Dependence of the Ion-Aerosol Equivalent Attachment Coefficient on the Ratio of Polar Conductivities in a Steady State

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ABSTRACT

The article discusses certain theoretical problems of the diffusion charging of aerosol particles in a bipolar ion environment. The ratio of polar conductivities, induced by cluster ions of either polarity, may vary in a wide range. New results are obtained for the calculation algorithm of the ion-aerosol equivalent attachment coefficient in a steady state. Applying the Poisson sum formula, an analytical approximation equation is derived for the ion-aerosol equivalent attachment coefficient as a function of the ratio of polar conductivities and of the particle diameter. This equation could simplify calculations of ion-aerosol interaction characteristics in the range of sufficiently large particle diameters. A possibility for the creation of a related approximation equation for the range of smaller particle diameters is briefly outlined.

Keywords: Aerosol; Ion; Attachment coefficient.

INTRODUCTION WITH A BRIEF HISTORICAL OVERVIEW

The charge of aerosol particles has an effect on their combination with cluster ions, on their transport, coagulation, dispersion, deposition, and other processes. This effect is quantitatively taken into account in various theoretical models of aerosol charging and interaction, which are often put into use in larger atmospheric physical models, and also in technical appliances, such as filters, precipitators, electrical air cleaners, neutralizers, and especially in aerosol measuring apparatus. To accurately assess the role of charge and electrical effects in theoretical models and practical devices, it is important to know the charge distribution of aerosol particles and the ion-aerosol attachment coefficients as functions of particle size. In a bipolar ion atmosphere and in fixed conditions, the charge distribution approaches a steady state distribution, and it is possible to proceed with analytical calculations for the single size or equivalent attachment coefficient, which takes into account the charge distribution (Hoppel, 1985).

Atmospheric aerosol particles are charged mainly by their combination with randomly moving cluster ions. Such a basic concept is applicable also for many technical appliances. McClelland and Kennedy (1912) were the first to describe mathematically the interactions between cluster ions (small ions), neutral and charged atmospheric aerosol particles using differential equations. The neutral and charged aerosol particles were represented by integral concentrations without size and charge distributions, and the interactions were represented by coefficients that were denominated as combination coefficients or attachment coefficients thereafter. Such an approach was dominant in a number of papers on atmospheric electricity in the 1910–1930s and later (e.g. Schweidler, 1918; Nolan and de Sachy, 1927; Whipple, 1933), and it is used at present as well. An overview of the subject up to the 1960s can be found in (Chalmers, 1967; Israël, 1971).

In the beginning of the 1920s, several researchers studied the physical mechanism of aerosol particle charging in an ion atmosphere. On the basis of Smoluchowski coagulation theory, Arendt and Kallmann (1926) derived the equation for the charge evolution of an aerosol particle in an unipolar ion atmosphere. The first constructive results for the theory of bipolar diffusion charging of aerosol particles were probably obtained by Fuchs in the 1930s, but due to repressions in the Soviet Union at that time, the results were published with a delay by Fuchs's colleague Lissowski (1940) and by Fuchs (1947). Since the 1940s, a number of researchers have studied various aspects of ion-aerosol interactions and the mechanism of aerosol particle charging (e.g. Bricard, 1949; Gunn, 1954; Fuchs, 1963; Salm, 1971). Adachi *et al.* (1986) studied theoretically the dynamics of the particle diffusion charging process in asymmetrical bipolar ion atmosphere, using the theory by Fuchs (1963), and checked the theoretical results experimentally for quasi-monodisperse particles with the geometric mean diameter in the range of 20–60 nm. They

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found that the Fuchs's theory is reasonably exact for the ratio of the concentrations of negative and positive ions from 0.8 to infinity. Alonso and Alguacil (2008) studied the effect of particle diffusion charging on their size distribution. Overviews of the study of charge distributions in bipolar particle charging from the 1950s to the 1990s are given in (Matsoukas, 1994; Reischl *et al.*, 1996).

