Introduction of a simple Markov chain particle growth model

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Introduction

For the simulation of coagulation simple models can reproduce the qualitative behaviour of the particle size number distribution of nanoaerosols. A simple Markov chain model has been implemented with a Mathcad® simulation and a comparison with the nodal GDE (general dynamics equation) code of Prakash *et al.* (2003) has been made.

Markov chain model

The Markov chain model makes use of the transition probabilities and allows for growth or decay of particles for the whole particle size distribution. The advantage in the simple Markov chain is that only the probability matrix and the initial concentration is necessary to calculate the following state. The probability matrix can be simplified further by taking the coagulation constant. The preceding size distribution is independent due to the Markov chain relation. Each state as a function of time can be gained by a matrix potency (Durett 1999, Heiden et al. 2004).

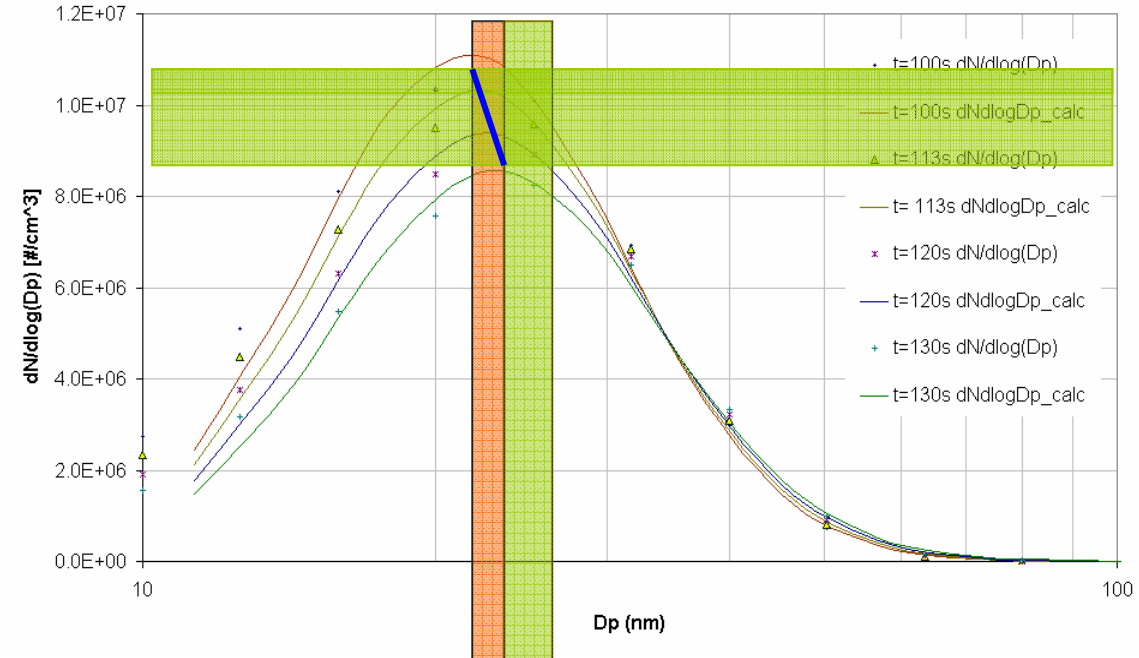

figure 1

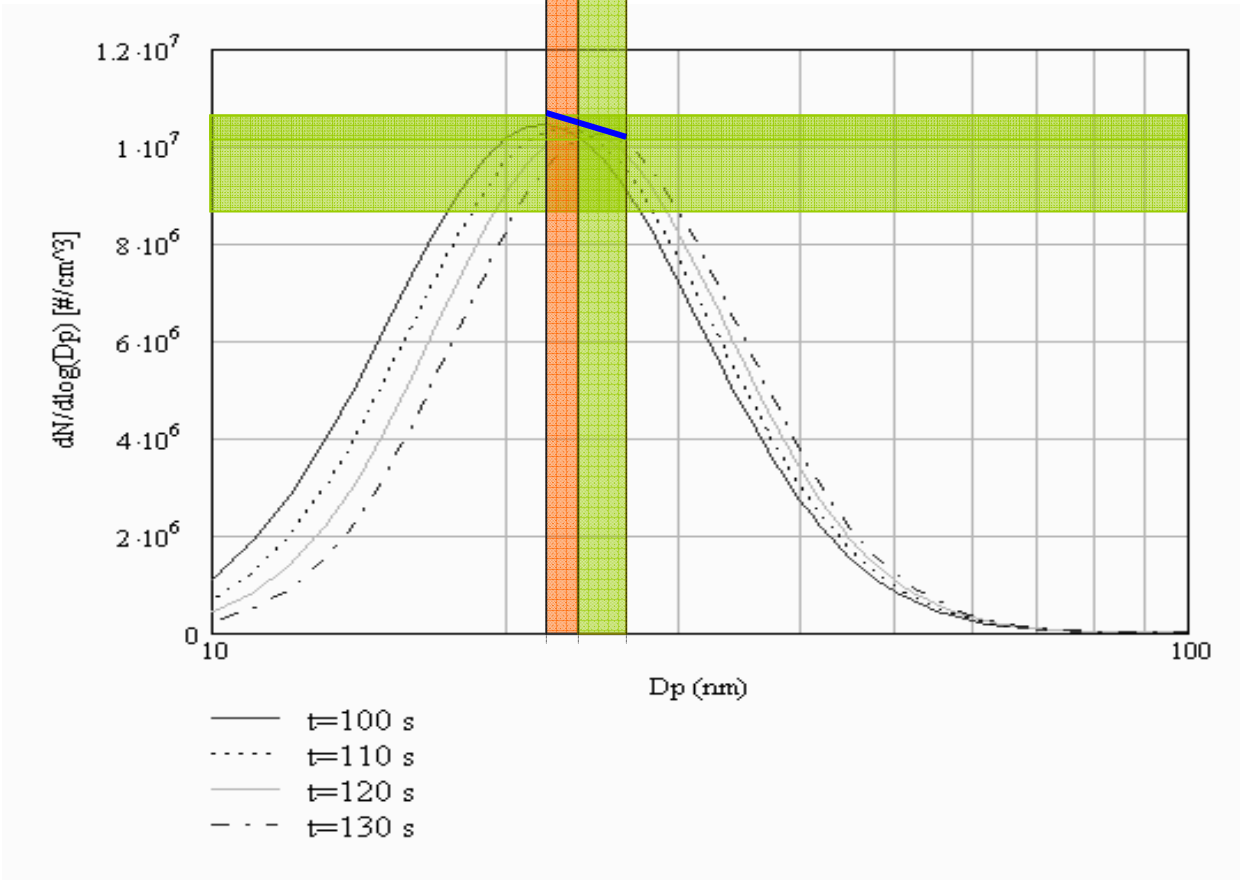

figure 2

In figure 1 a simulation with the nodal GDE code (Prakash *et al.* (2003) is shown in figure 2 the Markov chain model presented for the same initial state (t=100s) with the introduced Markov chain model is shown.

Formulation of the model

The application of the Markov chain can be imagined as stochastic process where the particles enter in a flow through the matrix. Primary particles enter and build small aggregates. The primary particles "diffuse" from smaller to bigger aggregates, till they leave at the upper end of the observation window. In the simplified case the growth is described by the diagonal and the above diagonal elements only.

The Markov chain of a sequential reaction of three chemical species A, B, C can be described by four transition coefficients (velocities, reaction rates).

$$A \underset{k_{ba}}{\overset{k_{ab}}{\rightleftharpoons}} B \qquad B \underset{k_{cb}}{\overset{k_{bc}}{\rightleftharpoons}} C \qquad \textbf{equation 1}$$

In analogy to the chemical reaction equation 1 can be thought in the dimension of the quantities number concentrations and size for the particle growth. Each section of a particle number size distribution, an area of a certain particle diameter width multiplied by the specified number is equivalent to one chemical species in terms of a diameter fraction here called *particle diameter concentration*. Instead of the reaction rates the probability that one state changes to the other state (one particle diameter concentration changes to another) can be taken. This is shown in equation 2 for the probabilities p_i and the species A, B, C for continuous growth. Each species has a probability to grow. The probability to grow from A to B is p_1, the probability to grow from B to C is p_2.

