growth rate and $\beta$ is the interpolative collision frequency function ([13]); the superscript * denotes the critical state.

Two methods for the numerical solution of the GDE will be presented below, namely the method of moments and the nodal method.

**Method of Moments (MoM)**

In this method the GDE is expressed in a different form to obtain a set of equations easier to handle; the first three moments of the PSDF are defined as:

$$M_k = \int_0^{\infty} v_p^k n(v_p) dv_p \quad (2)$$

with $k = (0,1,2)$. $v_p$ is the particle volume and $n(v_p)$ is the PSDF. As mentioned above, the method usually assumes a lognormal distribution for the nanoparticle size in order to obtain a mathematical closure.

The zeroth moment represents the total concentration of the nanoparticles and the first moment their total volume, whilst the second moment is proportional to the light scattered by the nanoparticles. The GDE then becomes a system composed by the transport equations of the three moments:

$$\frac{\partial M_k}{\partial t} = [\dot{M}_k]_{nucleation} + [\dot{M}_k]_{condensation/evaporation}$$
$$+[\dot{M}_k]_{coagulation} + [\dot{M}_k]_{diffusion} \qquad k = (0,1,2) \quad (3)$$

where the terms $[\dot{M}_k]$ represent the net production rates due to nucleation, condensation, coagulation and diffusion. Hence, with the assumption of a lognormal PSD the system is mathematically closed by the definitions of geometric standard deviation $\sigma_g$ and geometric mean volume $v_g$ and the relation between the moments:

$$\ln^2 \sigma_g = \frac{1}{9}\ln\left(\frac{M_0 M_2}{M_1}\right) \quad (4)$$

$$v_g = \frac{M_1^2}{M_0^{\frac{3}{2}} M_2^{\frac{1}{2}}} \tag{5}$$

$$M_k = M_0 v_g^k \exp\left(\frac{9}{2} k^2 \, ln(\sigma_g)\right) \tag{6}$$

NUCLEATION, DIFFUSION AND COAGULATION

In the present work, a zero-dimensional form of the system is used and, furthermore - given that the aim is to study the effect of evaporation - for the sake of simplicity the coagulation and nucleation processes are neglected. Therefore, we have

$$\left[\dot{M}_k\right]_{diffusion} = \left[\dot{M}_k\right]_{coagulation} = \left[\dot{M}_k\right]_{nucleation} = 0$$

CONDENSATION AND EVAPORATION

Regarding heterogenous condensation and evaporation the source terms are calculated through the formula

$$\left[\dot{M}_k\right]_{c/e} = \begin{cases} 0 & k = 0 \\ \xi(S-1) M_{\frac{2}{3}} & k = 1 \\ 2\xi(S-1) M_{\frac{5}{3}} & k = 2 \end{cases} \tag{7}$$

$$\xi = v_{mon} N_S (36\pi)^{\frac{1}{3}} \left(\frac{k_B T}{2\pi m_{mon}}\right)^{\frac{1}{2}} \tag{8}$$

Where $v_{mon}$ and $m_{mon}$ are the volume and mass of the considered monomer, $N_s$ the monomer concentration at the saturated state, while $M_{\frac{2}{3}}$ and $M_{\frac{5}{3}}$ can be calculated through equation (6).

$S$ is the supersaturation ratio, given by $S = \frac{p_s}{p_s^{sat}}$, with $p_s$ the partial pressure of the generic s molecule species and $p_{sat}^s$ the saturated vapor pressure. Therefore, when $S > 1$, we have condensation on the particles surface and $\left[\dot{M}_k\right]_{c/e}$ is positive, while when $S < 1$, $\left[\dot{M}_k\right]_{c/e}$ becomes negative and it reduces the particles volume.

Heterogenous condensation and evaporation do not affect the total concentration, consequently the source term for $M_0$ is generally assumed as null [3,5]; nevertheless, it is clear that in case of prolonged evaporation the particles might re-evaporate completely, and the concentration should actually decrease. This is a serious shortcoming in the common formulation of the model, since it leads to the prediction of unphysical behaviour in the simulation of the evaporation process (particles with volumes smaller than $v_{mon}$ can be obtained, for instance). To solve this problem a new term is proposed in the following paragraph which takes into account the disappearing of the particles.

