Journal of Nanoparticle Research **4:** 61–72, 2002.

A hybrid sectional-moment model for coagulation and phase segregation in binary liquid nanodroplets

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Received 15 June 2001; accepted in revised form 21 November 2001

Key words: collision probability, heterogeneous aerosols, Smoluchowski equation, log-normal distribution

Abstract

We describe a new formulation of the aerosol general dynamic equation (GDE) that incorporates the phase segregation in a binary aerosol. The model assumes that complete phase segregation is the thermodynamically favored state, that no thermodynamic activation energy exists, and that the segregation process is kinetically controlled. We develop a GDE formulation that involves the solution of a distribution function $N_{n,\sigma}(V)$, where $N_{n,\sigma}(V)$ is the number density of aerosols with volume V and n phase domains (which we might think of as enclosures) with an enclosure size distribution characterized by σ. The model improves our earlier efforts (Struchtrup H., M. Luskin & M. Zachariah, 2001. J. Aerosol Sci. 15(3)) which did not account for the enclosure size distribution. The description of the enclosures is based on a moment approach relying on a log-normal distribution (Park S., K. Lee, E. Otto & H. Fissan, 1999. J. Aerosol Sci. 30, 3–16). As with our earlier model, we obtain an increase of the mean number of enclosures per droplet in time, in disagreement to experimental results. The reasons for the disagreement are discussed.

Introduction

The study of aerosol dynamics is often limited to homogeneous, single-component aerosol particles. However, it is becoming increasingly apparent that multi-component aerosol particles are of both industrial importance and an area in need of significant research activity.

We have been involved in a number of multi-component aerosol dynamics studies with heterogeneous aerosol particles. One of our main goals in this research is to study the evolution of the internal state of the aerosol droplets. For example, we have conducted studies on the formation of binary metal oxide systems with application to removal of heavy metals (Biswas & Zachariah, 1997; Biswas et al., 1998) as well as the formation of materials with novel and interesting properties (Ehrman et al., 1998; 1999a,b).

Our initial success in growing interesting microstructures (Zachariah et al., 1995) indicated that further research into the mechanistic aspects of the growth was warranted. In subsequent studies, we have employed both *in situ* interrogation into the formation process (McMillin et al., 1996), multi-component aerosol dynamic modeling (Biswas et al., 1997) and molecular dynamics computation (Zachariah et al., 1996). One of the primary conclusions was that at the high temperatures where these materials are typically grown, nanodroplets are in a liquid like state, and that phase segregation taking place within the

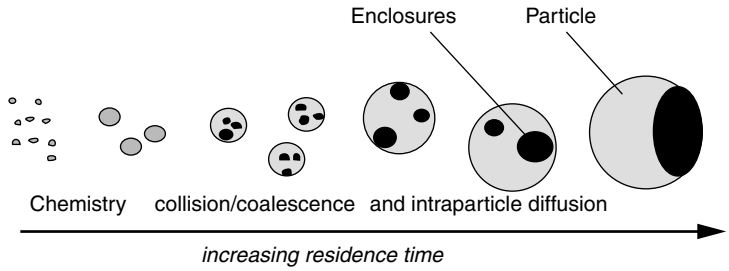

Figure 1. Schematic of the temporal evolution of a two-component aerosol.

nanodroplet was probably limited by transport within the nanodroplet.

In the course of this paper, we shall use the terms minor phase and enclosure interchangeable to refer to the component within each aerosol droplet, and droplet, aerosol when referring to the major phase. The enclosures are considered as an aerosol inside the droplet, where the coagulation takes place due to Brownian motion; both phases are in a liquid state. The temporal evolution of the aerosol phase is schematically depicted in Figure 1. Due to the surface tension the enclosures form spherical shapes inside the aerosol droplets. Obviously, it is not possible to describe the individual enclosures inside individual droplets since the numerical efforts would be tremendous. Therefore we supplement the usual statistical formulation for the droplets, i.e. the Smoluchowski equation, with the statistics of the enclosures.

The parametric model developed in the paper is applied to a binary system, SiO_2/Fe_2O_3, where SiO_2 is the major phase and Fe_2O_3 is the minor phase, for which we have experimental results (Ehrman et al., 1999a,b) see also Figure 2. In the figure, we can see that at short residence times the dark Fe_2O_3 enclosures are larger in number and smaller in size than those observed at later residence times. Our previous model in Struchtrup et al. (2001), however, could not describe this behavior, but gave an increasing number of enclosures per droplet with time. Our goal in this paper is to extend our model (Struchtrup et al., 2001) by incorporating the size distribution of the enclosures into the model in the hope to match the experimental results better.

For the model presented below, the main assumption will be that the enclosures in a droplet are distributed log-normally, a common assumption for the description of the long-time behavior of coagulating particles (Pratsinis, 1988; Park et al., 1999). The collision of

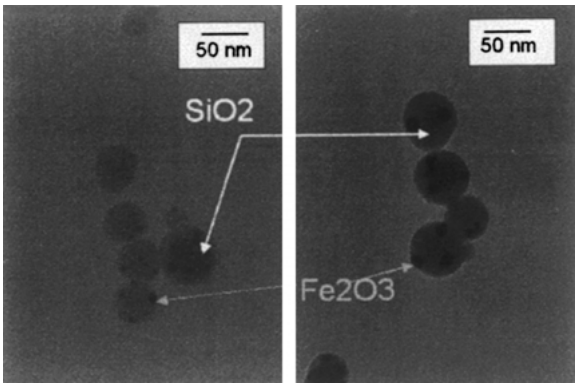

Figure 2. Aerosol droplet with enclosures. The droplets on the left are 'younger'.

two droplets leads to a new distribution of enclosures, which is assumed to be log-normal as well, see the section on 'Droplet collisions and the distribution of enclosures' for a discussion. Furthermore, we assume that the enclosure volume concentration is the same in all droplets (Efendiev & Zachariah, 2001b).

