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Simultaneous charging and Brownian coagulation of nanometre aerosol particles

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Abstract. The electric charging process, by bipolar ions, of nanometre-sized aerosol particles undergoing simultaneous Brownian coagulation is examined. Two approximate analytical models, valid for symmetrical charging and size-independent coagulation rate constant, are derived and compared with the numerical solution of the rigorous population balance equations. For each particle size, there exists an optimum mean aerosol residence time in the bipolar charging device for which the output concentration of charged particles is a maximum. The optimum residence time for the smallest particles is about one order of magnitude lower than the time required to attain the charge equilibrium state. In practical situations, the maximum attainable number concentration of charged particles is accordingly much lower than in equilibrium conditions.

1. Introduction

The gas-to-particle conversion process is becoming increasingly important to the preparation of high-purity functional materials with special mechanical, optical, electric or magnetic properties [1–3]. In this process, a supersaturated vapour phase of the precursor materials is cooled down to promote nucleation. The nuclei thus formed subsequently grow by (a) further vapour condensation onto their surface, and (b) Brownian coagulation between already formed particles.

Depending on the order of magnitude of the size of the generated particles, a number of methods are available to measure their size distribution. In the particle size range of a few nanometres, the most accurate measuring technique to date is the electrostatic classification [4]. In this method, the aerosol particles must be previously charged, usually in a radioactive ionizer. To avoid particle detection problems, it is desirable to have a concentration of charged particles as high as possible at the outlet of the charging chamber. This goal becomes harder to achieve for smaller particles, because of their higher wall deposition loss rate and lower charging probability. Normally, the processes of charging and diffusion to the walls are accompanied by Brownian coagulation, whereby a further loss of small particles occur.

The concentration and size of the charged particles exiting the charging chamber depend on the aerosol residence time. Too short residence times result in few ion–particle collisions and, hence, very low charging efficiency. As the aerosol residence time increases, charging efficiency improves but, at the same time, the loss of small particles increases by diffusion to the wall and Brownian coagulation. Clearly, for each particle size there exists an optimum residence time which maximizes the output concentration of charged particles. In a recent

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experimental investigation [5] it has been shown that the optimum residence time for 2–3 nm particles can be about one order of magnitude lower than the time required to attain charging equilibrium.

Most of the work done in the coagulation field during the last several decades has been devoted to finding the analytical solution of Smoluchowski's equation for different forms of the kernel $K_{i,j}$ (see, for instance, the recent papers [6–10] and references therein). In contrast, very few investigations have addressed the problem of coagulation coupled with other mechanism(s) of particle size distribution modification. The simultaneous consideration of all the possible mechanisms affecting the aerosol dynamics (nucleation, condensation, evaporation, coagulation, diffusion losses, charging, etc) results in the so-called general dynamic equation (GDE) [11]. A number of authors have numerically solved the GDE involving all or a part of the above cited mechanisms [12–17]. However, numerical methods usually make difficult the evaluation of the relative importance of the mechanisms involved and prevent a better physical understanding of the phenomena.

In this paper, the process of simultaneous charging and coagulation is first described rigorously by means of the full population balance equations. The rigorous equations are then simplified by the introduction of certain assumptions, leading to two analytical solutions which are compared with the numerical rigorous solution.

2. Formulation of the problem

Consider a population of uncharged aerosol particles flowing through a cloud of bipolar ions while undergoing Brownian coagulation. We will restrict ourselves to nanometre-sized particles (<20 nm), for which the charging probability at equilibrium is less than about 0.01 [18], i.e. at most 1% of the uncharged particles become charged upon passing through the ion cloud. This implies that the fraction of ions spent in particle charging is negligible and, hence, one can assume that the ion number concentration remains constant through the process, and equal to its equilibrium value. The equilibrium number concentration of ions can be calculated upon knowledge of the ion generation rate by the radioactive source, the recombination rate constant between ions of opposite polarity, and their wall deposition loss rate. In this type of ionizer, the negative ions are usually more mobile than the positive ones and are accordingly lost to the wall at a higher rate. Therefore, the equilibrium number concentrations of positive and negative ions are different. However, normally this difference is not significantly large and we will neglect it.

Another important feature of the charging of nanoparticles by collision with ions is that the probability of multiple charging is vanishingly small, so that the nanometre-sized aerosol particles leave the charging device with at most one net charge of either sign. In the rest of the discussion, when we refer to charged particles we implicitly mean singly charged particles.

If charging is carried out just immediately after the particle generation process, the number concentration of uncharged particles at the inlet of the charging chamber is normally very high. In these conditions, diffusion losses to the wall are negligible in comparison with particle number concentration decrease by coagulation.

The particle size will be expressed as the number of 'monomers' or minimal units the particle is composed of. Denoting by u_j , c_j^+ and c_j^- the number concentration of uncharged, positive and negative particles, respectively, composed of j monomers, the population balance equations can be expressed as

$$\frac{du_j}{dt} = \eta_j^{+-} N c_j^- + \eta_j^{-+} N c_j^+ - \eta_j^{-0} N u_j - \eta_j^{+0} N u_j + \sum_{i=1}^{j-1} \frac{1}{2} K_{i,j-i} u_i u_{j-i}$$

$$+ \sum_{i=1}^{j-1} K'_{i,j} c_i^+ c_{j-i}^- - \sum_{i=1}^{\infty} K_{i,j} u_j (u_i + c_i^- + c_i^+) \quad (1)$$

$$\frac{dc_j^+}{dt} = \eta_j^{+0} N u_j - \eta_j^{-+} N c_j^+ + \sum_{i=1}^{j-1} K_{i,j} u_i c_{j-i}^+ - \sum_{i=1}^{\infty} c_j^+ (K_{i,j} u_i + K'_{i,j} c_i^-) \quad (2)$$

$$\frac{dc_j^-}{dt} = \eta_j^{-0} N u_j - \eta_j^{+-} N c_j^- + \sum_{i=1}^{j-1} K_{i,j} u_i c_{j-i}^- - \sum_{i=1}^{\infty} c_j^- (K_{i,j} u_i + K'_{i,j} c_i^+). \quad (3)$$

In the above equations, $\eta_j^{\mu\nu}$ is the attachment rate constant of an ion of polarity μ with a particle of polarity ν and size j , a superscript '0' standing for neutral; N is the ion-pair equilibrium number concentration; $K_{i,j}$ is the coagulation rate constant for particles of sizes i and j in the case where at least one of the colliding particles is uncharged; and $K'_{i,j}$ is the coagulation rate constant in the case that the i and j particles are charged with opposite polarity. Coagulation between charged particles of equal polarity has been neglected because the corresponding rate constant is extremely low.

