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CLUSTER POPULATION SIMULATIONS AS A TOOL
TO PROBE PARTICLE FORMATION MECHANISMS

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Cluster population simulations as a tool to probe particle formation mechanisms

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University of Helsinki, 2015

Abstract

Formation of aerosol particles from condensable vapors is a ubiquitous phenomenon in the atmosphere. Aerosols can affect regional and global climate, as well as visibility and human health. The work of this thesis contributes to the numerous efforts made to build understanding of atmospheric particle formation mechanisms. The focus is on the first molecular-level steps, where clustering of individual gas-phase molecules initiates the process, and the applied method is dynamic cluster population modeling. Sets of sub-2 nm molecular clusters are simulated in conditions relevant to the atmosphere or laboratory considering vapor production, external sinks for clusters and vapors, cluster collision and evaporation processes, and in some cases also ionization and recombination by generic ionizing species. Evaporation rates are calculated from the cluster formation free energies computed with quantum chemical methods.

As sulfuric acid has been shown to be the key component in particle formation in most boundary layer locations, the majority of the work presented here concentrates on simulating sulfuric acid-containing clusters in the presence of potentially enhancing species, namely ammonia and amines. In laboratory experiments, these base compounds have been found to be capable of enhancing sulfuric acid driven particle formation to produce formation rates around the magnitude observed in the atmosphere. This result is reproduced by the cluster model. In this work, the performance of the modeling tools is validated against experimental data also by comparing simulated concentrations of charged sulfuric acid–ammonia clusters to those measured with a mass spectrometer in a chamber experiment. Examination of clustering pathways in simulated sulfuric acid–ammonia and sulfuric acid–dimethylamine systems shows that the clustering mechanisms and the role of ions may be very different depending on the identity of the base.

In addition to predictions related to cluster formation from different precursor vapors, the model is applied to study the effects of varying conditions on the qualitative behavior of a cluster population and quantities that have been deduced from measured cluster concentrations. It is demonstrated that the composition of the critical cluster corresponding to the maximum free energy along the growth pathway cannot be reliably determined from cluster formation rates by commonly used methods. Simulations performed using a simple model substance show that cluster growth rates determined from the fluxes between subsequent cluster sizes are likely to differ from the growth rates deduced from the time evolution of the concentrations as in experiments, with the difference depending on the properties of the substance as well as ambient conditions. Finally, the effect of hydration and base molecules on sulfuric acid diffusion measurement is assessed by mimicking an experimental setup. Applications of cluster population simulations are diverse, and the development of these types of modeling tools provides useful additions to the palette of theoretical approaches to probe clustering phenomena.

Keywords: atmospheric new particle formation, growth rate, molecular cluster, kinetic modeling, quantum chemistry, sulfuric acid, ammonia, amines

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List of publications

This thesis consists of an introductory review, followed by five research articles. In the introductory part, the papers are cited according to their roman numerals.

- I Olenius, T., Schobesberger, S., Kupiainen-Määttä, O., Franchin, A., Junninen, H., Ortega, I. K., Kurtén, T., Loukonen, V., Worsnop, D. R., Kulmala, M., and Vehkamäki, H.: Comparing simulated and experimental molecular cluster distributions, *Faraday Discuss.*, 165, 75–89, 2013.
- II Olenius, T., Kupiainen-Määttä, O., Ortega, I. K., Kurtén, T., and Vehkamäki, H.: Free energy barrier in the growth of sulfuric acid–ammonia and sulfuric acid–dimethylamine clusters, *J. Chem. Phys.*, 139, 084312, 2013.
- III Olenius, T., Kurtén, T., Kupiainen-Määttä, O., Henschel, H., Ortega, I. K., and Vehkamäki, H.: Effect of hydration and base contaminants on sulfuric acid diffusion measurement: a computational study, *Aerosol Sci. Tech.*, 48, 593–603, 2014.
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- V Olenius, T., Riipinen, I., Lehtipalo, K., and Vehkamäki, H.: Growth rates of atmospheric molecular clusters based on appearance times and collision–evaporation fluxes: Growth by monomers, *J. Aerosol Sci.*, 78, 55–70, 2014.

