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A Study of the
Temperature and Pressure Variation
of Air Ion Mobilities

Final Report

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Abstract

The air ion mobility distribution gives valuable information about air pollution. Measurements in atmospheric air are carried out in highly variable conditions. The measured mobilities should be transformed into temperature and pressure independent quantities to extract information of environmental importance. Traditionally, the small ion mobilities are reduced to standard conditions according to the Langevin rule. The Langevin rule is correct in case of zero-size ions. The Stokes-Millikan equation provides an alternative valid in the limit of large charged particles. A problem is the conflict between the Stokes-Millikan equation and the Langevin rule in the transition region.

The physical mechanism of the air ion mobility is analyzed in the present study, and a new model using the specified concept of size is proposed. The macroscopic model of a particle as a sphere with an exactly determined surface is not adequate in the nanometer size range. The size of a microscopic particle is a parameter of a model and its common meaning is ambiguous. The difference between the collision radius and the mass radius of a particle is estimated to be 0.115 nm fitting a new semiempirical model to the experimental data.

An innovation is the explanation of the transition from the elastic collisions specific for molecules to the inelastic collisions specific for macroscopic particles using the Einstein factor of the “melting” of the particle internal energy levels. Dipole polarization interaction is included into the model using the $(\infty-4)$ potential. The new model is valid in the full mobility range. It approaches the Chapman-Enskog equation in the free molecule limit and the Millikan equation in the macroscopic limit.

The temperature and pressure variation of atmospheric ion mobilities is examined using the new model. Algorithms are derived to calculate the particle mass size according to the mobility or diffusion coefficient, and to reduce the measured mobilities to the standard conditions. The temperature variation of the mobility occurs to be strongly suppressed in a narrow size interval between 1 and 2.5 nm. This peculiar effect is explained by the temperature variation of the transition size in the Einstein factor. The errors caused by the common usage of the Langevin rule proved to be important even in case of atmospheric ions of the highest mobility. Thus the old data about atmospheric ion mobilities are distorted and should be critically revised.

The results of the study have been published in papers (*Tammets*, 1995a, 1995b, 1996a, 1996b, 1996c) and submitted for publication in the *Journal of Geophysical Research*.

Introduction

Air ions

The term “air ions” signifies all airborne particles which are carriers of the electrical current in the air and have drift velocities determined by the electric field. The physical parameters of an air ion are mass, size, electrical charge, and electrical mobility. Introduction to the physics of air ions and the role of ions in the atmospheric environment can be found in publications (*Israël, 1970; Tammet, 1993*).

A directly measurable parameter of an air ion is the electrical mobility K characterizing the drift velocity in the unit electric field. Additional parameters are the mechanical mobility B and the diffusion coefficient D . Non-linear effects that are essential in high electric fields (e.g. *Mason, 1984*) are not discussed in the present study and the zero field limit is expected considering the electric mobility. The three parameters are bound with two exact equations

$$D = kTB, \quad K = qB \quad (1)$$

where q is the particle charge. Because the parameters B , D and K are equivalent attributes of the particle, one of them is enough to express the mobility of an ion or particle.

The air ions are produced by ionizing radiation's as atomic or molecular ions. The enhanced chemical activity of an ion results in a chain of ion-molecule reactions with the colliding neutrals. During the first microsecond of the life of an air ion a charged molecular cluster called the *cluster ion* is formed. According to the mobility the air ions are called: fast or small ions with mobility $K > 0.5 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, intermediate ions, and slow or large ions with mobility $K < 0.01 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. The boundary between intermediate and large ions is conventional. Small ions are cluster ions. Intermediate and large ions are charged aerosol particles. They can be called the *aerosol ions* according to their physical nature.

Air ion mobility distribution or spectrum is a traditional subject of atmospheric electric research. The mobility spectrum of ions in tropospheric air is continuous with a depression in the region of intermediate ions (*Hörrak et al., 1994, 1996b*). The electric mobility is well correlated with the particle size in the range of intermediate and large air ions. Correspondingly, a space charge mobility spectrum $\rho(K) = d\rho/dK$ can be transformed into a size spectrum of particle number concentration $n(r) = dn/dr$, and the atmospheric electric measurements can be used as a source of information about the atmospheric aerosol particle size distribution (*Hörrak et al., 1995a, 1996a*). The equation of correlation is (e.g., *Salm, 1988*)

$$\rho(K) = \sum_{q=1}^{\infty} q n(r_{qK}) p_q(r_{qK}) \left| \frac{dr}{dK} \right|_{r_{qK}} \quad (2)$$

where r_{qK} is the radius of an aerosol particle that corresponds to the prearranged values of K and q , $p_q(r_{qK})$ is the probability of carrying charge q , and $\left| \frac{dr}{dK} \right|_{r_{qK}}$ is the Jacobian of the transform of the differential distribution function of air ions from r -space to K -space at a known radius r_{qK} .

Nanometer particles and intermediate air ions

Aerosol particles of diameter less than 10 nm are called the *nanometer particles*. Intermediate air ions are electrically charged nanometer particles. Low concentration complicates the measuring of nanometer particles in atmospheric air. The role of nanometer particles as carriers of air pollution and a factor of air turbidity is negligible. Nevertheless, they have turned out as a subject of extensive research during last few years.

Pollock (1915) was the first, who distinctly wrote about intermediate ions. He found a group of air ions with mobilities of about $0.02 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ in natural atmosphere. The measurements by *Pollock* cannot be qualified as reliable. *Misaki et al.* (1972) measured the mobility spectra of air ions in a continuous interval from 0.0001 to $3.2 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ and found a deep depression between small and large ions. The range of depression is considered as the range of intermediate ions. The upper border of the depressed mobility range lies at about $0.5\text{--}0.6 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ and the lower border at about $0.03\text{--}0.1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, depending on the measurement site and time. The result by *Misaki et al.* was confirmed and confined by many of scientists, e.g. *Salm and Reinart* (1992a), *Kojima* (1984) *Dhanorkar and Kamra* (1991), *Hörrak et al.* (1994).

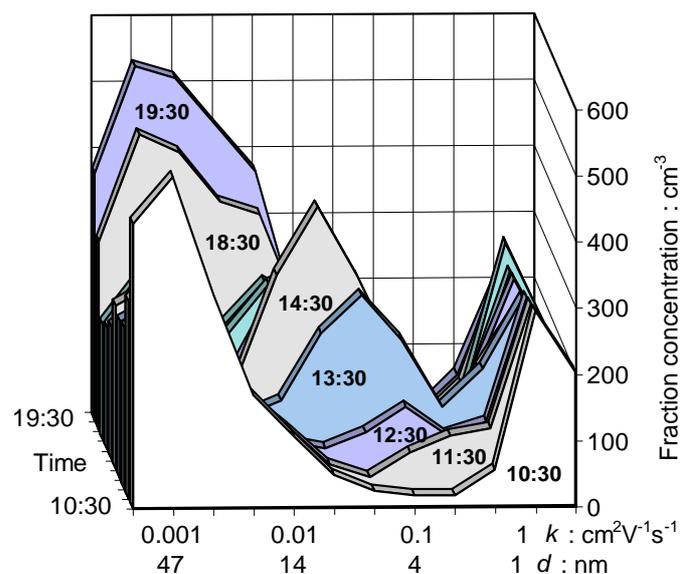


Fig 1. Evolution of air ion mobility spectrum at Tahkuse Observatory, October 20, 1994 (*Hörrak et al.*, 1995b).

The measurements at Tahkuse Observatory showed occasional enhancements or outbursts of the intermediate air ions (*Tammet et al.*, 1988; *Hörrak et al.*, 1994, 1996c). A hypothesis was advanced stating that an outburst could be explained by ion-induced nucleation in atmospheric air (*Tammet et al.*, 1988). An outburst follows in evolution of atmospheric aerosol size distribution as shown in Figure 1. The intermediate ions act as embryos of optically active aerosol particles, and they control the process of gas-to-particle conversion in the atmosphere.

Theoretical models and experimental data about ion mobilities

Mobilities of molecular particles have been carefully studied in the kinetic theory of gases (*Chapman and Cowling*, 1970) and in the theory of ion mobilities (*McDaniel and Mason*, 1973; *Mason and McDaniel*, 1988). A discussion of the problem from a viewpoint of applications has been given by *Mason* (1984). If the interactions between a particle and ambient gas molecules were quantitatively known, the mobility of the particle could be exactly calculated. Unfortunately, the *ab initio* calculation of interactions is extremely complicated in case of molecule-molecule collisions and practically impossible in case of cluster-molecule collisions. Thus the measurements are the main source of reliable information about the mobilities of real particles and empirical or semiempirical models are the tools for practical calculations.

The Millikan equation is considered to be an essence of empirical knowledge about the mobilities of spherical macroscopic particles (*Annis et al.*, 1972). *Ramamurthi and Hopke* (1989) proposed an improved empirical equation fitted to the kinetic theory in the lower size limit and to the Millikan equation in the higher size limit. Another empirical model for full size range composed as a modification of the Millikan equation has been suggested by *Tammet* (1988). The idea is developed in the present study. Some shortcomings of earlier model are eliminated:

- the concept of the particle size is specified,
- the model of transition from elastic to the inelastic collisions is essentially improved,
- the Sutherland approximation of polarization interaction is replaced by the ($\infty-4$) potential model,
- an error caused by the interpretation of the mobilities reduced to the standard conditions by *Kilpatrick* (1971) as real mobilities in the standard conditions, is rectified.

A weak spot of the present study is the experimental data (*Kilpatrick*, 1971) used estimating the empirical parameters of the model. The data does not fully cover the size range of the transition from elastic to inelastic collisions. The data by *Kilpatrick* (1971) are discussed by various authors (e.g. *Meyerott et al.*, 1980, *Böhringer et al.*, 1987) and there is no more complete data set available today. The conclusion was confirmed during special discussion in seminar of the Ion

Physics Institute, University of Innsbruck, 5 Sep. 1996. It is to be hoped that the gap in the experimental knowledge will be filled owing to the advances in development of the electrospray ionization – mass spectrometry (*Smith et al.*, 1991). When combined with an ion mobility spectrometer, the electrospray ionization – mass spectrometer is a promising instrument to obtain the data required for testing the models of the size-mobility relation for nanometer particles.

Problem of the temperature and pressure variation of the mobility

The classic theory of the ion mobilities founded by Langevin results in an equation where the mobility is inversely proportional to the gas density. Commonly, the mobilities of small air ions measured in the atmosphere or in the laboratory are numerically reduced to the standard conditions using the Langevin rule

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

and the reduced mobilities are presented in the publications without any notice about the method of reduction. It is known (e.g., *Mason*, 1984) that the Langevin rule is correct only in the limit of zero-size ions and considerable errors are possible when applying the rule to the cluster ions. However, no quantitative estimate of the error was available and the warning by Mason has been neglected in atmospheric electricity. The air ion mobility temperature and pressure variation should be known to estimate the error and improve the procedure of mobility reduction.