Equations (1)–(3) must be solved with initial condition

$$u_j = u_j^0 \quad \text{and} \quad c_j^+ = c_j^- = 0 \quad \text{at time} \quad t = 0 \quad (4)$$

which express that at the charger inlet all the aerosol particles are neutral.

The coagulation rate constant in the free molecule regime (i.e. for nanometre-size aerosol particles) is given by [19]

$$K_{i,j} = (3kT d_m / \rho)^{1/2} (i^{1/3} + j^{1/3})^2 \left(\frac{1}{i} + \frac{1}{j} \right)^{1/2} \quad (5)$$

where k is Boltzmann constant, T the absolute temperature, d_m the monomer diameter, and ρ the particle density. The latter is assumed independent of particle size.

The rate constant for the coagulation of charged particles of opposite polarity can be calculated with the expression [20]

$$K'_{i,j} = \frac{\lambda_{i,j}}{1 - \exp(-\lambda_{i,j})} K_{i,j} \quad (6)$$

with

$$\lambda_{i,j} = \frac{e^2}{2\pi \epsilon_0 k T d_m (i^{1/3} + j^{1/3})} \quad (7)$$

where e is the elementary charge and ϵ_0 the dielectric constant of the medium (air), taken to be that of a vacuum.

3. Approximate analytical models

In order to arrive at an analytical solution of the coagulation–charging process, some simplifications are required. First, because of the low charging probability for nanometre particles, most of the particles in the chamber are neutral ones. Therefore, the formation of neutral particles through coagulation between charged particles of opposite polarity, and the depletion of neutral particles by coagulation with charged ones, are both insignificant in comparison with the formation–depletion of neutral particles by coagulation among themselves. On the other hand, at most 1% of the uncharged particles are lost by charging.

Accordingly, the time variation of the number concentration of uncharged particles can be approximately expressed as

$$\frac{du_j}{dt} = \sum_{i=1}^{j-1} \frac{1}{2} K_{i,j-i} u_i u_{j-i} - \sum_{i=1}^{\infty} K_{i,j} u_i u_j. \quad (8)$$

Equation (8) simply describes the coagulation of uncharged particles, as if the presence of ions and charged particles had no effect whatsoever. This approximation is only valid for nanometre aerosol particles, with extremely low charging probability.

In practical situations, the mean aerosol residence time in the ionizer is less than 1 s, and the inlet number concentration is usually less than 10^{16} m^{-3} . In these conditions, the mean particle volume of the aerosol leaving the ionizer is less than about 1.4 times the mean particle volume at the chamber inlet. According to equation (5) the coagulation rate constant for equal-sized particles is proportional to $j^{1/6}$. Therefore, in a practical charging process the ‘average’ coagulation rate constant at the ionizer outlet is, at most, 6% larger than that at the inlet. This justifies the use of a size-independent coagulation rate constant, K , so that equation (8) can be further simplified to

$$\frac{du_j}{dt} = \frac{1}{2} K \sum_{i=1}^{j-1} u_i u_{j-i} - K U u_j \quad (9)$$

where

$$U = \sum_{j=1}^{\infty} u_j \quad (10)$$

is the total number concentration of uncharged particles at time t .

To derive the corresponding equation for charged particles, we will first assume symmetric charging, i.e. equal physical properties of positive and negative ions (in addition to the equal concentration assumption already introduced in the preceding section). The assumption of symmetric charging has two implications. First, the otherwise four different ion attachment coefficients are reduced to just two, one for charging of neutral particles ($\eta_j^{+0} = \eta_j^{-0} \equiv \eta_j^C$), the other for neutralization of charged particles ($\eta_j^{+-} = \eta_j^{-+} \equiv \eta_j^N$). Second, the concentration of positive and negative particles are equal throughout the process, $c_j^+ = c_j^- \equiv c_j$. As a further approximation, we will neglect coagulation effects for charged particles. This is not, however, a justified assumption, because the formation–depletion rate of charged particles through collisions with uncharged ones can be of the same order of magnitude as the charging rate terms. Comparison with the results obtained from numerical solution of the rigorous equations (1)–(3) will show that, in spite of its lack of *a priori* justification, this assumption is fairly valid.

With these considerations, the simplified population balance for charged particles of either polarity can thus be expressed as

$$\frac{dc_j}{dt} = \eta_j^C N u_j - \eta_j^N N c_j. \quad (11)$$

Equations (9) and (11) are the proposed simplified population balance equations to describe the process of charging of a coagulating nanometre aerosol. Equation (9) can be solved independently because the concentration of charged particles, c_j , does not appear in it. Once the $u_j(t)$ are known, the $c_j(t)$ can be found by integration of (11). In words, we are assuming that the presence of ions and charged particles does not affect the growth of neutral particles by coagulation. Secondly, we treat the charging process in a conventional way, except that the size distribution of neutral particles is varying with time due to coagulation.

