Air Ions and Aerosol Science

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Abstract. Collaboration between Gas Discharge and Plasma Physics, Atmospheric Electricity, and Aerosol Science is a factor of success in the research of air ions. The concept of air ion as of any carrier of electrical current through the air is inherent to Atmospheric Electricity under which a considerable statistical information about the air ion mobility spectrum is collected. A new model of air ion size-mobility correlation has been developed proceeding from Aerosol Science and joining the methods of neighboring research fields. The predicted temperature variation of the mobility disagrees with the commonly used Langevin rule for the reduction of air ion mobilities to the standard conditions. Concurrent errors are too big to be neglected in applications. The critical diameter distinguishing cluster ions and charged aerosol particles has been estimated to be 1.4–1.8 nm.

INTRODUCTION

Air ions are a common research subject of Atmospheric Electricity, Gas Discharge and Plasma Physics, and of Aerosol Science. During the development of the science, the research fields are expanding and folding over each other as shown in Fig. 1.

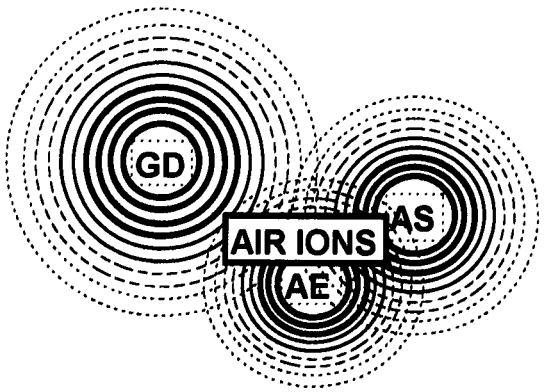

FIGURE 1. An illustration of the expanding research fields and of the position of air ions as a common research subject. GD – Gas Discharge and Plasma Physics, AE – Atmospheric Electricity, AS – Aerosol Science.

The overlapping of GD&AE and AE&AS in Fig. 1 is an old feature and the study of air ions has been a roundabout bridge between GD and AS for many years. A new direct bridge between GD&AS is created by the research of the dusty plasma. However, the bridge is built only from one side and it is almost idle by now.

Separated research fields form their own paradigms (1). Each paradigm consists of specific knowledge about the carriers of electric current in the air. Today, the study of electrical phenomena in natural air is expanding, owing to applications in air quality control and monitoring. Interaction of paradigms is a factor of success in the study of shared subjects. The aim of the present paper is to help the scientists engaged in separated research fields to join their efforts for a better understanding of air ions.

CONCEPT OF AIR ION

When J. J. Thomson started the study of the passage of electricity through gases, the nature of the carriers of electrical current was unknown and the word "ion" was denoting any carrier, the electrons excluded. This original meaning has steadily been preserved in Atmospheric Electricity. A considerable role in the formation of terminology was played by the prestige of Paul Langevin whose paper "Sur les ions de l'atmosphère" (2) is often cited as a first description of charged particles of a mobility of about 1/3000 $cm^2V^{-1}s^{-1}$. These particles are now called the Langevin ions or large ions. They carry up to one per cent of the electrical current in the atmospheric air. The diameter of a single charged Langevin ion is about 0.09 μm and it consists of about 10^7 atoms. In Aerosol Science, the Langevin ions are called the charged aerosol particles.

Originating from Atmospheric Electricity, the term "air ion" or "atmospheric ion" has been fixed by Atmospheric Electricity and other narrow research fields are not authorized to redefine the meaning of this word combination. There are no gaps in the air ion mobility spectrum in a range of 0.0001–2.5 $cm^2V^{-1}s^{-1}$. The term "air ion" denoting all these particles could be considered an inseparable phrase independent of the term "ion" used in general physical context. The terms "small ion", "intermediate ion" and "large ion" used in Atmospheric Electricity have been derived from "air ion", not from the term "ion" denoting ionized atoms or molecules.