The Langevin rule is commonly accepted as adequate when considering atomic and molecular ions. However, some facts are indicating the problems. The mobility of O_2^- in oxygen has been measured in many laboratories. The variation of the results essentially exceeds the estimate of measuring errors. The unconformity of measurements has no explanation. The measurements have been carried out at different temperatures and the reduced mobilities have been published. A hypothetical explanation of the unconformity is the error of the temperature reduction of the mobility. A numerical example Figure 13 shows considerable error in mobilities of molecular ions when reduced according to the Langevin rule.

Possible practical value of the knowledge about the real temperature variation of big cluster ions in the environmental physics becomes evident when analyzing the results by *Salm et al.* (1992b). The covariation of the average mobilities of small air ions and temperature was studied on basis of long-term continuous measurements of natural ions in atmospheric air. The regression was different for negative and positive ions. Two main factors of the mobility variation are: 1) the physical temperature and pressure variation of the ions of certain chemical composition, 2) the variation of the chemical composition of the ions with temperature. The second factor is of environmental importance. However, no envi-

ronmental conclusions could be drawn because lack of reliable information about the first factor. On the other hand, the temperature variation of the ion chemical composition obscures the physical effect and does not enable to draw conclusions about the first factor.

The temperature and pressure variation of large air ion mobilities is determined by the variation of air viscosity. The temperature variation can be easily calculated and it is opposite when compared with Langevin variation. However, the mobilities of large air ions are presented in publications as measured, and a question about possible reduction to the standard conditions has not been raised.

The air ion mobility spectrum is continuous. The opposite laws of the temperature variation should alter and to join together in the region of intermediate ions. The importance of intermediate air ions in the processes of ion-induced nucleation and gas-to-particle conversion makes it essential to know the law of temperature and pressure variation in the full scale of air ion mobilities. Thus, the limits of the Langevin rule should be examined and alternative procedures of mobility reduction should be discussed.

As affirmed above, consistent *ab initio* theoretical calculation of cluster ion mobilities is not a realistic task. The attempts to find method for direct empirical measuring of the temperature variation of cluster ions (e.g., *Thuillard*, 1995) have had no success because of the temperature instability of the clusters. Thus the solution is to be attempted building a semiempirical model based on theoretical considerations and available indirect experimental information. The model used in the present research is essentially based on the concept of the size of an air ion (*Tamm*, 1995b).

Size of air ions

Concept of the size in the nanometer range

We are using the term *particle* in a wide sense referring to macroscopic and microscopic particles. The term *microscopic* is used when dealing with molecules and clusters. The central symmetry of the particles under discussion is expected, i.e. the interactive force between two particles is assumed to be unambiguously determined by the distance between the centers of the two particles.

The traditional macroscopic model of a particle as a sphere with an exactly determined geometric surface is not adequate in the nanometer size range. In atomic physics, the microscopic particles are characterized by continuous coordinate functions and the concept of the particle size does not play any fundamental role. The concepts of mass and mobility are considered as well defined for any particle. The concepts of size and density of particulate matter are considered as well defined only for macroscopic particles. Modern aerosol physics deals with particles of a wide size range and it is desirable to have the concept of size unambiguously well defined for all particles including the clusters and molecules.

When two colliding particles approach each other, the distance between the particle centers reaches the rebounding interval where the repulsive component of the interaction force is rapidly increasing. The magnitude of the interval is about 0.1 nm. If the size of the particle is ten nanometers or more, the width of the interval is small enough to be neglected. If nanometer particles are examined, a specification of the concept of the size is required.

A result by *Winklmayr et al.* (1991) can be considered as an example pointing out the need to specify the concept of size. A new wide-range particle size spectrometer that is able to measure ultrafine particles down to the molecular size is described in the paper. The directly measured parameter of a particle is the electric mobility and the size of the particle is calculated as a solution of the Millikan mobility equation. The diameter of a single-charged particle of mobility of $1.9 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ is estimated to be 1.1 nm by *Winklmayr et al.* (1991). An ion of indicated mobility has a mass of about 130 amu (*Mason*, 1984). The density of matter in a sphere of diameter of 1.1 nm and mass of 130 amu has an unrealistic value of 0.31 g cm^{-3} . If the density is estimated to be 2 g cm^{-3} , the diameter of the particle should be 0.59 nm. Both estimations of the particle diameter are based on correct calculations but on different concepts of the particle size. The controversy can be solved only when the concept of the particle size is specified.

Collision size

The collision radius or diameter of a particle cannot be considered to be an exact parameter of any precise model in the kinetic theory of gases. A similar

situation exists in structural chemistry and crystallography. The distance between the centers of two atoms called the bond length in a molecule or crystal can be precisely measured using the X-ray technique. The length of a bond is interpreted as a sum of two atomic radii. Several definitions of the atomic radius have been used in structural chemistry (e.g. *Wells*, 1984). However, the measured lengths of bonds differ from the sum of radii up to few percent in any model. The additivity of radii is expected in all models, but it is not exactly satisfied in the nature. Nevertheless, the concept of the atomic radius is fruitful in practice and commonly accepted as a fundamental concept of structural chemistry and crystallography.

The physical collision distance is defined as the closest approach between the centers of two colliding particles. The collision radius of the first kind is defined as a half of the average physical collision distance between two identical particles. We are not using the concept of the collision radius of the first kind in the present paper and the term “collision radius” is defined as the collision radius of the second kind given below. The concept of the collision radius of the second kind is based on the particle collision cross-section and the rigid sphere model of a particle.

In the kinetic theory, the scattering cross-section of the ambient gas molecules by a particle is a well-determined parameter. When two ideal hard spheres of radii r_1 and r_2 elastically-specularly collided, the cross-section is $\Omega = \pi(r_1 + r_2)^2$. The collision distance defined as $\delta = \sqrt{\Omega/\pi}$ is nearly equal to the average distance of the closest approach between the molecules. We can estimate the value of collision distance fitting the calculated values of the transport phenomena to the measured values. The collision radius of the second kind is defined as $r_p = \delta/2$ in case of an encounter of two identical particles. There is no perfect additivity of radii in force when a mixture of various particles is considered, but the errors are small enough to be neglected solving practical problems. The actual values of the collision size can be calculated using the measured values of gas viscosity η and the well-known equation of the kinetic theory (*Chapman and Cowling*, 1970):

$$\eta = 0.1792 \frac{\sqrt{m_g k T}}{\delta^2} . \quad (4)$$

The collision diameter depends on temperature. It follows that the simple rigid sphere model is not adequate. A model of force centers e.g. the Lennard-Jones model or the Tang-Toennies model (*Chapman and Cowling*, 1970; *Tang and Toennies*, 1984) can explain the dependence of viscosity on temperature. Unfortunately, there is no simple concept of particle size in a model where the interaction potential is a continuous function of the distance. An alternative is the model of spheres of variable radii (*Chapman and Hainsworth*, 1924), where the radius is expected to decrease with an increase in temperature. The Chapman-

Hainsworth model is considered to be obsolete and it is not used in the kinetic theory today. However, the idea of variable size cannot be disregarded when the estimation of the size is the aim of an analysis. Empirical values of the efficient collision size of molecules in nitrogen and air calculated according to Equation (4) are presented in Table 1.

Table 1. Collision diameter of nitrogen and “air molecule” according to the experimental data (*CRC Handbook*, 1993) and Equation (4)

Temperature	200	300	400	500	600	K
Viscosity of nitrogen	12.9	17.9	22.2	26.1	29.6	μPa s
Viscosity of air	13.3	18.6	23.1	27.1	30.8	μPa s
δ of nitrogen molecule	0.397	0.373	0.360	0.351	0.345	nm
δ of “air molecule”	0.394	0.369	0.356	0.347	0.341	nm

The empirical formulas

$$\left. \begin{aligned} \text{N}_2: \quad \delta &= 0.2996 \left(1 + (40\text{K} / T)^{0.7}\right) \text{nm} \\ \text{air:} \quad \delta &= 0.3036 \left(1 + (44\text{K} / T)^{0.8}\right) \text{nm} \end{aligned} \right\} \quad (5)$$

approximate the sizes calculated above with an error less than 0.0003 nm. Empirical formulas (5) and Equation (4) can be used interpolating the tabulated values of viscosity. The approximation error is less than 0.06 μPa s in case of viscosity of air at T = 600 K and less than 0.03 μPa s in case of all other values presented in Table 1.

Mobility size

The Cunningham-Knudsen-Weber-Millikan equation

$$B \approx B_M = \frac{1 + \frac{l}{r} \left[a + b \exp\left(-c \frac{r}{l}\right) \right]}{6\pi\eta r} \quad (6)$$

is an accepted representation of empirical knowledge about the dependence of mechanical mobility on the radius of a macroscopic particle. For the sake of brevity Equation (6) is called the Millikan equation. Theoretically derived equations are usually verified by comparing them with the Millikan equation accepted as a standard (e.g. *Annis et al.*, 1972).

The slip factor coefficients have been estimated in different ways by various authors (see *Annis et al.*, 1972; *Allen and Raabe*, 1985; *Rader*, 1990; *Hutchins et al.*, 1995). We are using the round average values $a = 1.2$, $b = 0.5$ and $c = 1$ in numerical calculations. The estimates of the additional parameters of the new

model suggested in this paper essentially depend only on the sum of first two coefficients $a + b$.

Every possible equation of the mobility-size relation can be used to define the mobility size. The Millikan mobility diameter is defined as a solution of Equation (6) where B_M is replaced by the measured value of mobility. When coarse particles moving at low Reynolds numbers are considered, the slip factor in Equation (6) can be omitted and the Stokes mobility diameter can be calculated. The value of the Stokes mobility diameter will differ from the value of the Millikan mobility diameter. The various definitions of the mobility diameter can be evaluated only when an independent value of a more fundamental diameter is available. Hence, the mobility diameter of a spherical particle is not a fundamental parameter. Its physical meaning is a transformed value of the mobility.

The Millikan equation has proved to be precise enough to avoid any practical complication when the size of ambient gas molecules is negligible. The state of affairs will be different when microscopic particles are studied.

Mass size

We are looking for a fundamental parameter that could be interpreted as a simple and natural extension of the macroscopic concept of size. A pragmatic approach is issued from the problem how to calculate the aerosol mass concentration according to the number concentration and vice versa. A common solution is based on the postulate that the density of the particulate matter ρ does not depend on particle size and particle volume is determined by the mass $V = m/\rho$. The radius defined by the equation

$$r_m = \sqrt[3]{\frac{3V}{4\pi}} = \sqrt[3]{\frac{3m}{4\pi\rho}} \quad (7)$$

is called the volume radius or the mass radius. We concur with *Mason* (1984) in using the last term and recommending the mass radius as a fundamental measure of the particle size.

It is assumed that the density of the particle substance is independent of the particle size. According to the experimental data (e.g. *Gamarnik*, 1993), the maximum variation of the lengths of the structural bonds in nanometer particles and clusters is estimated to be about few percent. The same value can be considered as the characteristic of the roughness of the model of particle mass size in practice.