3.1. Analytical solution for uncharged particles

Summing up equation (9) over all the particle sizes j , and recalling the definition (10), the global population balance for uncharged particles becomes $dU/dt = -\frac{1}{2}KU^2$. Hence,

$$U = \frac{U^0}{1 + \frac{1}{2}KU^0t} \tag{12}$$

where $U^0 = \sum_{j=1}^{\infty} u_j^0$ is the total aerosol number concentration at the ionizer inlet ($t = 0$). With the help of (12) the solution of (9) can be written as

$$u_j = (U/U^0)^2 \left[u_j^0 + \int_0^t \frac{1}{2}K(U/U^0)^{-2} \sum_{i=1}^{j-1} u_i u_{j-i} dt \right]. \tag{13}$$

The concentration decrease with time for uncharged monomers ($j = 1$) is readily computed from (13) because, in this case, the integral vanishes. Thus

$$u_1 = \left(\frac{U}{U^0} \right)^2 u_1^0 = \frac{u_1^0}{(1 + \frac{1}{2}KU^0t)^2}. \tag{14}$$

The concentration of monomers decrease as $1/t^2$, while the total concentration decreases as $1/t$: monomers are lost much faster than the total population as a whole. For the discussion that follows it is convenient to express the concentrations in dimensionless form, by referring them to the initial total concentration of aerosol particles U^0 ($u_j^* \equiv u_j/U^0$, etc). (14) then becomes $u_1^* = (U^*)^2 u_1^{0*}$. Once the solution for monomers has been found, one can easily obtain the solution for dimers ($j = 2$):

$$u_2^* = (U^*)^2 [u_2^{0*} + (u_1^{0*})^2 (1 - U^*)]. \tag{15}$$

Similarly, the solutions for the following values of j are found to be

$$u_3^* = (U^*)^2 [u_3^{0*} + 2u_1^{0*}u_2^{0*}(1 - U^*) + (u_1^{0*})^3(1 - U^*)^2] \tag{16}$$

$$u_4^* = (U^*)^2 \{ u_4^{0*} + [(u_2^{0*})^2 + 2u_1^{0*}u_3^{0*}](1 - U^*) + 3(u_1^{0*})^2u_2^{0*}(1 - U^*)^2 + (u_1^{0*})^4(1 - U^*)^3 \} \tag{17}$$

$$u_5^* = (U^*)^2 \{ u_5^{0*} + 2(u_1^{0*}u_4^{0*} + u_2^{0*}u_3^{0*})(1 - U^*) + 3[u_1^{0*}(u_2^{0*})^2 + (u_1^{0*})^2u_3^{0*}](1 - U^*)^2 + 4(u_1^{0*})^3u_2^{0*}(1 - U^*)^3 + (u_1^{0*})^5(1 - U^*)^4 \}. \tag{18}$$

In this manner one can proceed to find the solution up to any desired value of j . However, from the above equations for small values of j we can understand the way in which the solutions are constructed, so that for larger j there is no need to solve (13) for each of the $(j - 1)$ preceding u_j^* . All the solutions consist in $(U^*)^2$ multiplied by a certain number of terms. Each of these terms contains the time-dependent factor $(1 - U^*)^m$, where m is the number of collision steps in succession required to yield a particle of size j . As an example, consider the term $3[u_1^{0*}(u_2^{0*})^2 + (u_1^{0*})^2u_3^{0*}](1 - U^*)^2$ appearing in (18). The factor $(1 - U^*)^2$ corresponds to a two-step collision process. There are two different two-step processes by which particles of size $j = 5$ can be formed: one involves two dimers and one monomer, hence the term $u_1^{0*}(u_2^{0*})^2$, and the other involves two monomers and one trimer, represented by the term $(u_1^{0*})^2u_3^{0*}$. These two terms must be multiplied by the factor three, the number of particles participating in each of the two-step processes, because one must also consider the order in which collisions occur. In contrast, the last term in (18), $(u_1^{0*})^5(1 - U^*)^4$, which is a four-step collision process, involves only one type of particles (monomers in this case), hence the order in which collisions occur is irrelevant and this term must be counted only once.

Consequently, the general solution for coagulation with size-independent rate constant can be expressed thus

$$\frac{u_1^*}{(U^*)^2} - u_1^{0*} = 0 \quad (j = 1) \quad (19a)$$

$$\begin{aligned} \frac{u_j^*}{(U^*)^2} - u_j^{0*} &= \sum_{i=1}^{j-1} u_i^{0*} u_{j-i}^{0*} (1 - U^*) \\ &+ \sum_{i=1}^{j-2} \sum_{k=1}^{j-(1+i)} u_i^{0*} u_k^{0*} u_{j-(i+k)}^{0*} (1 - U^*)^2 \\ &+ \sum_{i=1}^{j-3} \sum_{k=1}^{j-(2+i)} \sum_{l=1}^{j-(1+i+k)} u_i^{0*} u_k^{0*} u_l^{0*} u_{j-(i+k+l)}^{0*} (1 - U^*)^3 \\ &+ \sum_{i=1}^{j-4} \sum_{k=1}^{j-(3+i)} \sum_{l=1}^{j-(2+i+k)} \sum_{m=1}^{j-(1+i+k+l)} u_i^{0*} u_k^{0*} u_l^{0*} u_m^{0*} u_{j-(i+k+l+m)}^{0*} (1 - U^*)^4 \\ &+ \dots + (u_1^{0*})^j (1 - U^*)^{j-1} \quad \text{for } j > 1. \end{aligned} \quad (19b)$$

A specially simple solution is obtained when at time $t = 0$ (ionizer inlet) there are only monomers, that is, when $u_1^0 = U^0$ and $u_{j>1}^0 = 0$. In this case, (19) is reduced to the simple form

$$u_j^* = (U^*)^2 (1 - U^*)^{j-1} \quad \text{for } j = 1, 2, \dots, \infty \quad (20)$$

or in dimensional form

$$u_j = \frac{U^2}{U^0} \left(1 - \frac{U}{U^0} \right)^{j-1} \quad \text{for } j = 1, 2, \dots, \infty \quad (21)$$

where the total aerosol number concentration U at time t is given by (12). Equation (21), which was first obtained by Smoluchowski [21], is then the solution to the coagulation process for an initially monodisperse aerosol.