Our main result is a generalized Smoluchowski equation which is solved using a sectional discretization. The problem could also be tackled by means of Monte Carlo (MC) methods (Shah et al., 1977; Kruis et al., 2000; Efendiev & Zachariah, 2001a,b). The disadvantage of the MC approach in comparison to our model are the large CPU times required for the simulation of the droplets and the enclosures inside the droplets. The results in the present paper indicate that one droplet may have several hundreds of enclosures, so that the number of variables (= [number of droplets]∗[number of enclosures in droplet]) is much higher. The advantage of MC is that other collision mechanisms can be incorporated more

easily. It must be emphasized that both methods can only be as good as the underlying models for the collision probabilities for enclosures and droplets. As will become clear in the course of the paper, the disagreement between the simulations and experiments can be traced to the model for enclosure collisions. Indeed, the MC simulations in Efendiev and Zachariah (2001a,b) rely on the same collision probabilities as our present model, and show the same characteristics.

The model will be developed and discussed in the section on 'The generalized Smoluchowski equation'. In the section on 'Reduced models', we shall consider certain limits of our model, which show the relation to our previous work. A more elaborate but simplified model is considered in the section on 'A hybrid model: Updating standard deviation', where we also present some numerical solutions.

The generalized Smoluchowski equation

We consider aerosol droplets which consist of two immiscible components. Due to surface tension, one phase forms sphere-like enclosures inside the aerosol droplets. Due to their Brownian motion, the enclosures collide and coagulate. At the same time, the droplets collide because of their free molecular motion. The coagulation of the droplets and the enclosures are assumed to occur by instantaneous coalescence of spherical particles. Our goal is to determine the distribution of the droplet volumes and the internal state of the droplets as a function of time.

In our previous study (Struchtrup et al., 2001), we considered a model where the internal state of the droplets is described by the number of the enclosures alone. In the present work, our goal is to extend the model by incorporating the size distribution of the enclosures.

Our basic assumption will be that the distribution of the enclosures in each droplet remains log-normally distributed at all times (Friedlander, 2000; Park et al., 1999).

Log-normal distribution

In the log-normal distribution theory for aerosol coagulation, it is assumed that the volume distribution of coagulating particles can be described by a log-normal size distribution at all times. The log-normal distribution is given by

$$n(v) = \frac{1}{3v}\frac{n}{\sqrt{2\pi}\ln\sigma}\exp\left(\frac{\ln^2(v/v_g)}{18\ln^2\sigma}\right), \tag{1}$$

where v_g is the geometric mean particle volume and σ is the geometric standard deviation based on the mean particle radius (Pratsinis, 1988; Park et al., 1999). For the enclosures in an aerosol droplet, $n(v)\,\mathrm{d}v$ is the number of the enclosures with volumes between v and $v + \mathrm{d}v$, and n is the total number of enclosures in that droplet. A monodisperse distribution with enclosures of volume v_g is characterized by $\sigma = 1$.

The moments of the log-normal distribution are easily computed as

$$m_k = \int v^k n(v)\,\mathrm{d}v = n v_g^k \exp\left(\frac{9}{2}k^2 Z\right),$$
$$\text{where } Z = \ln^2\sigma, \quad k = 0, 1, 2, \ldots. \tag{2}$$

The log-normal distribution is characterized by the three quantities n, v_g, and σ, or, alternatively, by the first three moments. These are the total number n, the total volume of the enclosures m_1, and the second moment m_2,

$$\begin{aligned} &m_0 = n, \quad m_1 = n v_g \exp\left(\tfrac{9}{2}Z\right), \\ &m_2 = n v_g^2 \exp(18Z). \end{aligned} \tag{3}$$

Our objective is to find the number density of the heterogeneous droplets of volume V whose enclosure size distribution is log-normal with the given parameters n, v_g, and σ or m_0, m_1, and m_2, respectively.

Throughout this paper, we shall assume that the volume fraction c of the enclosures in the droplets is the same for all droplets initially. Evidently, this means that the concentration will be a constant at all times. Thus, the total volume of enclosures in a droplet, the first moment, is given by

$$m_1 = cV, \tag{4}$$

so that m_1 is not an independent variable. The assumption of constant volume concentration is backed by MC simulations of nucleation and coagulation in two-component aerosols (Efendiev & Zachariah, 2001b): initially, when nucleation prevails, the concentration differs between nuclei. But as soon as coagulation prevails, the concentration of the aerosol droplets shows almost no variance.

Since $\sigma \geq 1$, and therefore $Z \geq 0$, it follows from Eqs. (3) and (4) that

$$m_2 \geq \frac{m_1^2}{m_0} = \frac{(cV)^2}{n}. \tag{5}$$

Evolution of moments in a single nanodroplet

In this section, we consider the evolution of the moments in a single droplet. The enclosures move inside the liquid droplet due to Brownian motion, and coagulate instantaneously when they collide. The distribution of number density for the enclosures $v(t, v) = n(t, v)/V$ obeys the Smoluchowski equation (Friedlander, 2000):

$$\frac{\mathrm{d}v(t, v)}{\mathrm{d}t} = \frac{1}{2}\int_0^v \sigma_\mathrm{B}(u, v-u)v(t, u)v(t, v-u)\,\mathrm{d}u - v(t, v)\int_0^\infty \sigma_\mathrm{B}(v, u)v(t, u)\,\mathrm{d}u, \tag{6}$$

where the appropriate collision kernel for Brownian motion is given by (Pratsinis, 1988; Park et al., 1999)

$$\sigma_\mathrm{B}(u, v) = K_0\left(u^{1/3} + v^{1/3}\right)\left(\frac{1}{u^{1/3}} + \frac{1}{v^{1/3}}\right) \quad \text{with } K_0 = \frac{2kT}{3\mu}. \tag{7}$$

Here, k denotes Boltzmann's constant, T, the temperature and μ, the viscosity of the surrounding media. This is the collision kernel for the continuum regime, where the mean free path of the particles impinging on the enclosure is assumed to be much smaller than the enclosure diameter. The mean free path in the liquid droplet is of the order of the molecule diameter (if not zero), so that this choice is justified for all enclosures.