1 From vapors to particles

If one thinks about the Earth's atmosphere, the most probable vision is a sky with clouds. In the boundary layer clouds originate from *aerosol particles*. These very small, liquid or solid particles act as condensation nuclei for water to form cloud droplets. In this way the particles indirectly affect the Earth's radiation budget, as the optical properties of the clouds depend on the number and properties of the condensation nuclei (Twomey, 1991; Andreae and Rosenfeld, 2008). This indirect effect via cloud formation is probably the most significant issue related to aerosols, because it gives rise to one of the largest uncertainties in the global radiation budget predictions (IPCC, 2013). Aerosols also affect the incoming solar radiation directly by reflecting and absorbing it (Yu et al., 2006). Furthermore, the particles diminish visibility, affect regional weather and precipitation, and cause adverse health effects (see *e.g.* Ramanathan et al., 2001; Nel, 2005; Chang et al., 2009). The particles can be divided into two categories by their origin: *primary aerosols* enter the atmosphere directly as particulate matter as, for example, soot, pollen, or sea salt particles. *Secondary aerosols* are formed in the atmosphere from condensable vapors. According to current knowledge, a significant fraction of the cloud condensation nuclei originate from secondary aerosols (Pierce and Adams, 2009; Kerminen et al., 2012).

The first steps in the formation of secondary atmospheric aerosol particles involve the aggregation of individual gas phase molecules into molecular clusters. The clusters can grow into larger sizes by colliding with vapor molecules and each other, evaporate back into smaller sizes, or deposit onto pre-existing surfaces. Together, these dynamic processes determine the formation rate of larger clusters that are stable enough to grow further into aerosol particles. However, the exact mechanisms of the initial clustering and the compounds participating in it remain uncertain. This has served as a starting point and motivation for numerous studies, including the research of this thesis. The work presented here aims to obtain insights to atmospheric clustering processes and measurable quantities related to them by simulations of *molecular cluster populations*.

It is evident that sulfuric acid is the key component in atmospheric particle formation in many locations in the boundary layer (Weber et al., 1997; Kuang et al., 2008; Nieminen et al., 2009). It is equally evident that sulfuric acid alone or with water is not able to explain the observed particle formation rates, but other compounds must be participating in the process. Compounds proposed to enhance sulfuric acid driven particle formation include bases, ions, and organic species (Ball et al., 1999; Yu and Turco, 2000; Zhang et al., 2004; Kurtén et al., 2008; Schobesberger et al., 2013). Regarding the very first steps of atmospheric clustering, bases are promising candidates: they are capable of binding to acids and forming stable clusters. Ammonia has been the topic of interest in numerous studies for a long time; it is abundant in the atmosphere and has been detected in sulfate particles in field studies (Seinfeld and Pandis, 2006). Ammonia has been found to increase particle formation rates in laboratory measurements (Ball et al., 1999; Kirkby et al., 2011); on the other hand, the

enhancing effect of ammonia is not likely to be strong enough to explain atmospheric observations (Kirkby et al., 2011). Other base candidates are amines, ammonia derivatives in which one or more hydrogen atoms are replaced by organic functional groups. Amines are stronger bases than ammonia and are thus expected to form more stable clusters with acids. Indeed, the enhancing effect of different methylamines on particle formation has been observed in experiments (Erupe et al., 2011; Yu et al., 2012; Almeida et al., 2013), and found to exceed that of ammonia at atmospherically relevant base concentrations (Almeida et al., 2013). According to theoretical calculations, small sulfuric acid–amine clusters are clearly more stable than corresponding ammonia-containing clusters (Kurtén et al., 2008; Loukonen et al., 2010; Nadykto et al., 2011; Ortega et al., 2012). Dimethylamine, in which two hydrogen atoms are replaced by methyl groups, has often been studied as a representative amine compound (Ortega et al., 2012; Almeida et al., 2013; Loukonen, 2014). Chamber experiments carried out with sulfuric acid and dimethylamine have produced particle formation rates of the order of magnitude of those observed in the atmosphere (Almeida et al., 2013). However, the oxidative lifetime of dimethylamine in ambient air is of the order of hours (Atkinson et al., 1977), and thus the compound is likely to have a prominent effect mainly near its sources (Almeida et al., 2013).

Ions are another widely studied candidate for the missing piece in the aerosol formation puzzle (Raes et al., 1986; Yu and Turco, 2000). Although both theory and experiments indicate that ions have a stabilizing effect on sulfuric acid clusters (Lovejoy et al., 2004; Kirkby et al., 2011; Ortega et al., 2014), this stabilization is not sufficient to explain ambient observations, as is also the case for ammonia (Kirkby et al., 2011). Low volatile organic compounds are known to dominate the growth of larger particles (Riipinen et al., 2012; Yli-Juuti, 2013), and it has been recently shown that oxidized organic species composed of ten carbon atoms and a few oxygen and hydrogen atoms are also capable of participating in the first steps of clustering (Schobesberger et al., 2013; Riccobono et al., 2014). All in all, it is likely that atmospheric particle formation events are not caused simply by one or two key species; instead, the principal players behind the phenomenon in different environments vary depending on the vapor concentrations and the relative stabilizing strengths of different compounds.