3.2. Analytical solution for charged particles—model I

The solution to the first-order linear differential equation (11) with initial condition $c_j = 0$ at $t = 0$ is

$$c_j = N \eta_j^C \exp(-N \eta_j^N t) \int_0^t u_j \exp(N \eta_j^N t) dt. \quad (22)$$

To solve the general case, one should insert (19) into (22) and perform the integration. We will, however, restrict ourselves to the simple case in which the aerosol consists of monomers, so that the concentration of uncharged particles at time t is given by the much simpler equation (21). Inserting (21) into (22), making the substitution $x = 2N \eta_j^N / KU$, and applying the binomial theorem, the last equation can also be rewritten as

$$\begin{aligned} c_j &= U^0 \frac{\eta_j^C}{\eta_j^N} \exp\left(-\frac{2N \eta_j^N}{KU}\right) \sum_{m=0}^{j-1} \frac{(-1)^m (j-1)!}{(j-m-1)! m!} \left(\frac{2N \eta_j^N}{KU^0}\right)^{m+2} \\ &\times \int_{2N \eta_j^N / KU^0}^{2N \eta_j^N / KU} x^{-(m+2)} \exp(x) dx. \end{aligned}$$

In the exponential term before the summation, as well as in the upper limit of the integral, appears the factor $N \eta_j^N / KU$, which represents the ratio of neutralization rate to coagulation

rate at time t for a particle of size j . Similarly, the factor $N\eta_j^N/KU^0$ appearing in the lower limit of the integral is the ratio of neutralization to coagulation rate at time $t = 0$.

Expanding $\exp(x)$ in a power series and integrating term by term, the solution for singly charged particles of either polarity can be finally written as

$$c_j = U^0 \frac{\eta_j^C}{\eta_j^N} \exp\left(-\frac{2N\eta_j^N}{KU}\right) \sum_{m=0}^{j-1} \frac{(-1)^m (j-1)!}{(j-m-1)!m!} \left(\frac{2N\eta_j^N}{KU^0}\right)^{m+2} \times \left\{ \frac{\ln\left(\frac{U^0}{U}\right)}{(m+1)!} + \sum_{\substack{s=0 \\ s \neq m+1}}^{\infty} \frac{\left(\frac{2N\eta_j^N}{KU}\right)^{s-m-1} - \left(\frac{2N\eta_j^N}{KU^0}\right)^{s-m-1}}{s!(s-m-1)} \right\}. \tag{23}$$

The time dependency of c_j is included in U , the total number concentration of uncharged particles given by (12). Equation (23) is the rigorous solution to the simplified model expressed by equation (11). This solution will be referred to as ‘Analytical I’, to distinguish it from a still simpler solution to be derived next.

3.3. Analytical solution for charged particles—model II

In the second approximate analytical model, the simultaneous coagulation and charging process is idealized as a two-step process. First, uncharged aerosol particles are let to coagulate in a coagulation chamber with no ionizing source in it. The size distribution of the uncharged particles leaving the coagulation chamber is still given by (21) in the case that the aerosol population initially consisted of monomers alone. Next, the coagulated particles are admitted into a second chamber where ions are being continuously generated by a radioactive source. In the charging chamber the aerosol is not allowed to coagulate any further and, hence, because of the extremely low charging probabilities, the concentration of uncharged particles, u_j , can be assumed to be constant.

The solution to this idealized process is simply given by (22) with the particularity that u_j can be taken out of the integral sign. Thus we find

$$c_j = \frac{\eta_j^C}{\eta_j^N} u_j [1 - \exp(-N\eta_j^N t)] \tag{24}$$

where u_j is given by (21). The simple solution (24) will be referred to as ‘Analytical II’.

4. Mean particle size

The mean size of uncharged particles, J_{um} , can be determined as

$$J_{um} = \frac{\sum_{j=1}^{\infty} j u_j}{\sum_{j=1}^{\infty} u_j} = \frac{1}{U} \sum_{j=1}^{\infty} j u_j \approx \frac{U^0}{U} = 1 + \frac{1}{2} K U^0 t \tag{25}$$

because the concentration of uncharged particles is much larger than that of charged particles.

Similarly, for the mean size of charged particles and using the Analytical II solution, one finds

$$J_{cm} = \frac{\sum_{j=1}^{\infty} j c_j}{\sum_{j=1}^{\infty} c_j} = \frac{\sum_{j=1}^{\infty} \frac{\eta_j^C}{\eta_j^N} j u_j [1 - \exp(-N\eta_j^N t)]}{\sum_{j=1}^{\infty} \frac{\eta_j^C}{\eta_j^N} u_j [1 - \exp(-N\eta_j^N t)]}. \tag{26}$$

Because of the presence of the size-dependent attachment coefficients η_j , it is not possible to arrive at an analytical expression for the mean size of charged particles. Equation (26) will anyway be compared with the results of the rigorous numerical solution.

5. Optimum aerosol residence time in the charger

The optimum residence time for particles of size j is defined as the time at which their concentration is a maximum. This can be determined analytically for uncharged particles using equation (21) of the approximate model. Differentiating (21) with respect to time and setting to zero yields

$$t_{u,opt}(j) = \frac{j-1}{KU^0}. \quad (27)$$

Therefore, the optimum residence time for neutral particles is proportional to the particle volume and inversely proportional to the coagulation rate KU^0 .