Hoppel (1977) calculated the attachment coefficients of positive or negative cluster ions to an individual aerosol particle taking into account such factors as image capture and three-body trapping. Tammet (1984) studied the depletion of cluster ions by aerosol particles applying equations by Fuchs (1947) and introducing a correction factor that approximates the results to the coefficients in (Hoppel, 1977). The idea of equivalent attachment coefficient (see Eq. (2)) was also used in (Tammet, 1984). The concept of the equivalent attachment coefficient was comprehensively introduced in (Hoppel, 1985; Hoppel and Frick, 1986). Shimo (1985) published an extensive historical overview of equations for the calculation of attachment coefficients. The terminology by Shimo is somewhat different of that by Hoppel. Salm (1987) made an attempt to develop approximating equations for the equivalent attachment coefficient in the case of charge symmetrical steady state ionization. Tammet (1991) continued the use of the equations by Fuchs (1947), updating the correction factor for the range of ultrafine aerosol particles. The correction factor was determined by fitting the results to the data by Hoppel and Frick (1990). Tammet and Kulmala (2005) developed software for the simulation of aerosol nucleation bursts, where the attachment of ions to aerosol particles plays a substantial role. The equations describing the attachment are similar to those in (Tammet, 1991), but contain a few refinements. The attachment coefficients are fitted to the numerical results by Hoppel and Frick (1986) and experimental results by Reischl *et al.* (1996), and they converge to the experimental values of the ion-ion recombination coefficient at the limit of very small particles. Tammet *et al.* (2006) used similar methodology in a subsequent model for the calculation of air ion balance in coniferous forest.

In the present study, we will consider the diffusion charging of sufficiently large aerosol particles in a bipolar ion atmosphere, where the ratio of polar conductivities, induced by ions of either polarity, may vary in a wide range. New results are obtained for the calculation algorithms of the ion-aerosol equivalent attachment coefficient in a steady state. The results are briefly outlined in abstracts (Salm, 2004; 2005). The goal of the study is to extend the sphere of application of equations based on the diffusion charging theory (Fuchs, 1947) in order to get sufficiently simple analytical equations for the use in various theoretical models that include aerosol charging, e.g. similar to (Tammet and Kulmala, 2005).

BASIC CONCEPTS AND EQUATIONS

Let us consider a spatially homogeneous aerosol environment that comprises a large number of aerosol particles and cluster ions (small ions) in a gas. In many cases, the cluster ions can be distinguished from aerosol particles, since a clear vacancy is observed between the two particle classes in the size distribution. For example, long-term measurements in rural atmosphere have distinctly shown very low average concentrations of intermediate ions between cluster ions and aerosol ions (charged aerosol particles) (Hõrrak *et al.*, 2000). Cluster ions were found in a mobility interval of 0.5–3.2 $cm^2/V/s$, which approximately correspond to the particle diameter interval of 0.4–1.6 nm. Obviously this is the case also in other clean gas environments. However, in certain cases, the region between cluster ions and larger charged particles can be rather populated, and the distinguishing is complicated (e.g. Hõrrak *et al.*, 1998). The cluster ions and aerosol particles are in a continuous Brownian motion and randomly collide with each other. During each collision, an aerosol particle acquires one negative or one positive elementary charge from the colliding cluster ion; the reverse process is not probable (Fuchs, 1963).

The flux of positive or negative cluster ions onto an aerosol particle with a diameter of d and charge number j is expressed as:

$$\Phi_j^\pm(d) = \beta_j^\pm(d) n^\pm \qquad (1)$$

where $\beta_j^\pm(d)$ is the attachment coefficient of positive or negative cluster ions to an individual aerosol particle with the diameter of d and charge number j, and $n^\pm$ are the concentrations of positive or negative cluster ions, respectively. In the case of negative charges, j is negative. The flux may also be called the collision frequency and the attachment coefficient the combination coefficient. The calculation or the measurement of attachment coefficients has been the goal of a large number of papers since the work (Arendt and Kallmann, 1926). Information about the numerical values of the coefficients can be found in (Hoppel and Frick, 1986; Tammet and Kulmala, 2005).

In consequence of charging by collisions, aerosol particles acquire different charges from negative to positive values. If the charge distribution of particles at a given particle diameter is known, the *equivalent* or single-size ion-aerosol attachment coefficient is determined as follows:

$$\beta_\delta^\pm(d) = \sum_{-\infty}^\infty \beta_j^\pm(d) p_j(d) \qquad (2)$$

where $p_j(d)$ is the charge distribution, i.e. the probability of a particle with the diameter of d to carry j elementary charges. The equivalent attachment coefficient integrates the attachment effects of all neutral, single charged and multiple charged particles at the given diameter of d. The evolution of charge distribution due to the attachment of cluster ions is calculated by the following equation (e.g. Hoppel 1985; Adachi *et al.*, 1986):

$$\frac{dp_j}{dt} = \Phi_{j-1}^+ p_{j-1} + \Phi_{j+1}^- p_{j+1} - \Phi_j^+ p_j - \Phi_j^- p_j \qquad (3)$$

The argument d has been omitted here. It is always possible to carry out numerical calculations on the basis of Eq. (3) in order to find charge distributions, but our objective is to derive explicit and synoptic equations that can help the compilation of theoretical or semiempirical models.