DISSOLUTION TERM

As stated above, if the evaporation process is long enough to cause the complete disappearance of the particles, it is necessary to introduce a negative source term for the zeroth moment. The term proposed and used throughout this work is defined as following:

$$\left[\dot{M}_k\right]_{dissipation} = \xi \, (S-1) \, v_m^{2/3} \, n_m \tag{9}$$

where

$$n_m = \frac{M_0}{v_m \sigma_g \sqrt{2\pi}} e^{\frac{\ln^2 \frac{v_m}{v_g}}{2\sigma_g}} \tag{10}$$

$$v_m = v_g e^{-\sigma_g \sqrt{2} erfc^{-1}(\beta)}. \tag{11}$$

$\beta$ is the only parameter and it is related to the fraction of nanoparticles that is consumed by evaporation (i.e. "removed" from the lognormal distribution) per second, such as:

$$\beta = \frac{1}{M_0} \int_{-\infty}^{v_m} n(v) dv = \frac{1}{2} erfc\left(-\frac{\ln(v_m - \mu)}{\sigma_g \sqrt{2}}\right). \tag{12}$$

Therefore $\beta$ (and consequentially $v_m$) remains a factor that can be chosen empirically to reduce the error in the prediction and that can be fitted to different conditions of the simulation.

**Nodal method**

In the nodal method a discretised form of the PSDF is assumed and the total volume range to be considered for the nanoparticles is linearly discretised on a logarithmic scale:

$$v_{k+1} = f v_k \qquad (k = 1,2, \dots, k_{max}) \tag{13}$$

where $v_k$ is the particle volume at node $k$. The number of nodes $k_{max}$ and the geometric spacing factor $f$ should be selected to give a good compromise between accuracy and computational cost. According to [1] 42 nodes separated by a factor of 1.6 and with an initial volume equal to ten times the volume of the monomer should be sufficient to cover the size range of the nanoparticles synthesised in an ICTP reactor. However, in this work a finer mesh was chosen, and all the results presented below were obtained with $f = 1.3$ and $k = 60$; this corresponds to a range of volumes from $10^{-29}$ to $10^{-22}$.

CONDENSATION AND EVAPORATION

The source term for condensation and evaporation is:

$$\dot{N}_k^{cond/evap} = \sum_i \frac{(\psi_{ik}^{cond/evap} - \delta_{ik}) N_{p_i}}{\Delta t} \tag{14}$$

Where $\Delta t$ is the condensation time lag and $\delta_{ik}$ is the Kronecker delta. The volume of the particles at node $i$ may either decrease or increase, depending on the phenomenon occurring (i.e. evaporation or condensation); the new particles are then redistributed into different adjacent nodes depending on their new volume $v_i \pm \Delta v_i$ (see [1,14] and Figure 1 for further clarification). The term $\psi_{ik}^{cond}$ is a weighting factor used for the reallocation of the particles and it is calculated according to the following algorithm:

$$\psi_{ik}^{cond/evap} = \begin{cases} \dfrac{v_{k+1} - (v_i + \Delta v_i)}{v_{k+1} - v_k} \; if \; (v_k < v_i + \Delta v_i < v_{k+1}) \\ \dfrac{(v_i + \Delta v_i) - v_{k-1}}{v_k - v_{k-1}} \; if \; (v_{k-1} < v_i + \Delta v_i < v_k) \\ 0 \; otherwise \end{cases} \tag{15}$$

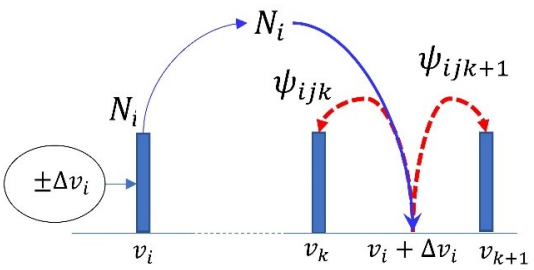


*Figure 1 - Relocation of new particles in the nodal model: Condensation and evaporation*