In the general physical context, the small air ions could be called the cluster ions, and the large air ions – the aerosol ions (3). The term "cluster ion" is commonly acknowledged, in spite of the controversy with the usage of the word "ion" in a general physical context. The principle of discrimination between cluster ions and aerosol ions is explained hereinafter.

The lowest size of a particle considered a subject of Aerosol Science has been decreased during recent years. In the last volumes of *Journal of Aerosol Science*

one can find the titles "A new electromobility spectrometer for the measurement of aerosol size distributions in the size range from 1 to 1000 nm" (4), "Electric mobility measurements of small ions ..." (5), etc. Today, all kinds of air ions are accepted as research subjects of Aerosol Science.

CHARACTERISTICS OF AIR IONS

The frequently used characteristics of air ions are: mass and electrical mobility in Gas Discharge and Plasma Physics, electrical mobility in Atmospheric Electricity, size and mass in Aerosol Science. Mass, electrical mobility, and size of air ions are closely correlated.

Direct measurement of the mass of a microscopic particle is possible when the particle has been transmitted into the vacuum. The processes of composition and decomposition of clusters, and condensing and evaporating of compounds from particles during the rapid expansion of the air are disturbing the measuring of mass of an air ion as it is in the normal air. Nevertheless, important results in small air ion research are achieved using mass spectrometers that enable an excellent resolving power and the best capacity for identification of chemical compounds. There is a huge amount of clusters of the same mass assembled from various compounds. Reliable information about chemical composition of small air ions in the ground layer of the atmosphere was first obtained by Eisele who introduced a sophisticated technique in case of which the clusters are disassembled in the first section of the instrument (6). After this the masses of molecular fragments are measured and identified.

The electrical mobility is an in situ measurable parameter of an air ion; most of the information available about air ions is expressed in terms of mobility. Measurement of air ion mobilities in the natural air is complicated when compared with the mobility measurements in laboratory experiments. The reason is the low concentration of air ions combined with the low mobility that follows in extremely low values of electrical current of the collected air ions. The instrumental broadening of the mobility lines, on the occasion of tropospheric measurements, is typically exceeding ten per cent. Better resolution is achieved, when the ions artificially created in the natural air are measured to get the information about trace gases. This method is known as plasma chromatography (7).

A simple equation of empirical regression between mass and mobility presented in the handbook (8) is based on the classic data set by Kilpatrick (9, 10) where the measured mobilities and masses of 36 ions are presented over the mass range of 35–2122 u. The original data set (9) is slightly deformed because Kilpatrick has reduced the mobilities to standard conditions using an incorrect procedure. While correcting the data according a new model (11), the numerical values of regression coefficients presented in (8) should be changed, and the improved equation for standard conditions would be:

$$K \approx \left(\sqrt[3]{\frac{1210u}{m}} - 0.21 \right) \mathrm{cm^2 V^{-1} s^{-1}}. \quad (1)$$

While restoring the mobilities measured by Kilpatrick, the mean-square and maximum relative errors of the equation above are 3.3% and 7.8%, respectively. If the smallest ion and biggest ion in the Kilpatrick data set are neglected, the mean square and maximum errors for other 34 ions will be 2.8% and 5.3%.

A real particle has no exactly determined geometric surface; and it can be non-spherical. Size is a parameter for a model of air ion. The concepts of collision size, mobility size, and mass size are discussed in the paper (11). The mass size is preferred as a simple and natural extension to the macroscopic concept of size. The mass diameter of a particle is defined as

$$d_m = \sqrt[3]{\frac{6m}{\pi\rho}}, \quad (2)$$

where ρ is the density of the particle matter.

The size of large ions can be measured directly using an electron microscope. Usually, the size is a parameter to be determined by an indirect way, e.g. measuring the mobility, and calculating the value with the help of the size-mobility relation.

MOBILITY SPECTRUM OF AIR IONS

A typical air ion is encountering about 10^{12} neutral molecules during its existence in the atmosphere as a cluster ion. Therefore, the trace admixtures of relative concentration down to 10^{-12} can participate in forming the composition and determining the mobility of a cluster. The result is a big variety of cluster ions in the air, and the mobility spectrum consisting of many neighboring lines not resolvable in measurements. The mobility spectrum of cluster ions is ultrasensitive to some trace gases; the mobility spectrometry is accepted as a promising technique for environmental analysis (12).