It should be pointed out that the density of the particulate matter can exceed the density of the condensed matter of packed particles. An array of packed spheres has the density of 0.52ρ in case of the simple cubic lattice and 0.74ρ in case of the closest packing.

Basic models of the free molecule regime

Kinetic theory of elastic particles

In the free molecule regime, the velocities of ambient gas molecules are independent of the particle velocity. According to the Chapman-Enskog kinetic theory, the first approximation for the mobility of a particle of mass m_p among the molecules of mass m_g and number concentration n_g is

$$B_1 = \frac{3}{8n_g\Omega^{(1,1)}} \sqrt{\frac{\pi(1+m_g/m_p)}{2m_gkT}} \quad , \quad (8)$$

where collision cross-section is represented by the average first collision integral $\Omega^{(1,1)}$. An estimate of the relative error of the first approximation is

$$\frac{B_2 - B_1}{B_1} = \frac{m_g^2(6\Omega^{(1,2)} / \Omega^{(1,1)} - 5)^2}{30m_p^2 + 10m_g^2 + 16m_gm_p\Omega^{(2,2)} / \Omega^{(1,1)}} \quad , \quad (9)$$

where B_2 is the second approximation of the mobility, $\Omega^{(1,2)}$ and $\Omega^{(2,2)}$ are the higher collision integrals (*McDaniel and Mason, 1973*).

The collision integrals depend on the conservation of energy during a collision between a particle and a gas molecule. The molecule-molecule collisions are elastic-specular but the molecule-macroscopic particle collisions are inelastic as shown in Figure 2.

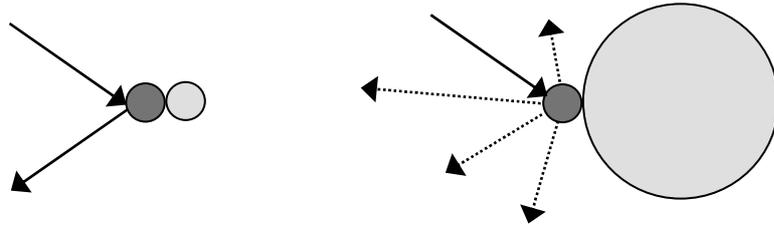


Figure 2. An illustration of elastic and inelastic collisions.

Collision integrals are calculated and tabulated for various models of interaction between colliding particles. The elastic interactions are described using the interaction potential. Two simple model potentials are of special importance. When a charged particle is colliding with a neutral molecule, the interaction between the point charge q and the induced dipole separated by the distance r is described by the potential

$$U_{\text{pol}}(r) = -\frac{\alpha q^2}{8\pi\epsilon_0 r^4} \quad , \quad (10)$$

where α is the dipole polarizability of the molecule. The effect of quadrupole and higher order polarisation as well the effect of the polarity of the charge are not considered in the present paper.

Another simple model potential is the potential of elastic rigid sphere:

$$U_{\text{sph}}(r) = \begin{cases} \text{if } r < \delta & \text{then } \infty \\ \text{if } r \geq \delta & \text{then } 0 \end{cases} . \quad (11)$$

The results are well known in both cases (*McDaniel and Mason, 1973*). In the first case of $U(r) = U_{\text{pol}}(r)$:

$$\Omega^{(1,1)} = 0.9206 \frac{q}{e} \sqrt{\frac{\alpha}{\epsilon_0 kT}} , \quad (12)$$

$$B = B_2 = B_1 = 0.5105 \frac{q}{en_g} \sqrt{\frac{\epsilon_0 (1 + m_g / m_p)}{\alpha m_g}} , \quad (13)$$

where q/e is the number of elementary charges. Equation (13) is known as the polarisation limit or the contemporary expression of the Langevin formula. It has been proved fairly useful when interpreting the measured mobilities of atomic and small molecular ions (*Böhringer et al., 1987*). In the second case of $U(r) = U_{\text{sph}}(r)$:

$$\Omega^{(1,1)} = \pi \delta^2 , \quad (14)$$

$$\frac{B_2 - B_1}{B_1} = \frac{1}{10 + 16(m_p / m_g) + 30(m_p / m_g)^2} . \quad (15)$$

The relative error expressed by Equation (15) decreases rapidly when $m_p > m_g$:

$m_p / m_g =$	1	2	5	10
$(B_2 - B_1) / B_1 =$	1.8%	0.6%	0.1%	0.03%

Effect of inelastic interaction on the collision cross-section

When collisions between particles and molecules of ambient gas are inelastic, the actual collision cross-section exceeds the calculated value assuming that the gas molecules are elastically scattered by the particle. Inelastic collisions will occur when the internal energy of a particle or an ambient gas molecule is interconvertible with the energy of translation. Thus a violation of the law of elastic-specular scattering occurs and there is a corresponding increase in collision cross-section.

The success of the elementary theory of heat capacity of gases demonstrates that the energy of the rotation of polyatomic molecules is interconvertible with the energy of translation at room temperature. However, the mobilities of atomic and small molecular ions in diatomic gases calculated according to Equation (13)

have proved to be acceptable (*McDaniel and Mason, 1973; Böhringer et al., 1987*). Obviously, the separation of the rotational energy levels of diatomic molecules is too large to have a significant effect on the collision cross-section. Therefore, the internal energy of ambient gas molecules can be neglected when calculating the mobilities.

The separation of the internal energy levels of a macroscopic particle is very small and interconversion between the translational energy and the internal energy of the particle is actual. A result is heat transfer between gas and a particle. The corresponding microscopic phenomenon is called the accommodation of the kinetic energy of a molecule to the temperature of the particle surface. An experimental and theoretical analysis of the issue has been carried out first by *Millikan (1923)* and *Epstein (1924)*.

An inelastic interaction cannot be described by potential. The collision cross-sections have been calculated using sophisticated techniques for various regimes of inelastic scattering of gas molecules by a rigid sphere (*Chapman and Cowling, 1970*). The collision cross-section of an inelastic sphere exceeds the geometrical cross-section $\pi\delta^2$ and can be written using a factor $s = s(r_m, T)$ as

$$\Omega^{(1,1)} = s(r_m, T)\pi\delta^2(T) . \quad (16)$$

The mass radius is used above as a characteristic of the particle size and the dependence of the collision distance δ on temperature is pointed out in Equation (16). When all gas molecules are assumed to be thoroughly accommodated to temperature of the particle, the value of the factor s should be of 1.393 as calculated by *Epstein (1924)*. The actual value of the factor s varies between 1 in case of atomic ions and $s_\infty = 2.25/(a+b) \approx 1.32$ in case of macroscopic particles, depending on the real law of the reflection of gas molecules by a particle. The law of the reflection of gas molecules is not determined by the Knudsen number but by the absolute size of the particle. Therefore, the low pressure techniques used for the measurement of the slip factor cannot be used when studying the factor s .

Improved Model of the Ion Mobility

Mobility of a neutral particle in the free molecule regime

Equation (8) and the approximation $B \approx B_1$ are exact enough to satisfy the requirements of experimental aerosol research. The problem of the size-mobility relation is reduced to the calculation of the collision integral $\Omega^{(1)}$. Equation (16) is used as the basis for further discussion which makes it possible to interpret the results in terms of the particle size.

The collision distance is the sum of the particle collision radius r_c and the average collision radius of an ambient gas molecule r_g : $\delta(T) = r_c(T) + r_g(T)$. The function $r_g(T)$ is estimated on the basis of gas viscosity measurements. The function $r_c(T)$ is spliced into two addends:

$$r_c(T) = r_m + h(T) \quad (17)$$

linking the concepts of the mass radius and the collision radius of a particle. The temperature-dependent addend h is called the *extra-distance*. Theoretical evaluation of the function $h(T)$ is a hopeless task. An empirical model is useful in applications if the temperature-dependent addend $h(T)$ is presented by a simple parametric approximation and the parameters can be estimated fitting the model to the measurements. An example is the equation $h = h_o + h_T/T$ where h_o and h_T are the empirical parameters. However, the measurement data available in the present study are not informative enough to enable to evaluate the parameters of a two-parametric model. Therefore, the value of the parameter h is considered to be an empirical constant when analysing the measurement data below.

The extra-distance h as an empirical quantity is automatically taking into account all possible undiscussed effects including the effect of Van der Waals forces.

When clusters and nanometer particles are considered, the law of the transition of the internal energy factor $s = s(r_m, T)$ from the initial value 1 to the saturation level s_∞ will present a problem. A fitting of a two-parametric formal mathematical approximation of the transition function to the empirical data was performed in an earlier study by the author (*Tammets*, 1988). It was shown that the transition from elastic collisions to inelastic collisions should take place at the particle mass diameter of about 1–2 nm.

The physics of collisions is rather complicated (*Billing*, 1990) and the existing knowledge is not sufficient for theoretical calculation of the transition function $s(r_m, T)$. A semiempirical model is thus built on the basis of limited knowledge. Two physical statements are used:

1. The melting of internal degrees of freedom of the particle energy is described by the Einstein factor

$$\left(\frac{\Delta E}{kT}\right)^2 \frac{\exp\left(\frac{\Delta E}{kT}\right)}{\left(\exp\left(\frac{\Delta E}{kT}\right) - 1\right)^2}$$

where ΔE is the separation of energy levels. The statement is based on an analogy of the process considered with the melting of the rotational and vibrational degrees of freedom by the heating of polyatomic gas or a solid body.

2. The average separation of internal energy levels in a cluster is inversely proportional to the number of the atoms in the cluster (*Petrov, 1986*) or to the value of r_m^3 .

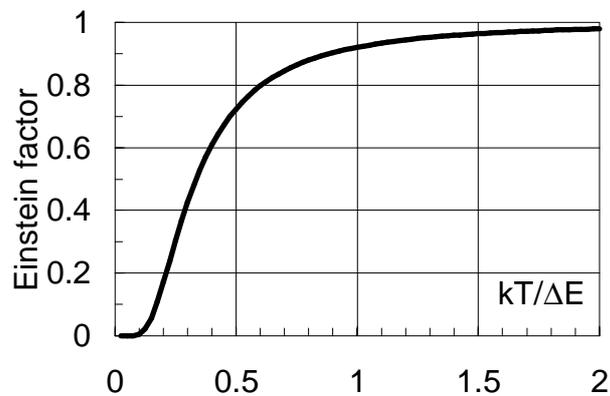


Figure 3. The Einstein factor of melting of internal degrees of freedom of the particle energy

The separation of the energy levels in the expression of the Einstein factor is replaced by the average separation in an approximate model:

$$x = \frac{\Delta E}{kT} = \frac{273\text{K}}{T} \left(\frac{r_{\text{cr}}}{r_m}\right)^3, \quad s = 1 + (s_{\infty} - 1)x^2 e^x / (e^x - 1)^2. \quad (18)$$

The model consists of one parameter r_{cr} to be evaluated fitting the model to the empirical data. Nevertheless, the error of the fitting of the model to the measurements is less than in case of the two-parametric formal approximation used in the earlier study (*Tammet, 1988*).