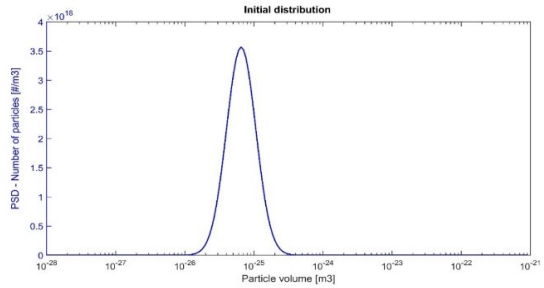


*Figure 2 - Initial distribution of the nanoparticles (diameter)*

The volume variation $\Delta v_i$ (during the time lag $\Delta t$) is obtained through the calculation of the net molecular flux from the vapour phase to the condensed phase with the formula:

$$\frac{dv_i}{dt} = 2\pi d_i D_{vap} v_{mon} (n_g - n_{S_i}) \left[ \frac{0.75\alpha(1+Kn_i)}{0.75\alpha + 0.283\alpha Kn_i + Kn_i + Kn_i^2} \right] \quad (16)$$

where $\alpha$ is an accommodation coefficient, $n_g$ is the vapour concentration, $n_{S_i}$ is the vapour concentration at saturation, $Kn_i$ the Knudsen number for particle at node $i$ and $D_{vap}$ is the vapour diffusion coefficient calculated through the Chapman-Enskog method [15]. A value of 0.05 was assigned to $\alpha$, following the suggestion in [10].

## 3. Results and discussion

To compare the behaviour of the two models during the evaporation process, two different setups were tested. The same particle distribution was imposed as initial condition in both the setups but in the first one the temperature was kept constant whilst in the second one a temperature gradient representative of plasma environment was imposed; for each setup different conditions were studied, and all the simulations were run until all the particle population decreased by a factor of 10 in a logarithmic scale. The initial distribution is shown in Figure 2. The idea behind the imposed conditions is to exemplify the temperature variation to which the nanoparticles are exposed in an ICTP reactor due to recirculation. The occurrence and impact of these zones of recirculation has been studied in different works [5,10] .

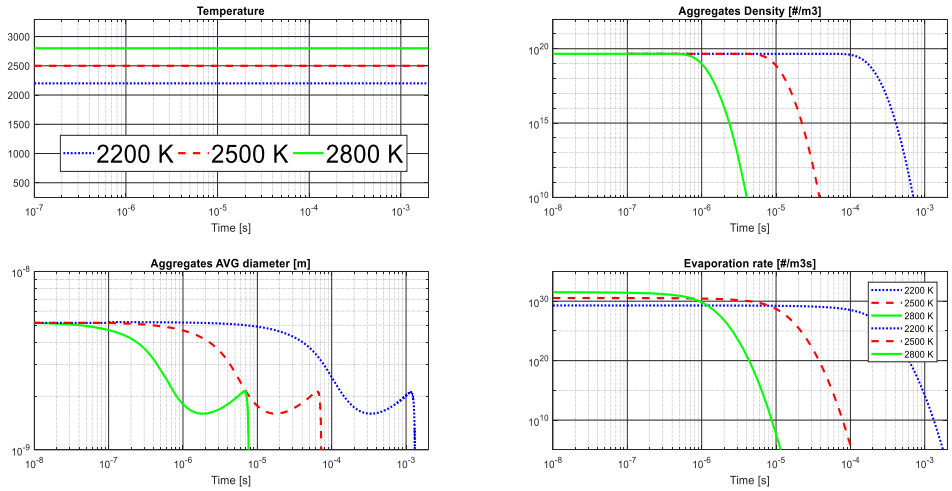


*Figure 3 - Nodal method: Time evolution of the main characteristics of the particles population at three different constant temperatures.*