Modeling the atmospheric clustering process is an extremely complicated task. Already the fact that there are a huge number of possible contributing compounds is challenging: one needs to decide which compounds are worth studying in detail. The ultimate objective of any modeler is to develop theoretical tools, based on fundamental physics, that are both capable of reproducing experimental observations as well as possible and giving a physical explanation for them. On the other hand, often the main focus of interest in cluster population modeling is not highly accurate quantitative results on, for example, cluster formation rates in specific systems, but rather the relative effects and trends related to different representative compounds. These effects can include, for instance, the relative changes in cluster concentrations or formation rates in the presence of a stabilizing (or de-stabilizing) species, and the relative participation of different compounds in cluster stabilization and growth in a multicomponent system (*e.g.* Bork et al., 2014b).

In addition, elementary understanding of the dynamic behavior of a cluster population is in itself essential. The implementation of theoretical approaches may suffer from the lack of sufficient computational resources; this has been a severe problem especially in the past and has led to the use of various approximations and assumptions. Approximations may also be required to make the computations feasible. Simplified theories may, however, fail to describe the behavior of a highly non-linear system of colliding and decaying clusters under different conditions. Therefore, model substances should be used to test the general behavior of a system as well as the sensitivity of the quantities of interest to different assumptions.

The work of this thesis concentrates on modeling the dynamics of a cluster population in atmospherically relevant conditions, principally with quantum chemical cluster free energies used as input. The main objectives can be summarized as:

- To combine quantum chemical data with a dynamic cluster population model to study the formation and growth of electrically neutral and charged molecular clusters containing sulfuric acid, ammonia, amines and water (**Papers I–III**).
- To compare cluster distributions obtained from simulations with mass spectrometer measurements (**Paper I**).
- To study the effect of different compounds and/or ambient conditions on measurable quantities related to atmospheric cluster formation (**Papers I, III and V**).
- To apply a dynamic model to examine and explain the behavior of cluster populations under different conditions (**Papers IV and V**) and to assess the validity as well as impacts of commonly used assumptions related to cluster formation (**Paper IV**).

2 Thermodynamics of molecular cluster formation

The formation of a cluster in vapor is generally evaluated using *thermodynamics*: if the formation process is thermodynamically favorable, the cluster is likely to hold together instead of decaying. It must be noted, though, that cluster formation may involve kinetic barriers that are not considered in the thermodynamic treatment, and thus the cluster may not form even if the formation would be energetically favorable. These kinetic barriers can be related to, for instance, rearrangement of molecules in order to reach a low-energy configuration, or breaking of chemical bonds. The energetics of the process is not solely determined by the change of internal energy when molecules form clusters. Instead, due to the connection to the environment via a thermodynamic bath and the entropy of this combined system, the relevant quantity is the *free energy*. The choice of a suitable free energy depends on which quantities are kept constant through the connection to the bath. In atmospheric cluster formation, the temperature and pressure as well as the numbers of molecules are most often assumed to remain constant, and the freely exchanged quantities between the system and the environment are heat and volume work. Therefore, the relevant free energy is the Gibbs free energy

$$G = U + P_0V - T_0S = H - T_0S, \quad (2.1)$$

where U is the internal energy of the system, V is its volume, S is its entropy, and P_0 and T_0 are the pressure and temperature determined by the environment, respectively. The last equality follows from the definition of enthalpy $H = U + P_0V$, and is very often used for the Gibbs free energy. It allows the calculation of the Gibbs free energy at different temperatures when the enthalpy and entropy at one temperature are known, since the latter two can be approximated to be temperature-independent over atmospherically relevant temperature range. The formation free energy of a cluster from monomers $\Delta G_{\text{cluster}} = G_{\text{cluster}} - \Sigma G_{\text{monomers}}$ characterizes the *stability* of the cluster. Clusters that have the lowest formation free energies are the most stable and are, thus, likely to be relatively abundant (although the abundances are affected also by cluster kinetics, see Section 3). In atmospheric multi-component particle formation studies, the significance of different species in the initial clustering can be assessed by examining the relative stabilities of clusters containing these species. For instance, dimethylamine forms more stable clusters with sulfuric acid than does ammonia (Kurtén et al., 2008; Loukonen et al., 2010; Nadykto et al., 2011; **Paper II**).

