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Growth rates of atmospheric molecular clusters based on appearance times and collision–evaporation fluxes: Growth by monomers

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ABSTRACT

Formation of secondary atmospheric aerosol particles starts with the formation and growth of small molecular clusters. The probability that freshly formed clusters reach larger sizes depends on the rate at which they grow with respect to the rate at which they are lost on pre-existing surfaces. At present, advances in condensation particle counter and mass spectrometer techniques enable the observation of cluster growth via time evolution of size resolved cluster concentrations, and recent studies have utilized measured concentrations to deduce growth rates from the appearance times of different cluster sizes. In this work, we use a dynamic model to simulate the time development of a population of clusters of up to ~2 nm in mass diameter, and examine the relation of the growth rates determined from the appearance times to the growth rates calculated from the molecular fluxes between the clusters. This study concentrates on a simple model substance where the clusters grow only by monomer additions and the growth involves a single free energy barrier. Each cluster size defined by the number of molecules in the cluster is explicitly treated instead of dividing the clusters into size classes. Effects of finite size resolution and cluster–cluster collisions will be discussed in future work. We find that the growth rates determined with the two different approaches may differ significantly, both quantitatively and qualitatively, for the smallest clusters with the highest evaporation rates. The relative difference decreases with increasing cluster size and decreasing evaporation rate. In addition to cluster size, the difference depends on ambient conditions including external losses and time profile of the monomer concentration. Thus a quantitative comparison requires information not only on the substance, but also on the external conditions. We also show that the size of a critical cluster, corresponding to the maximum of an energy barrier in cluster formation, cannot be inferred from the size-dependent growth rates in realistic conditions.

1. Introduction

The first steps of atmospheric new particle formation process involve clustering of individual molecules and growth of the clusters by collisions with gas-phase molecules and each other. Aerosol particle concentrations are ultimately limited by

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the formation rate of the initial molecular clusters, but the survival probability of freshly formed particles to larger sizes depends on the rates at which the particles grow and are lost on pre-existing larger particles or surfaces (Kerminen et al., 2001; Kuang et al., 2010). The time evolution of particle size distribution during a new particle formation event can be described considering these competing processes. The time derivative of particle concentration C_{D_p} in a size class with a mean particle diameter D_p and a width of ΔD_p is (see, for example, Sihto et al., 2006; Kulmala et al., 2012)

$$\frac{\mathrm{d}C_{D_\mathrm{p}}}{\mathrm{d}t}=J_{D_\mathrm{p}}-\frac{\mathrm{GR}_{D_\mathrm{p}}}{\Delta D_\mathrm{p}}C_{D_\mathrm{p}}-S_{D_\mathrm{p}}, \tag{1}$$

where J_{D_p} is the formation rate of particles in the size range, $\mathrm{GR}_{D_\mathrm{p}}$ is the growth rate of the particles to larger sizes (as the change of particle diameter per unit time), and S_{D_p} is an external loss term due to deposition onto pre-existing particles or surfaces. If the particles are formed via growth from the preceding smaller size class $D_\mathrm{p}-\Delta D_\mathrm{p}$, the formation rate J_{D_p} equals to the growth term of the smaller size range $J_{D_\mathrm{p}}=\mathrm{GR}_{D_\mathrm{p}-\Delta D_\mathrm{p}}C_{D_\mathrm{p}-\Delta D_\mathrm{p}}/\Delta D_\mathrm{p}$, where it is assumed that the size classes have equal width ΔD_p. The formation and growth terms (the first and second term on the right-hand side of Eq. (1)) include the effects of condensation and evaporation of vapor monomers, and possibly also collisions and fragmentations involving two clusters.