$$A \underset{P_3}{\overset{P_1}{\Longleftrightarrow}} B \underset{P_4}{\overset{P_2}{\Longleftrightarrow}} C \qquad \textbf{equation 2}$$

$$\left(\bar{A}\ \bar{B}\ \bar{C}\right) = (A\ B\ C)\cdot\begin{pmatrix} 1-p_1 & p_1 & 0 \\ 0 & 1-p_2 & p_2 \\ 0 & 0 & 1 \end{pmatrix}$$

Each species is in the transformed imagination a *particle diameter concentration* $c_{i,}$ which corresponds to the particle number size distribution as a whole. The particle diameter concentration for three species is shown in equation 3. When we pick out one particle with one diameter, then the growth process can be described by the addition of another particle to a bigger particle. In the case we have one constant primary particle this process can be described in terms of a stochastic coagulation by the DLA (diffusion limited aggregation) model (e.g. Jullien and Botet (1987)). As diameter change is not linear with growth, a time correction has to be considered with proceeding growth, which is in the simple model according to each neighbor size, i.e. in the diagonal and the above and below diagonal elements of the probability matrix, which corresponds to the time evolution of the particle growth.

In equation 3 the properties of the Markov chain can be seen for particle distribution steady state, growth and decay. For the steady state the above and below diagonal elements are nonzero. The probability $p_{i,j}$ is the probability to change from the state i to the state j. The states correspond to the *particle diameter concentration* classes. The above diagonal elements are meaning that growth occurs the below diagonal elements the same with decay. The process is in terms of the model reversible.

steady state:

$$\left(\overline{c_0}\ \ \overline{c_1}\ \ \overline{c_2}\right) = \left(c_0\ \ c_1\ \ c_2\right)\cdot\begin{pmatrix} 1-p_{1,2} & p_{1,2} & 0 \\ p_{2,1} & 1-p_{2,1}-p_{2,3} & p_{2,3} \\ 0 & p_{3,2} & 1-p_{3,2} \end{pmatrix}$$

growth:

$$\left(\overline{c_0}\ \ \overline{c_1}\ \ \overline{c_2}\right) = \left(c_0\ \ c_1\ \ c_2\right)\cdot\begin{pmatrix} 1-p_{1,2} & p_{1,2} & 0 \\ 0 & 1-p_{2,1} & p_{2,3} \\ 0 & 0 & 1-p_{3,4} \end{pmatrix}$$

equation 3

decay:

$$\left(\overline{c_0}\ \ \overline{c_1}\ \ \overline{c_2}\right) = \left(c_0\ \ c_1\ \ c_2\right)\cdot\begin{pmatrix} 1-p_{1,0} & 0 & 0 \\ p_{2,1} & 1-p_{2,1} & 0 \\ 0 & p_{3,2} & 1-p_{3,2} \end{pmatrix}$$

In a further step equation 3 can be transformed in a more simple form in equation 4. Assuming reversibility the transposed elements orthogonal above and below the diagonal are the same, leading to equilibrium. Net growth has to give a net difference. The assumption of DLA simplifies the model in that sense the each probability of one to the other is the same. The probability of one particle to grow into one of the next size class can be regarded as "jumping" of a primary particle to the next bigger particle, or the stochastic attachment of one free particle to agglomerates, which is the definition for the DLA algorithm. So the results for these numerical investigations should also be applicable to the simple Markov chain model.

steady state:

$$\left(\overline{c_0}\ \ \overline{c_1}\ \ \overline{c_2}\right) = \left(c_0\ \ c_1\ \ c_2\right)\cdot\begin{pmatrix} 1-p_{1\circ} & p_{1\circ} & 0 \\ p_{1\circ} & 1-p_{2\circ}-p_{1\circ} & p_{2\circ} \\ 0 & p_{2\circ} & 1-p_{2\circ} \end{pmatrix}$$

growth:

$$\left(\overline{c_0}\ \ \overline{c_1}\ \ \overline{c_2}\right) = \left(c_0\ \ c_1\ \ c_2\right)\cdot\begin{pmatrix} 1-p_{1\circ} & p_{1\circ} & 0 \\ 0 & 1-p_{2\circ} & p_{2\circ} \\ 0 & 0 & 1-p_{2\circ} \end{pmatrix} \qquad \textbf{equation 4}$$

decay:

$$\left(\overline{c_0}\ \ \overline{c_1}\ \ \overline{c_2}\right) = \left(c_0\ \ c_1\ \ c_2\right)\cdot\begin{pmatrix} 1-p_{1\circ} & 0 & 0 \\ p_{2\circ} & 1-p_{2\circ} & 0 \\ 0 & p_{2\circ} & 1-p_{2\circ} \end{pmatrix}$$

Difficulties may arise for the exact application for two reasons:

- The DLA algorithm is only an approximation for growth
- The time diameter dependency is in general more complicated due to different possible particle size shapes inherent to different particle properties like e.g. liquid/solid phase.