2.1 Concept of a critical cluster reconsidered

The gas-to-liquid phase transition involved in atmospheric new particle formation is generally assumed to proceed via *nucleation*, which implies that the growing clusters must overcome an energy barrier in order to become stable particles. The alternative process is *barrierless clustering* of vapor molecules, where the formation and growth of clusters is energetically

ically favorable throughout the cluster size range. In the case of nucleation, the growth becomes favorable after the *critical cluster size* corresponding to the maximum in the Gibbs free energy of formation. Clusters smaller than the critical size are more likely to decay by evaporation than to grow further by collisions with vapor molecules, and clusters larger than the critical size are more likely to grow than to evaporate. Therefore the formation of a critical cluster has been considered as the bottleneck for new particle formation.

The widely established assumption that the formation free energy along the growth route exhibits one maximum originates from the traditional classical liquid droplet model (Section 2.2). However, the droplet model is based on macroscopic properties of matter and does not consider molecular and atomic interactions. Formation free energies of small molecular clusters may be significantly affected by, for instance, details of proton transfers between acid and base molecules that are not taken into account by the classical model. Moreover, bulk properties such as liquid density and surface tension are not well defined quantities in the case of small clusters. The bulk droplet model is thus not a reasonable approximation for clusters consisting of a few molecules, and the free energy surface of molecular clusters may be more complex than is assumed in the droplet model.

Despite these issues, it has been commonly assumed that there is a critical cluster involved in atmospheric aerosol formation, and numerous studies have concentrated on assessing the size and composition of the critical cluster in atmospheric conditions. From the experimental perspective, the critical cluster cannot be identified by examining cluster energies, as the free energy profile of growing clusters cannot be directly measured. A widely applied method to indirectly deduce the composition of the critical cluster from particle formation measurements is the first nucleation theorem in its most readily applicable form (McGraw and Wu, 2003; **Paper IV** and references therein)

$$\left(\frac{\partial \log J}{\partial \log C_i}\right)_{T, C_{j \neq i}} = n_i^* + \varepsilon_i. \quad (2.2)$$

Here J is the steady-state nucleation rate, C_i is the gas-phase concentration of compound i , T is the temperature, n_i^* is the number of molecules of species i in the critical cluster and ε_i is a small correction term, which is usually assumed to be negligible. The theorem is not limited to the classical droplet approach, but is valid regardless of the model used for cluster energies. However, the derivation of the theorem in the form of Eq. (2.2) contains very restrictive assumptions related to the cluster growth mechanism and ambient conditions, which have usually not been considered when applying the theorem. In realistic situations, various non-idealities may result in violation of these assumptions, and application of the nucleation theorem can easily lead to erroneous conclusions concerning the critical cluster size (Vehkamäki et al., 2012; **Paper IV**). Also, while the theorem is independent of the quantitative free energies, Eq. (2.2) assumes that the qualitative energy profile contains one distinct maximum.

Sections 2.2–2.4 summarize the methods for determining cluster formation free energy that are used or discussed in this thesis. The theoretical approaches include electronic structure

calculations, referred to as quantum chemistry, and the classical droplet model. Other approaches not discussed here are methods based on classical molecular interaction potentials, namely molecular dynamics simulations (see *e.g.* Haile, 1997), Monte Carlo simulations (Metropolis and Ulam, 1949), and classical density functional theory (Oxtoby and Evans, 1988). From a theoretical point of view, methods based on macroscopic substance properties or classical force fields are relatively easy to apply and can, for example, be used to study the behavior of a model substance for which no chemical reactions occur. To calculate thermodynamic properties of specific atmospheric molecular clusters consisting of arbitrary real chemical compounds, the most accurate –or in fact the only realistic– method is electronic structure calculations.

2.2 Classical liquid droplet model: a simplified approach for bulk substance

The classical expression for the cluster formation free energy follows from examining the formation of a liquid droplet in vapor based on *macroscopic properties of matter*. The droplet model is used in the classical nucleation theory framework (Becker and Döring 1935; Zeldovich 1943; for a review, see *e.g.* Vehkamäki, 2006, and Vehkamäki and Riipinen, 2012), that has often been applied to make theoretical predictions on particle formation rates. In short, the formation free energy is the free energy difference between the liquid and vapor phases plus the free energy required to form the surface separating the phases. For a one-component system, the Gibbs free energy of formation ΔG_i of a cluster consisting of i molecules is