About 3% of cluster ions in the ground level atmospheric air is neutralized encountering another cluster ion of opposite polarity. Most of the cluster ions are attaching to initially neutral or charged aerosol particles. Some of cluster ions are collecting an unlimited number of ligand molecules, and become aerosol particles. The latter process is called the ion induced nucleation (13), its role in the nature is a hot research problem today.

Mobility spectrum of air ions is formed in the process of all possible ion-molecular reactions, ion-to-particle attachment, ion induced nucleation, particle coagulation and sintering. The elementary processes are well known in the limits of low and high Knudsen numbers (the ratio of the molecule mean free path to the particle size), and satisfactorily known in the domain of medium Knudsen numbers. The

models of Aerosol Science for high Knudsen numbers consist of the knowledge that could be useful in the research of dusty plasma.

The processes involving all components of the real air are too complicated to be covered by a universal model. Even the narrow partial models are technically complicated. A model by Luts and Salm (14) has been presented as a huge system of differential equations, it contains 1518 kinds of ion-molecular reactions. The model is satisfactorily describing the early stages of the evolution of cluster ions. A possible application of the model in Gas Discharge Physics is calculation of the current-voltage characteristics of corona discharge, where the evolution of mobility in the discharge gap is a reason of the inconsistency of the simplified models and experimental results. The models simulating the evolution of aerosol systems can be used in order to solve other partial problems. A new model by Kerminen (15) includes the Van der Waals forces and can be applied to the particles with a size down to 1 nm. Unfortunately, the model by Kerminen does not include the effect of free charges.

Today, the most reliable information about the mobility spectrum of air ions can be obtained by measurements. Long term measurements of air ion mobility spectrum in full range of mobilities are running in Tahkuse, Estonia. The published results (3, 16) are describing the statistical distributions, averages, and some exceptional processes. The long-term average mobility distribution of aerosol ions is consistent with the average aerosol particle size spectrum, and the theoretical model of ion-particle attachment (3). The spectrum over high mobility subrange is shown in Fig. 2. The resolving power of the instrument is not high and the data about the fraction of 2.5–3.2 $cm^2V^{-1}s^{-1}$ can be a result of instrumental broadening of the spectrum lines.

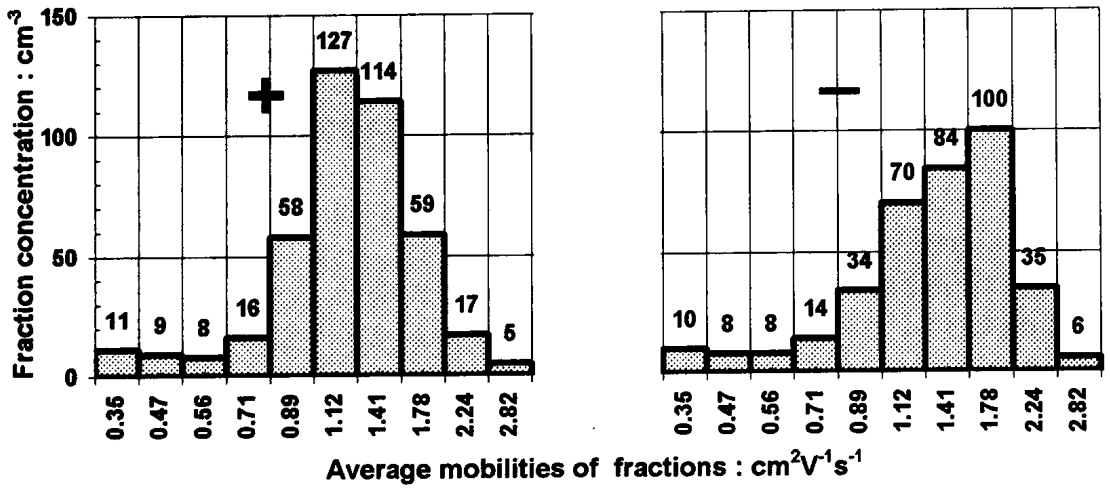

FIGURE 2. The average spectrum of positive and negative air ions with the mobility of 0.32–3.2 $cm^2V^{-1}s^{-1}$ in a rural observatory Tahkuse, Estonia during June–September 1985.