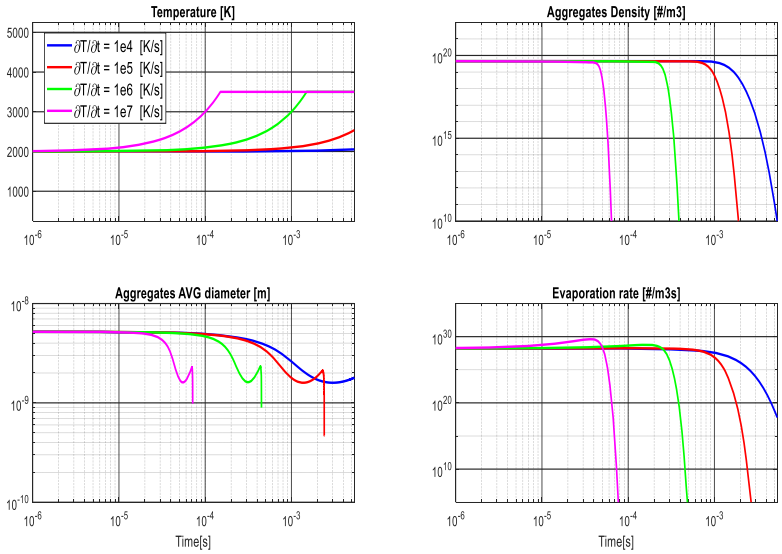


*Figure 4 – Nodal method: Time evolution of the main characteristics of the particles population at four different temperature gradients.*

The evolution in time of the main characteristics of the population for the sectional model alone is shown in Figure 3 and Figure 4; furthermore, in Figure 5 it is possible to see the time development of the PSD. At the very beginning, the only effect of evaporation is to reduce the mean diameter of the population while the total density (i.e. the total number of particles) remains constant. After a short period of time -which depends on the evaporation rate – the smaller particles start to evaporate completely and therefore the total number of particles begins to decrease. As expected, the three cases with different temperatures show exactly the same trend, the only difference

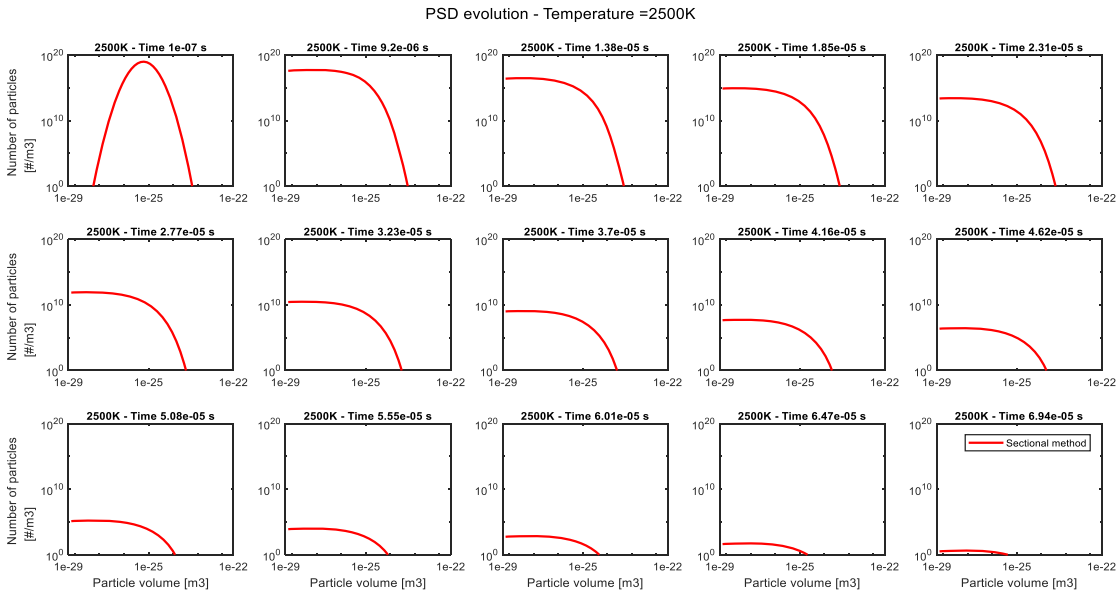


*Figure 5 - Nodal method: Particle Size Distribution evolution in a logarithmic scale at a constant temperature of 2500 K*

between them being the velocity of evaporation and therefore the time scale, as can be seen from Figure 3 and Figure 4; the same can be said for the cases with different temperature gradients.