Mobility of a charged particle in the free molecule regime

Considering a nonpolar ambient gas like nitrogen or oxygen, the electric charge of the particle induces a dipole moment of an initially nonpolar gas molecule. The charge-dipole interaction results in the enhanced cross-section of a collision between a particle and a molecule. The induced quadrupole and higher moments are neglected in the present paper.

The energy of polarization interaction at the moment of the collision $U_{\text{pol}}(\delta)$ can be calculated using Equation (10). *Hopke and Ramamurthi (1988)*, *Strydom et al. (1990)* and *Ramamurthi et al. (1993)* have corrected the equation of the mobility of charged nanometer particles using the Sutherland approximation according to *Chapman and Cowling (1970)*

$$B_q = \frac{B_{q=0}}{1 + \frac{0.2011|U_{\text{pol}}(\delta)|}{kT}} \quad (19)$$

When the size of the rigid sphere decreases and approaches zero, the expression of the mobility must approach to the polarization limit (13). The requirement is not satisfied when using the Sutherland approximation (19). It follows the limits of the Sutherland approximation should be examined. An improved theoretical model is required for the examination of the quality of the approximation.

Two kinds of the interaction potential models consisting of both a rigid sphere and polarization interaction are known in the kinetic theory of ion mobility (*McDaniel and Mason, 1973*). In the simple ($\infty-4$) potential model, the particle charge is located in the center of the particle and the potential is:

$$U = \begin{cases} \text{if } r < \delta(T) & \text{then } \infty \\ \text{if } r > \delta(T) & \text{then } U_{\text{pol}}(r) \end{cases} \quad (20)$$

In the sophisticated core models the particle charge is assumed to be distributed on a spherical surface. Unfortunately, a core model consists of additional parameters that should be evaluated according to the empirical data. Available data are not sufficient for estimating the values of the additional parameters. Therefore, the simple ($\infty-4$) potential model is used in the present paper.

Dimensionless parameters

$$\left. \begin{aligned} \Omega_{\infty-4}^{(1,1)*} &= \Omega^{(1,1)} / (\pi\delta^2) \\ T^* &= kT / U(\delta) \end{aligned} \right\} \quad (21)$$

are traditionally used in numerical calculations. We mark the collision integral for the ($\infty-4$) model with an index $\infty-4$. The table of the function $\Omega_{\infty-4}^{(1,1)*}(T^*)$ presented by *McDaniel and Mason (1973)* can be replaced by the interpolation algorithm:

$$\Omega_{\infty-4}^{(1,1)*} = \begin{cases} \text{if } T^* \leq 1 & \text{then } 1.4691 \times T^{*-1/2} - 0.341 \times T^{*-1/4} + 0.185 \times T^{*5/4} + 0.059 \\ \text{if } T^* \geq 1 & \text{then } 1 + 0.106 \times T^{*-1} + 0.263 \times T^{*-4/3} \end{cases} \quad (22)$$

The approximation is correct in the limit $T^* \rightarrow 0$ and the relative error of the calculated values is less than 0.09% for the values presented in the table published by *McDaniel and Mason (1973)*.

The effect of the dipole polarization increases the collision integral calculated for a neutral rigid sphere by an addend $(\Omega_{\infty-4}^{(1,1)*} - 1)\pi\delta^2$. The addend does not depend on the factor s when considering the polarization limit. Hence, Equation (16) is expanded in the following way

$$\Omega^{(1,1)} = [s(r_m, T) + \Omega_{\infty-4}^{(1,1)*} - 1]\pi\delta^2(T) , \quad (23)$$

where $\Omega_{\infty-4}^{(1,1)*}$ is calculated for an elastic-specular interaction.

An original alternative approach has been proposed by *Phillips* (1993). The molecule trajectories near the charged particle were numerically calculated using a computer program not available in the publication. Numerical results presented by *Phillips* (1993) have not been compared with the results of Chapman-Enskog theory and cannot be judged in the present paper.

Electrical compression of the collision distance

The collision distance between a neutral particle and a gas molecule has been considered as a function of temperature. The true argument of the function is the average maximum deformation energy that is determined by temperature in case of a neutral particle. If the particle is charged, the energy of polarization interaction is added to the maximum deformation energy. As a result the collision distance will decrease when compared with the collision distance between a neutral particle and a molecule. The effect is expected to be similar to the effect of equivalent increase in temperature.

When expressed in the reference system of the mass center, the average kinetic energy of a pair of neutral colliding particles is $2kT$ (*Chapman and Cowling*, 1970). The kinetic energy will be fully transformed to the deformation energy in case of a direct collision only. If the collision angle is φ , the average maximum deformation energy will be $2kT\cos^2\varphi$. The average maximum deformation energy integrated over all collision angles E_{def} equals to kT for a neutral particle. In the first approximation, the average deformation energy for a charged particle is

$$E_{\text{def}} = kT + |U_{\text{pol}}(\delta)| . \quad (24)$$

The effect can be easily taken into account when the argument of the collision distance is replaced by an effective temperature

$$T_{\delta} = E_{\text{def}}/k = T + |U_{\text{pol}}(\delta)|/k . \quad (25)$$

T_{δ} is expressed as a function of δ (Equations 25 and 10), and δ as a function of T_{δ} (Equation 5). Thus, a system of equations should be solved to determine the values of both variables. A simple iterative procedure presented in the appendix rapidly converges when testing the equation under realistic conditions.

The electrical compression is a peculiarity of the $(\infty-4)$ potential model when interpreted in terms of the Chapman-Hainsworth “soft” spheres. The same physical effect is automatically included when using any of the models based on a continuous interaction function

Modified Millikan equation

The radius of a particle and the collision distance are not distinguished in the classic Millikan equation (6). The Millikan equation is based on the assumption of size independent temperature accommodation of gas molecules on the surface of a particle that is not adequate in the nanometer size range. When the particle diameter decreases, the accommodation coefficient approaches to zero and the kinetic theory model of the mobility will be valid.

Replacement of the particle radius by the collision distance δ is a precondition for perfect conversion of the Millikan equation to the free molecule regime equation as the particle size decreases. Additional improvements are required to take into account the finite mass of the particle, the polarization interaction and transition to the elastic-specular collisions in the limit of $r \rightarrow 0$. A modified equation written as a product of three factors is thus proposed

$$B = f_1 f_2 \frac{1 + \frac{l}{\delta} \left[a + b \exp\left(-c \frac{\delta}{l}\right) \right]}{6\pi\eta\delta} . \quad (26)$$

The collision distance is calculated as a sum

$$\delta = r_m + h + r_g(T_\delta) \quad (27)$$

where the possible dependence of the addend h on temperature is neglected because the available empirical information is not sufficient to estimate the parameters of the dependence. The value of r_g is estimated to be a half of the collision distance between two gas molecules calculated according to Equation (5) by the effective temperature considering the effect of electrical compression.

The first correction factor in Equation (26) accounts for the finite mass of the particle

$$f_1 = \sqrt{1 + \frac{m_g}{m_p}} . \quad (28)$$

The second factor takes into account the inelastic collisions and the polarization interaction

$$f_2 = \frac{2.25}{(a + b) \left(\Omega_{\infty-4}^{(1,1)*}(T^*) + s(r_m, T_\delta) - 1 \right)} , \quad (29)$$

where a and b are the slip factor coefficients, $\Omega_{\infty-4}^{(1,1)*}$ is calculated according to Equation (22) and s according to Equation (18). In case of electrically neutral particles $\Omega_{\infty-4}^{(1,1)*} = 1$.

Arguments of the algorithm (26–29) are the parameters of ambient gas and any combination of two values from the set of three particle parameters (mass radius, mass and density). The algorithm consists of two parameters that are not evaluated above:

- the extra-distance h (parameter of the collision distance δ),
- the critical radius r_{cr} (parameter of the function $s(r_m, T_\delta)$).

We are considering the above parameters to be empirical constants that should be evaluated when fitting the model to the measured data.

Equation (26) is approaching the Chapman-Enskog equation (6) in the fine particle limit and the Millikan equation (4) in the coarse particle limit.

Fitting of the model to the experimental data

The mass and the electrical mobility of charged nanometer particles can be independently measured using a mass spectrometer and a drift tube. There is no available instrumentation for the direct measurement of the geometric size in the nanometer range. The gap could be filled with information about the density of the particulate matter.

Available empirical data are poor. Reliable results of the simultaneous measurement of ion mass and mobility have been published by *Böhringer et al.* (1987) together with a careful analysis of the available data by other authors. Ions with mass up to 2000–3000 amu must be presented in the data set to make it possible to estimate the value of the parameter r_{cr} . The original measurements by *Böhringer et al.* (1987) cover the mass range up to 188 amu. The only available data set covering the mass range up to 2122 amu has been published by *Kilpatrick* (1972). The agreement between the data by Kilpatrick and Böhringer *et al.* in the common mass subrange is fair. Charged nanometer particles are a traditional subject of atmospheric electricity where they are called the atmospheric ions. In the literature about atmospheric electricity, the most quoted source of information about ion mass-mobility correlation is a paper by *Meyerott et al.* (1980) where the results by Kilpatrick are reproduced as the most complete data for big cluster ions. There is no newer satisfactory data set available in the literature. Therefore, the classic data set by *Kilpatrick* (1972) is used in the present paper to evaluate the empirical parameters fitting the model to the measurement data.

The mobilities of the particles were measured by Kilpatrick in dry nitrogen at a pressure of 760 torr and temperature of 200°C. Before publication the data were converted to the standard conditions by multiplying the measured mobilities by the ratio of temperatures 273/473 according to the Langevin rule. How-

ever, the converted values presented in the report cannot be interpreted as the real values of the mobility at standard conditions (*Böhringer et al.*, 1987). The Langevin rule is valid in the polarization limit only and the ratio of the real mobilities of the particles measured by Kilpatrick differ essentially from the ratio of the absolute temperatures. Therefore, the measured values of the mobility were restored multiplying the presented values by 473/273 before using the data in the present study.

In the Kilpatrick data set, the mass and electrical mobility of a single-charged particle are presented. The size and density of the particle remain unknown. The comparison of the model and the data is not possible without any knowledge about the size or the density. To fill the gap, a hypothesis is advanced stating that the correlation between the mass and density of a particle is negligible when considering the full data set. The average density of the particles is assumed to be an unknown constant. The mathematical problem is to choose the values of the three free parameters (extra-distance h , critical radius r_{cr} and the average particle density ρ) so that the mean-square relative deviation between the calculated and measured mobilities will reach the minimum value. The solution acquired using a numerical procedure is:

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

The data and the results of fitting the model to the data are presented in Table 2. The errors are distributed randomly along the table with a mean-square value of 2.59%. The variability of the real densities of the particles is a possible origin of the fitting errors.

The density of an array composed of the spheres of density of 2.07 g cm^{-3} is 1.08 g cm^{-3} in case of the simple cubic lattice and 1.53 g cm^{-3} in case of the closest packing.

