

Cambridge Centre for Computational Chemical Engineering

University of Cambridge

Department of Chemical Engineering

Preprint

ISSN 1473 – 4273

Two Approaches to the Simulation of Silica Particle Synthesis

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submitted: 16th January 2003

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Preprint No. 5



c4e

Key words and phrases. Material Synthesis, Coagulation Dynamics, Population Balances.

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Abstract

In this paper the flame synthesis of silica particles is studied. A model is presented that combines the detailed kinetics of gaseous species including the SiO_2 -precursor and the coagulation process of silica particles in a regime governed by Brownian motion. To describe the particle dynamics of the aerosol synthesis two different numerical techniques are studied; first, the method of moments (MoM), and second, a new stochastic particle method (SPM), which results in a complete representation of the evolution of the particle size distribution function (PSDF). Both methods are economical regarding CPU time, which makes them attractive for modelling. This exact stochastic particle method is used to quantify the numerical error introduced by the closure of the source terms in the method of moments. It is found that the first three moments obtained with the MoM are in good agreement with the results from the SPM. The numerical error increases for moments of higher order. For validation of the model a low pressure flame of H_2/O_2 diluted with Ar and doped with a SiH_4 precursor is simulated and the results are compared with measurements. This comparison shows fair agreement and a result from literature obtained by a sectional method could be confirmed. Finally, the PSDF obtained from the SPM was used to produce a presumed shape fit of a lognormal distribution. Although based on one parameter only the fit shows very good agreement with the exact PSDF.

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1 Introduction

Nano structured materials have drawn attention in recent years. Reducing the size of materials down to a nanometer scale leads to a significant change of their physical and chemical properties. These are the subject of extensive research ranging from fundamental investigations on the chemical and physical qualities of such materials to optimizing engineering routes of nanoparticle synthesis. An established way of producing the smallest particles is by aerosol flame reactors, which allow large scale production of materials such as carbon black or fumed silica. This work focuses on the formation of fumed silica by gas phase synthesis. For optimizing purposes a thorough understanding of the process is crucial and there is a demand for models that incorporate the complex gasphase reactions of the combustion process and particle dynamics in the reactor environment, which are generally characterized by small residence times.

In this paper a model is presented that combines the gas phase kinetics of all reacting species including the SiO_2 -precursor and the coagulation process of silica particles in a regime governed by Brownian motion. To describe the particle dynamics of the aerosol synthesis two different techniques are introduced. The first, the method of moments, was used for the first time by Frenklach [4] describing the particle dynamics in soot formation. In this method evolution equations for the moments of the particle distribution are solved.

The second approach uses a stochastic particle system with an optimized solution algorithm developed in [2] and improved for the special case of nano-particle dynamics in the free molecular regime in [9]. This algorithm does not include any assumptions on the form of the particle size distribution. Only the initial conditions and an expression for the nucleation rate have to be formulated to result in a complete representation of the evolution of the particle size distribution function. The accuracy depends on the numerical parameter N , which is a normalization factor that can be considered to correspond to the volume of a sample. The beauty of this method is that in the limiting case for $N \rightarrow \infty$ it has been proved that the stochastic particle system converges to the solution of the limiting equation, which is in our case the population balance equation consisting of the Smoluchowski equations with an additional source term describing particle nucleation. To achieve convergence for the first 2 moments the approximation parameter N has to be set to 1000. This means one single run takes about 8s CPU time for the residence time of the flame studied in this paper. To achieve convergence for the first five moments we set $N = 10000$, which leads to a CPU time in the order of a minute. The efficiency of the algorithm has been investigated in detail in [9]. The introduction of the majorizing kernel leads to a reduction in complexity from order N^2 to order N , which can be considered to be a significant improvement over the standard direct simulation Monte Carlo algorithm introduced by Gillespie [7].

The described methods are validated by comparison to experimental and numerical results published by Lindackers *et al.* [14]. The tested system is a low pressure

flame reactor in which an Ar diluted H₂/O₂ flame was doped with a SiH₄ precursor. Simulation results are compared and used to find and an appropriate presumed shape PSDF to combine the advantages of the Method of Moments (computational speed) with the ability to resolve the entire particle size distribution.