With the choice of this collision kernel, we ignore the finite size of the droplets. Indeed, the derivation of σ_B includes that enclosures are uniformly distributed in space. The finite droplet size should reduce the collision probability $\sigma_\mathrm{B}(u, v)$ to some extent. Moreover, experimental data suggests a tendency of the enclosures to stay at the edge of the droplets (see Figure 2), implying a surface diffusion of enclosures, see the discussion in Struchtrup et al. (2001).

One might also argue, that the description of the enclosures on statistical terms, i.e. by the Smoluchowski equation, makes sense only, if the number of enclosures is sufficiently large. This criticism can be resolved, however, since the aerosol contains a large number of similar droplets. While the behavior of enclosures in a single droplet may not be well described by a distribution function and the Smoluchowski equation, the behavior of the enclosures in a large number of similar droplets (ensemble) can be described statistically. In this sense, we consider the most likely behavior of enclosures in a droplet.

From the Smoluchowski equation (6) with collision kernel (7) one can derive moment equations for the first moments m_0, m_1, m_2 and close them by means of the log-normal distribution (1), see (Park et al., 1999) for a detailed account. In Park et al. (1999), the authors present an analytical solution for the resulting moment equations. In the following, we shall employ these results in order to determine the coagulation probability of the enclosures. For Brownian coagulation, i.e. in the continuum regime, the evolution of n, the number of the enclosures in a droplet, v_g, the mean geometric volume of the droplet, and $Z = \ln^2\sigma$, σ, the geometric standard deviation, in a droplet of volume V, is given in Park et al. (1999) as

$$n = \frac{n_0}{1 + K_0(1 + \exp[Z_0])(n_0/V)t}, \tag{8a}$$

$$v_\mathrm{g} = v_{\mathrm{g}0}\frac{n_0}{n}\exp\left[\frac{9}{2}(Z_0 - Z)\right], \tag{8b}$$

$$Z = \frac{1}{9}\ln\left[2 + (\exp[9Z_0] - 2)\frac{n}{n_0}\right]. \tag{8c}$$

Here, the quantities with subscript zero refer to the initial values. According to these equations, the number of enclosures, n, is decreasing as one expects. Furthermore, $Z = \ln^2\sigma$ is approaching its stationary value $Z_\mathrm{stat} = \frac{1}{9}\ln 2$, corresponding to a mean standard deviation of $\sigma_\mathrm{stat} = \exp\left[\sqrt{\ln 2/3}\right] = 1.32$.

We shall make use of corresponding equations for the evolution of the moments in the subsequent sections. Denoting the initial values of the moments by k_i and their actual values by m_i, we obtain from (8a) to (8c)

$$m_0 = \frac{k_0}{1 + K_0[1 + (k_2k_0/k_1^2)^{1/9}](k_0/V)t}, \tag{9a}$$

$$m_1 = k_1, \tag{9b}$$

$$m_2 = k_2 + 2k_1^2\frac{k_0 - m_0}{m_0k_0}. \tag{9c}$$

It should be kept in mind that, by Eq. (4), we have $m_1 = k_1 = cV$. Since the zeroth moment $m_0 = n$ is

decreasing in time, and the first moment m_1 is constant, it follows that the second moment is strictly increasing.

Also, it must be noted that m_0 is an integer (the number of enclosures), which cannot be less than 1. It follows that Eqs. (9a)–(9c) are only valid for finite times, i.e. as long as $m_0 \gg 1$.

Droplet collisions and the distribution of enclosures

Next, we consider the coagulation of two droplets with volumes V' and V'', and enclosure distributions $n'(v)$ and $n''(v)$, respectively. The volume of the resulting droplet is $V = V' + V''$, the resulting enclosure distribution is $n(v) = n'(v)+n''(v)$ and the moments of $n(v)$ are obviously given by $m_0 = m'_0 + m''_0$, $m_1 = m'_1 + m''_1$ (or $cV = cV' + cV''$), $m_2 = m'_2 + m''_2$.

For our model, we shall assume that the moments m_0, m_1, m_2 of the new droplet will evolve according to Eqs. (9a)–(9c). Since these solutions of the moment equations rely on the closure by means of the log-normal distribution (1), this assumption is tantamount with the statement that the enclosures are distributed log-normally in the new droplet. In general, however, the resulting distribution $n(v)$ – the sum of two log-normal distributions with different parameters – will not be log-normal. Therefore, the use of the solutions (9a)–(9c) for the evolution of the moments in newly combined droplets must be seen as an approximation.

It is difficult to estimate the error which is introduced by this assumption into the model. As the discussion of our model will show, the disagreement with experimental data can be traced back to inaccurate models for the enclosure collision probability. The choice of a log-normal distribution certainly has some influence, but it seems that the neglect of finite size effects seems to be more important, see the section on 'Relaxation times'.

Smoluchowski equation for droplets and enclosures

Under the assumption of log-normal distributions of the enclosures, the aerosol population can be described by the distribution function $N_{m_0,m_2}(V)$ which is defined such that $N_{m_0,m_2}(V)\,\mathrm{d}V\,\mathrm{d}m_2$ gives the number density of droplets with volumes in $(V, V + \mathrm{d}V)$ and a log-normal enclosure distribution with moments m_0, $m_1 = cV$, and m_2 in $(m_2, m_2 + \mathrm{d}m_2)$.