It is recommended that the estimated values $h = 0.115 \text{ nm}$ and $r_{cr} = 1.24 \text{ nm}$ be treated as a preliminary approximation using the algorithm presented by Equations (26–29) and in the Appendix. The values of the parameters should be adjusted when the advanced experimental data becomes available.

Table 2. The empirical data by Kilpatrick
and the best fit of the data using the model (26–29)

Mass (amu)	Sign	Mobility ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$)			Error (%)
		reduced	measured	calculated	
35.5	–	2.49	4.31	4.41	2.2
46	–	2.36	4.09	4.00	–2.3
60	–	2.06	3.57	3.61	1.3
60	+	2.07	3.59	3.61	0.8
84	+	1.84	3.19	3.19	0.0
90	–	1.83	3.17	3.11	–2.0
114	–	1.69	2.93	2.85	–2.8
114	+	1.73	3.00	2.85	–5.0
127	–	1.52	2.63	2.74	3.8
130	+	1.56	2.70	2.71	0.3
152	–	1.46	2.53	2.56	1.1
152	+	1.44	2.50	2.56	2.5
168	+	1.47	2.55	2.46	–3.4
188	+	1.34	2.32	2.36	1.6
215	+	1.21	2.10	2.24	6.8
222	–	1.27	2.20	2.21	0.5
240	+	1.24	2.15	2.15	0.1
244	+	1.27	2.20	2.13	–3.1
244	+	1.28	2.22	2.13	–3.8
256	+	1.26	2.18	2.09	–4.1
292	–	1.14	1.98	1.99	0.6
292	–	1.13	1.96	1.99	1.5
292	+	1.14	1.98	1.99	0.6
295	–	1.19	2.06	1.98	–4.0
361	–	1.06	1.84	1.83	–0.6
407	–	0.984	1.71	1.74	2.0
430	–	0.976	1.69	1.70	0.6
430	+	0.976	1.69	1.70	0.6
499	–	0.906	1.57	1.60	1.8
499	+	0.906	1.57	1.60	1.8
511	–	0.922	1.60	1.58	–1.0
660	–	0.820	1.42	1.41	–0.6
660	+	0.842	1.46	1.41	–3.2
1061	–	0.607	1.05	1.10	4.5
1612	–	0.497	0.86	0.84	–2.1
2122	–	0.411	0.71	0.71	–1.0

Comparison of the new and traditional models of the mobility

If the size of a particle in the Millikan equation (6) is represented by the mass radius, the difference between the Millikan model and the present model is less than 1% for particles with diameters greater than 103 nm and less than 0.1% for diameters above 720 nm. The main source of error is the neglecting of the difference between the mass radius and the collision distance in a straightforward usage of the Millikan model. Simple replacement of the radius in Equation (6) by the collision distance δ defined by Equation (27) will dramatically reduce the difference. The residual deviation is less than 1% for particles of a diameter above 2.8 nm and less than 0.1% for particles of a diameter above 4.2 nm.

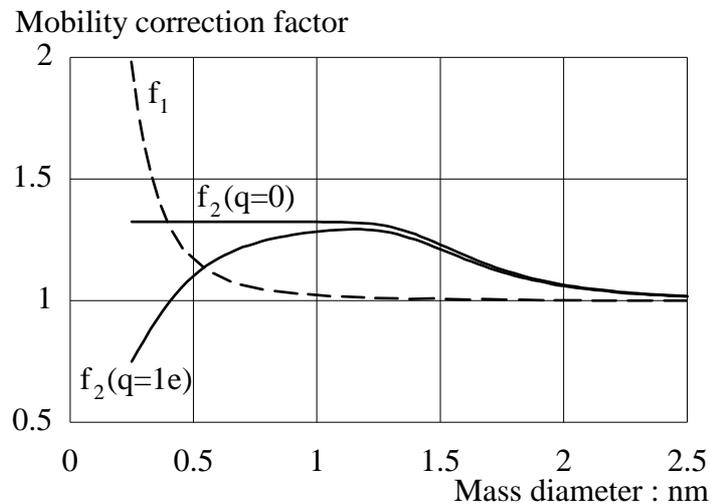


Figure 4. Dependence of the mobility correction factors (26–27) on the size of neutral and single-charged particles in air. Standard conditions and the particle density of 2 g cm^{-3} are assumed.

Both correction factors in Equation (26) are essential only in the case of very small particles. The behavior of the factors is illustrated in Figure 4. The effect of the finite mass f_1 is considerable in case of molecules and small clusters. The second factor is different for neutral and charged particles. In case of neutral particles, the polarization effect is zero and f_2 demonstrates the transition from elastic-specular collisions to inelastic scattering that is characteristic of the macroscopic particles. The curve $f_2(q=0)$ in Figure 4 can be used to discriminate between macroscopic particles and clusters. Traditionally, the particles are called clusters if their behavior differs from the behavior of the macroscopic particles because of the discrete structure of their internal energy (*Petrov, 1986*). The scattering law is just the effect of the structure of the internal energy of the particle. If the internal energy levels are frozen during the collisions, the particles should be considered to be molecules or clusters. If the internal energy levels are

melted out, then the scattering of the molecules is inelastic and a particle can be considered to be a macroscopic body. Thus, the curve illustrates the transition from the molecular or cluster state into the macroscopic particle state. Particles of diameter below 1.4 nm could be called the clusters or molecules and particles of diameter above 2 nm could be called macroscopic particles according to the dominant mechanism of energy transfer by collisions.

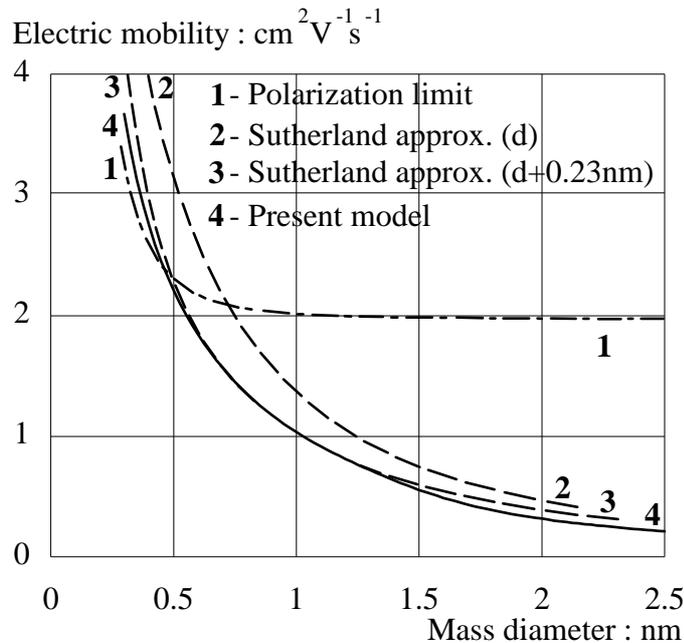


Figure 5. Dependence of mobility on the particle mass diameter in air according to Equations (8, 13, 14, 19, and 26–29). Standard conditions and the particle density of 2 g cm^{-3} are assumed. Curve 1 is presenting the mobility of particles of zero diameter and finite mass calculated according to the plotted fictitious diameter.

The cluster ion mobilities have been interpreted using various models. In the gas discharge physics, the Langevin model (Equation 13) is used to estimate the zero field mobilities. In the aerosol research, the rigid sphere model (Equations 8 and 14) is more common. The effect of the polarization interaction is usually included according to the Sutherland approximation (19). The mobilities calculated using these models and the present model are compared in Figure 5. Curve 1 confirms the well-known fact (e.g. *Mason*, 1984) that the Langevin formula cannot be used to interpret the mobilities in standard conditions below $2.2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. The error of the rigid sphere model combined with the Sutherland approximation depends on the specification of the particle size and collision distance. Curve 2 in Figure 5 is calculated assuming that the collision radius of the particle is equal to the mass radius. When drawing curve 3, the extra-

distance of 0.115 nm was added to the mass radius. As a result, the curve is close to the continuous curve 4 representing the present model. The agreement is very good in the diameter range from 0.6 to 1.3 nm or in the mobility range from 0.7 to 1.8 $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ that is typical for cluster ions. The results are worse for high mobilities where the Sutherland approximation is not exact enough, and for low mobilities where the scattering of gas molecules is not elastic–specular.

The difference between the present model and the Sutherland approximation is demonstrated in Figure 6 where the ratio of the mechanical mobilities of charged and neutral particles is compared. The difference is not important for particles with diameter above 0.7 nm.

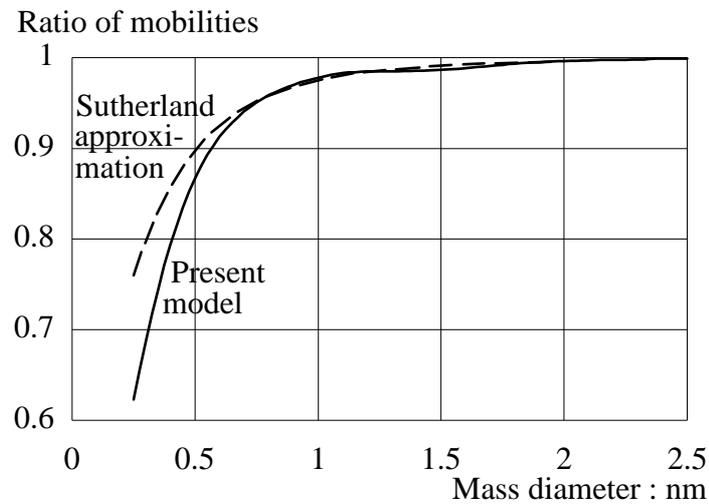


Figure 6. Ratio of the mobility of a single–charged particle to the mobility of a neutral particle in air according to the Sutherland approximation by the diameter $d_m+0.23$ nm, and the present model. Standard conditions and the particle density of 2 g cm^{-3} are assumed.

When considering aerosol particles above of the nanometer scale, the Millikan equation can be accepted as quite good approximation. The approximation can be improved including the effective size of the gas molecule. The error of such an approximation is illustrated in Figure 7.