$$\Delta G_i = -(i - 1)k_B T \ln S + (A_i - A_1)\sigma, \quad (2.3)$$

where S is the saturation ratio, k_B is the Boltzmann constant, T is the temperature, A_i is the surface area of a cluster consisting of i molecules, and σ is the surface tension, which is dependent on the temperature. The saturation ratio is defined as $S = P / P_{\text{eq}}$, where P is the vapor pressure of the nucleating compound and P_{eq} is the temperature-dependent saturation vapor pressure over a flat liquid surface. The vapor monomer concentration C_1 is connected to the saturation ratio via the ideal gas law as $C_1 = S \times P_{\text{eq}} / (k_B T)$. The first term on the right-hand side of Eq. (2.3) corresponds to the free energy difference related to the formation of a liquid droplet from gas-phase molecules. The term is negative for saturation ratios greater than one, that is, for supersaturated vapor for which the phase transition from gas to liquid is energetically favorable. The second term corresponding to the surface energy is always positive. The classical ΔG curve with a single maximum results from the sum of the volume and surface terms, as shown in Figure 1.

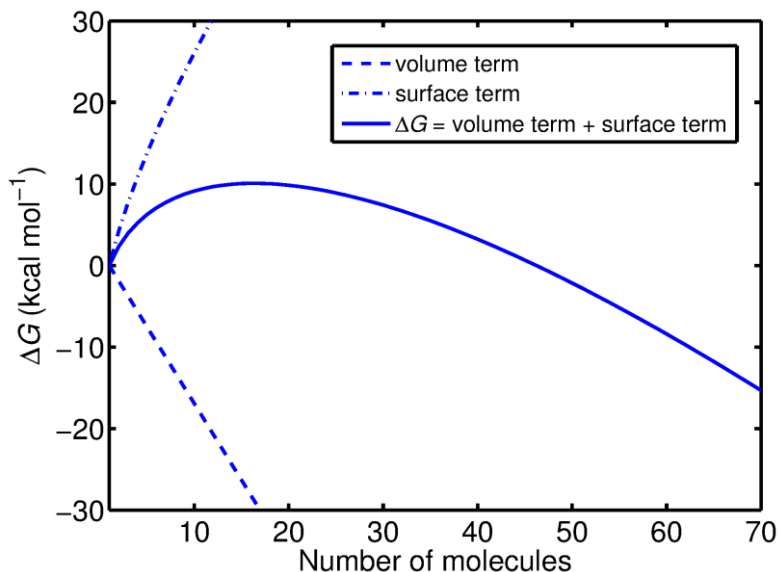


Figure 1: Gibbs free energy of formation as a function of cluster size according to the classical liquid droplet model, calculated using the properties of the model substance of **Paper V** at a saturation ratio of $S = 30$ and a temperature of 278 K.

The classical model has been applied also to ion-induced nucleation of a single polarity (Yue and Chan, 1979). This approach assumes that clusters are formed on an ion core, which decreases the formation free energy compared to the electrically neutral case due to electrostatic forces. However, in the presence of generic ionizing species of both polarities, as in natural atmospheric ionization, the clustering may proceed simultaneously through electrically neutral and negatively and positively charged pathways. Clusters can move from one charging state to another via collisions with each other, or ionization and recombination by the ionizing species (**Paper II**). In this case cluster formation free energy with respect to monomers is not even an unambiguously defined quantity, as *e.g.* electrically neutral clusters may be formed from neutral monomers, or from charged monomers of opposite polarities.

2.3 Quantum chemical calculations: free energy from the electronic structure

The most accurate theoretical method to study the properties of molecular clusters and compute their free energies are *electronic structure calculations*, often referred to as *quantum chemistry*. These methods are based on solving the time-independent Schrödinger equation of the cluster or molecule, treated as a system of N electrons and K nuclei

$$\hat{H}\Psi(\mathbf{r}_1, \dots, \mathbf{r}_{N+K}) = E\Psi(\mathbf{r}_1, \dots, \mathbf{r}_{N+K}), \quad (2.4)$$

where \hat{H} is the Hamiltonian operator of the system, E is its ground-state energy, Ψ is its wavefunction, and \mathbf{r}_i is the vector coordinate of particle i . The Hamiltonian includes operators for the kinetic energy of the electrons and nuclei, and the potential energy between the electrons, the nuclei, and the electrons and nuclei. In practice, solving the equation requires several approximations, namely the omission of relativistic effects, the Born-Oppenheimer approximation and the approximation for electron correlation (for a review, see *e.g.* Szabo and Ostlund, 1996; Jensen, 2007). The Born-Oppenheimer approach refers to separating the movement of nuclei and electrons, that is, considering the atomic nuclei from the point of view of electrons as fixed masses since they are much heavier and slower than the electrons. The wavefunction can thus be split into electronic and nuclear components, and the electronic wavefunction can be solved for each set of nuclear coordinates. The treatment of electron correlation, a small but essential and important component of the electronic energy, depends on the specific quantum chemical method used, as discussed below. The minimum-energy configuration is found by solving Eq. (2.4) iteratively based on an initial starting guess.