It is not possible to arrive at an analytical expression for the optimum residence time for charged particles. However, an inspection of (24) shows that, if the ion-pair number concentration N is not too low, the exponential factor practically vanishes after very short residence times. Thus, except in the very early stages of the process, we have $c_j \approx (\eta_j^C / \eta_j^N) u_j$ and hence,

$$t_{c,opt}(j) \approx t_{u,opt}(j) = \frac{j-1}{KU^0}. \quad (28)$$

This last equation indicates that the optimum residence time for charged particles is completely controlled by Brownian coagulation; charging itself plays no role. It must be pointed out that (28) is *not* valid for charged monomers ($j = 1$). Indeed, according to (28) the optimum residence time for charged monomers is zero, which is not true because at time $t = 0$ there are no charged monomers at all! For other, but not too large, values of the particle size j , equation (28) gives results in fair agreement with those obtained by the rigorous numerical model, as will be shown below.

6. Calculation procedure

6.1. Evaluation of ion attachment rate coefficients

The ion attachment rate coefficients $\eta_j^{\mu\nu}$ were calculated using Fuchs theory [22] as recently reviewed by Reischl *et al* [23], using ion electric mobilities $Z^+ = 1.15 \times 10^{-4}$ and $Z^- = 1.65 \times 10^{-4} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$, and ion masses $m^+ = 150$ and $m^- = 80$ amu. These are typical values for air ions generated in the radioactive ionizers commonly used in aerosol research [24]. To reduce the computing time the ion attachment coefficients were fitted by polynomials of the form

$$\eta_j^{\mu\nu} = 10^{-15} \sum_{i=0}^5 a_i^{\mu\nu} (d_m)^i (j)^{1/3} \quad (29)$$

where $\eta_j^{\mu\nu}$ is expressed in $\text{m}^3 \text{ s}^{-1}$ and the monomer diameter d_m in nm. The constants $a_i^{\mu\nu}$ given in table 1 are valid for the particle size range 1–25 nm.

6.2. Rigorous solution

The rigorous population balance equations (1)–(3) with initial condition (4) were solved numerically using a simple forward integration scheme, with a time step of 0.001 s, and maximum size of $j = 150$. Total aerosol mass conservation was fully satisfied up to times between 1 and 2 s (depending on the specific initial aerosol concentration). At longer times, the total mass decreased gradually because concentrations of newly formed particles of size

Table 1. Values of the constants $a_i^{\mu\nu}$ for the evaluation of the ion attachment rate coefficients (equation (29)).

$i \rightarrow$	0	1	2	3	4	5
a_i^{+0}	-2.7680	3.6247	0.4294	-0.0052	0	0
a_i^{-0}	-3.9515	5.0171	0.5992	-0.0076	0	0
a_i^{+-}	455.20	381.13	-55.20	3.93	-0.13	0.0018
a_i^{-+}	256.77	350.16	-31.12	1.30	-0.02	0

larger than 150 monomers were not stored in memory. In all the cases reported below, the mass loss at the end of the calculation was always less than 10%.

6.3. Approximate solutions

In order to use the approximate analytical expressions (21), (23) and (24), we have first to assign a value to the size-independent coagulation rate constant K . It has been decided to take the value of K which best reproduces the numerically-calculated time variation of the mean size J_{um} of uncharged particles. According to (25), a plot of J_{um} against time should yield a straight line from whose slope one can determine the coagulation rate constant K . Such a plot is shown in figure 1 for different values of the initial concentration U^0 of uncharged monomers of size $d_m = 2$ nm. The data points are mean sizes calculated with the numerical model. The lines are the best fittings to the numerical data using (25). The numerical calculations show that the mean size of uncharged particles is not exactly a linear function of time as suggested by (25), but it is very nearly so. The values of K obtained from the slope of the fitting lines will be used throughout the rest of the discussion. Using equation (5) with $i = j$, it is found that the values of K obtained from the fittings (see caption of figure 1) correspond to particle sizes of $j \approx 2, 5, 6$ and 12 for initial aerosol concentrations U^0 of 10^{15} , 5×10^{15} , 10^{16} and $5 \times 10^{16} \text{ m}^{-3}$, respectively.

It must be noted that in a practical case one does not know *a priori* which is the value of K that would reproduce best the rigorous numerical solution, unless one solves previously the numerical model! However, it must not be forgotten that the purpose of this paper is to assess the validity of the simple approximate solutions derived above. As will be shown below, the approximate equations give fairly good results provided an appropriate value of the coagulation rate constant K is chosen. The selection of the appropriate value of K without the need to solve previously the full population balance equations should be the subject of further research.

7. Comparison between numerical and analytical solutions

Figures 2 and 3 show the comparison between numerical calculations and the two analytical solutions, for two different initial number concentrations of uncharged monomers. For uncharged particles (figures 2(a) and 3(a)) there is only one analytical curve because equation (21) is common to Analytical I and Analytical II models. As seen, the approximate analytical solutions reproduce reasonably well the numerical data. Considering the drastic assumptions under which the analytical solutions have been obtained (size-independent K and, specially, the non-inclusion of gain-loss terms due to coagulation between charged and uncharged particles) the agreement between numerical and approximate solutions is quite good. It is also striking that Analytical II gives better results than Analytical I despite the fact that the former is still a less rigorous approach.