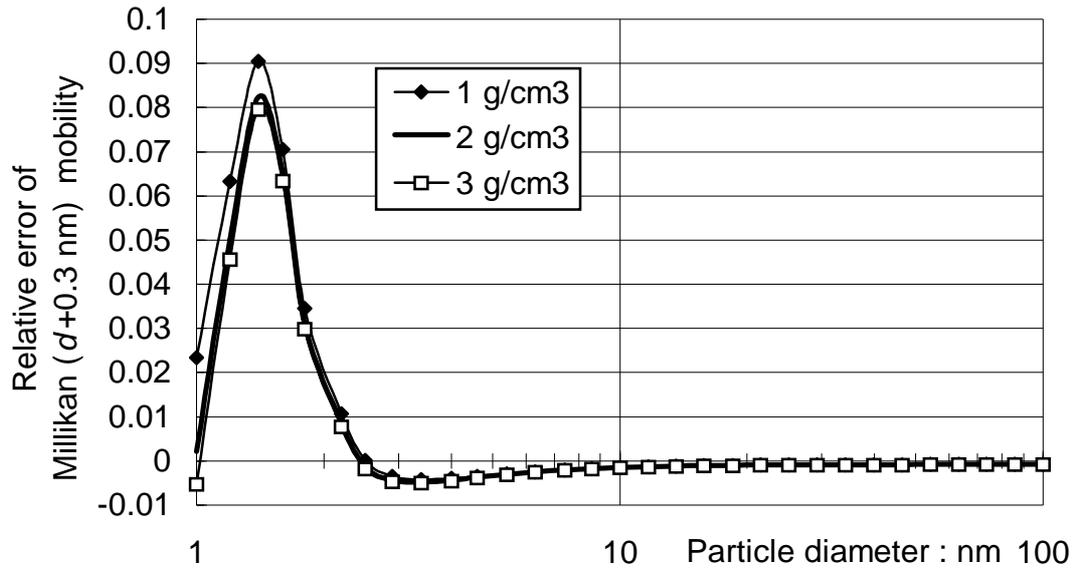


Figure 7. Relative error of the mobility, calculated according to the Millikan equation where particle diameter is substituted by $(d + 0.3 \text{ nm})$, when compared with the advanced model (*Tammet, 1995b*). Temperature 20°C and standard pressure are assumed. Three values of particle density are considered.

Temperature and pressure variation of the mobility

Temperature and pressure variation in the full range of mobility

In the high mobility limit the polarization interaction dominates and the temperature and pressure variation of the mobility follow the Langevin rule. A simple generalization of the Equation (3) is:

$$K = \text{const} \frac{T^\tau}{p^\psi} . \quad (30)$$

According to the Langevin rule, $\tau = \psi = 1$ in the high mobility limit. When the partial variations (the second parameter is unchanged) are considered, the mobility is proportional to the temperature and inversely proportional to the air pressure.

In the limit of big particles the Knudsen number l/r is approaching zero and the mobility is determined by the particle radius and air viscosity. The pressure variation of the air viscosity is negligible and the temperature variation can be expressed by an approximate equation

$$\eta = 0.192 (T:\text{K})^{0.8} \mu\text{Pa s} , \quad (31)$$

where $T:\text{K}$ is the numeric value of the temperature by the Kelvin scale. The function $\text{const} \times T^{0.8}$ can be fitted to the well proved Sutherland approximation with a relative deviation less than $\pm 0.2\%$ in the temperature interval of $-50^\circ \dots 50^\circ\text{C}$. The corresponding parameters of Equation (30) in big particle limit are $\tau = -0.8$ and $\psi = 0$, which are far from the parameters of the Langevin model.

Air ions are never very big particles in the sense of the slip factor. The Knudsen number for single charged particles is reaching a value of 1 at the mobility less than $0.0002 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ that is close or below of the lower mobility limit of most of the large air ion mobility spectrometers. In the fine particle limit, Equation (7) is approaching

$$\lim_{r \rightarrow 0} K_{\text{Millikan}} = \frac{e(a+b)l}{6\pi\eta r^2} . \quad (32)$$

The ratio l/η is expressed in the kinetic theory (*Chapman and Cowling, 1970*)

$$\frac{l}{\eta} = \frac{1.256}{p} \sqrt{\frac{kT}{m_g}} \quad (33)$$

and the limit (32) yields the values of the parameters $\tau = 0.5$ and $\psi = 1$. The pressure variation is the same as in the Langevin model, but the temperature variation is essentially different.

Equation (32) does not produce correct values for small ion mobilities. The Stokes-Millikan equation neglects polarization interaction and assumes inelastic scattering of molecules by particles that is not true in the molecular size range.

The smooth transition from the Stokes-Millikan law to the Langevin law is described by the new model (26–29). The character of temperature variation of the particle mobilities in a wide size range is shown in Figure 8. The detailed discussion is presented below.

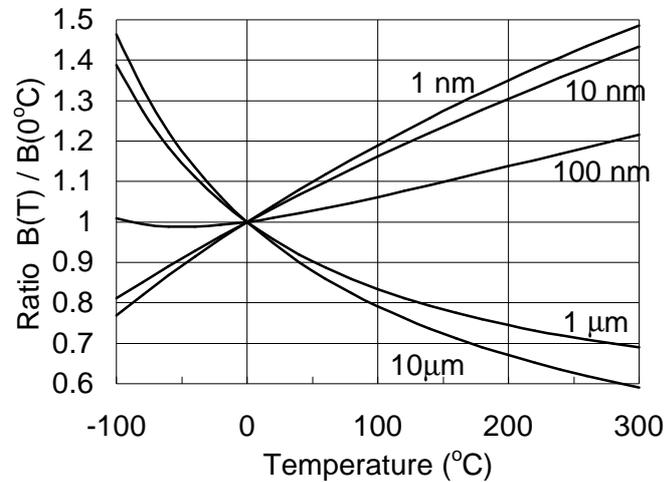


Figure 8. Temperature dependence of neutral particle mobility according to the model (26–29).

Peculiarities of the temperature variation

Temperature-mobility curves for a wide size range plotted in Figure 8 are determined by the temperature dependence of the viscosity of the air and peculiarities are not visible in the diagram. Spherical particles of density 2 g/cm^3 in air under standard atmospheric pressure are considered in all numerical examples below. Particle size is given by the mass diameter. The mobilities are calculated according to the model (*Tammets*, 1995b) and expressed by values of the mechanical mobility B that can easily be converted into the electrical mobility of the diffusion coefficient. The peculiarities are visible when the temperature effect $B(T)/B(0^\circ\text{C})$ is plotted as a function of size in Figure 9. The temperature sensitivity of the mobility is essentially suppressed in a narrow size interval of 1.5–2 nm.

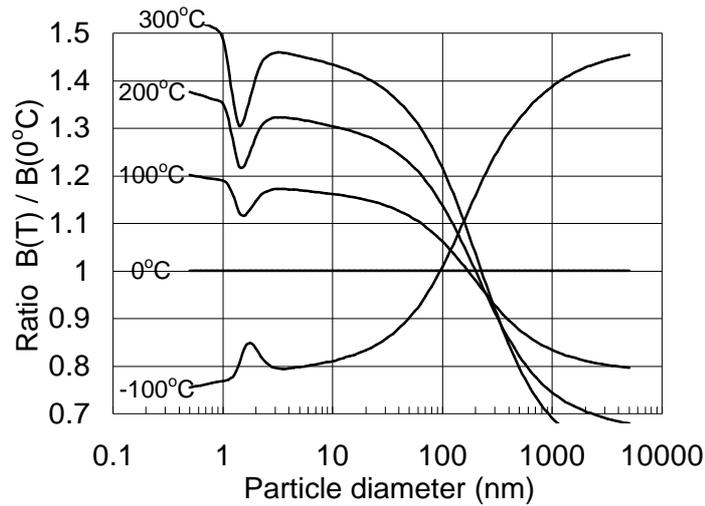


Figure 9. Size dependence of the temperature sensitivity of neutral particle mobility.

The peculiarity demonstrated in Figure 9 is a result of the temperature shift of the characteristic size of transition from the Stokes-Millikan law to the kinetic theory law. The temperature shift of the transition size is shown in Figure 10, where the factor f_2 of Equation (26) is plotted.

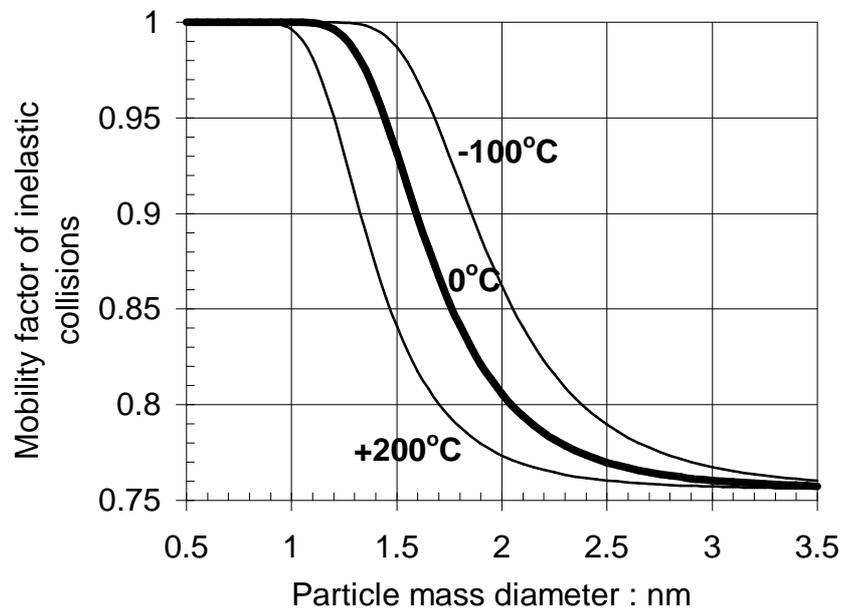


Figure 10. The temperature shift of the air ion transition size and the mobility factor f_2 .

Deviations from the Langevin rule

The Langevin rule assumes $\tau = \psi = 1$ and it is valid only when this assumption is adequate. When the temperature and pressure variation of the mobility is given not by Equation (30) but in some different way, the parameters τ and ψ are estimated as follows

$$\tau = \frac{dK}{dT} \frac{T}{K}, \quad \psi = -\frac{dK}{dp} \frac{p}{K}. \quad (34)$$

The deviations of the parameters τ and ψ from the Langevin value 1 measure the errors of the Langevin rule.

If the temperature and pressure variation of the mobility does not follow the power law, Equation (30) is valid as an approximation in a narrow temperature and pressure range. In this occasion the values of τ and ψ determined according to Equation (34) depend on the temperature and pressure in the wide temperature and pressure range.