2 Model

2.1 Gasphase

An accurate description of the flame structure is important for the prediction of particle formation. Therefore the gasphase reactions were described by a combined mechanism, consisting of a detailed H₂/O₂/Ar- and a skeletal SiH₄/O₂ reaction scheme [14]. The species profiles for the laminar premixed flame in steady state were computed using the PREMIX code [13].

2.2 Particle Formation and Particle Dynamics

In the nucleation process new particles are formed from matter that is not in a particulate state [10]. The actual process is still a matter of research; within this work the existing theory is adopted. In our test case silica powder is generated from the precursor SiH₄ by high temperature reactions. SiO₂ is formed by reactions which are driven by a detailed representation of the gas-phase kinetics. This reaction mechanism includes a detailed scheme for the H₂/O₂-reactions and the precursor species. The common approach to describe the transition from gaseous to condensed solid state is given in [18], [17], [12] or [14]. The combustion product SiO₂ is considered to become the smallest stable member of the particle representation. Hence the rate of particle formation is directly coupled to the gas phase production rates of SiO₂. A population balance equation for N_i can be written as:

$$\dot{N}_i = \frac{dN_i}{dt} = J\delta_{i^*} + \frac{1}{2} \sum_{j=1}^{i-1} \beta_{j,i-j} N_j N_{i-j} - \sum_{j=1}^{\infty} \beta_{i,j} N_i N_j, \quad (2.1)$$

where N_i represents the number concentration of particles formed of i SiO₂ molecules. The first term on the RHS is a source term corresponding to the formation of new particles. J is the production rate (e.g. a chemical reaction rate) and i^* stands for the size of the smallest stable particle. RHS terms two and three were formulated by Smoluchowski [19]; they describe the coagulation of particles. An expression for the collision frequency $\beta_{i,j} = \alpha\beta_{i,j}^\circ$ in the free molecular regime was derived earlier and is stated here while referring to [6] and [15] :

$$\alpha = \sqrt{\frac{6kT}{\rho}} \left(\frac{3m_1}{4\pi\rho} \right)^{\frac{1}{6}} \quad (2.2)$$

$$\beta_{i,j}^{\circ} = \left(\frac{1}{i} + \frac{1}{j} \right)^{\frac{1}{2}} \left(i^{\frac{1}{D_f}} + j^{\frac{1}{D_f}} \right)^2. \quad (2.2b)$$

Here k is the Boltzmann constant, T the temperature, ρ the density of the particles and m_1 the mass of the monomer unit; in our case an SiO_2 molecule. The indices i and j refer to the particle size, i.e. the number of monomer units making up a particle.

3 Two numerical approaches

3.1 Method of Moments

An accurate and computationally inexpensive way to describe the Smoluchowski equations was introduced by Frenklach [3], [4], [5]; the method of moments. It was utilized in various papers on the modelling of soot formation. Rather than solving the equations for all particle size classes this method considers equations for the moments of the size distributions, where the r th-Moment is defined as

$$M_r = \sum_{i=1}^{\infty} m_i^r N_i \quad r = 0, 1, \dots, \infty \quad (3.1)$$

with m_i denoting the mass of one particle of class i . The total particle number density is expressed by the **zeroth moment** M_0

$$M_0 = \sum_{i=1}^{\infty} N_i = N \quad (3.2)$$

which is used to define **reduced moments** μ_r according to:

$$\mu_r = \frac{M_r}{M_0}. \quad (3.3)$$

The first reduced moment μ_1 is a measure for the mean of the particle distribution, i.e. the mean mass of one particle in the ensemble, an important quantity, which allows comparison with measured data.

The method of moments describes dynamics of particle coagulation by moment evolution equations. Their form depends on the specified problem and the transport operator \mathcal{L} denotes the considered case, which can be simple evolution in time or spatially evolving processes including convection and diffusion. The transport

equations for the moments M_r are:

$$\mathcal{L}(M_0) = J + \frac{1}{2} \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} \beta_{i,j} N_i N_j \quad (3.4)$$

$$\mathcal{L}(M_r) = J + \frac{1}{2} \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} ((i+j)^r \beta_{i,j} N_i N_j) - \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} (i^r \beta_{i,j} N_i N_j) \quad , r = 2, \dots, \infty \quad (3.5)$$

where $\mathcal{L}(M_1) = J$ follows from mass conservation. The model applied within this study accounts for nucleation of particles J as a source term which is linked directly to gas-phase kinetics, i.e. the production rate of SiO_2 . The coagulation of particles is described by the Smoluchowski equations, which are rewritten in terms of the moments of the particle size distribution (3.1) resulting in the source terms of the moment evolution equations due to coagulation in (3.4-3.5).