The spectrum has a steady minimum near the mobility of 0.5 $cm^2V^{-1}s^{-1}$ for both polarities. Two fraction concentrations are positively correlated in time if they both are below or above the border of 0.5 $cm^2V^{-1}s^{-1}$. Concentrations of fractions separated by this border are statistically independent in the measurement series. It could be concluded, that the air ions with the mobility below 0.5 $cm^2V^{-1}s^{-1}$ and above 0.5 $cm^2V^{-1}s^{-1}$ have different nature. This observation will be essential when the discrimination between cluster ions and charged aerosol particles is discussed.

A phenomenon of special interest is the sporadic enhancement of air ion concentration in the mobility interval of 0.32–0.5 $cm^2V^{-1}s^{-1}$ observed in Tahkuse. In most occasions the concentration of both positive and negative ions was enhanced but in some occasions the concentration was enhanced only for one polarity that can be positive or negative. An example is given in Fig. 3.

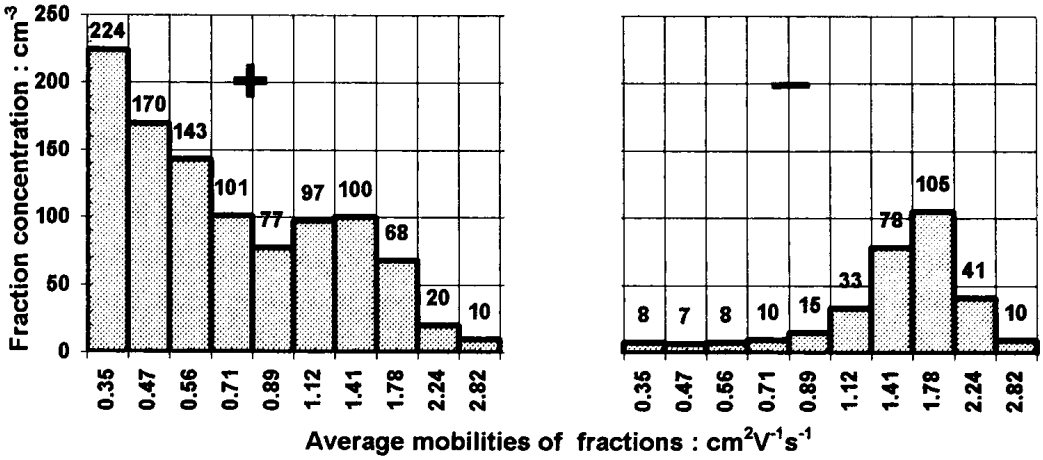

FIGURE 3. Hourly average air ion mobility spectrum in Tahkuse 13 June 1985 at 3 a.m.

The phenomenon above cannot be explained using the standard model of creating the ions with the mobility of 0.32–0.5 $cm^2V^{-1}s^{-1}$ by diffusion attachment of cluster ions to initially neutral nanometer particles. A hypothesis was advanced that the ions of this mobility range are intermediate products of ion induced nucleation (17). According to the hypothesis, the enhanced concentration of air ions with the mobility of 0.32–0.5 $cm^2V^{-1}s^{-1}$ is indicating the appearance of some trace gases in the air, which are able to condense on positive or negative cluster ions, or on cluster ions of both polarities. Fig. 3 is demonstrating the situation where a trace gas is condensing on positive cluster ions. The origin and chemical composition of such gases in the Tahkuse Observatory has remained unknown.

