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Estimating atmospheric nucleation rates from size distribution measurements: Analytical equations for the case of size dependent growth rates

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ABSTRACT

While laboratory and field measurements indicate that atmospheric nucleation most likely initiates with the formation clusters of ~1.0–1.5 nm diameter, most atmospheric observations to date measure only particles larger than 3–10 nm in size. Because of this, several analytical formulations have been developed to estimate the real nucleation rate at the initial cluster size from the "apparent" nucleation rate at the measured larger sizes. All previous analytical formulations have assumed a constant particle growth rate below the instrument detection limit; however, recent atmospheric measurements have shown that the growth rate is often strongly size dependent. This study presents new analytical equations to connect the real and "apparent" nucleation rates in two special cases, i.e. when the cluster growth rate follows a (1) linear, or (2) power-law dependence on the particle size. The accuracy of these equations is tested with an ensemble of numerical model simulations of new particle formation events. Both new formulations are capable of estimating the nucleation rate at 1.5 nm fairly accurately (largest normalised mean bias −1.4% for the power-law and −23% for the linear events). We find, however, that the power law formulation gives a more accurate estimate of the nucleation rate even for a majority of the events with linear growth rate dependence. Further analysis indicates that previous studies of atmospheric nucleation events, which have assumed a constant cluster growth rate, may have clearly underestimated the real nucleation rate.

1. Introduction

Atmospheric new particle formation via nucleation and growth is known to contribute significantly to total aerosol number as well as to cloud condensation nuclei concentration (Kerminen et al., 2012). However, despite recent progress in controlled laboratory experiments (Kirkby et al., 2011), field observations (Kuang et al., 2012) and theoretical studies (Chen et al., 2012; Loukonen et al., 2010), many details of the initial steps of atmospheric nucleation still remain unknown (Zhang et al., 2012; Kulmala et al. 2013). The first direct observations of atmospheric nucleation have confirmed that new particle

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formation initiates at a cluster size of about 1–2 nm in diameter (Jiang et al., 2011; Kulmala et al., 2013). Unfortunately instruments capable of measuring down to such small sizes are not yet in wide use, and the vast majority of measurement sites still employ techniques that have a lower cut-off diameter in the range between 3 and 10 nm. Therefore, obtaining a global picture of the first steps of atmospheric new particle formation requires reliable ways to estimate the initial nucleation rate at 1–2 nm based on the size distribution of larger particles.

To this end, methods to estimate the initial nucleation rate have been developed by assuming a constant (Weber et al., 1996; Kerminen & Kulmala, 2002; Lehtinen et al., 2007; Kuang et al., 2008) or partially constant (Kerminen et al., 2004) growth rate between the initial nucleation size (in this study $d_{1.5}=1.5$ nm) and the detectable size (d_x, typically 3 nm), despite observations that the growth rate below 3 nm is typically clearly smaller than above this threshold (Hirsikko et al., 2005; Yli-Juuti et al., 2011; Häkkinen et al., 2013). However, the most recent atmospheric measurements, which can directly detect particles as small as 1 nm in diameter, indicate that the particle growth rates below 3 nm may be strongly size dependent. Analysing new particle formation events in Atlanta and Boulder, Kuang et al. (2012) found that the growth rate increased approximately linearly with particle diameter below 3 nm. This behaviour was attributed to unidentified condensing species (i.e., other than sulphuric acid) which accounted for up to 95% of the observed growth. Similarly, Kulmala et al. (2013) observed a strongly size dependent growth rate below 3 nm diameter at the Hyytiälä boreal station and interpreted it as contribution of organic vapours to initial particle growth.

To incorporate these new findings into future analyses of atmospheric nucleation events, we present analytical formulations for calculating the initial nucleation rate (hereafter: $J_{1.5}$) from the "apparent" nucleation rate at a detectable size in two special cases: when the growth rate below the detectable size follows a (1) linear, or (2) power-law dependence on the particle size. We then test the derived formulae against an ensemble of model-generated nucleation events, for which the initial nucleation rates as well as particle growth rates are known exactly.

2. Theory

The evolution of the particle flux J for a growing nucleation mode (i.e. the number of nucleation mode particles reaching a certain size per unit volume and time) is described by (Lehtinen et al., 2007)

$$\frac{dJ}{dd_p} = -\frac{CoagS(d_p)}{GR(d_p)}J \tag{1}$$

Here $GR(d_p)$ is the size-dependent growth rate and the coagulation sink of particles of diameter d_p is given by

$$CoagS(d_p) = \int_0^\infty \beta(d_p, \overline{d}_p) n(\overline{d}_p) d\overline{d}_p, \tag{1a}$$

where $\beta(d_p, \overline{d}_p)$ is the coagulation coefficient between particles of diameters d_p and $\overline{d}_p$, and $n(\overline{d}_p)$ is the particle size distribution function. The particle flux for size d_p can be calculated from

$$J(d_p) = GR(d_p) n(d_p) \tag{1b}$$

Note that Eq. (1) assumes that particle loss occurs only through coagulation with the background aerosol (i.e. self-coagulation of the nucleation mode is negligible).

To solve Eq. (1) for J analytically, approximations of the size dependencies of $CoagS$ and GR are required. Previously Kerminen and Kulmala (2002) assumed that the particle growth rate is constant within the nucleation mode and that $CoagS \sim d_p^{-2}$. Later, this analysis was improved by Lehtinen et al. (2007) by replacing the $CoagS$ dependence by a general power-law dependence

$$CoagS(d_p) = CoagS(d_{1.5}) \left(\frac{d_p}{d_{1.5}} \right)^m \tag{2}$$

However, also the Lehtinen et al. (2007) formulation still assumed a constant GR as a function of size.

Fortunately, the analysis of Lehtinen et al. (2007) can be generalised to two other special cases still providing analytical solutions:

(1) By assuming GR linearly dependent on d_p:

$$GR(d_p) = a + b d_p \tag{3}$$

$$a = GR(d_{1.5}) - b d_{1.5} \tag{3a}$$

$$b = \frac{GR(d_x) - GR(d_{1.5})}{d_x - d_{1.5}} \tag{3b}$$