The collision frequency $\beta_{i,j}$ for this work was derived earlier and is given in equations (2.2). Introduced in (3.4-3.5), the coagulation terms cannot be reduced because the expression $(i+j)^{\frac{1}{2}}$ does not allow further simplification. Based on the Method II in [4], where the authors proposed a interpolation scheme between assigned grid functions, a similar expression $\langle \phi_{x,y} \rangle$ is introduced:

$$\langle \phi_{x,y} \rangle = \alpha \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} (i+j)^{\frac{1}{2}} \left(i^{\frac{1}{D_f}} + j^{\frac{1}{D_f}} \right)^2 i^{x-\frac{1}{2}} j^{y-\frac{1}{2}} n_i n_j, \quad (3.6)$$

where α was defined in eq. (2.2) and $n_i = N_i/N$ denotes the number of particles of size class i normalized with the sum of all particles. $\langle \phi_{x,y} \rangle$ is calculated by l^{th} -order logarithmic Lagrangian interpolation between equidistant grid functions ${}^l f_{x,y}$ of the form

$${}^l f_{x,y} = \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} (i+j)^l \left(i^{\frac{1}{D_f}} + j^{\frac{1}{D_f}} \right)^2 i^{x-\frac{1}{2}} j^{y-\frac{1}{2}} n_i n_j. \quad (3.7)$$

The functions ${}^l f_{x,y}$ are obtained by another logarithmic Lagrangian interpolation scheme between the non-negative integer reduced moments μ_r . The accuracy of the methods of moments can be adjusted by the order of the applied interpolation schemes. The performance of the method of moments with respect to accuracy and computational costs compared to the stochastic particle method described next is one objective of this work.

3.2 Stochastic Particle Method

To find the solution to the population balance equation (2.1) we use a stochastic particle method. The particle size distribution is approximated by a stochastic particle system, in which the particle sizes are stored in an array.

Each event (either one particle being formed or one coagulation taking place) is dealt with individually; the waiting time between each event (also known as the interval

of quiescence) is an exponentially distributed random variable that depends on the current state of the system [8].

The event that occurs after this waiting time (either particle inception or coagulation) is chosen probabilistically according to the relative rates of the two processes; furthermore, if coagulation is chosen, two particles, of sizes i and j , are chosen probabilistically according to the relative rates of coagulation, given by $\beta_{i,j}$. The stochastic particle system is then updated accordingly.

For more efficient generation of the waiting time parameter and the particle indices, we follow the method described in [9], that of majorant kernels and fictitious jumps. The general simulation algorithm we use is given as follows:

1. Generate the initial state of the stochastic particle system. This is chosen so as to approximate the real initial particle size distribution.
2. Wait an exponentially distributed time step τ with parameter derived from the total rates of coagulation and inception
3. With probability based on the relative total rates of coagulation and inception choose either step 4 or step 5.
4. Perform a source step, i.e.
 - (a) Add a particle of size 1 to the system.
 - (b) Go to step 2.
5. Perform a coagulation step, i.e.
 - (a) Choose particles of sizes i and j according to the probabilities given by the majorant kernel.
 - (b) If the coagulation step is to be real, remove the particles of sizes i and j and add a particle of size $i+j$ to the stochastic particle system. Otherwise the interaction is fictitious, i.e. nothing changes.
 - (c) Go to step 2

4 Results

The population balance given in (2.1) was solved using the method of moments and the stochastic particle method for constant $\alpha = 1$ and $J = 0.5$. In **Fig. 1** the resulting moment evolutions are plotted for the first six moments. The SPM converges towards the exact solution of equation (2.1) using approximation parameter $N = 10^6$. The upper and lower bounds express the confidence bands that include 99.9% of all solutions. The Method of Moments can cope with the exact solution for the moments 0 - 2 and in general for low coagulation times. The higher moments are predicted incorrectly due to increasing interpolation errors.