In figures from Figure 6 to Figure 9 it is shown a comparison between the results obtained with the nodal model and the method of moments with the additional term (9) for the dissipation of the nanoparticles; in this comparison, the NM is used as a benchmark for the MoM, since, as stated above, the NM has an higher accuracy and it is already capable of automatically handling the evaporation and dissolution process. With the new term the MoM yields a comparable match with the nodal model: it correctly captures the trend and furthermore, from a quantitative point of view, all the predictions give an absolute error no larger than an order of magnitude both for the particles density and the average diameter; this, given the simplicity of the model, can be considered a good approximation.

Figure 8 and Figure 9 show the time evolution of the PSD during the evaporation for the two different models. The comparison is good for particles of small size whilst the method of moments overpredicts the density of the larger particles. However, this discrepancy was somewhat expected, since the Method of Moments can only represent lognormal distributions. The overall agreement can be considered more than acceptable.

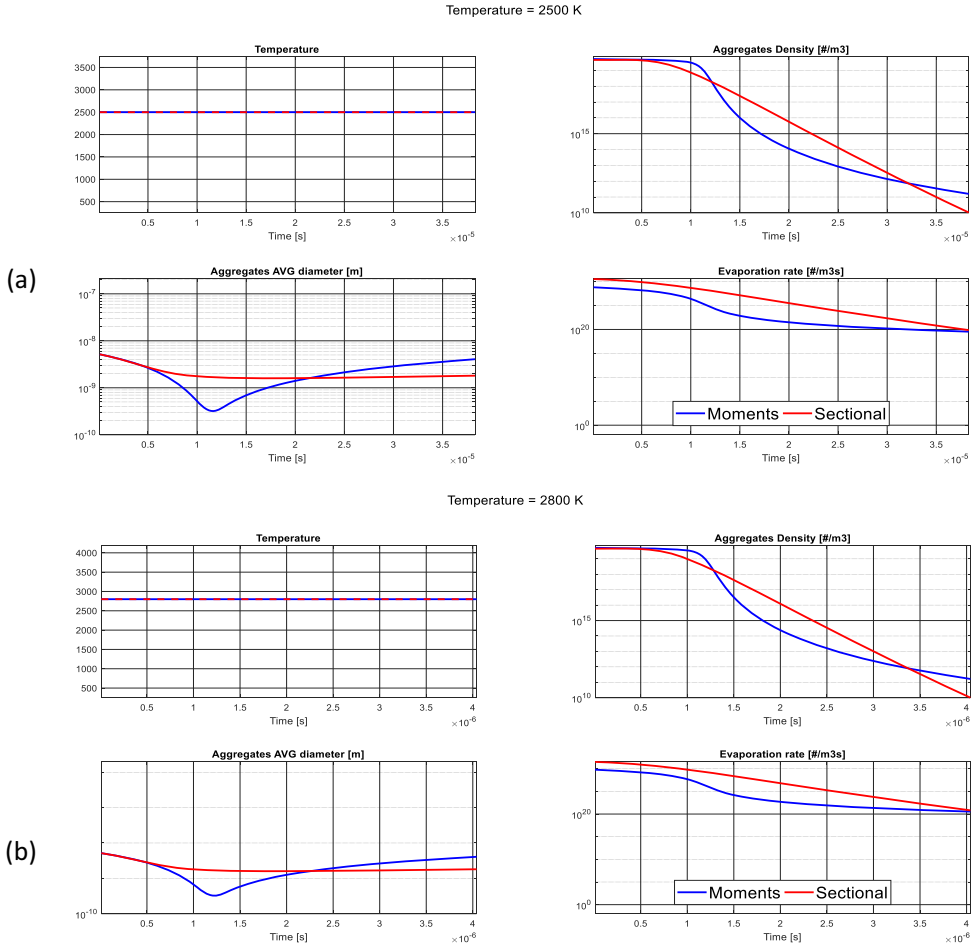


*Figure 6 – Comparison between Nodal Method (red) and Method of Moments (blue): Time evolution of particle characteristics at different imposed temperatures: (a) 2500 K (b) 2800 K*