The equivalent attachment coefficient has a special relevance in a steady state (equilibrium conditions), when the charge distribution is invariable. In a steady state, the following equation between neighboring charge probabilities is valid:

$$\Phi_j^+ p_j = \Phi_{j+1}^- p_{j+1} \qquad (4)$$

In most cases, aerosols are polydisperse, covering a wide range of particle diameters. If the size distribution of aerosol particles is known, the attachment effects can be integrated into an *effective* attachment coefficient. In principle, aerosol particles may be differentiated by their sizes into either discrete size classes (histograms) or continuous size distribution. In the case of continuous representation, the size distribution may be expressed by a normalized differential distribution function $f(d)$, where d is the diameter of a particle, so that the concentration of particles in an infinitesimal size interval dd around d is $N_{tot}f(d)dd$, where N_{tot} is the total number concentration of aerosol particles. The effective ion-aerosol attachment coefficient can be expressed as:

$$\beta_{eff}^\pm = \int \beta_\delta^\pm (d) f(d) dd \qquad (5)$$

The evolution and balance of the concentrations of unimobile cluster ions in a uniform aerosol environment is described by equation

$$\frac{dn^\pm}{dt} = q - \alpha n^- n^+ - \beta_{eff}^\pm n^\pm N_{tot} \qquad (6)$$

where q is the ionization rate and α is the recombination coefficient of cluster ions.

Eq. (6) may also contain a term describing the cluster ion loss by ion-induced nucleation (Turco *et al.*, 1998; Enghoff and Svensmark, 2008). Eventual ion-induced nucleation and any generation of aerosol particles are neglected in the present study. The coagulation of aerosol particles is also neglected.

For further calculations, let us consider monodisperse aerosol particles with a diameter of d. Negative and positive cluster ions have single elementary charges, concentrations n^- and n^+, diffusion coefficients D^- and D^+, and electrical mobilities Z^- and Z^+. The concentrations of cluster ions and aerosol particles are assumed to be spatially uniform. Any significant external electric field is lacking. The diffusion fluxes of cluster ions onto an aerosol particle will be expressed analogously as in (Fuchs, 1947). Various refinements of the theory will not be introduced here, since our aim is to derive analytical equations of a simple shape. E.g. image forces and polarization forces of particles will not be taken into account.

The diffusion fluxes of single charged negative and positive cluster ions onto a neutral aerosol particle are:

$$\Phi_0^\pm (d) = 2\pi d D^\pm n^\pm = 2\pi k T d Z^\pm n^\pm / e \qquad (7)$$

where k is the Boltzmann constant, T is the absolute temperature, $Z^\pm$ is the mobility of a negative or positive charged particle, e is the elementary charge.

Let us introduce the dimensionless reciprocal of the aerosol particle diameter

$$\kappa = e^2 / (4\pi\varepsilon_0 k T d) \qquad (8)$$

where ε_0 is the electric constant.

The diffusion flux of negative cluster ions onto an aerosol particle with a charge of je is

$$\Phi_j^- (d) = \Phi_0^- (d) \frac{2j\kappa}{1 - \exp(-2j\kappa)} \qquad (9)$$

The number of elementary charges j is negative for negative charges and positive for positive charges.

The diffusion flux of positive cluster ions onto an aerosol particle with a charge of je is

$$\Phi_j^+ (d) = \Phi_0^+ (d) \frac{2j\kappa}{\exp(2j\kappa) - 1} \qquad (10)$$

Eqs. (7)–(10) are sufficiently accurate in the range of larger particle diameters roughly above 100 nm, where the use of diffusion theory for the calculation of cluster ion fluxes is justified. The accuracy is lower for the range of medium particle diameters, which are comparable with the mean free path of cluster ions, and it is even lower for small particle diameters, if the molecule kinetics theory of interaction is valid. By means of proper correction factors, it is still possible to extend the equations also into the range of smaller diameters (Tammet, 1984; Salm, 1987; Tammet, 1991; Tammet *et al.*, 1998; Tammet and Kulmala, 2005; Tammet *et al.*, 2006; Hõrrak *et al.*, 2008).