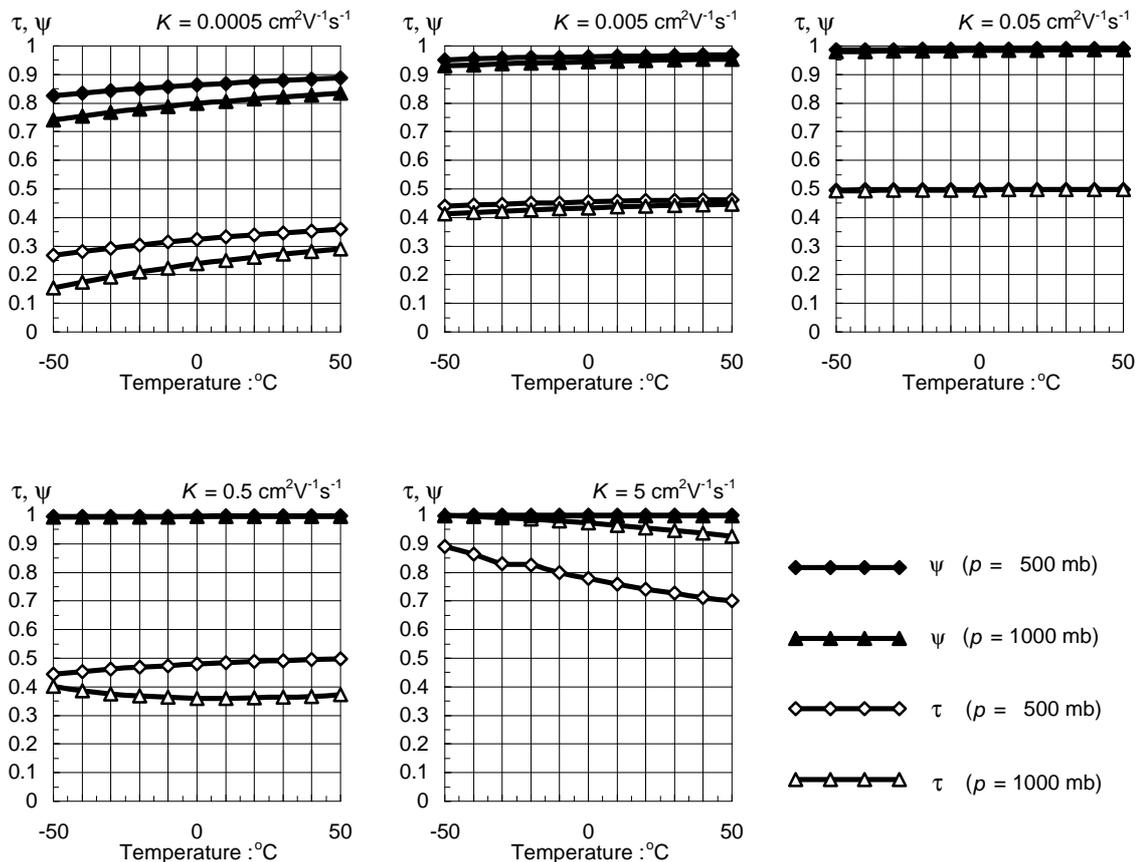


Figure 11. Temperature and pressure variation of parameters τ and ψ for the air ions of various mobility.

The model developed in the present study can be used to evaluate the correctness of the procedure of reducing various mobilities to the standard conditions. A function expressed by an iterative algorithm (26–29) cannot be differentiated in a

closed form as a rule. The results of the numerical differentiation of the mobility according the temperature (see Appendix) are presented in Figure 11. The incorrectness of the relation (3) for the temperature dependence is dramatic even in case of molecular ions. The character of variation is different for the air ions of different mobility. A variation of the pressure factor ψ is relatively simple. It will differ from the Langevin value 1 in the range of large air ions due to the decrease in the role of the slip factor with the decrease in Knudsen number. The macroscopic limit of ψ is zero but the real values of ψ for large air ions are far from this limit.

The variation of the temperature factor τ does not follow simple rules because the temperature effect is influenced by many different physical factors.

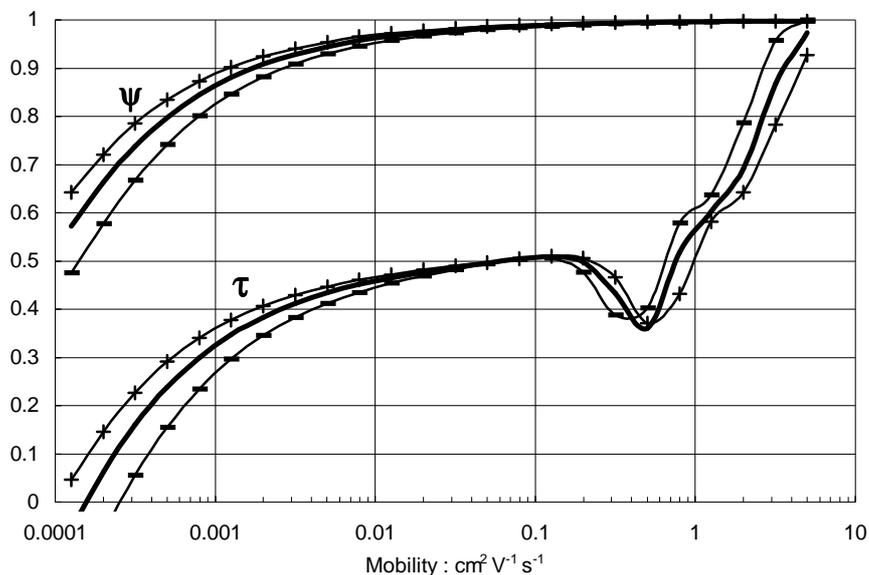


Figure 12. Mobility variation of parameters τ and ψ at pressure 1000 mb. The unmarked curves correspond to temperature 0°C , the curves marked with $+$ and $-$ correspond to temperatures $+50^{\circ}\text{C}$ and -50°C .

The dependence of the parameters τ and ψ on the air ion mobility is shown in Figure 12. The value of τ is far from the Langevin value 1 even in case of small atmospheric ions, typical mobility of which is about $1.5 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$. The Langevin model could be considered as a fair approximation only in case of extremely high mobilities characteristic of atomic and pure molecular ions created in specific laboratory experiments.

The relevance of the error of the Langevin rule is shown by the following example. The air ion mass-mobility correlation in the mass interval of 35–2122 u has been measured by *Kilpatrick* (1971) at 200°C , and the mobilities have been published as reduced to standard conditions using the Langevin rule. The fitting of these data yields a regression equation

$$K \approx \left(\sqrt[3]{a/m_p} - b \right) \text{cm}^2 \text{V}^{-1} \text{s}^{-1} \quad (35)$$

with coefficients of $a = 850$ u and $b = 0.3$ (Tammet, 1993). In the paper (Tammet, 1995b) the original 200°C data were restored and the mobilities at 0°C were recalculated according to the new model. When using the recalculated data the best fit of the mass-mobility regression is achieved at the numerical values of the coefficients of $a = 1200$ u and $b = 0.2$. The ratio of air ion masses (1200/850) estimated according to different approximations is too big to be neglected. The difference between the Langevin reduction and the corrected reduction is illustrated in Figure 13.

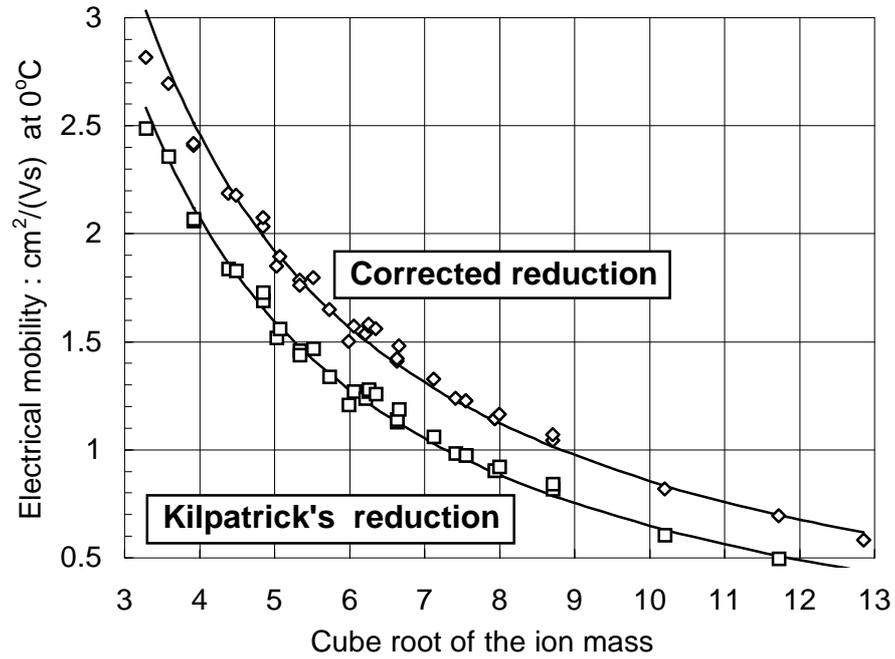


Figure 13. Kilpatrick's data as reduced according to the Langevin rule and according to the new algorithm.

Summary and conclusions

The model of the particle size–mobility relation developed in the present study is a combination of empirical knowledge stored in the Millikan equation, particular physical laws and mathematical approximation of available measurements. Some features of the model are:

- specification of the radius of a particle discriminating between the concepts of the collision size and the mass size,
- approaching the Chapman–Enskog equation when the particle size decreases sufficiently and the Millikan equation when the particle size increases sufficiently,
- accounting for the dependence of the law of the reflection of gas molecules on the particle size,
- consideration of the polarization interaction according to the ($\infty-4$) potential model,
- consideration of the collision distance as a function of the interaction energy.

The particle radius is replaced by an effective collision distance when calculating the mobility of a nanometer particle. Three addends are included into the equation for the collision distance: the collision radius of an ambient gas molecule, the particle mass radius, and an extra–distance that covers the difference between the particle mass radius and the collision radius. The estimated value of the extra–distance of 0.115 nm takes into account all of the interactions between a particle and ambient gas molecules that are not considered in the theoretical model.

Collisions between the molecular particles and ambient gas molecules can be assumed to be elastic–specular. When the particle size increases, the internal energy of a particle will be interconvertible with the energy of collisions and the character of collisions changes to the inelastic one. The transition process is described by the Einstein factor

$$(\Delta E/kT)^2 e^{\Delta E/kT} / (e^{\Delta E/kT} - 1)^2 ,$$

where the average separation of energy levels ΔE is inversely proportional to the particle mass. If the particle mass diameter is less than 1.4 nm, elastic collisions dominate and the particle can be considered as a molecule or a cluster characterized by frozen internal energy. If the particle mass diameter is greater than 2 nm, inelastic collisions dominate and the particle can be considered as a macroscopic body.

According to the long term measurements of atmospheric ions the mobility of $0.5 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ appears as critical in statistical behavior of air ion fraction concentrations. The mass diameter of critical air ions 1.6 nm is just the same as the critical diameter of the transition from elastic to inelastic collisions. Therefore, the term *macroscopic particles* could be preferred when speaking about particles

of diameter greater than 1.6 nm and the term *molecular clusters* when considering the particles of diameter less than 1.6 nm.

The dependence of mobility on temperature at a constant pressure is essentially different from the proportionality expected in the traditional procedure for the reduction of the mobilities of ions to the standard conditions. The mobilities of the nanometer particles can be reduced to the standard pressure without any considerable error but proportional reduction to the standard temperature cannot be recommended.

The algorithm of air ion mobility reduction according to the model consists of two stages: first, the particle size should be calculated at a given temperature and pressure and then the reduced mobility should be calculated according to the size, standard temperature and standard pressure. The Pascal-statement where the functions presented in the Appendix are used is:

```
ReducedMobility := 1.602 * Mobility (28.96, 0.00171, 0.3036, 44, 0.8, 1013.25, 273.15, 2.07, 1,
MassDiameter (Pressure_mb, 273.15 + Temperature_C, 2.07, 1, MeasuredMobility / 1.602));
```

The mobilities above should be expressed in $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$.