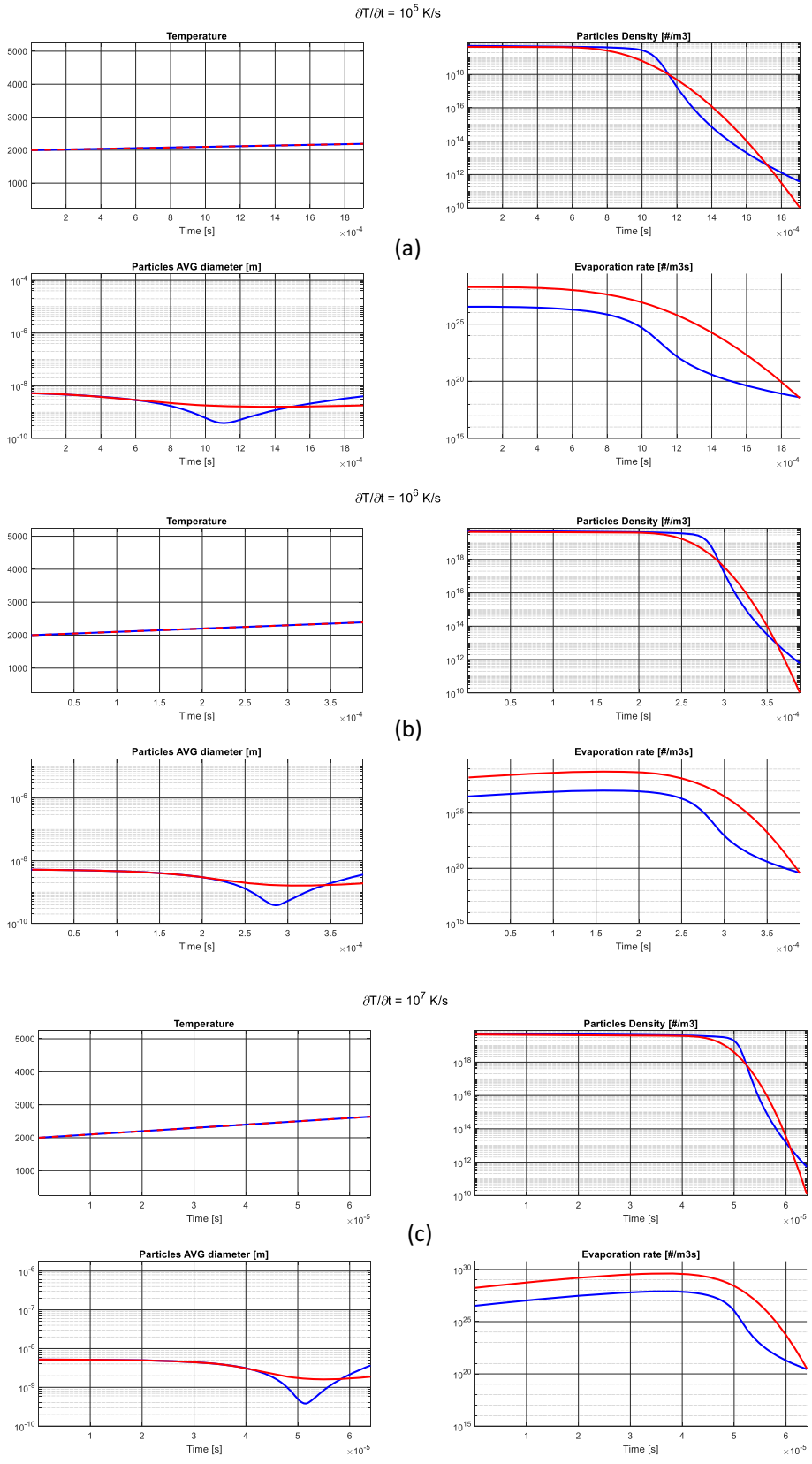


*Figure 7 - Comparison between Nodal Method (red) and Method of Moments(blue): Time evolution of particle characteristics at different imposed temperature gradients: (a) 1e5 K/s (b) 1e6 K/s (c) 1e7 K/s*