SIZE-MOBILITY CORRELATION

In the free molecule regime, the velocities of ambient gas molecules are independent of the air ion velocity; the equation of size-mobility correlation is given in the Chapman-Enskog kinetic theory. A complication occurs on the occasion of big clusters. In this case the inelastic interactions between air ions and gas molecules become essential. The drag on macroscopic particles at low Knudsen numbers is given by the Stokes-Cunningham-Knudsen-Weber-Millikan equation called below the Millikan equation for the sake of brevity. The Millikan equation considers the inelastic effect of collisions independent of the particle size and it is not valid in the domain of cluster ions. Ramamurthi and Hopke (18) proposed the first empirical equation fitting the kinetic theory in the free molecule limit, and Millikan equation in macroscopic limit. An advanced model is developed in the paper (11).

While discussing the size of a particle, the model of particle-molecule interaction should include a parameter which could be interpreted as the size. A continuous potential model like the Lennard-Jones model or the Tang-Toennies model does not include a proper parameter. Therefore, some modification of the model of rigid spheres should be used in the discussion.

The basic features of the size-mobility correlation model proposed in (11) are:

◊ The interaction between an air ion and ambient gas molecule is described by the $(\infty - 4)$ potential, where the collision distance is written as a sum of three addends: the collision radius of the gas molecule, the mass radius of the air ion and an extra distance that is completing the mass radius to fit the collision radius of the air ion.

◊ The collision radius of the gas molecule is considered to depend on the temperature as in the Chapman-Hainsworth model, and on the energy of the polarization interaction.

◊ The extra distance is regarded as an empirical parameter that should be estimated fitting the model to the experimental data.

◊ The transition from the elastic collisions specific of molecules to the inelastic collisions specific of macroscopic particles is described using the Einstein factor of "melting" of the particle internal energy levels.

◊ The model is written as Millikan equation completed by additional factors describing the transition to the Chapman-Enskog equation in the microscopic limit.

Three parameters should be determined while fitting the model to the experimental data: the density of the ionic matter ρ, the extra distance h and the critical radius of transition from elastic to inelastic collisions r_{cr}. The fitting of the model to the data by Kilpatrick (9) yields following estimates:

$$\rho = 2.07 \text{ g cm}^{-3}, \quad h = 0.115 \text{ nm}, \quad r_{cr} = 1.24 \text{ nm}.$$

The model cannot be presented by an explicit function and it is presented for applications by a computational algorithm (11). The size-mobility curve covering the transition region for air ions in standard conditions is presented in Fig. 4.

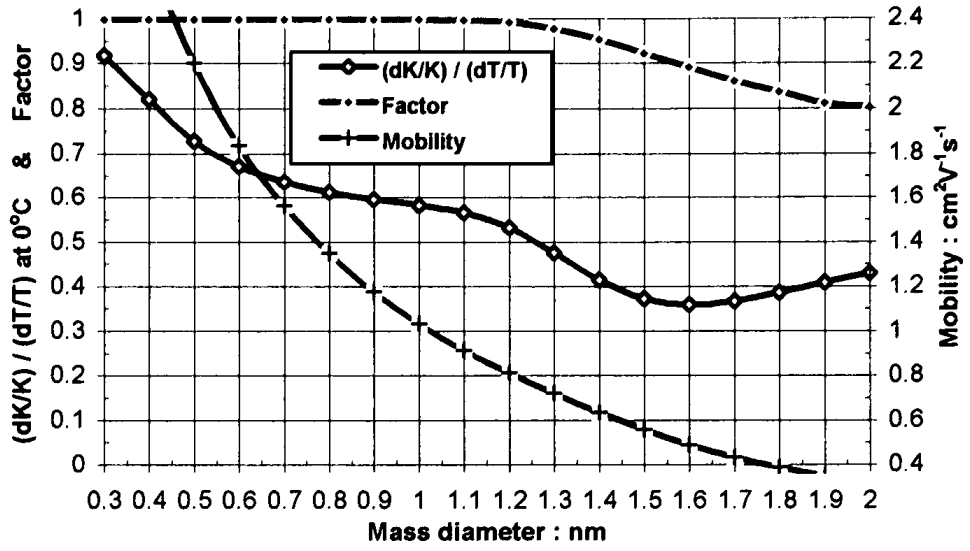

FIGURE 4. Size-mobility correlation, the mobility factor of inelastic collisions, and relative temperature coefficient of the mobility according to the model (11) for air ions in the standard conditions (101325 Pa and 0°C). The mobility factor of inelastic collisions is approaching a value of 0.754 in the macroscopic limit.