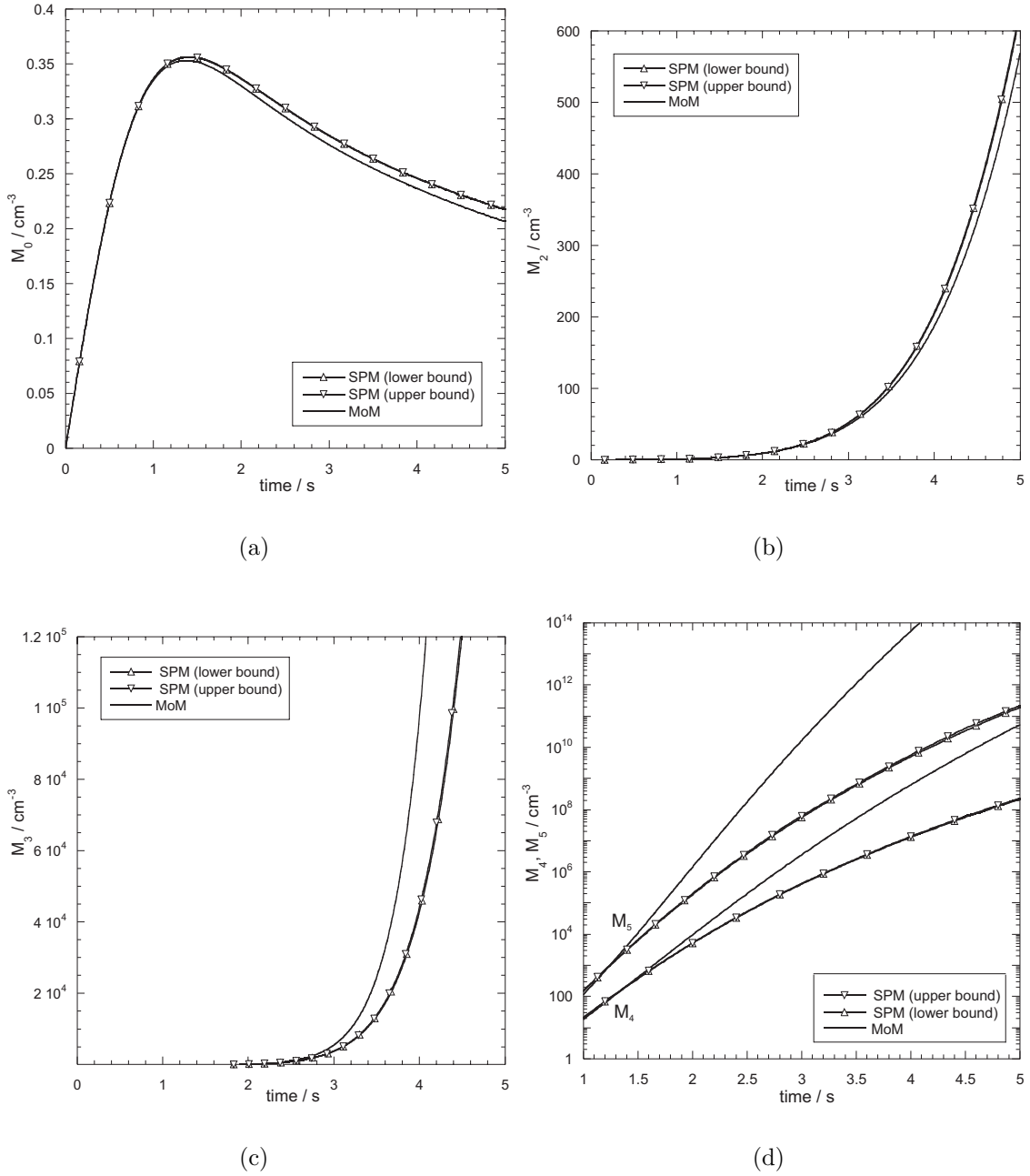


Figure 1: Comparison of SPM and MoM for $D_f = 2.1$, $\alpha = 1$ and zero initial concentration

The composition of a non-reacted gas mixture is given in **Table 1**. The gas has a temperature of 305K and enters a low pressure flame reactor with a velocity of 1.44m/s. The species profiles were computed at the pressure level of the combustion chamber, $p = 30$ mbar. Heat losses were accounted for by applying a temperature profile throughout the post flame zone [11]. Based on the species profiles shown in **Fig. 2** the particle formation was computed in a postprocessing step employing a

Table 1: *Composition of non-reacted mixture.*

Molar Ratio	H ₂ /O ₂	Ar/(H ₂ + O ₂)	SiH ₄ /(H ₂ +O ₂ +Ar)
	1.69	1.36	0.000262

Lagrangian view of particles in a reference volume that propagates along the flame. The production rate of SiO₂ exhibits a significant peak early in the reaction zone, which means that the particle formation process is located in the zone near the flame front. The post flame zone and the areas downstream the chamber are governed only by coagulation processes. The evolution of the mean particle mass is shown in **Fig. 3** using the Method of Moments and the Stochastic Particle Method. The results for both methods correspond very well to the numerical investigations in [14]. The discrepancy to the measured data is explained by the fact that the particles were ionized during the experiments, which increased the coagulation probability. This is thoroughly discussed in [14].