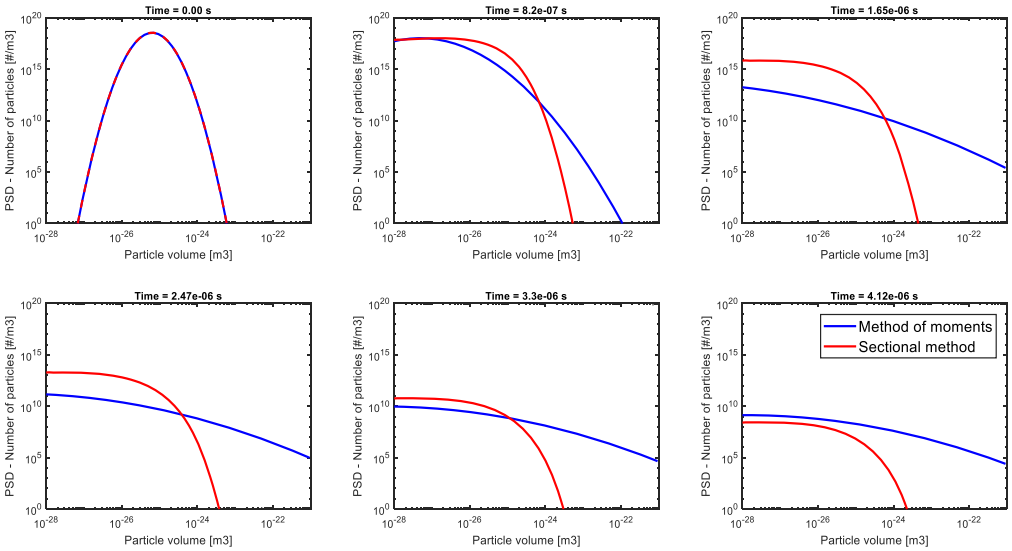


*Figure 8 - Comparison between Nodal Method(red) and Method of Moments(blue) Particle Size Distribution evolution in a logarithmic scale at a constant temperature (2500K)*

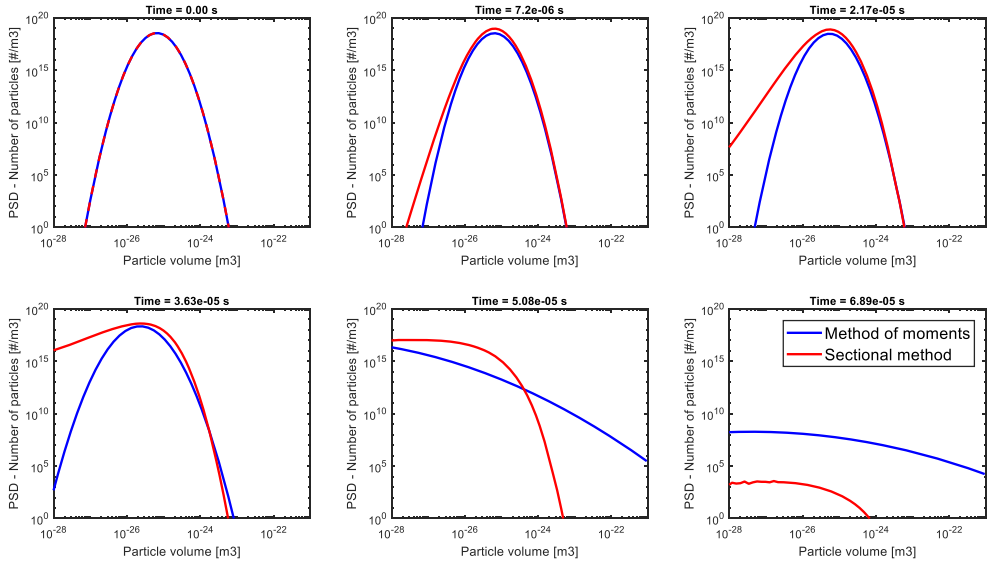


*Figure 9 -- Comparison between Nodal Method(red) and Method of Moments(blue): Particle Size Distribution evolution in a logarithmic scale at a constant temperature gradient ($10^7$ K/s)*

## 4. Conclusions

In this article two simple numerical methods for the simulation of the evaporation of nanoparticles population in a plasma environment were tested and compared; since the method of moments does not include a term to consider the complete evaporation of the nanoparticles a new term was proposed and validated in this work. The results presented show a good agreement between the two models on predicting the time evolution of the main characteristics of the particle population and a lesser but still acceptable agreement – also given the intrinsic limitation of the Method of Moments - on the development of the Particle Size Distribution during the evaporation process.

## 5. Acknowledgements

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