There are two approaches to obtain the ground-state energy: wavefunction-based methods and density functional theory. In wavefunction methods, often called *ab initio* methods (although the term *ab initio* may sometimes refer to all electronic structure methods in general), the electronic wavefunction is first formed as a combination of non-interacting one-electron wavefunctions via a Slater determinant (for more detailed information, see *e.g.* Jensen, 2007). The one-electron wavefunctions, also called spin orbitals, are approximated as a linear combination of some basis functions, known as the basis set. The N -electron Schrödinger equation is then solved by converting it into N Hartree-Fock equations and minimizing the energy by finding the optimal set of linear combination coefficients (Jensen, 2007). Density functional theory, or in short DFT, is based on the fact that the ground-state energy of a system of interacting electrons is unambiguously determined by the electron density. That is, the ground-state energy is a functional of the electron density (Hohenberg and Kohn, 1964) –however, this functional is not known. Thus the electron density is in practice expressed via one-electron wavefunctions constructed using a basis set as in wavefunction methods, and the energy functional is converted into Kohn-Sham equations, which are analogous to the Hartree-Fock equations.

In practice, the main difference between the two electronic structure calculation methods is the treatment of electron correlation. In the wavefunction scheme, the correlation is considered as a correction on top of the solution for non-interacting electrons, while in density functional theory it is included in the energy expression as an exchange–correlation functional. Physically, the correction related to wavefunction methods corresponds to including excited energy levels in the electronic wavefunction. The level of the method depends on the number of excitations. There are several approaches for including excited states, of which the most relevant are Møller-Plesset perturbation theory (Møller and Plesset, 1934) and the coupled cluster method (Coester, 1958; for a review, see Bartlett and Musial, 2007). Nevertheless, high-level corrections are limited to very small systems due to heavy computational burden, and clusters of the sizes studied in this work must be treated with somewhat

less accurate, but computationally more affordable levels of theory. In DFT, while the exchange–correlation functional is the only unknown term in the energy expression, it is also substantially important for the calculations. Therefore constructing good exchange–correlation functionals is essential for the success of DFT methods. At present, various functionals, developed for different purposes have been benchmarked against high-level theoretical data, experimental results, or both (see *e.g.* Jensen, 2007; Becke, 2014).

The free energy at non-zero temperatures is obtained by adding the contributions of translational, vibrational and rotational degrees of freedom to the ground-state electronic energy solved from Eq. (2.4). Thermodynamic quantities are calculated from the statistical mechanical partition function q of the system. The partition function is normally expressed as the product of the different factors $q = q_{\text{elec}}q_{\text{trans}}q_{\text{vib}}q_{\text{rot}}$, assuming that the corresponding degrees of freedom are decoupled. The contribution of each factor q_X to the enthalpy and entropy is given as

$$H_X = k_B T^2 \left(\frac{\partial \ln q_X}{\partial T} \right)_V + k_B T V \left(\frac{\partial \ln q_X}{\partial V} \right)_T \quad (2.5)$$

$$S_X = k_B T \left(\frac{\partial \ln q_X}{\partial T} \right)_V + k_B \ln q_X. \quad (2.6)$$

The total enthalpy and entropy can then be calculated as the sum of the contributions $H_{\text{tot}} = \Sigma H_X$ and $S_{\text{tot}} = \Sigma S_X$, and the Gibbs free energy is given by Eq. (2.1) as $G_{\text{tot}} = H_{\text{tot}} - TS_{\text{tot}}$.

In general, the thermal contributions are computed assuming ideal gas behavior for the translational component, and applying the harmonic oscillator-rigid rotor assumption for the vibrational and rotational components. While these approximations need to be made due to finite computational resources, they may be rather poor for realistic systems. Especially, the assumption of harmonic vibrations is not valid in the case of hydrogen bonded molecular clusters, and may cause significant errors in the quantitative results (Kathmann et al., 2007; Loukonen et al., 2014a). The problem is that there is, in general, no reliable method for including anharmonic effects. For very small systems, anharmonicity can be considered using various theoretical approaches (Chaban et al., 1999; Barone, 2004; Partanen et al., 2012). The results can be used to derive anharmonic scaling factors for harmonic frequencies, and these factors can then be applied for larger clusters (Kurtén et al., 2007; Loukonen et al., 2010). However, this simple correction may lead to errors: scaling factors derived from specific clusters are by no means universally applicable, as they depend on the relative fractions of inter- and intramolecular vibrational modes of the chosen clusters. If these fractions are significantly different for the clusters to which the scaling is applied, the vibrational corrections may be erroneous.