The volume distribution of droplets with volume V and an *arbitrary* internal state is given by the number density

$$N(t, V) = \sum_{m_0=1}^{\infty} \int_{(cV)^2/m_0}^{\infty} N_{m_0,m_2}(t, V)\,\mathrm{d}m_2. \quad (10)$$

The number density $N(t, V)$ evolves according to the Smoluchowski equation (6) as well, where now the appropriate collision probability for the droplets must be inserted. We consider droplets in the free-molecular regime where the collision probability for droplets with volumes V and U is given by Friedlander (2000):

$$\sigma_{\mathrm{F}}(U, V) = \left(\frac{3}{4\pi}\right)^{1/6} \left(\frac{6kT}{\varrho}\right)^{1/2} \left(\frac{1}{U} + \frac{1}{V}\right)^{1/2} \times \left(U^{1/3} + V^{1/3}\right)^2, \quad (11)$$

where ϱ is the mass density of droplets.

The evolution of the distribution $N_{m_0,m_2}(t, V)$ is due to the coagulation of both, droplets and enclosures. The generalized Smoluchowski equation for the evolution of $N_{m_0,m_2}(t, V)$ can be written as

$$\begin{aligned}
&\frac{\mathrm{d}N_{m_0,m_2}(t, V)}{\mathrm{d}t} \\
&= \frac{1}{2} \int_0^V \sigma(U, V - U) \\
&\quad \times \sum_{k_0=1}^{m_0-1} \int_{k_1^2/K_0}^{m_2-((m_1-k_1)^2/(m_0-k_0))} N_{k_0,k_2}(t, U) \\
&\quad \times N_{m_0-k_0,m_2-k_2}(t, V - U)\,\mathrm{d}k_2\,\mathrm{d}U \\
&\quad \times \left[m_2 \geq \frac{k_1^2}{k_0} + \frac{(m_1 - k_1)^2}{m_0 - k_0}\right] \\
&\quad - N_{m_0,m_2}(t, V) \int_0^{\infty} \sigma(U, V) \\
&\quad \times \sum_{k_0=1}^{\infty} \int_{(cU)^2/k_0}^{\infty} N_{k_0,k_2}(t, U)\,\mathrm{d}k_2\,\mathrm{d}U \\
&\quad + \sum_{k_0=m_0+1}^{\infty} \int_{(cV)^2/k_0}^{m_2} \gamma_{k_i \to m_i}(V) N_{k_0,k_2}(t, V)\,\mathrm{d}k_2 \\
&\quad - \sum_{k_0=1}^{m_0-1} \int_{m_2}^{\infty} \gamma_{m_i \to k_i}(V) N_{m_0,m_2}(t, V)\,\mathrm{d}k_2.
\end{aligned} \quad (12)$$

In this equation, the first term accounts for the gain of droplets with volume V and enclosure moments, m_0,

m_2 due to collisions of droplets with volumes U and $V-U$ and moments k_0, k_2 and m_0-k_0, m_2-k_2, respectively. The limits of integration for k_2 follow from the minimum values for the second moments as given in (5). In particular we have $k_2 \geq k_1^2/k_0 = (cU)^2/k_0$ and $(m_2-k_2) \geq (m_1-k_1)^2/(m_0-k_0) = (c(V-U))^2/(m_0-k_0)$. Since the moments of the colliding droplets are added, this term contributes only for values of the second moment m_2 larger than $k_1^2/k_0 + (m_1-k_1)^2/(m_0-k_0)$.

The second term accounts for the loss of droplets with volume V and moments m_0 and m_2 due to collisions of these with droplets of arbitrary internal state and arbitrary volumes.

The third term represents the gain of droplets with volume V and internal state m_0, m_2 due to coagulation of the enclosures in a droplet with volume V and initial moments k_0, k_2. Similarly, the fourth term represent the loss of droplets with volume V and internal state m_0, m_2 due to the coagulation of the enclosures with any final state k_0, k_2. The quantity $\gamma_{k_i\to m_i}(V)\,\mathrm{d}k_2\,\mathrm{d}t$ denotes the probability that in a droplet of volume V the moments of the distribution of enclosures changes from k_i to m_i $(i = 0, 2)$ during the time $\mathrm{d}t$. The limits of summation for k_0 take into account that coagulation will decrease the number of enclosures while the limits for the k_2-integration follow from the fact that the second moment will be increasing as coagulation proceeds.

Collision probability of enclosures

We shall now determine the probability $\gamma_{k_i\to m_i}(V)\,\mathrm{d}k_2\,\mathrm{d}t$ for the change of the enclosures with moments from $\{k_0, k_2\}$ to $\{m_0, m_2\}$ during $\mathrm{d}t$ from Eqs. (9a)–(9c). The reasoning is similar to the arguments given in Struchtrup et al. (2001). The probability can be written as the product of the probabilities for a change from k_0 to m_0 and for a change from k_2 to m_2, that is

$$\gamma_{k_i\to m_i}(V)\,\mathrm{d}t\,\mathrm{d}k_2 = \gamma_{k_0\to m_0}(V)\,\mathrm{d}t\,\gamma_{k_2\to m_2}(V)\,\mathrm{d}k_2.$$

The first quantity is the inverse mean time for the change of enclosure number from k_0 to m_0. This time can be found by solving (9a) for time, so that

$$\gamma_{k_0\to m_0}(V)\,\mathrm{d}t = \frac{\mathrm{d}t}{t_{k_0\to m_0}} = \frac{K_0}{V}\left[1+\left(\frac{k_2k_0}{k_1^2}\right)^{1/9}\right] \times \frac{k_0m_0}{k_0-m_0}\mathrm{d}t.$$

