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Technical note

Extrapolating particle concentration along the size axis in the nanometer size range requires discrete rate equations

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ABSTRACT

For modeling or data analysis purposes, the concentration of atmospheric aerosol particles measured or modeled at a certain size is often extrapolated to a different size along the particle size axis. This is normally done using compact analytical formulae which are based on the assumption that particles of the same size move synchronously together in size space at the same rate, and thus a monodisperse population is not allowed to disperse. However, in reality the individual uncorrelated collision processes with vapor molecules introduce natural spreading to the particle distribution, which is fundamentally described by a set of discrete rate equations for each particle size. In the present work, predictions based on synchronous growth are compared to the results of the discrete treatment in the free molecular regime for particles of circa 1.5–3.3 nm in mass diameter in a situation where the population is affected by irreversible vapor condensation and scavenging losses. The comparison demonstrates that the results given by approaches that do not consider the discrete nature of the growth process may be distorted. In the studied cases, the differences to the discrete result are a factor of less than around ten, and the deviations are larger for faster particle formation events and often also for higher particle loss rates. Therefore, the discrete treatment should be used for obtaining reliable estimates on the size-dependent concentration of nanometer-sized particles.

1. Introduction

Exploring the growth dynamics of freshly formed aerosol particles has been the topic of numerous studies on atmospheric new particle formation. For some experimental data analysis or modeling purposes, the concentration or formation rate observed or modeled at a specific particle size needs to be extrapolated to another size. These purposes include testing the agreement between experimental particle formation rates and molecular clustering models by extrapolating the observed rate to a size smaller than what can be detected (*e.g.* Kerminen & Kulmala, 2002; Kürten, Williamson, Almeida, Kirkby, & Curtius, 2015), or providing input for models that do not include very small particles by

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extrapolating a formation rate predicted at a small size (where for example determining cluster properties from quantum chemistry is feasible) to a larger size that is treated by the model (*e.g.* Lee, Pierce, & Adams, 2013; Spracklen et al., 2006). Extrapolation can also be applied to generally assess the survival probability of small particles to larger, climatically relevant sizes.

Various studies have discussed the extrapolation of particle concentration along the size axis considering growth by vapor condensation and removal of particles due to external scavenging (see *e.g.* Lehtinen, Dal Maso, Kulmala, & Kerminen, 2007; Kerminen & Kulmala, 2002; Kerminen, Anttila, Lehtinen, & Kulmala, 2004; Kürten et al., 2015; Weber et al., 1997). Sometimes the condensational growth rate includes an estimated evaporation rate of molecules from the particle surface. In general the evaporation rate, which may be affected by complex chemistry in the particle phase, is considerably more difficult to assess than the molecular collision rate, calculated from gas kinetics. Thus, in many cases the assumption of irreversible condensation has been made to obtain an upper-limit estimate for the growth rate. This assumption is also justified if the vapors responsible for the major growth of stabilized particles are very low-volatile, as often suggested (Ehn et al., 2014; Kulmala et al., 2013). The effect of self-coagulation processes among the population of growing particles has often been assumed to be negligible in many atmospheric situations (Lehtinen et al., 2007; Kerminen and Kulmala, 2002), as the phenomenon is likely to become significant only at relatively high particle concentrations (Anttila, Kerminen, & Lehtinen, 2010; Kürten et al., 2015).

In most extrapolation approaches, including the widely applied Kerminen-Kulmala equation (Kerminen & Kulmala, 2002), all particles of the same size are approximated to change their size at the same rate. In other words, if a subset of particles is monodisperse at a given time, it will remain monodisperse as the particles grow, since each particle is assumed to move along the size axis at the same size-specific pace. However, in reality the growth occurs due to addition of individual molecules to the particles, and thus a more fundamental description of the process is provided by discrete rate equations (*e.g.* Goodrich, 1964a, 1964b). In this approach, each particle size, defined by the molecular content, is examined separately. The approximation of synchronous growth enormously simplifies the mathematical treatment of the problem, as analytical solutions to the set of discrete equations, even in cases where they exist, are often extremely complex (see *e.g.* Goodrich, 1964a, 1964b), and may not be very useful as such. However, the discrete collision processes may cause significant spreading in the size distribution, which decreases the concentration at a given size compared to the synchronous result. The spreading also affects the effective growth rate driving particles to larger sizes (Wang, McGraw, & Kuang, 2013).

The spreading of the particle size distribution, also referred to as size diffusion, has been studied in the past in terms of moment equations, which describe the mean particle size and the variance (Clement & Wood, 1979, 1980; Clement, Lehtinen, & Kulmala, 2004; Goodrich, 1964a). Previous work has addressed the width of the size distribution versus the mean size mostly for the case of a growing particle population with no external sources or sinks (see *e.g.* Clement & Wood, 1979; Clement et al., 2004). The relative spreading is often expected to become less significant as the mean size increases, but for some specific functional forms of a size-dependent condensation rate (Clement & Wood, 1979) or for a case where particles also evaporate (Clement et al., 2004), the spreading may be prominent even at large sizes. The effect of the discrete collisions has been recognized also in cloud droplet studies. Telford (1955) and Twomey (1964) studied the evolution of a droplet size spectrum in the absence of external sinks, and pointed out that the widening leads to a fraction of the growing cloud droplets reaching sizes larger than predicted by assuming that the droplets grow synchronously. In the context of particle formation, on the other hand, efforts have mainly been made to examine whether the width of the population remains narrow enough for the approximation of a sharp peak to be justified, and the effect of the widening on the particle number concentration within a given size interval has not received as much attention. However, concentration is the main focus of interest for instance when assessing the fraction of particles surviving to larger sizes. In the presence of a size-dependent particle sink, the effective particle loss rate is affected by the widening, and estimates of the survival probability based solely on the mean size of the population may be distorted.

The present work applies a discrete particle model to explore the validity of the approximation of synchronous growth on the size-dependent particle concentration. A population of growing particles in the size range of circa 1.5–3 nm in mass diameter is simulated with molecular resolution by numerically solving the set of discrete rate equations, and the results are compared to the simplified synchronous predictions. The focus is on a case where the only dynamic processes affecting the population are irreversible vapor condensation and scavenging losses. It must be noted that several studies (Sihto et al., 2006; Riipinen et al., 2007) have extrapolated the particle formation rate, defined as the number of particles grown into a certain size per unit time, instead of the particle number concentration studied in this work. However, extrapolation approaches have very often been applied to experimental data, and the directly measurable quantity is the concentration, from which the formation rate is deduced using estimated condensation and loss rates (Kulmala et al., 2012) or with some other method (*e.g.* Glasoe et al., 2015). Therefore, examining the concentration is considered more fundamental.

2. The discrete and continuous approaches to describe the time evolution of a particle population

The discrete equations for describing the condensational growth of a particle population in the presence of external sinks, as well as corresponding equations in which the particle size is approximated as a continuous variable, are briefly reviewed below. The result given by the continuous approximation, with certain assumptions (see below), is very likely the basis for the widely spread conception that a subset of particles of the same size retains its monodispersity as the particles grow. The discrete approach refers to explicitly considering each particle size consisting of a different number of molecules,