In the research of this thesis, the quantum chemical free energies were calculated with a multistep method (Ortega et al., 2012) that combines geometry optimizations and frequency calculations performed with the Gaussian09 program (Frisch et al., 2009) using the B3LYP density functional (Becke, 1993) and a CBSB7 basis set (Montgomery et al., 1999) with single point energy calculations performed with the TURBOMOLE program (Ahlrichs et

al., 1989) using the wavefunction-based RI-CC2 method (Hättig and Weigend, 2000) and an aug-cc-pV(T+d)Z basis set (Dunning et al., 2001). The harmonic oscillator-rigid rotor scheme was used, since the effect of anharmonicity is very difficult to assess, and prone to errors for clusters of the sizes studied here. The combination of geometries and frequencies calculated at a lower level of theory and single point energies calculated at a higher level of theory is a common practice: the geometry optimizations and vibrational frequencies can be computationally the most expensive quantities to calculate, but are less sensitive to the level of theory than the energies. In general, atmospheric clusters have been studied with a variety of methods (*i.a.* Kurtén et al., 2007 and 2008; Loukonen et al., 2010; Nadykto and Yu, 2007; Nadykto et al., 2011; Temelso et al., 2012). While the quantitative results given by different methods may differ, the general trends, such as the composition of the most stable clusters, are similar.

Extensive comparisons of the performance of different methods have been conducted by, for example, Leverentz et al. (2013), Elm et al. (2012 and 2013), and Bork et al. (2014a). The benchmark studies have aimed at determining which methods provide the optimal balance between accuracy and computational cost. The work by Leverentz et al. (2013) shows that the RI-CC2/aug-cc-pV(T+d)Z method used to compute the single point energy in the work of this thesis somewhat overestimates the binding of the clusters compared to higher level methods. Therefore, for more accurate free energy estimates, the electronic energies should be calculated at a level recommended by the benchmark studies, such as the M06-2X functional (Zhao and Truhlar, 2008).

The free energies used in this work correspond to the global minimum-energy structure of each cluster. In reality, there can exist multiple local minima, and a more appropriate approach may be to use the Boltzmann averaged free energy of an ensemble of low-energy configurations (see *e.g.* Kurtén et al., 2007, and Temelso et al., 2012). However, while aiming to find the configuration having the absolutely lowest energy is rather straightforward, finding a representative set of local minimum structures requires very effective configurational sampling methods especially for larger clusters. The free energy averaged over an ensemble of configurations may be distorted if some essential low-energy structures have not been found, and thus the ensemble-averaged energies may have considerably larger uncertainties than the absolute minimum energies.

The free energies are normally computed by default at the standard pressure P_{ref} of 1 atm, and can be converted to another pressure P by

$$G(P) = G(P_{\text{ref}}) + k_{\text{B}}T \ln\left(\frac{P}{P_{\text{ref}}}\right). \quad (2.7)$$

The formation free energy of a cluster with respect to monomers is also generally given at the reference pressure P_{ref} at which the absolute free energies of all the species are computed. This quantity can be cast in terms of the actual vapor pressures of the clustering compounds by (see *e.g.* Silbey et al., 2005; Vehkamäki, 2006; **Paper II**)

$$\Delta G(P_1, P_2, \dots, P_n) = \Delta G(P_{\text{ref}}) - k_B T \sum_{i=1}^n N_i \ln \left(\frac{P_i}{P_{\text{ref}}} \right), \quad (2.8)$$

where n is the number of components in the cluster, N_i is the number of molecules of type i in the cluster, and P_i is the partial pressure of component i in the vapor phase. The quantity given by Eq. (2.8) is used to determine the free energy surface in the classical theory framework (Section 2.2) and to identify a possible energy barrier corresponding to a critical cluster (Section 2.1).