For given initial values k_0, k_2 and final number m_0 the moment m_2 must assume the value given by (9c) and therefore

$$\gamma_{k_2\to m_2}(V)\,\mathrm{d}k_2 = \delta\left(m_2-k_2-2k_1^2\frac{k_0-m_0}{m_0k_0}\right)\mathrm{d}k_2,$$

where $\delta(x)$ is the Dirac delta function. Thus, the enclosure collision probability reads

$$\gamma_{k_i\to m_i}(V) = \frac{K_0}{V}\left[1+\left(\frac{k_2k_0}{k_1^2}\right)^{1/9}\right]\frac{k_0m_0}{k_0-m_0} \times \delta\left(m_2-k_2-2k_1^2\frac{k_0-m_0}{m_0k_0}\right). \tag{13}$$

The evolution equation for $N_{m_0,m_2}(t, V)$

The substitution of $\gamma_{k_i\to m_i}(V)$ into (12) yields

$$\begin{aligned}
&\frac{\mathrm{d}N_{m_0,m_2}(t,V)}{\mathrm{d}t} \\
&= \frac{1}{2}\int_0^V \sigma(U, V-U) \\
&\times \sum_{k_0=1}^{m_0-1}\int_{(cU)^2/k_0}^{m_2-(c(V-U))^2/(m_0-k_0)} N_{k_0,k_2}(t,U) \\
&\times N_{m_0-k_0,m_2-k_2}(t, V-U)\,\mathrm{d}k_2\,\mathrm{d}U \\
&\times \left[m_2 \geq \frac{(cU)^2}{k_0} + \frac{(c(V-U))^2}{m_0-k_0}\right] \\
&- N_{m_0,m_2}(t,V)\int_0^\infty \sigma(U,V) \\
&\times \sum_{k_0=1}^{\infty}\int_{(cU)^2/k_0}^{\infty} N_{k_0,k_2}(t,U)\,\mathrm{d}k_2\,\mathrm{d}U \\
&+ \frac{K_0}{V}\sum_{k_0=m_0+1}^{\infty}\left[1+\left(\frac{k_2k_0}{(cV)^2}\right)^{1/9}\right] \\
&\times \frac{k_0m_0}{k_0-m_0}N_{k_0,k_2}(t,V) \\
&- \frac{K_0}{V}\left[1+\left(\frac{m_2m_0}{(cV)^2}\right)^{1/9}\right] \\
&\times \sum_{k_0=1}^{m_0-1}\frac{k_0m_0}{m_0-k_0}N_{m_0,m_2}(t,V).
\end{aligned} \tag{14}$$

Here, we have introduced $k_1 = m_1 = cV$. Moreover, k_2 in the third term stands as an abbreviation for

$$k_2 = m_2 - 2(cV)^2\frac{k_0-m_0}{m_0k_0}.$$

The coagulation equation (14) has two conservation properties. First, the coagulation of the enclosures does not change the dynamics of the droplet coagulation. That is, the droplet distribution $N(t, V)$, Eq. (10), evolves according to the Smoluchowski equation (6). Indeed, it can be readily shown that after summation over m_0 the last two terms in (14) cancel, since the sequence of summation can be inverted as

$$\sum_{m_0=1}^{\infty}\sum_{k_0=1}^{m_0=1} = \sum_{k_0=1}^{\infty}\sum_{m_0=k_0+1}^{\infty} .$$

The second conservation property of the coagulation equation (14) is the conservation of the total volume density of droplets, given by

$$\begin{aligned} V_{\text{total}} &= \sum_{m_0=1}^{\infty}\int_0^{\infty}\int_{(cV)^2/m_0}^{\infty} V N_{m_0,m_2}(t, V)\,\mathrm{d}V\,\mathrm{d}m_2 \\ &= \int_0^{\infty} V N(t, V)\,\mathrm{d}V = \text{const.} \end{aligned}$$

Reduced models

Constant standard deviation

In our previous paper, we characterized the internal morphology of the aerosol only by the number of enclosures. The extended model of this paper can be compared to the previous results if we assume a constant value for the standard deviation for all droplets. By Eqs. (3), the second moment is related to enclosure number n, droplet volume V and standard deviation $\sigma = \exp\sqrt{Z}$ as

$$m_2 = \frac{(cV)^2}{n}\exp(9Z).$$

Under the assumption that all droplets have the same constant value for the standard deviation, m_2 is not an independent variable anymore and we can write

$$N_{m_0,m_2}(t, V) = N_{m_0}(t, V)\delta\left(m_2 - \frac{(cV)^2}{m_0}\exp(9Z)\right).$$

Then, after integration with respect to m_2, the generalized Smoluchowski equation (14) reduces to

$$\begin{aligned} &\frac{\mathrm{d}N_{m_0}(t, V)}{\mathrm{d}t} \\ &= \frac{1}{2}\int_0^V \sigma(U, V-U)\sum_{k_0=1}^{m_0-1} N_{k_0}(t, U) \\ &\quad\times N_{m_0-k_0}(t, V-U)\,\mathrm{d}U \\ &\quad - N_{m_0}(t, V)\int_0^{\infty}\sigma(U, V)\sum_{k_0=1}^{\infty} N_{k_0}(t, U)\,\mathrm{d}U \\ &\quad + \frac{\tilde{K}_0}{V}\sum_{k_0=m_0+1}^{\infty}\frac{k_0 m_0}{k_0 - m_0}N_{k_0}(t, V) \\ &\quad - \frac{\tilde{K}_0}{V}\sum_{k_0=1}^{m_0-1}\frac{k_0 m_0}{m_0 - k_0}N_{m_0}(t, V). \end{aligned} \tag{15}$$

Here, we have abbreviated

$$\tilde{K}_0 = [1 + \exp Z]K_0 = [1 + \exp Z]\frac{2}{3}\frac{kT}{\mu}. \tag{16}$$