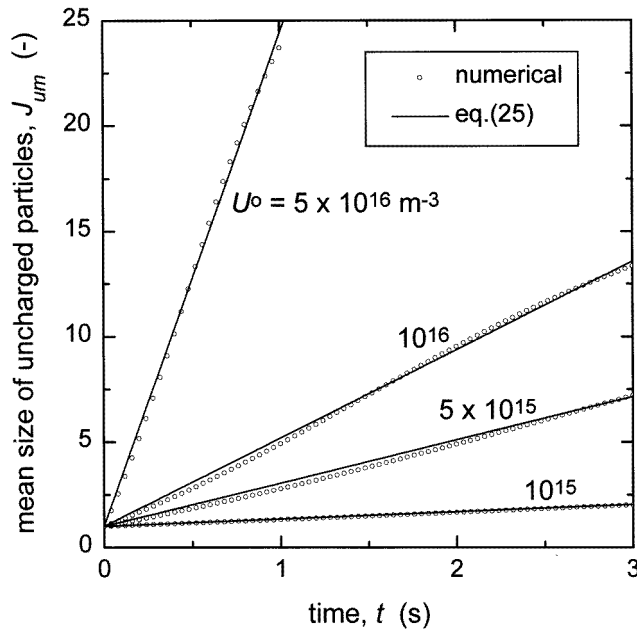


Figure 1. Variation with time of the mean size of uncharged particles for different initial monomer concentrations. Monomer diameter $d_m = 2$ nm; ion-pair number concentration $N = 2 \times 10^{13} \text{ m}^{-3}$. From the slopes of the fitting lines, the size-independent coagulation rate constants K were determined to be 6.92×10^{-16} , 8.20×10^{-16} , 8.38×10^{-16} and $9.36 \times 10^{-16} \text{ m}^3 \text{ s}^{-1}$ for initial monomer number concentrations U^0 of 10^{15} , 5×10^{15} , 10^{16} and $5 \times 10^{16} \text{ m}^{-3}$, respectively.

In summary, we can conclude that the simple equations (21) and (24), although approximate, describe very well the process of simultaneous coagulation and charging of nanometre aerosol particles, provided a suitable value is chosen for the size-independent coagulation rate constant K .

Figure 4 shows the comparison between numerical and analytical mean size of charged particles for different initial monomer concentrations. The numerical mean size has been evaluated using the numerically calculated concentrations of negatively charged particles. Again, the matching between the rigorous and approximate approaches is quite good.

Figure 5 shows the practically insignificant effect of the ion-pair number concentration N on the particle size growth with time. This figure also serves to compare the mean sizes of charged and uncharged particles. The mean size of charged particles is always larger than that of uncharged particles; the reason is simply that the charging probability η_j^C / η_j^N increases with particle size.

The optimum residence time in the ionizer is plotted in figure 6. It is seen that the predictions using the approximate equation (28) are in reasonable agreement with the numerical calculations except for large values of particle size and initial monomer number concentration. Also, the numerical calculations show that the optimum residence time is practically the same for charged and neutral particles, in agreement with (28).

Finally, it must be mentioned that the rigorous model (1)–(4) has already been successfully tested with experiments [5]. Moreover, these experiments showed that the optimum residence time for very small particles (2–4 nm) in the charging device was less than 0.05 s, which is one order of magnitude smaller than the time required to attain the aerosol charging equilibrium

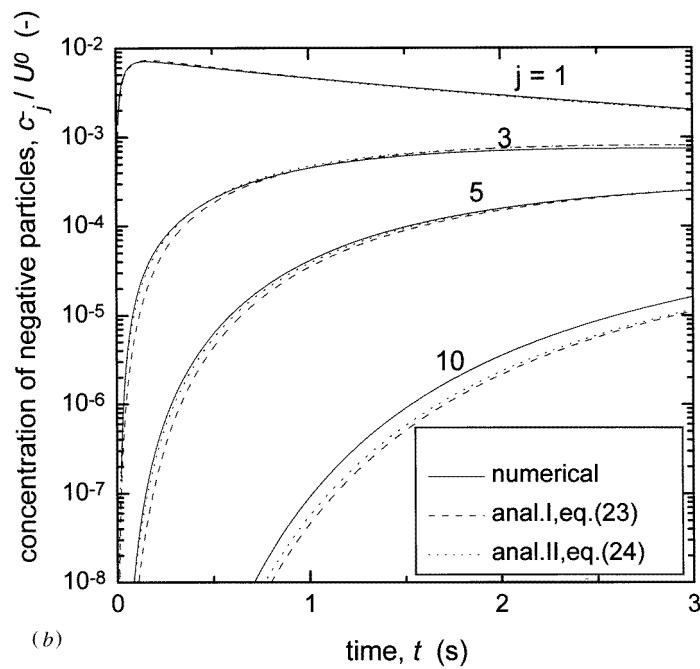
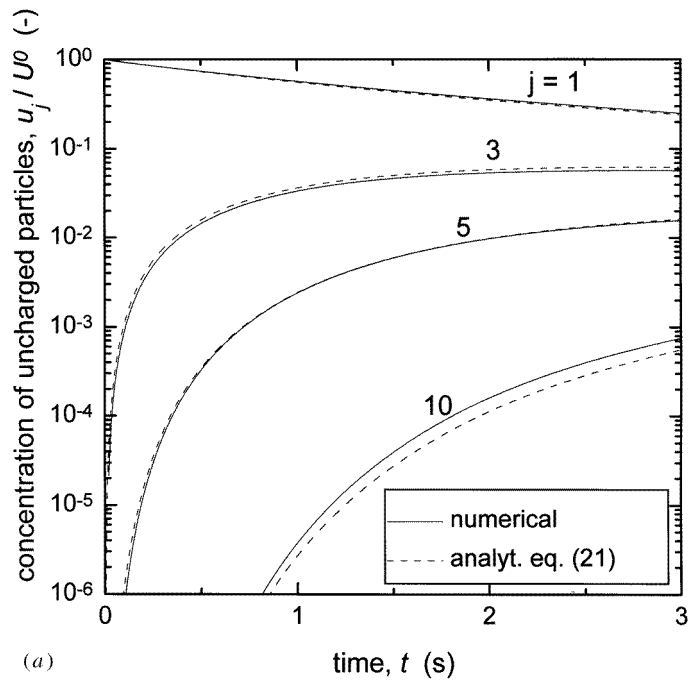


Figure 2. Comparison between numerical and approximate analytical solutions for (a) uncharged and (b) negatively charged particles. Monomer diameter $d_m = 2$ nm; ion-pair number concentration $N = 2 \times 10^{18} \text{ m}^{-3}$; initial monomer number concentration $U^0 = 10^{15} \text{ m}^{-3}$. In this and the following figures, the size-independent coagulation rate constants for analytical solutions are the same as in figure 1.

