Geophysical Research Abstracts
Vol. 17, EGU2015-1614, 2015
EGU General Assembly 2015

Growth rates of atmospheric molecular clusters determined from cluster appearance times and collision–evaporation fluxes

Jenni Kontkanen, Tinja Olenius, Katrianne Lehtipalo, Hanna Vehkamäki, and Markku Kulmala
Department of Physics, University of Helsinki, Helsinki, Finland

The probability of freshly formed particles to survive to climatically relevant sizes is determined by the competition between the coagulation loss rate and the particle growth rate. Therefore, various methods have been developed to deduce the growth rates from measured particle size distributions. Recently, the growth rates of sub-3nm clusters have been determined based on the appearance times of different cluster sizes. However, it is not clear to what extent these growth rates are consistent with the growth rates corresponding to molecular fluxes between clusters. In this work, we simulated the time evolution of a population of sub-3 nm molecular clusters and compared the growth rates determined (1) from the cluster appearance times and (2) from the collision–evaporation fluxes between different cluster sizes.

We performed a number of simulations by varying the ambient conditions and the properties of the model substance. In the first simulation set, the Gibbs free energy of the formation of the clusters was assumed to have a single maximum and no minima, corresponding to a monotonically increasing stability as a function of cluster size. The saturation vapor pressure was selected so that the growth proceeded solely via monomer additions. The growth rates were determined separately for each cluster. However, to see the effect of finite size resolution, we also performed simulations where the clusters were grouped into size bins, for which we determined the growth rates. In the second simulation set, the saturation vapor pressure was lowered so that the collisions of small clusters significantly contributed to the growth. As the growth rate of a single cluster is ambiguous in this case, the growth rates were determined only for different size bins. We performed simulations using a similar free energy profile as in other simulations but we also used a free energy profile containing a local minimum, corresponding to small stable clusters.

Our simulations show that there may be significant differences between the growth rates determined with the two approaches. The growth rates determined from the appearance times of clusters were generally higher than the flux-equivalent growth rates. The difference between the growth rates was largest for the smallest clusters but its magnitude varied depending on the properties of the model substance and on the ambient conditions, such as the external sink. The use of size bins increased the difference, especially if the width of the size bins was large. In the simulations where non-monomer collisions significantly contributed to the growth, the difference between the two growth rates was smallest in the conditions with high cluster concentrations. Furthermore, when the free energy profile had a minimum, the difference was generally smaller than in the simulations with no minima. While this work assesses the qualitative behavior of the size-dependent growth rates, and calls for caution in the interpretation of growth rates deduced from experiments, quantitative comparisons require information on the specific substance and conditions of interest.