STEADY STATE CHARGE DISTRIBUTION

Let us introduce the ratio of polar conductivities

$$s = Z^+ n^+ / Z^- n^- = \Phi_j^+ / \Phi_{-j}^- \qquad (11)$$

This ratio has also been called the ion asymmetry ratio (Clement and Harrison, 1992) or the coefficient of the unipolarity of cluster ion polar conductivities (Tammet *et al.*, 2006).

We will retain the symbols for $p_j(d)$ and $\beta_\delta^\pm (d)$ also in a steady state. The steady state charge distribution of aerosol particles can be calculated by recurrent application of Eq. (4), and the charge distribution is expressed as in (Salm,

1971; Clement and Harrison, 1992):

$$p_j(d) = p_0(d)s^j \exp(-j^2\kappa)\frac{\sinh(j\kappa)}{j\kappa} \qquad (12)$$

Taking into account the identity $s^j \exp(-j^2\kappa)$
$= \exp\left(-j^2\kappa + \ln s - \frac{\ln^2 s}{4\kappa} + \frac{\ln^2 s}{4\kappa}\right)$, Eq. (12) can be
transformed into an equivalent shape

$$p_j(d) = p_0(d)\exp\left(\frac{\ln^2 s}{4\kappa}\right)\exp\left(-\frac{(j\kappa - 0.5\ln s)^2}{\kappa}\right)\frac{\sinh(j\kappa)}{j\kappa} \qquad (13)$$

The concentration p_0 is calculated as follows:

$$p_0(d) = \left[\sum_{j=-\infty}^{\infty} s^j \exp(-j^2\kappa)\frac{\sinh(j\kappa)}{j\kappa}\right]^{-1} \qquad (14)$$

or in an equivalent shape:

$$p_0(d) = \left[\exp\left(\frac{\ln^2 s}{4\kappa}\right)\sum_{j=-\infty}^{\infty}\exp\left(-\frac{(j\kappa - 0.5\ln s)^2}{\kappa}\right)\frac{\sinh(j\kappa)}{j\kappa}\right]^{-1} \qquad (15)$$

In the range of sufficiently large particle diameters, the quotient $\sinh(j\kappa)/(j\kappa) \approx 1$, and Eq. (13) shows the symmetry of the charge distribution $p_j(d)$ with respect to the point

$$\bar{j} = \frac{\ln s}{2\kappa} \qquad (16)$$

In this case, $\bar{j}$ represents the average charge number. A similar result was obtained in (Gunn, 1954; Clement and Harrison, 1992). Eq. (16) represents a one-to-one relationship between the average charge number of large aerosol particles and the polar conductivity ratio in steady state conditions.

Eqs. (12)–(16) are accurate in the range of larger particle diameters, if the use of the diffusion theory for the calculation of cluster ion fluxes is justified. By means of the above-mentioned correction factors, it is possible to derive modified steady state equations also for the range of smaller diameters. However, the recurrent application of Eq. (4) with the corrected equations does not give similar simple equations for charge distribution as Eqs. (12)–(15). In the present paper, the correction factors are not specially studied.

EQUIVALENT ATTACHMENT COEFFICIENT IN STEADY STATE

Taking into account all the particles with the same diameter and different charges, the equivalent attachment coefficient is determined by means of Eq. (2). Transforming the variables on the right hand side of Eq. (2) by means of Eqs. (1), (9), (10), and (12), we obtain for steady state:

$$\beta_\delta^\pm(d) = \beta_0^\pm(d)p_0(d)\sum_{j=-\infty}^{\infty}s^j\exp\left(-(j^2 \pm j)\kappa\right) \qquad (17)$$

At some particular calculations of the equivalent attachment coefficient, a complicacy arises that an accumulative number of addends should be summed in Eqs. (14) and (17). If the diameter is about 10 nm, it is sufficient to sum 1, 2 or 3 largest addends. At a diameter of 40 nm, five addends suffice, but the necessary number of addends grows rapidly with the increasing diameter. This complicacy can be overcome by means of the Poisson sum formula (Salm, 1987; 2004).