The values of parameters in the size-mobility model can be justified after improved experimental data of mass-mobility or size-mobility correlation becomes available, and advanced models can be proposed. If the measurements are published as reduced to standard conditions according to a certain model, a correction of the data could be required in the future. Thus, the actual values of mobility completed by the values of temperature and pressures are recommended for publication. If only the reduced mobilities are published, the algorithms of reduction and restoration of original data should be indicated.

The results of the study have been published in papers (Tammet, 1995a, 1995b, 1996a, 1996b, 1996c) and submitted for publication in the *Journal of Geophysical Research*.

Nomenclature

a, b, c	slip factor coefficients, dimensionless
B	particle mechanical mobility, $\text{m N}^{-1} \text{s}^{-1}$
B_M	particle mechanical mobility according to the Millikan equation, $\text{m N}^{-1} \text{s}^{-1}$
d_m	particle mass diameter $2r_m$, m
D	particle diffusion coefficient, $\text{m}^2 \text{s}^{-1}$
e	elementary charge, $1.60 \times 10^{-19} \text{ C}$
E	deformation energy, J
f_1, f_2	correction factors in the modified Millikan Equation (26), dimensionless
h	difference between particle collision radius and mass radius $r_p - r_m$, m
k	Boltzmann constant, $1.38 \times 10^{-23} \text{ J K}^{-1}$
K	particle electrical mobility (zero field limit), $\text{m}^2 \text{V}^{-1} \text{s}^{-1}$
l	mean free path of gas molecules, m
m_g	gas molecule mass, kg
m_p	particle mass, kg
n_g	number concentration of gas molecules, m^{-3}
q	particle electric charge, C
r	radius, m
r_g	gas molecule collision radius, m
r_c	particle collision radius, m
r_m	particle mass radius, m
s	factor of reflection law in expression of collision cross-section (16), dimensionless
s	coarse particle limit of the factor s , dimensionless
T	gas temperature, K
T_δ	effective collision temperature, K
T^*	dimensionless temperature (21)
U	potential energy, J
U_{pol}	potential energy of polarisation interaction, J
V	particle volume, m^3

Greek letters

α	dipole polarizability of gas molecules, m^3
δ	collision distance or collision diameter, m
ϵ_0	electric constant $8.85 \times 10^{-12} \text{ F m}^{-1}$
η	gas viscosity, Pa s
ρ	particle density, kg m^{-3}
Ω	collision cross-section, m^2
$\Omega_{\infty-4}^{(1,1)*}$	dimensionless first collision integral for ($\infty-4$) potential (21)

All equations are written in SI. When expressing numerical values, the practical measurement units nm, amu, g cm^{-3} , $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ and $\mu\text{Pa s}$ are used.

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Algorithms

```

function Mobility
  {velocity/force }      (GasMass      {amu},      { air      nitrogen }
  { (m/s) / fN } Polarizability      {nm3},      { 28.96    28.02 }
  VisCon1              {nm},          { 0.00171  0.00174 }
  VisCon2              {K},           { 0.3036   0.2996 }
  VisCon3,             { 0.8        0.7        }
  Pressure             {mb},
  Temperature          {K},
  ParticleDensity      {g cm-3},
  ParticleCharge       {e},
  MassDiameter         {nm} : real;

function Omega11 (x : real) : real;      { $\Omega(1,1)^*(T^*)$  for ( $\infty-4$ ) potential}
  var p, q : real;                       {and elastic-specular collisions}
  begin
    if x > 1 then Omega11 := 1 + 0.106 / x + 0.263 / exp ((4/3) * ln (x))
    else begin p := sqrt (x); q := sqrt (p); Omega11 := 1.4691 / p - 0.341 / q + 0.181 * x * q + 0.059 end;
  end;

const  a = 1.2; b = 0.5; c = 1; {the slip factor coefficients}
  ExtraDistance = 0.115 {nm}; TransitionDiameter = 2.48 {nm};
var    GasDiameter, MeanVelocity, Viscosity, FreePath, DipolEffect,
  DeltaTemperature, CheckMark, ParticleMass, CollisionDistance, Kn, Omega, s, x, y : real;

begin
  Viscosity { $\mu$ Pa s} := 0.02713 * sqrt (GasMass * Temperature) /
    sqrt (VisCon1 * (1 + exp (VisCon3 * ln (VisCon2 / Temperature))));
  MeanVelocity {m/s} := 145.5 * sqrt (Temperature / GasMass);
  FreePath {nm} := (166251 * Viscosity * Temperature) / (GasMass * Pressure * MeanVelocity);
  ParticleMass {amu} := 315.3 * ParticleDensity * exp (3 * ln (MassDiameter));
  DeltaTemperature := Temperature;
  repeat
    CheckMark := DeltaTemperature;
    GasDiameter {nm} := VisCon1 * (1 + exp (VisCon3 * ln (VisCon2 / DeltaTemperature)));
    CollisionDistance {nm} := MassDiameter / 2 + ExtraDistance + GasDiameter / 2;
    DipolEffect := 8355 * ParticleCharge * Polarizability / sqrt (sqrt (CollisionDistance));
    DeltaTemperature := Temperature + DipolEffect;
  until abs (CheckMark - DeltaTemperature) < 0.01;
  if ParticleCharge = 0 then Omega := 1 else Omega := Omega11 (Temperature / DipolEffect);
  Kn := FreePath / CollisionDistance;
  if Kn < 0.03 {underflow safe} then y := 0 else y := exp (- c / Kn);
  x := (273.15 / DeltaTemperature) * exp (3 * ln (TransitionDiameter / MassDiameter));
  if x > 30 {overflow safe} then s := 1
    else if x > 0.001 then s := 1 + exp (x) * sqrt (x / (exp (x) - 1)) * (2.25 / (a + b) - 1)
    else {underflow safe} s := 1 + (2.25 / (a + b) - 1);
  Mobility := ((2.25 / (a + b)) / (Omega + s - 1)) * sqrt (1 + GasMass / ParticleMass) *
    (1 + Kn * (a + b * y)) / (6 * PI * Viscosity * CollisionDistance);

end;
{Electrical mobility (cm2 V-1 s-1) = 1.602 * Particle charge (e) * Mobility (m fN-1 s-1)};

```

$$\{\text{Diffusion coefficient (cm}^2 \text{ s}^{-1}) = \text{Temperature (K)} * \text{Mobility (m fN}^{-1} \text{ s}^{-1}) / 7244\}$$

```

function MassDiameter      {Air environment}
  {nm}      (Pressure      {mb},
            Temperature   {K},
            ParticleDensity {g cm-3},
            ParticleCharge {e},
            MechMobility   {m fN-1 s-1} : real) : real;
            {MechMobility = 0.624 * ElectricalMobility / ParticleCharge}
var   c, d, test : real;
      n : integer;
begin
  c := 300; n := 0;
  repeat
    n := n + 1;
    d := (0.6 + sqrt (0.36 + 200 * c * MechMobility)) / (c * MechMobility) - 0.3;
    test := Mobility (28.96, 0.00171, 0.3036, 44, 0.8,
                    Pressure, Temperature, ParticleDensity, ParticleCharge, d);
    c := (1.2 / (d + 0.3) + 200 / sqrt (d + 0.3)) / test;
  until (abs (test / MechMobility - 1) < 0.0001) or (n = 99);
  if n < 99 then MassDiameter := d else MassDiameter := 0;
end;

```

The function *Mobility* is an implementation of the algorithm defined by Equations (26–29). It is presented to enable the data verification. The function can be immediately used in a computer program to calculate the mobility of a particle of any known size, charge and density.

The function *MassDiameter* is a simple demonstration how to solve the inverse problem and calculate the size of a particle of known mobility in a computer program. The function is written for the air environment but it can be easily modified changing the numerical values in the body of the function. The simple iterative procedure used in the example is not converging in some unrealistic extreme situations (very high charge and a very small size simultaneously). The zero value of the function. indicates a failure.

Aeroioonide liikuvuste temperatuuri- ja rõhusõltuvuse uurimine

Aeroioonide liikuvusjaotus sisaldab väärtuslikku informatsiooni õhu saastatuse kohta. Atmosfääriõhus tehtud vaatluste välistingimused on muutlikud. Saasteaineid iseloomustava informatsiooni saamiseks peab vahetud mõõtmistulemused teisendama temperatuurist ja õhurõhust sõltumatuteks suurusteks. Traditsiooni kohaselt kasutatakse kergete ionide liikuvuste standardtingimustele taandamiseks Langevini reeglit, mis on teoreetiliselt korrektne nullmõõtmetega ionide jaoks. Suurte osakeste puhul on alternatiiviks Stokes-Millikani võrrand. Probleeme tekitab üleminekupiirkonnas esinev konflikt Stokes-Millikani võrrandi ja Langevini reegli vahel.

Uurimistöös analüüsitakse aeroioonide liikuvuse füüsikalist mehhanismi ja esitatakse uus liikuvuse mudel, mis kasutab iooni lineaarmõõdu mõistet. Osakese mudel kui defineeritud geomeetrilise pinnaga sfäär ei ole nanomeeterpiirkonnas adekvaatne. Seetõttu on osakese mõõt vaid mudelparameeter mille tähendus tuleneb kokkuleppest. Üldkeelelisele lineaarmõõdu mõistele vastab mitu erinevat mudelparameetrit. Uue mudeli sobitamisel katseandmetega leiti osakese pörkeraadiuse ja massiraadiuse erinevuse hinnanguks 0.115 nm.

Liikuvuse mudeli üks uuendusi on Einsteini energianivoode "sulamise" faktori kasutamine kirjeldamiseks üleminekut elastsetelt pörgetelt mitte-elastsetele pörgetele osakeste mõõdu suurendamisel. Polarisatsioonijõud võetakse arvesse ($\infty-4$) potentsiaalimudeli kohaselt. Uus liikuvusmudel ei esita kitsendavaid tingimusi osakese mõõtmetele. Vaba molekulaarliikumise piiril läheneb uus mudel Chapman-Enskogi mudelile ja suurte osakeste piiril Stokes-Millikani mudelile.

Uus liikuvusmudel võimaldab aeroioonide liikuvuste temperatuuri- ja rõhusõltuvust senisest paremini kirjeldada. Osakeste liikuvus-raadius teisenduste algoritmid sobivad ka liikuvuste taandamiseks standardsetele välistingimustele. Liikuvuse temperatuurikoefitsient osutub tugevalt allasurutuks kitsas diameetrivahemikus 1–2.5 nm. Selle iseärasuse põhjuseks on Einsteini faktoris sisalduva üleminekudiametri temperatuurisõltuvus ja faktori end järsk sõltuvus osakese suurusest. Seni üldiselt tarvitatud Langevini reegli viga osutub oluliseks isegi kõige suuremate liikuvustega atmosfääriioonide puhul. Seetõttu on varasemad atmosfääriioonide liikuvuste andmed reeglina moonutatud ja vajavad kriitilist läbivaatamist.

Töö tulemused on avaldatud publikatsioonides (*Tamm*, 1995a, 1995b, 1996a, 1996b, 1996c) ja esitatud avaldamiseks ajakirjas *Journal of Geophysical Research*.