4.1 Particle Size Distributions

The Stochastic Particle Method, although slower than the Method Of Moments, has the benefit of being able to provide a complete statistical description of the particle population at any point in time. This can be used to obtain a very accurate approximation of the solution of (2.1). It is common, while trying to solve the population balance equation, to use an assumed shape probability density function (PDF) for the particle size distribution. These assumed shapes include monodisperse [16] and lognormal [20], and this second case is the one we examine; we try to find a fit for the distributions obtained from stochastic simulation of the test case described above.

The lognormal distribution is given as:

$$f_X(x) = \frac{1}{Bx\sqrt{2\pi}} \exp\left(-\frac{1}{2}\left(\frac{\ln x - A}{B}\right)^2\right) \quad (4.1)$$

where A and B are parameters describing the location and scale of the distribution. From this distribution, the following relationships (among others) can be obtained:

$$E(X) = \exp\left(A + \frac{B^2}{2}\right) \quad (4.2)$$

$$\text{var}(X) = \exp(2A + B^2) (\exp(B^2) - 1) \quad (4.3)$$

$$\text{Mode} = \exp(A - B^2) \quad (4.4)$$

and one has a choice of which two characteristics of the distribution to use to select the parameters A and B in order to obtain a fit for the particle size distribution.

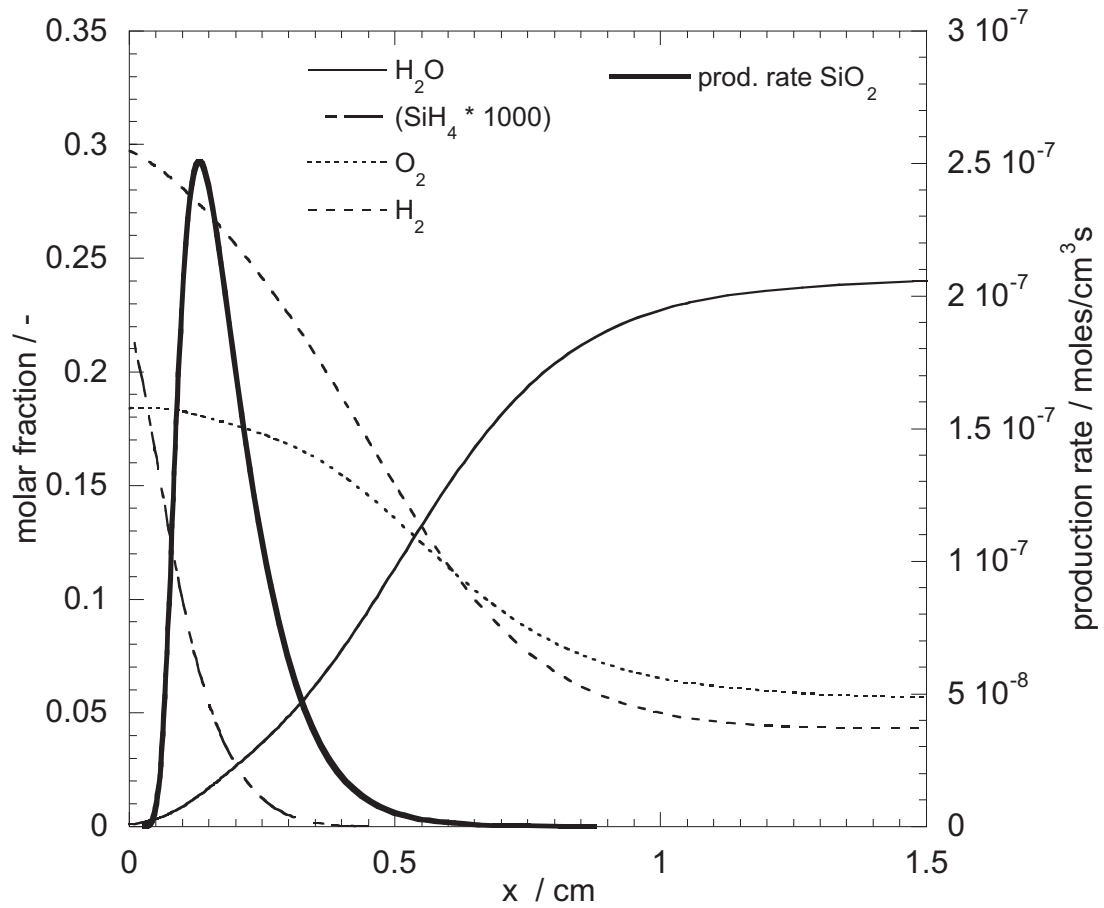


Figure 2: Molefraction profiles of major gas-phase species and production rate of SiO₂.

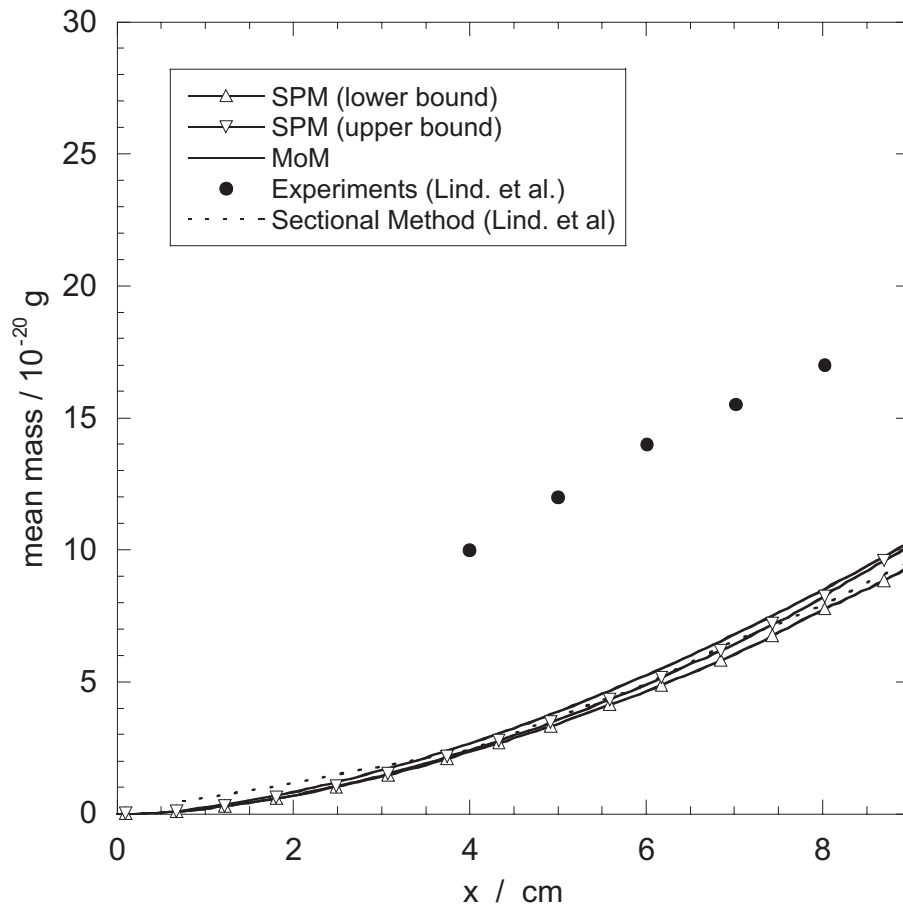


Figure 3: Mean particle mass as a function of the flow coordinate x for the Method of Moments (MoM) and the Stochastic Particle Method (SPM). The discrepancy to the measurements is explained by the fact that the ionization of the particles in the experiments are not accounted for in the model.

