Unsteady bipolar diffusion charging in aerosol neutralisers: A non-dimensional approach to predict charge distribution equilibrium behaviour

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ABSTRACT

High total particle concentration and small particle size are common features of aerosols encountered in the field of aerosol-based nanotechnology that can potentially lead to non-equilibrium issues in the neutraliser upon SMPS characterisation, resulting in large errors in size distribution measurements. Experiments show that the commonly assumed $n \cdot t$ product rule fails to predict equilibrium behaviour in aerosol neutralisers under these conditions, as it does not capture the influence of total particle concentration and particle size. The aim of this work is to provide an equilibrium indicator that identifies situations where equilibrium is not reached in the neutraliser as a function of residence time, ion generation rate, total particle concentration, and particle size. Bipolar diffusion charging equations are solved numerically in a one-dimensional model first, and a non-dimensional analysis of the results is carried out in order to map equilibrium behaviour as a function of two non-dimensional groups, the non-dimensional ion concentration, and the non-dimensional neutraliser residence time. Solving the three-dimensional form of the charging equations in the geometry of the neutraliser then enables one to find good agreement in terms of equilibrium behaviour between experiments and predictions from the non-dimensional model. The three-dimensional model captures the complexity of the physics of unsteady particle charging inside a neutraliser. This work then discusses this as a new approach to non-equilibrium behaviour prediction in neutralisers, providing a tool supplementing the $n \cdot t$ product rule that can be used in practice.

1. Introduction

Growing interest in the characterisation of the smaller diameter range (< 35 nm) of ultrafine particles at high concentrations (up to 10^{13} m^{-3}) for purposes of combustion analysis and nanomaterial production has led to increasingly stringent demands on aerosol instrumentation (Biskos, Yurteri, & Schmidt-Ott, 2008). Under these conditions, typical methods of mobility characterisation that rely on diffusion charging prove problematic. The collision kernel between particles and ions decrease with particle diameter, where particle attachment coefficients with a typical neutraliser ion is

Nomenclature

α	ion–ion recombination rate (m^3 s^{-1})
$\beta_{\pm i}^{\pm}$	attachment coefficient of a $\pm$ ion with a particle of a given diameter bearing $\pm i$ net elementary charges (m^3 s^{-1})
d_p	particle diameter (nm)
$f_{\pm i}^{Unsteady}$	fraction of particles of a given diameter bearing $\pm i$ net elementary charges as computed by the charging model or measured experimentally
$f_{\pm i}^{Wied}$	fraction of particles of a given diameter bearing $\pm i$ net elementary charges as predicted by Wiedensohler equilibrium interpolation
J	equilibrium indicator: relative difference to equilibrium levels in terms of $+1$ charge fraction
$\hat{N}$	non-dimensional ion concentration
$\hat{\tau}$	non-dimensional neutraliser residence time
$n^{\pm}$	concentration of $\pm$ polarity ions (m^{-3})
$\overline{n_0}$	particle-weighted ion concentration (m^{-3})
$N_{\pm i}$	concentration of particles of a given diameter bearing $\pm i$ net elementary charges (m^{-3})
N_{tot}	total particle concentration (m^{-3})
P_{Coll}	collision probability between the average ion entering the limiting sphere and a neutral particle of a given diameter
q	ion generation rate (m^{-3} s^{-1})
τ_{plug}	neutraliser residence time assuming plug-flow (s)
$\overline{\tau_{res}}$	particle-averaged neutraliser residence time (s)

ten times higher for neutral particles with diameters of 50 nm than particles 10 nm in diameter (Hoppel & Frick, 1986). High concentrations of particles reduce the ratio of ions to particles, thus decreasing the number of excess ions available for charging. Ion–ion recombination, which typically occurs at a rate $\alpha = 1.6 \cdot 10^{-12}$ m^3 s^{-1} inside a neutraliser (Hoppel & Frick, 1990), limits neutraliser ion concentrations. The strongest commercially available neutralisers have ion concentrations of $\sim 10^{14}$ m^{-3}, a value that is of the same order of magnitude as total particle concentration in many practical cases. As a consequence, ion availability might become a limiting factor in the diffusion charging process.

Particle mobility characterisation by differential mobility analysis (DMA) is a NIST-traceable standard for reference particle sizing (Vasiliou, 2005) and is described by an ISO standard (BS ISO 15900:2009(E), 2009). Scanning mobility particle sizers (SMPS) classify particles according to their electric mobility with a DMA and then count the classified particles with a condensation particle counter (CPC). In order to determine the initial particle size distribution from the CPC raw counts by a data inversion, it is necessary to control the charge distribution of the aerosol upstream of the DMA (Flagan, 2008). The typical method of controlling the particle charge is accomplished with a bipolar diffusion charger (also known as neutraliser), where particles are introduced into an ionisation chamber that contains ion species of both polarities. Ions may be generated by a variety of sources and the charging process differs only to the extent that the mass and mobilities of the ions are distinct (Kallinger, Steiner, & Szymanski, 2012). Most analyses of mobility-dependent particle charge fraction assume that the charge distribution reaches equilibrium, resulting from the balance of collisions with positive and negative ions. This equilibrium charge distribution was first described accurately by Fuchs (1963) and fundamental efforts directed at understanding ion–particle interactions at the nanoscale still continue (Gopalakrishnan, Meredith, Larriba-Andaluz, & Hogan, 2013; López-Yglesias & Flagan, 2013). Wiedensohler (1988) solved the equilibrium charging equations to give a convenient interpolation of charge distribution as a function of particle size for typical neutraliser ion properties, which is currently used for data inversion in most commercially available SMPS systems (Flagan, 2008). It is generally accepted that the validity of the equilibrium solutions can be determined using an approximation known as the $n \cdot t$ product, where n is the concentration of ion pairs inside the neutraliser and t is the aerosol residence time in the neutraliser. A steady state charge distribution is approached as the $n \cdot t$ product value increases. The ISO 15200:2009(E) standard states: "for an $n \cdot t$ product larger than about 10^{13} m^{-3} s the equilibrium charge distribution will be reached in most practical situations" (BS ISO 15900:2009(E), 2009). The ISO standard states $n \cdot t = -(1/\beta^{\pm})\ln(1-(N_{\pm p}/N_{tot}))$, where $\beta^{\pm}$ is an unspecified attachment coefficient $\sim 10^{-12}$ m^3 s^{-1}, N_{tot} is the total particle concentration and $N_{\pm p}$ the concentration of particles bearing $\pm p$ net elementary charges. This expression is a simplified result derived by integrating ion and aerosol conservation equations followed an approach used by Adachi, Kousaka, and Okuyama (1984) among others. Liu and Pui (1974) coined the term $n \cdot t$ product in a paper where they developed a more complete microscopic model in a similar approach to the seminal paper by Fuchs (1963), relying on the flux of positive and negative ions colliding with the particle, that result in a different expression for the $n \cdot t$ product needed to reach equilibrium. Both approaches fail to capture the influence of total particle concentration, and the use of a fixed $n \cdot t$ value in all situations fails to capture the influence of particle size. The ISO standard acknowledges the limitation of the $n \cdot t$ product, stating that an "upper particle concentration limit exists beyond which the charge equilibrium condition will not be reached", but does not provide a method for determining the concentration limit. As methods for robust measurement at small particle diameters and high concentrations are sought, there is an increased need for an equilibrium charge indicator that accounts for particle size and concentration.

This work therefore aims to understand the complex influence of ion concentration, neutraliser residence time, total particle concentration, and particle size on the non-equilibrium behaviour of aerosol bipolar diffusion charging inside a