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Critical cluster size cannot in practice be determined by slope analysis in atmospherically relevant applications

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ABSTRACT

The first nucleation theorem is the most widely used method to assess atmospheric new-particle formation mechanisms from particle formation rate measurements. The theorem states that the slope $(\partial \log J)/(\partial \log C)$ of the nucleation rate J versus the concentration C of a nucleating compound gives the number of molecules of that species in the critical cluster. In principle, the derivation of the theorem is solid, but it contains very restrictive assumptions, the validity of which is questionable in realistic situations. It applies only for systems where clusters grow by addition of single molecules, and there are no external losses. In addition, application of the theorem to experimental data requires that the nucleation rate can be determined from particle concentration observations. This work presents simulation results on particle formation rates in atmospherically relevant conditions. We show that the slope of the nucleation rate in realistic conditions differs from that in an ideal situation. The slope analysis can easily lead to erroneous conclusions on the critical cluster size, and should therefore not be used to interpret experimental data.

1. Introduction

Formation of aerosol particles from precursor vapors is an important and widely studied topic in the field of atmospheric sciences. Numerous experimental and theoretical studies have focused on assessing the formation mechanism of aerosols in varying environments (Kulmala et al., 2004; Young et al., 2008; Zhang et al., 2012). The phenomenon begins with vapor-phase molecules colliding with each other to form small molecular clusters and continues with the clusters growing by further collisions, at the same time also being able to lose molecules by evaporation. While sulfuric acid has been recognized as the key compound of the process in many environments (Sihto et al., 2006; Weber et al., 1996), identities and roles of other compounds still remain uncertain.

The gas-to-liquid phase transition related to the particle formation process is in general assumed to proceed via nucleation, where the cluster formation free energy surface exhibits an energy barrier that the growing cluster must

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overcome in order to become a stable particle. Another option is barrierless condensation, where already the smallest clusters are stable and particle formation is kinetically limited. In case of nucleation, the location of the energy barrier is called the critical cluster size. Clusters that are smaller than the critical size are more likely to evaporate into smaller sizes than to grow further, and clusters that are larger than the critical size are more likely to grow than to decay. A central question concerning the nucleation mechanism is the size and composition of the critical cluster. As cluster energies cannot be measured directly, the critical cluster cannot simply be identified from the energy profile of the nucleating system. A seemingly easy-to-use, and thus very widely employed, method to deduce indirectly the composition of the critical cluster from experimental observations is the first nucleation theorem. According to its most generally used form, the number of molecules of any compound i in the critical cluster, n_i^*, is approximately equal to the slope of the logarithm of the nucleation rate J as a function of the logarithm of the gas-phase concentration C_i of the compound i:

$$\frac{\partial \log J}{\partial \log C_i} \approx n_i^*, \tag{1}$$

where other parameters such as temperature and concentrations of other vapors are assumed to be constant. As sulfuric acid has been identified as the main driving compound of atmospheric new-particle formation, several studies have focused on determining the number of sulfuric acid molecules in the critical cluster (Zhang, 2010; Zollner et al., 2012). In experimental studies, this is normally done by measuring particle concentrations at different sulfuric acid concentrations, determining the particle formation rate at each point, and applying a linear fit to the data presented on a log-log scale. Consequently, the observed formation rate is often reported as a power law $J \propto [H_2SO_4]^x$ (Kuang et al., 2008; Riipinen et al., 2007; Sihto et al., 2006). However, different experiments have given values for the exponent x ranging from 1.3 to 12.9 (Ball et al., 1999; Benson et al., 2008; Brus et al., 2010; Sipilä et al., 2010; Zollner et al., 2012), and the measured formation rates at similar H_2SO_4 concentrations have varied by several orders of magnitude. The formation rate is normally given at the assumed critical cluster size corresponding to a mobility diameter of 1–2 nm. On the other hand, the detection limit of particle counters is often significantly higher than the assumed critical size, and thus the formation rate at the size of interest must be calculated from the particle concentrations at the observed size by assuming a certain growth rate, and accounting for possible losses between these sizes (Kerminen & Kulmala, 2002; Korhonen et al., 2014; Lehtinen et al., 2007).

The nucleation theorem has also been widely used in fundamental nucleation studies not directly related to atmospheric aerosols. Critical cluster sizes determined using the nucleation theorem for measured nucleation rates of various molecular liquids have been compared with theoretical predictions using the classical liquid droplet model. For n-butanol, Viisanen & Strey (1994) found reasonably close agreement between the two approaches, although the slope values were slightly higher than the classical results. On the other hand, Brus et al. (2005) found later large discrepancies between critical cluster sizes of n-butanol determined using different measurement set-ups. For the ethanol–hexanol mixture, Strey & Viisanen (1993) found qualitative agreement between the critical cluster composition determined from measurements and theory, while especially the critical cluster size of pure hexanol deviated by several tens of percent between the slope approach and the liquid drop model. Also in the n- and i-octane mixture, Vehkamäki & Ford (2001) found notable differences between slope values and classical theory. Slope values that are considerably lower than classical predictions have been reported for n-propanol (Brus et al., 2006) and slopes slightly lower than predicted have also been observed for n-pentanol (Hrubý et al., 1996). Also for water, classical predictions may be slightly or even significantly higher than experimental results, especially for larger critical sizes or higher temperatures (Fransen et al., 2013; Manka et al., 2010 and references therein), but there are also some discrepancies between different experimental data sets (see Kim et al., 2004; Manka et al., 2010 and references therein).

Some recent studies (Ehrhart & Curtius 2013; Kupiainen et al., 2013; Malila et al., 2011, 2013) have pointed out that external losses affect the nucleation rate and thus the applicability of the nucleation theorem. In addition to requiring that there are no losses, the derivation of the nucleation theorem also involves several other assumptions. In this work, we present an overview of the derivation, and examine how breaking each of the assumptions affects the results obtained by applying the theorem. While our examples are related to atmospheric new-particle formation, the problems raised in this study are quite general and may affect the applicability of the nucleation theorem also in other systems.

We use a cluster population dynamics model to simulate the formation rate of sulfuric acid–base clusters at a mobility diameter of approximately 1.5 nm, a size at which experimental particle formation rates are often reported. We present the simulated formation rate and its slope with respect to sulfuric acid and base concentrations as a function of acid concentration, and show that the slope may be altered by various factors.

To study the uncertainties related to calculating the formation rate of sub-2-nm particles from the concentrations of larger particles, we also apply a separate aerosol microphysics model to simulate particle growth from 1.5 nm to larger sizes. In this case, the formation rate at 1.5 nm is assumed to follow a power-law dependence $J \propto [H_2SO_4]^x$. The nucleation rate is then back-calculated from the concentrations of 3–6 nm particles following the procedure used in the analysis of experimental data. We show that the exponent x obtained from the slope of the calculated nucleation rate differs from the actual value used as input in the growth simulation, leading to erroneous conclusions about the critical cluster size.

2. The first nucleation theorem

Relation (1), usually referred to as the first nucleation theorem, was first developed on the basis of the classical capillary drop model by Nielsen (1964), who applied it to crystallization from a melt. Kashchiev (1982) gave the result a more general