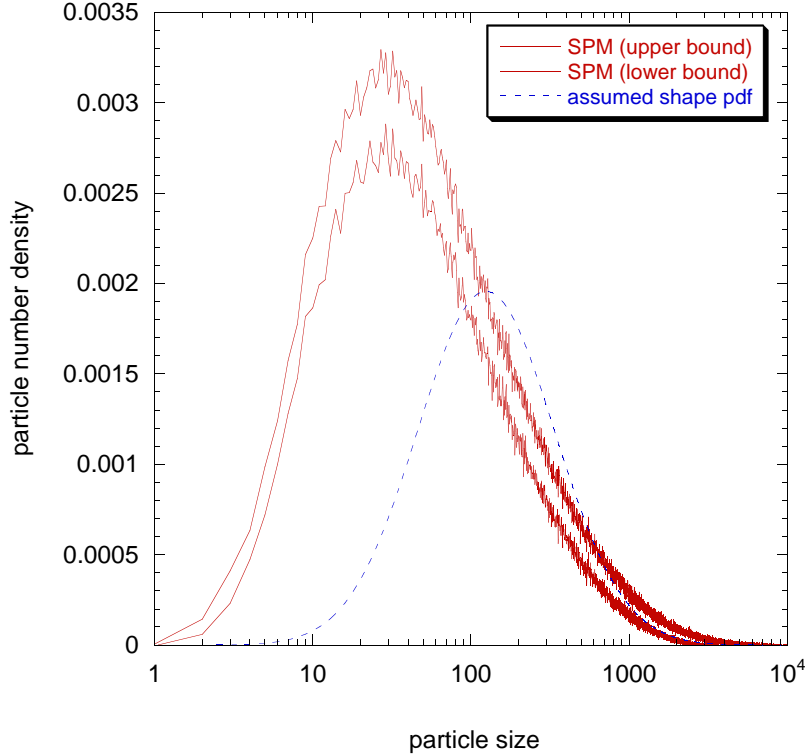


Figure 4: Comparison of the PSD obtained from stochastic simulation with an assumed shape lognormal PDF. The parameters for the assumed shape PDF were obtained from the expectation and variance of the distribution as $A = 5.818$, $B = 0.996$.

Taking the first two moments of the distribution (easily obtainable by using the Method Of Moments) to determine A and B from the expectation and the variance results in an assumed shape PDF that does not match up well with the particle size distributions obtained from the Stochastic Particle Method (see **Fig. 4**).

An alternative method is to use the mean and the mode of the distribution. This results in a much better fit, but requires knowledge of the location of the peak of the distribution, which is not available experimentally or from the Method Of Moments. However, it turns out from applying this method at various values of t that the **parameter B remains approximately constant**, in our case at a value of 1.37. Thus, there is one remaining parameter to be determined, which can be estimated from the expectation of the particle size distribution, which in turn can be obtained from experiments or from the Method Of Moments.

In **Fig. 5**, the particle size distribution obtained from stochastic simulation is compared with the assumed shape lognormal PDF using:

$$B = 1.37, \quad A = \ln(E(X)) - \frac{B^2}{2}. \quad (4.5)$$

This method even predicts closely the form of the particle size distribution at early times, when the lognormal form is not yet apparent and a peak is not observed. In

this case, the lognormal distribution with the parameters obtained as above needs to be renormalised to account for the fact that we do not encounter any particles of size less than one. (See **Fig. 5(a)**)

At the exit of the burner (distance co-ordinate = 90mm) the comparison of simulated and assumed shape PDFs is shown in **Fig. 5(d)**. Good agreement is still obtained.