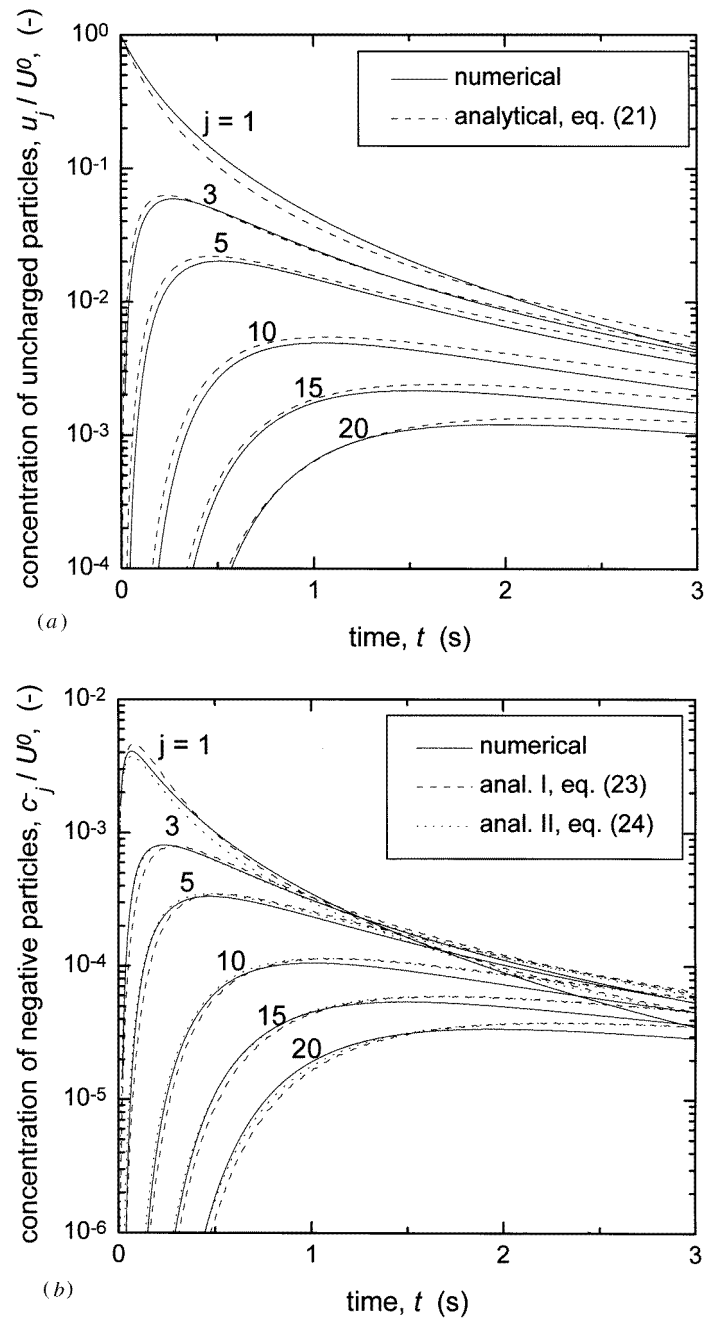


Figure 3. Comparison between numerical and approximate analytical solutions for (a) uncharged and (b) negatively charged particles. Monomer diameter $d_m = 2$ nm; ion-pair number concentration $N = 2 \times 10^{13} \text{ m}^{-3}$; initial monomer number concentration $U^0 = 10^{16} \text{ m}^{-3}$.

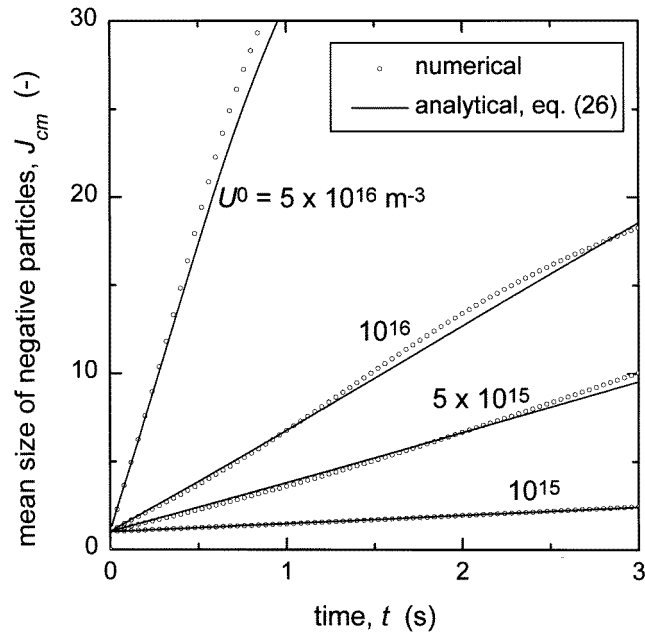


Figure 4. Variation with time of the mean size of charged particles as a function of the initial monomer number concentration. Ion-pair number concentration $N = 2 \times 10^{13} \text{ m}^{-3}$.