Equation (15) is – in slightly different notation – the generalized Smoluchowski equation of Struchtrup et al. (2001) which was derived by accounting only for the enclosure number, but not for higher moments, i.e. under the assumption of monodisperse enclosures of volume cV/m_0 and standard deviation $\sigma_{md} = 1$, i.e. $Z_{md} = 0$. Indeed, if we set $Z = 0$ in Eq. (16), we obtain $\tilde{K}_0\frac{4}{3}(kT/\mu)$ which is the value we found in Struchtrup et al. (2001) for monodisperse enclosures. For larger values of Z, we find larger values of $\tilde{K}_0$. We conclude, that a polydisperse size distribution of enclosures – i.e. $\sigma > 1, Z > 0$ – increases the value of K_0 and therefore gives a higher enclosure collision rate. For the stationary value of Z, according to (8c) given by $Z_{\text{stat}} = \frac{1}{9}\ln 2$, we obtain

$$\tilde{K}_0 = \left[1 + 2^{1/9}\right]K_0 = \frac{4.16}{3}\frac{kT}{\mu},$$

a value which is only slightly larger. We conclude that the variance of the enclosure size plays only a minor role for the enclosure coagulation rate.

Decoupled model

Here, we assume that Z is stationary, $Z_{\text{stat}} = \frac{1}{9}\ln 2$, and that the mean volumes of the enclosures are the same in all droplets, so that

$$v_{\text{g}} = \frac{cV}{\sqrt{2}n} = \text{const.}$$

The latter condition means that all droplets have the same number density of enclosures, which we shall denote by $\nu = n/V$. Also, the number of enclosures ceases to be an independent variable, so that we can write for the number density

$$N_{m_0}(t, V) = N(t, V)\delta(m_0 - \nu V).$$

Equation (15) reduces after summation with respect to m_0 to the standard Smoluchowski equation (6) for the droplet number density $N(t, V)$, where the collision probability is given by Eq. (11). The enclosure number density for all droplets changes according to (8a) as,

$$\nu = \frac{\nu_0}{1 + K_0(1 + 2^{1/9})\nu_0 t},$$

where ν_0 is the initial value of the enclosure number density. Thus, under these extremely simplified conditions, the coagulation processes of droplets and enclosures are independent of each other.

At the end of this section, we wish to stress that the reduced models of the section follow from our model under severe restrictions which will not be met in nature. They can only serve to give an basic idea of the coagulation processes in binary aerosols, but will not give a quantitatively correct picture.

A hybrid model: Updating standard deviation

For an accurate description of the process one needs to consider the second moment as an additional variable, i.e. one needs to solve Eq. (14). The solution of the complete equation requires extreme numerical efforts, a task which we defer to the future.

In the present paper, we consider a hybrid model, which improves our previous model by accounting for the first-order effects of an enclosure size distribution. For this we shall assume that all droplets have the same standard deviation for the enclosure distribution, however it is free to change in time. Then, we can use Eq. (15) – derived for the case of constant standard deviation – and replenish it with the equation for the time-evolution of Z, i.e. Eq. (8c).

The idea is as follows: For the jth time-step of the numerical solution of (15), Z is updated according to

$$Z_j = \frac{1}{9} \ln \left[2 + (\exp[9Z_{j-1}] - 2) \frac{\bar{n}_j}{\bar{n}_{j-1}} \right],$$

where $\bar{n}$ denotes the total number density of enclosures per unit volume of aerosol,[1]

$$\bar{n} = \sum_n \int n N_n(V)\, \mathrm{d}V.$$

[1]We have to mention that here the *mean* number of enclosures per droplet, given by $\bar{\bar{n}} = (\sum_n \int n N_n(V)\, \mathrm{d}V)/(\sum_n \int N_n(V)\, \mathrm{d}V)$, also seems to be a reasonable choice. This number, however, increases, and might therefore yield negative values of Z which are unphysical.

We use the same sectional model for the solution of (15) as in Struchtrup et al. (2001). In the following, we give a very short description of the procedure, for details, we refer the reader to Struchtrup et al. (2001).

Droplets with adjacent numbers of enclosures are subsumed into classes which are indicated by Greek indices, $\alpha = 1, 2, \ldots, \alpha_{\max}$, and the number of members in class α is given by μ_α. The boundaries of the classes are

$$M_\alpha = \sum_{\beta=1}^{\alpha} \mu_\beta \quad \text{for } \alpha = 1, 2, \ldots, \alpha_{\max}$$
$$\text{with } M_0 = 0,$$

where

$$\mu_\alpha = 2^{\alpha-2} \quad \text{for } \alpha = 2, \ldots, \alpha_{\max},$$
$$\text{so that } M_\alpha = 2^{\alpha-1} \quad \text{for } \alpha = 1, \ldots, \alpha_{\max}. \tag{18}$$

Similarly, the continuous volumes of the droplets are subsumed into sections, which are indicated by capital indices, $A = 1, 2, \ldots, A_{\max}$, and the volumes of the sections are Δ_A. Moreover, we define the boundaries of the sections by

$$V_A = \sum_{B=1}^{A} \Delta_B \quad \text{for } A = 1, 2, \ldots, A_{\max}$$
$$\text{with } V_0 = 0.$$

where

$$\Delta_A = 2^{A-2}\bar{V} \quad \text{for } A = 2, \ldots, A_{\max},$$
$$\text{so that } V_A = 2^{A-1}\bar{V} \quad \text{for } A = 1, \ldots, A_{\max}. \tag{19}$$

Here, $\bar{V}$ defines the smallest droplet volume of interest and must be chosen according to the process under consideration.