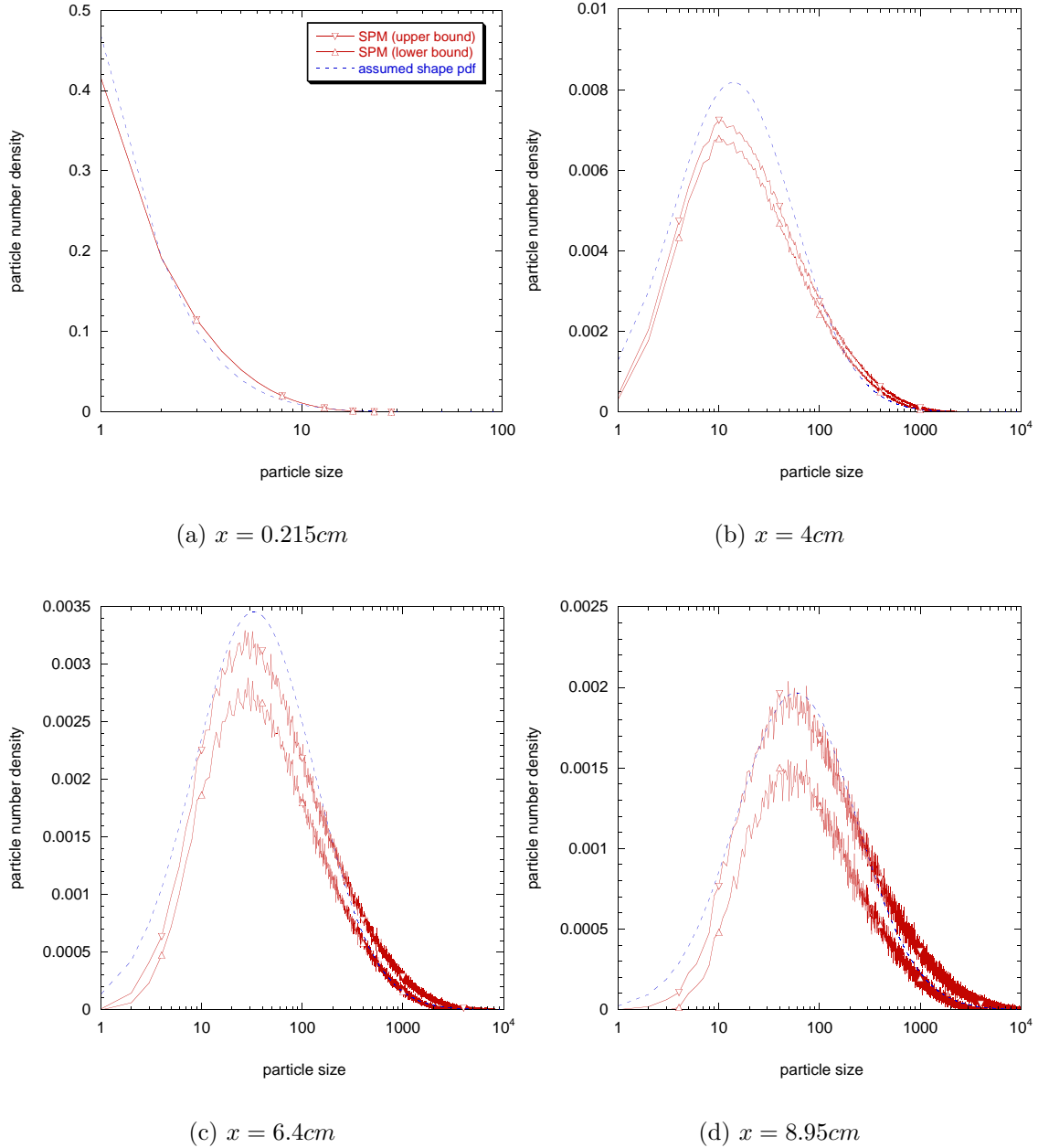


Figure 5: Comparison of SPM and lognormal fit for different heights above the burner

It should be noted that for very early times, when particle inception is still occurring, this method does not give such a good fit; indeed it seems only to work in the case

where coagulation is the only mechanism occurring. This numerical observation of a self preserving lognormal distribution provides further evidence of a phenomenon that has long been observed for pure coagulation processes but that has not been fully explained (see [1] for a mathematical examination).

5 Conclusion

A model has been studied combining detailed kinetics of gaseous species including the SiO_2 -precursor and the coagulation process of silica particles in a low pressure regime, which is governed by Brownian motion. To describe the particle dynamics of the aerosol synthesis two different techniques were applied. The Method of Moments allows accurate predictions of distribution characteristics such as the mean and variance, while at the same time being exceptionally economical. The second approach uses a new stochastic particle system that results in a complete representation of the evolution of the PSDF, which has not been feasible by any other approach so far. Furthermore, the optimized stochastic algorithm developed in [9] proved to be very effective regarding CPU time reduction.

Both methods were able to reproduce measured and numerical data very well. The PSDF obtained from the stochastic method was used to produce a presumed shape fit of a lognormal distribution, which depends on only one parameter and still shows very good agreement with the results from the SPM. This simplicity of the PSDF is quite remarkable and incorporated into the Method of Moments this fitting has the potential to become a powerful tool in engineering models.

6 Acknowledgements

The authors gratefully acknowledge financial support by *Kompetenznetz Verfahrenstechnik Pro 3* (DG) and the *EPSRC*, grant number 302275 (MG).

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