Let us transform Eq. (17) into an equivalent shape

$$\beta_\delta^\pm(d) = \beta_0^\pm(d)p_0(d)\exp\left(A_\pm^2\kappa\right)\sum_{j=-\infty}^{\infty}\exp\left(-(j-A_\pm)^2\kappa\right) \qquad (18)$$

where

$$A_\pm = \frac{1}{2}\left(\frac{\ln s}{\kappa} \mp 1\right) \qquad (19)$$

The series in Eq. (18) converges the slower, the larger is the particle diameter, or, the smaller is the reciprocal κ. By means of the Poisson sum formula, it is possible to transform Eq. (18) into a shape:

$$\beta_\delta^\pm(d) = \beta_0^\pm(d)p_0(d)\sqrt{\frac{\pi}{\kappa}}\exp\left(A_\pm^2\kappa\right)\times\sum_{j=-\infty}^{\infty}\exp\left(-\frac{j^2\pi^2}{\kappa}\right)\cos(2\pi j A_\pm) \qquad (20)$$

The series in Eq. (20) converges fast at large particle diameters. The dimensionless reciprocal κ depends on temperature. For example, at a temperature of 293 K, $\kappa = 57/d$, where d is in nanometers. At a diameter of 40 nm at the same temperature, if s is in the interval of 0.5–2 and the uncertainty is required to be under 1%, five addends are necessary in the series of Eq. (18). The necessary number of addends in Eq. (18) rapidly grows at larger diameters. However, in the same conditions, only one addend is necessary in Eq. (20), and a good precision is achieved by means of the following equation:

$$\beta_\delta^\pm(d) \approx \beta_0^\pm(d)p_0(d)\sqrt{\frac{\pi}{\kappa}}\exp\left(A_\pm^2\kappa\right) \qquad (21)$$

Eq. (21) yields an uncertainty below 1% at a particle diameter of 40 nm in the above-mentioned conditions, if we do not consider the uncertainty of p_0. A precise calculation of the concentration p_0 is still problematic. If we use an approximation $\sinh(j\kappa)/(j\kappa) \approx 1 + (j\kappa)^2/6$ for the range of large particles in Eq. (14), and if we apply

integration instead of summation, the concentration can be expressed as:

$$p_0\left(d\right) \approx \left[\sqrt{\frac{\pi}{\kappa}}\left(1+\frac{\kappa}{12}+\frac{\ln^2 s}{24}\right)\exp\left(\frac{\ln^2 s}{4\kappa}\right)\right]^{-1} \tag{22}$$

At a diameter of 40 nm and with the values of s in the interval of 0.5–2, Eq. (22) guarantees an uncertainty below 1.6% in comparison with Eq. (14). At larger diameters the uncertainty is lower. On the basis of Eqs. (109), (21), and (22), the equivalent attachment coefficient can be expressed as:

$$\beta_\delta^\pm\left(d\right) \approx \beta_0^\pm\left(d\right)\frac{\exp\left(\dfrac{\kappa}{4}\right)}{1+\dfrac{\kappa}{12}+\dfrac{\ln^2 s}{24}}s^{\mp\frac{1}{2}} \tag{23}$$

If the diameter of particles is larger than 50 nm and an uncertainty of 4% is admissible, then the exponent function may be replaced with the first two members of its power series, and

$$\beta_\delta^\pm\left(d\right) \approx \beta_0^\pm\left(d\right)\frac{1+\dfrac{\kappa}{4}}{1+\dfrac{\kappa}{12}+\dfrac{\ln^2 s}{24}}s^{\mp\frac{1}{2}} \tag{24}$$

Let us illustrate the exactness of Eq. (24) by a graphic presentation. For this purpose, we have made a comparison of the calculation results by Eq. (24) with corresponding precise calculations by Eqs. (14) and (17). Since the quantity $\beta_0^\pm\left(d\right)$ in Eq. (17) and in Eq. (24) is the same, we will consider the dimensionless ratio $R = \beta_\delta^\pm\left(d\right)\big/\beta_0^\pm$ for both cases. Let us denote by $R(17)$ the value of R from Eqs. (14) and (17), and by $R(24)$ the same from Eq. (24). The relative uncertainty of Eq. (24) per cent is expressed as $100 \times (R(17) – R(24))/R(17)$, and it is represented in Fig. 1 as a

function of $1/\kappa$ and s, where $1/\kappa$ is the dimensionless diameter of a particle. For example, if $1/\kappa = 1$, then $d = 57$ nm in standard atmospheric conditions. The ratio of polar conductivities s is presented with values 1; 2; 4. The values s and $1/s$ give identical results for R. The small uncertainty of about 0.3% for s = 4 at large $1/\kappa$ values is due to the approximation made in the derivation of Eq. (22).