With these definitions, we have for the number densities of droplets with number of enclosures in class α and volume in section A

$$\nu_\alpha^A = \sum_{n=M_{\alpha-1}+1}^{M_\alpha} \int_{V_{A-1}}^{V_A} N_n(V)\, \mathrm{d}V,$$
$$\text{for } \alpha = 1, 2, \ldots, \alpha_{\max};\ A = 1, 2, \ldots, A_{\max}. \tag{21}$$

The evolution equation for ν_α^A follows by summation and integration of (15) (Struchtrup et al., 2001). With the same dimensionless quantities as there, we have the dimensionless coefficient

$$\hat{K}_0 = [1 + \exp Z] \frac{K_0}{\sigma_0},$$

where

$$K_0 = \frac{2}{3}\frac{kT}{\mu} \quad \text{and} \quad \sigma_0 = \left(\frac{3}{4\pi}\right)^{1/6}\left(\frac{6kT}{\varrho\bar{V}}\right)^{1/2}\bar{V}^{2/3},$$

the volume $\bar{V}$ denotes the smallest possible droplet volume. Its value is determined by the initial conditions. The dimensionless time is defined as

$$\tilde{t} = \frac{\sigma_0}{\bar{V}}t.$$

We consider a case where initially all droplets have the same volume $\bar{V} = \frac{4}{3}\pi\bar{r}^3$ with a radius $\bar{r} = 5 \times 10^{-9}$ m; the initial number density of droplets is $\mathcal{N}_0(\bar{V}) = 10^{18}\,\mathrm{m}^{-3}$, and all enclosures are assumed to be of the same size, $Z = 0$. Density ϱ and viscosity μ of silica are given by

$$\varrho \simeq 2400\,\frac{\mathrm{kg}}{\mathrm{m}^3}, \quad \mu = 10^{-8.6625(1-3556.03K/T)}\,\frac{\mathrm{kg}}{\mathrm{m\,s}}.$$

Thus, we have for the dimensionless values of K_0/σ_0 at $T = 2300\,\mathrm{K}$

$$\frac{K_0}{\sigma_0}(2300\,\mathrm{K}) = 6.248 \times 10^{-10}.$$

As we have shown in Struchtrup et al. (2001), the result at larger times become independent of the initial number of enclosures per droplet. We chose the initial conditions

$$\nu_\alpha^A(t=0) = u_0\delta_{A,1}\delta_{\alpha,6},$$
$$u_0 = \bar{V}\mathcal{N}_0(\bar{V}) \simeq 5 \times 10^{-7}, \quad Z_0 = 0.$$

The contour plots in Figure 3 show, for $T = 2300\,\mathrm{K}$, the temporal development of the aerosol through ν_α^A (A: x-axis, α: y-axis, accounting for 15 sections and 12 classes). The gray levels refer only to the relative values inside one plot, where the darkest area corresponds to the highest values of ν_α^A. Recall that A is a measure of the droplet size, α is a measure of the number of enclosures and ν_α^A is the number density of droplets in class α, section A. We observe the development of a structure which moves in the (A, α)-plane almost without changing its shape in concordance with our previous results.

Figure 4 shows the temporal evolution of Z. Evidently, Z approaches its stationary value rapidly, so that the evolution follows Eq. (15) with

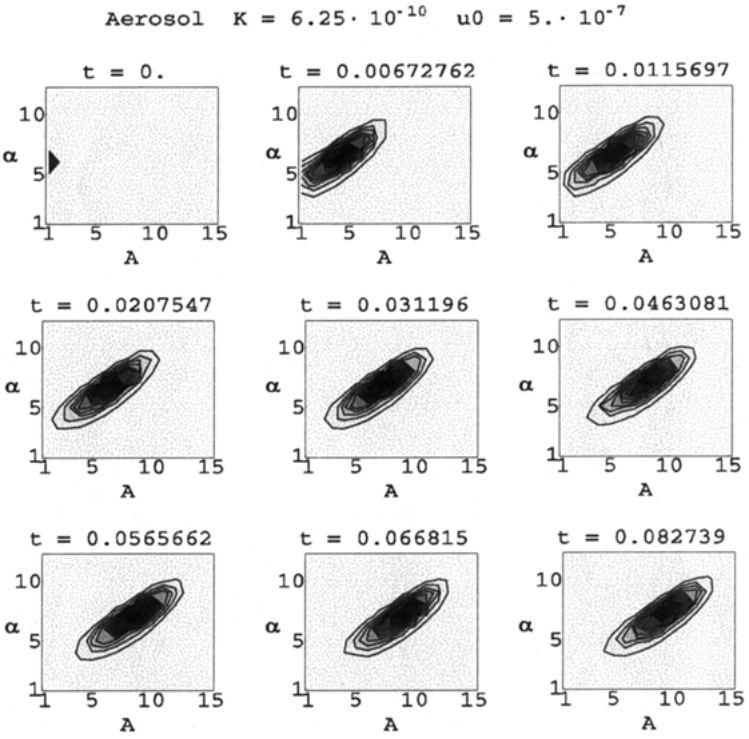

Figure 3. Temporal evolution of ν_α^A for $T = 2300\,\mathrm{K}$. Vertical axis: number of classes α (corresponds to number of enclosures), horizontal axis: number of sections A (corresponds to droplet volume). The gray levels refer only to the relative values inside one plot. t is the actual time in seconds. See Eqs. (17)–(19) for the definition of α, A, ν_α^A.