The growth rates of freshly formed particles of a few nanometers and upwards in diameter are in general deduced from measured particle concentrations during new particle formation events (Manninen et al., 2009, 2010; Yli-Juuti et al., 2011 and references therein), or calculated based on concentrations of condensable vapors (Nieminen et al., 2010; Yli-Juuti et al., 2013) and sometimes also coagulation (Stolzenburg et al., 2005; Leppä et al., 2011). The most widely used approaches to obtain the growth rates from experimental data include the mode fitting method (Dal Maso et al., 2005) and the maximum concentration method (Hirsikko et al., 2005). Another approach is to retrieve the growth rates from the time delay between the rise of concentrations measured with several particle counters with different detection threshold sizes (Riccobono et al., 2012). The time lag between the appearance of different sized particles has also been studied analytically (Wu, 1992 and references therein). Growth rates can also be determined by fitting analytical equations of the form of Eq. (1) to the time-dependent particle distribution data (Verheggen & Mozurkewich, 2006; Lehtinen et al., 2004; Kuang et al., 2012). Earlier, instrumental detection limit has restricted the determination of growth rates to particle sizes larger than a couple of nanometers in mobility diameter. Growth rates of particles below the detection limit have been estimated from the time lag between the increase in sulfuric acid concentration and the concentration of the smallest detected particles (Weber et al., 1997; Fiedler et al., 2005; Sihto et al., 2006). At present, condensation particle counters observe particles and molecular clusters down to the mobility diameter of 1 nm (Jiang et al., 2011; Vanhanen et al., 2011; Kulmala et al., 2013), and individual charged clusters can be detected and identified by high-resolution mass spectrometry (Junninen et al., 2010; Schobesberger et al., 2013). The growth rates of the smallest clusters can be likewise defined from the measured concentration time series. However, for example in chamber experiments with a constant vapor source, the cluster concentrations may increase to the steady state monotonously without exhibiting a maximum in which case methods based on determining the moment of the maximum concentration cannot be applied. Hence, in recent studies the growth rates have been determined based on cluster appearance times, generally defined as the time at which the concentration of the cluster reaches 50% of its maximum value (which may or may not equal to the steady-state value) or sometimes 50% of the total increase in the concentration in the case that there is a background level before the beginning of particle formation (Kulmala et al., 2013; Schobesberger et al., 2013; Lehtipalo et al., 2014; Wimmer et al., 2014). Alternative definitions for the appearance time have been tested by Lehtipalo et al. (2014). The appearance time method has been applied to simulation data from a condensation–coagulation aerosol microphysics model, and the results were found to roughly agree with the average condensational growth rates of different particle size classes (Lehtipalo et al., 2014).

From a theoretical perspective, the growth rates of the smallest clusters cannot be determined assuming irreversible vapor condensation or cluster coagulation, as also evaporation of molecules may be significant for the small sizes (Ortega et al., 2012; Yli-Juuti et al., 2013). In the case that the formation free energy profile of the growing clusters contains one global maximum corresponding to the critical cluster, the relative effect of evaporation with respect to growth by collisions is the most significant for clusters below the critical size. For clusters larger than the critical size, evaporation becomes less significant as the cluster size increases. It has been speculated that the critical size may be identifiable from observed cluster growth rates by rationalizing that evaporation substantially decreases the growth rate of sub-critical clusters, whereas at the critical size the growth rate starts to increase due to cluster stabilization. The critical size regime has thus been assessed by comparing measured growth rates to theoretical growth rates calculated assuming only vapor condensation and no evaporation (Kuang et al., 2012; Kulmala et al., 2013).

In this study we use a dynamic model to simulate the time evolution of a cluster population in a one-component system. We use a model substance that exhibits a critical cluster size, with the properties mimicking atmospherically relevant stabilized clusters. The cluster growth rates are determined from the simulation data with two different methods. First, we apply the experimental data analysis method to the simulated cluster concentration time series to extract the growth rates from the cluster appearance times in the same way as they are obtained from measurements. Second, we calculate the growth rates from the simulated collision–evaporation fluxes between different cluster sizes. The results give information on the qualitative relation between the effective growth rate calculated from the molecular fluxes that cannot be directly measured, and the apparent growth rate that can be deduced from cluster measurements. In addition, we examine the