From mathematical point of view, Eq. (24) is sufficiently exact in standard environmental conditions, if the diameter of particles is larger than 50 nm. However, in particular applications, corresponding physical presumptions also are to be considered. Eq. (24) can be applied in calculations, if the diffusion charging theory by (Fuchs, 1947) is posited. It is easy to replace the ratio of conductivities s by the average charge number $\bar{j}$ through Eq. (16), but the average charge number for any particle size is difficult to measure in observations, in comparison with the ratio of conductivities.

For completeness, it would be desirable to extend similar equations towards smaller diameters of particles. One way of the extension could be the application of the above mentioned correction factors for $\beta_j^\pm\left(d\right)$ from the papers (Tammet and Kulmala, 2005; Tammet *et al.*, 2006), which take into account the results of precise numerical calculations by Hoppel and Frick (1986) and experimental results by Reischl *et al.* (1996). In a steady state, the application of the correction factors does not give similar simple equations for charge distribution as Eqs. (12)–(15), however, there are only a few significant charge numbers around $j = 0$, if $d < 50$ nm, probably five j values from –2 to +2. Thus it would be possible to derive an analytical equation for approximate calculations of $\beta_\delta^\pm\left(d\right)$ also in the range of smaller particle diameters from 1 nm to 50 nm, and to match the equations for the entire range of aerosol particles. This derivation would be the subject for the next article. Another way to create compact analytical equations for the ranges of smaller particle diameters can open if the corresponding charging theory for the transient and free-molecule regimes will be developed; there are promising results in this respect by Lushnikov and Kulmala (2004; 2005).
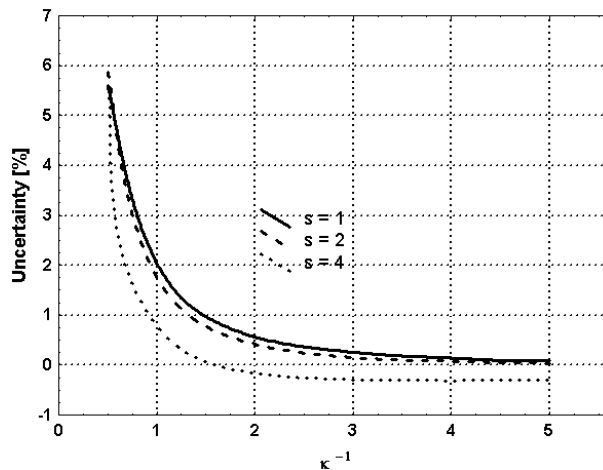

Fig. 1. The uncertainty of Eq. (24) in comparison with precise calculations by Eqs. (14) and (17). Explanations are given in the text.

CONCLUSIONS

Considering the diffusion charging of aerosol particles in a bipolar steady state ion environment and applying the Poisson sum formula, an explicit analytical approximation Eq. (24) for the ion-aerosol equivalent attachment coefficient as a function of the ratio of polar conductivities and of the particle diameter has been successfully derived. The merit of the equation lies in its simple and synoptic shape. It can be used as a component for the compilation of larger ion-aerosol interaction models like it has been done in (Hõrrak *et al.*, 2008). For example, through Eq. (5) the equivalent attachment coefficient determines the effective attachment coefficient, which in turn can be used in the balance Eq. (6). The creation of a related approximation equation for the range of smaller particle diameters is possible.

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NOMENCLATURE

α	recombination coefficient of cluster ions
$\beta_j^\pm(d)$	attachment coefficient of positive or negative cluster ions to an individual aerosol particle with a diameter of d and charge number j
$\beta_\delta^\pm(d)$	equivalent or single-size ion-aerosol attachment coefficient
$\beta_{eff}^\pm$	effective ion-aerosol attachment coefficient
d	diameter of a particle
$D^\pm$	diffusion coefficients of cluster ions
ε_0	electric constant
e	elementary charge
$f(d)$	normalized differential size distribution function
$\bar{j}$	average charge number
κ	reciprocal of the aerosol particle diameter
k	Boltzmann constant
$n^\pm$	concentrations of positive or negative cluster ions
N_{tot}	total number concentration of aerosol particles
$p_j(d)$	charge distribution, i.e. the probability of a particle with a diameter of d to carry j elementary charges
q	ionization rate
s	ratio of polar conductivities
T	absolute temperature
$\Phi_j^\pm(d)$	diffusion fluxes of single charged negative and positive cluster ions onto an aerosol particle
$Z^\pm$	mobility of a negative or positive charged particle

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