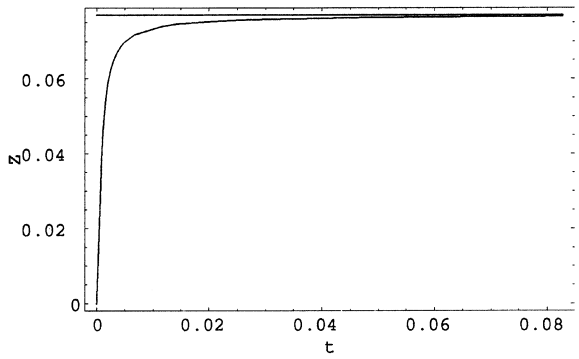

Figure 4. $Z = \ln^2 \sigma$ as a function of time ($T = 2300$ K). The straight line on the top is the stationary value $Z_{\text{stat}} = \frac{1}{9} \ln 2$.

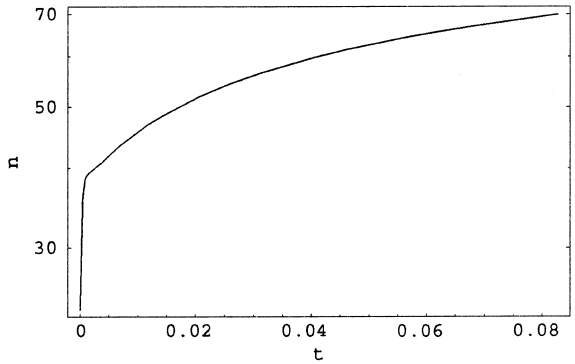

Figure 5. Mean number of enclosures for $T = 2300$ K as function of time.

$\tilde{K}_0 = [1 + 2^{1/9}]K_0 = (4.16/3)(kT/\mu)$. The result is very close to the calculation with constant Z, as in our first model. This holds also for other values of temperature, so that rather than present more further results we refer the reader to Struchtrup et al. (2001) instead. We note, however, that Z approaches its asymptotic value faster as temperature is increased due to the higher mobility and therefore higher growth rate of enclosures.

Relaxation times

Figure 5 indicates that there is an increase in the mean number of enclosures per droplet. This increase can be traced in a simple manner to the volume dependence of the collision frequencies for droplets and enclosures. In order to simplify the argument, let us consider monodisperse droplets of volume V which include monodisperse enclosures. Then, for the droplets, the Smoluchowski equation reduces to

$$\frac{\mathrm{d}N}{\mathrm{d}t} = -\frac{1}{2}\sigma_{\mathrm{F}}(V, V)N^2,$$

and we identify the collision frequency for the droplets as

$$\omega_{\mathrm{D}} = \frac{\sigma(V, V)}{2}N.$$

Since the total droplet volume is a constant, we have $N = \bar{V}\mathcal{N}_0/V$ and with Eq. (11), we can write the collision frequency as

$$\omega_{\mathrm{D}} = \frac{1}{2}\sigma_{\mathrm{F}}(V, V)N = 4\bar{V}\mathcal{N}_0\left(\frac{3}{4\pi}\right)^{1/6}\left(\frac{12kT}{\varrho}\right)^{1/2}\frac{1}{V^{5/6}}. \qquad (22)$$

For monodisperse enclosures, the Smoluchowski equation (6) reduces to

$$\frac{\mathrm{d}\nu}{\mathrm{d}t} = -\frac{1}{2}\sigma_{\mathrm{B}}(v, v)\nu^2,$$

and we identify the collision frequency for the enclosures as

$$\omega_{\mathrm{E}} = \frac{1}{2}\sigma_{\mathrm{B}}(v, v)\nu = \frac{8kT}{3\mu}\nu = \frac{8kT}{3\mu}n\frac{1}{V}. \qquad (23)$$

From (20) and (21), we see that both collision frequencies are decreasing with growing droplet volume V. However, the droplet collision frequency ω_{D} is growing faster than the enclosure collision frequency ω_{E}, and this is the reason for the increase of the mean enclosure number in our model. Also MC simulations show the same behavior of the evolution of the mean number of enclosures (Efendiev & Zachariah, 2001b).

The collision probabilities σ_{F} and σ_{B} are well established in infinite domains. The deviation from experimental observations is most likely due to finite size effects in the droplets, i.e. changes in the enclosure collision probability due to finite droplet size and migration of the enclosures to the droplet surface. Enclosures at the surface will also migrate in Brownian motion and collide, but the corresponding Smoluchowski equation will contain a different collision probability.

Moreover, the impact during the collision of droplets might enhance the enclosure collision rate – more so when the enclosures are at the droplet surface – and this effect is not accounted for in our model.

Conclusion

In this paper, we developed a model for the coagulation of binary aerosols which accounts for a distribution of the enclosure (i.e. the minority phase of the aerosol droplets) sizes. As in our first and simpler model (Struchtrup et al., 2001), where we considered monodisperse enclosures, we observe that the system evolves very quickly to a distribution that is independent of initial conditions and one in which there is a slow increase in the mean number of enclosures per droplet (see Figure 5) in contradiction to experimental evidence.

The size distribution of enclosures reaches its stationary value quite early in the aerosol coagulation process and remains constant from there on. The only difference to our previous model is a rather small change in the closure collision rate $\tilde{K}_0$, see Eq. (16). Altogether, we have to conclude that accounting for the variance of the enclosure size has no marked effect on the evolution of the binary aerosol. Thus, our initial hope – namely that the new model can describe the experimentally confirmed decreasing number of enclosures per droplet – is not fulfilled. From the comparison with experiments, we see that our models underestimate the enclosure collision rate for larger droplets.

From the above it follows that more work is needed in order to describe the enclosure processes accurately. Possible reasons for the apparent failure are the neglect of the confinement of the enclosures to the finite droplet volume, the neglect of surface effects – enclosures prefer regions at the droplet surface in order to minimize interfaces, and the influence of droplets collision on enclosure coagulation. Successful modeling, either with macroscopic models as in this paper, or with MC simulations will rely on a proper understanding of the enclosure collision probability.

Acknowledgement

H.S. gratefully acknowledges support by the Natural Sciences and Engineering Research Council of Canada (NSERC).

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