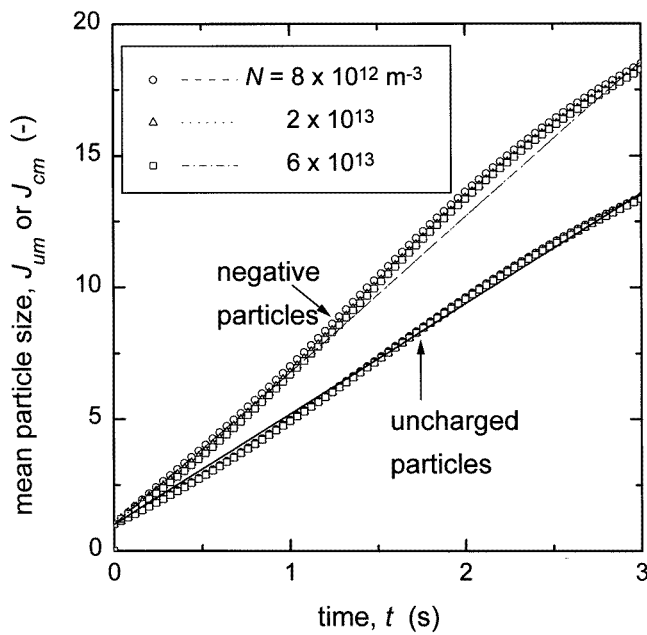


Figure 5. Variation with time of the mean size of charged and uncharged particles as a function of the ion-pair number concentration. Data points: numerical. Lines: Analytical II (equations (25) and (26)). Initial monomer number concentration $U^0 = 10^{16} \text{ m}^{-3}$.

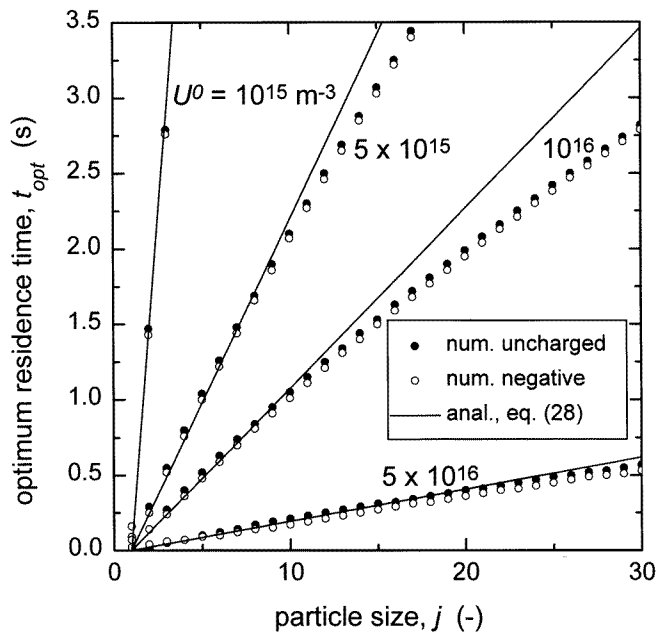


Figure 6. Optimum residence time as a function of the initial monomer number concentration. Ion-pair number concentration $N = 2 \times 10^{13} \text{ m}^{-3}$.

state. This further implies that the maximum attainable concentration of charged particles is, in practice, lower than the equilibrium concentration.

8. Conclusions

The charging process of a coagulating nanometre aerosol has been described by a simplified analytical model, expressed by equations (21) and (24), using a suitably chosen size-independent coagulation rate constant, and neglecting coagulation between charged and uncharged particles. The analytical solution is in good agreement with the rigorous solution obtained by numerical integration of the population balance equations. The optimum residence time for charged particles is controlled by Brownian coagulation and, as a consequence, is proportional to the particle volume and inversely proportional to the coagulation rate.

Acknowledgment

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References

- [1] Gurav A, Kodas T, Pluym T and Xiong Y 1993 *Aerosol Sci. Technol.* **19** 411
- [2] Kusters K A and Pratsinis S E 1995 *Powder Technol.* **82** 79
- [3] Pui D Y H and Chen D R 1997 *J. Aerosol Sci.* **28** 539
- [4] Chen D R, Pui D Y H, Hummes D, Fissan H, Quant F R and Sem G J 1998 *J. Aerosol Sci.* **29** 497
- [5] Alonso M, Hashimoto T, Kousaka Y, Higuchi M and Nomura T 1998 *J. Aerosol Sci.* **29** 263

- [6] Donnelly P and Simons S 1993 *J. Phys. A: Math. Gen.* **26** 2755
- [7] Krivitsky D S 1995 *J. Phys. A: Math. Gen.* **28** 2025
- [8] Boehm A B, Poor C and Grant S B 1998 *J. Phys. A: Math. Gen.* **31** 9241
- [9] Park S H, Lee K W, Otto E and Fissan H 1999 *J. Aerosol Sci.* **30** 3
- [10] Otto E, Fissan H, Park S H and Lee K W 1999 *J. Aerosol Sci.* **30** 17
- [11] Friedlander S K 1977 *Smoke, Dust and Haze* (New York: Wiley)
- [12] Warren D R and Seinfeld J H 1985 *Aerosol Sci. Technol.* **4** 31
- [13] Seigneur C, Hudischewskyi A B, Seinfeld J H, Whitby K T, Whitby E R, Brock J R and Barnes H M 1986 *Aerosol Sci. Technol.* **5** 205
- [14] Pratsinis S E 1988 *J. Colloid Interface Sci.* **124** 416
- [15] Oron A and Seinfeld J H 1989 *J. Colloid Interface Sci.* **133** 80
- [16] Lazaridis M and Koutrakis P 1997 *J. Aerosol Sci.* **28** 107
- [17] Katoshevski D and Seinfeld J H 1997 *Aerosol Sci. Technol.* **27** 550
- [18] Hoppel W A and Frick G M 1986 *Aerosol Sci. Technol.* **5** 1
- [19] Flagan R C and Seinfeld J H 1988 *Fundamentals of Air Pollution Engineering* (Englewood Cliffs, NJ: Prentice-Hall)
- [20] Zebel G 1966 *Coagulation of Aerosols in Aerosol Science* ed C N Davies (London: Academic)
- [21] Chandrasekhar S 1943 *Rev. Mod. Phys.* **15** 1
- [22] Fuchs N A 1963 *Geofis. Pura Appl.* **56** 185
- [23] Reischl G P, Mäkelä J M, Karch R and Necid J 1996 *J. Aerosol Sci.* **27** 931
- [24] Alonso M, Kousaka Y, Nomura T, Hashimoto N and Hashimoto T 1997 *J. Aerosol Sci.* **28** 1479