As a result in equation 5 the general equation in its implicit form is given with c(j) the particle diameter concentrations for the classes j, and in equation 6 M(n) the general probability matrix for the classes j=1..n, both given in its programmatic Mathcad® 11 definition form, following from the generalization of equation 4 .

$$c^{\langle j+1\rangle} = M^{T}\cdot c^{\langle j\rangle} \qquad \textbf{equation 5}$$

In equation 4 the p1=p1° and p2=p2°, which depicts the growing or decaying *particle diameter concentration* probability.

$$
\begin{aligned}
M(n) := \;& \text{for } i \in 0..n-1 \\
& \quad \text{for } j \in 0..n-1 \\
& \quad\quad \text{if } (j = i) \wedge (i \neq 0 \wedge i \neq n) \\
& \quad\quad\quad M_{i,j} \leftarrow (1 - p_1 - p_2) \\
& \quad\quad\quad M_{i,j+1} \leftarrow (p_1) \quad \text{if } j \leq n-2 \\
& \quad\quad\quad M_{i,j-1} \leftarrow (p_2) \\
& \quad\quad M_{i,j} \leftarrow 1 - p_1 - p_2 \quad \text{if } i = j = 0 \\
& \quad\quad M_{i,j} \leftarrow 1 - p_2 - p_1 \quad \text{if } i = j = n-1 \\
& \quad\quad M_{i,j} \leftarrow p_1 \quad \text{if } i = 0 \wedge j = 1 \\
& \quad\quad M_{i,j} \leftarrow p_2 \quad \text{if } i = (n-1) \wedge j = i-1 \\
& \quad\quad 0 \quad \text{otherwise} \\
& M
\end{aligned}
$$

equation 6

In equation 7 the generalized solution for the transition probability is given. K is proportionality constant. $\kappa_{i,j}$ is the velocity of growth for *particle diameter concentration* class i to j, β is the collision rate function as it occurs in the Smoluchowski (1917) equation[1], β° is the corresponding term for the particle decay and δt is the time step considered. In a crude estimation all parameters are taken constant e.g. as average then the equation can be simply calculated.

$$
\begin{aligned}
p1^\circ_j \cdot K = \kappa_{i,j} \cdot \delta t = \beta \cdot c_j \cdot \delta t \\
p2^\circ_j \cdot K = \kappa_{j,i} \cdot \beta \cdot c \cdot \delta t = \beta^\circ \cdot c_j \cdot \delta t
\end{aligned}
$$

equation 7

In further investigations the time dependency that one of morphology, temperature and subsequent diameter dependency can be investigated by modifying the coagulation kernel β (e.g. Heiden et al. 2004).

[1] referring to the GDE

Conclusion

The result of the comparison of the Markov chain model and the nodal GDE code of Prakash *et al.* (2003) is shown in figure 1 and figure 2. Only coagulation was investigated. The nodal GDE code begins with a monodisperse aerosol, which was initialized with 10 nm and a particle number concentration of 10^8 [particles/cm^3]. The self preserving size distribution is reached after 113 s. The Markov chain model is started for synchronization at the same values of the logarithmic size distribution for 100 s. There can be seen a different evolution of the particle diameter with the total number concentration approximately the same for both cases. As Friedlander (2000) states, the experiments and the theory show qualitatively different shapes for tobacco smoke. The theoretical results are similar to the nodal GDE code shown here whereas the Markov chain model comes nearer to the experiments.

The model has been introduced by means of its model construction, and its implementation in the general mathematic tool Mathcad® 11 has been indicated. By means of this simplified rules the calculation effort can be reduced. The particulate growth model is reduced to solving Matrix operations.

Literature

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