REDUCTION OF MOBILITY TO STANDARD CONDITIONS

Traditionally, the mobilities of molecular and cluster ions measured in various experiments are numerically reduced to the standard conditions according to the Langevin rule

$$K_{\text{reduced}} = K_{\text{measured}} \frac{273.15\text{K}}{T} \frac{p}{101325\text{Pa}}, \tag{3}$$

and the reduced values are presented in the publications. It is well known that the Langevin rule is correct only in the polarization limit and not exact when applied in the case of cluster ions. However, no alternative has been available and the error made while using the Langevin rule has been unknown. Therefore, most of the published data about small air ions with a mobility down to 0.5 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ is calculated according to Eq. 3 without any special notice.

The mobility is reduced to the standard conditions according to the model (11) in two steps: at first, the size of an air ion is calculated in the measurement conditions, and then, the standard mobility is calculated according to the size. A measure of the error made by using the Langevin rule is the relative temperature coefficient of the mobility $\frac{\mathrm{d}K}{K} \Big/ \frac{\mathrm{d}T}{T} = \frac{\mathrm{d}K}{\mathrm{d}T} \Big/ \frac{T}{K}$. If the Langevin rule were correct, the coefficient would equal one. The size variation of the relative temperature coefficient according to the model (11) is shown in Fig. 4. As it should be, the coefficient is

approaching one in the zero size limit. The values of the coefficient for the real air ions are considerably less than one and the error of the Langevin rule is essential even on the occasion of the air ions of the highest mobility. The size variation of the coefficient is peculiar in the size range of transition from elastic to inelastic collisions between air ions and molecules that is between 1.2 and 2 nm.

Langevin rule for the reduction of air ion mobilities can cause substantial errors as demonstrated by the following example. The mass-mobility data by Kilpatrick have been measured at a temperature of 200°C and the reduced values of the mobility have been published in the paper (9). Fitting of these data yields the regression equation similar to Eq. 1 but with numerical values of the coefficients of 850 and 0.3 (8). In the present research the original 200°C data were restored and the mobilities at 0°C were recalculated according to the model (11). The results are essentially different from the published data (9) and the best fit of the mass-mobility regression was achieved at numerical values of the coefficients of 1210 and 0.21. The ratio of air ion masses estimated according to the measured mobilities is 1210/850 which could not to be neglected in applications.

The quantitative results about the size and temperature variation of the cluster ion mobility above are depending on the values of the empirical parameters of the model (11) that are based on the old measurement data by Kilpatrick. The revision of numerical results will be required when improved experimental data become available.

DISTINCTION BETWEEN CLUSTERS AND MACROSCOPIC PARTICLES

According to the long term measurements (3) a border of 0.5 $cm^2V^{-1}s^{-1}$ appears as critical in statistical behavior of air ion fraction concentrations in atmospheric air. The same border is critical in the transition from elastic to inelastic collisions if the particle size is increasing. The distinction between clusters and macroscopic particles in physics is based on fitting of the models of the particle internal electron structure (19). If the orbital electron structure model is suitable, the particle is called the cluster. If the zone model is fitting, the particle is called the macroscopic particle. The transfer from elastic to inelastic collisions is closely related to the internal electron structure of the particle. The transfer curve is presented in Fig. 4. A conclusion is that the air ions of a size less than 1.4 nm or of a mobility greater than 0.6 $cm^2V^{-1}s^{-1}$ could be called the cluster ions, and the air ions of a size greater than 1.8 nm or of a mobility less than 0.4 $cm^2V^{-1}s^{-1}$ could be called the charged aerosol particles or aerosol ions.

ACKNOWLEDGMENTS

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