2.4 Experimental means to determine formation free energies

Experimental determination of cluster formation free energies is based on their thermodynamic relationship to the equilibrium cluster distribution. In the time-independent equilibrium situation with no net production of clusters, concentrations of clusters follow the statistical mechanical law of mass action, and the equilibrium constant $K_{A+B \rightarrow C}$ for the process $A + B \rightleftharpoons C$ where species C is formed from species A and B is

$$K_{A+B \rightarrow C} = \frac{[C]}{[A][B]} \propto \exp \left(-\frac{\Delta G_{A+B \rightarrow C}}{k_B T} \right),$$

where $[X]$ is the concentration of species X. For example, if A is a monomer and B is a cluster, the free energy of the addition of A to B to form cluster C at a reference pressure of P_{ref} can be obtained from the measured cluster concentrations $[B]$ and $[C]$ as

$$\Delta G_{A+B \rightarrow C}(P_{\text{ref}}) = -k_B T \ln \left(\frac{[C]}{[A][B]} \frac{P_{\text{ref}}}{k_B T} \right) = -k_B T \ln \left(\frac{[C]}{[B]} \frac{P_{\text{ref}}}{P_A} \right), \quad (2.9)$$

where P_A is the partial pressure of compound A. If measurements are performed at several temperatures T , the logarithm of the equilibrium constant can be presented as a function of T^{-1} to deduce the enthalpy and entropy (Eq. (2.1)) assuming that they are constant over the studied temperature range, a procedure known as the van't Hoff analysis. As determining the free energies from the observed cluster distributions requires a chemical composition measurement, performed by mass spectrometry, it can be applied only for electrically charged clusters (see Section 3.3). In atmospheric studies, free energies have been deduced from the equilibrium distribution for, for instance, positively and negatively charged sulfuric acid–water clusters (Froyd and Lovejoy, 2003a and 2003b; Sorokin et al., 2006), and positively charged sulfuric acid–ammonia clusters (Froyd and Lovejoy, 2012).

For electrically neutral clusters, experimental determination of cluster free energies is very challenging and requires some type of indirect method, as the cluster composition cannot be directly measured. Hanson and Eisele (2000) presented a method to deduce the free energies of sulfuric acid hydrates by measuring the diffusion coefficient of sulfuric acid as a function of relative humidity, which is based on the decreasing effect of hydrate formation on the diffusivity of acid. The results may, however, be affected by the assumed maximum number of water molecules that can be bound to the acid, and the presence of contaminant molecules

of other species (**Paper III**). Kupiainen-Määttä et al. (2013) proposed an experimental setup to determine the formation free energy of the sulfuric acid–dimethylamine dimer. The method is based on the theoretically predicted effect of dimer formation on the detection efficiency of vapor phase acid measured by chemical ionization; this type of experiment has however not yet been performed.

3 Cluster population dynamics: the ACDC model

Formation free energies give information on the relative stabilities of molecular clusters, but do not alone determine the relative abundances or the growth pathways in a system of clusters. To study the behavior of a population of clusters, kinetic effects must be considered. The time evolution of a cluster population is obtained by integrating the time derivatives of the cluster concentrations. The time derivatives, also called the *birth-death* or the *Becker-Döring equations*, include all possible processes where the clusters can be formed or destroyed. The birth-death equations have been solved for numerous systems (see *e.g.* Wyslouzil and Wilemski, 1995; McGrath et al., 2012, and references therein). In this thesis, cluster population dynamics was simulated using the Atmospheric Cluster Dynamics Code (ACDC; McGrath et al., 2012; **Paper II**). The code generates the birth-death equations for an arbitrary set of clusters, and solves them by numerical integration using the Matlab ode15s solver (Shampine and Reichelt, 1997).

The birth-death equation for each cluster or molecule is given as

$$\begin{aligned} \frac{dC_i}{dt} = & \frac{1}{2} \sum_{j < i} \beta_{j,(i-j)} C_j C_{i-j} + \sum_j \gamma_{(i+j) \rightarrow i,j} C_{i+j} \\ & - \sum_j \beta_{i,j} C_i C_j - \frac{1}{2} \sum_{j < i} \gamma_{i \rightarrow j,(i-j)} C_i + Q_i - S_i C_i, \end{aligned} \quad (3.1)$$

where C_i is the concentration of cluster i , $\beta_{i,j}$ is the collision rate coefficient of clusters i and j , and $\gamma_{k \rightarrow i,j}$ is the evaporation rate coefficient of cluster k evaporating into clusters i and j . Q_i is a possible source term that is most often relevant only for vapor monomers, and S_i is a loss rate coefficient corresponding to external coagulation losses onto pre-existing larger particles or other surfaces. The code also allows the concentration of a cluster or molecule to be set to a constant value, or to be determined as a function of time and/or concentrations of some other species. In new particle formation studies, the situation of interest is often the time-independent steady state of a cluster population, and in this case the dynamic simulation can be run until the cluster concentrations do not change anymore (**Papers I, II and IV**).

The system can include both electrically neutral and charged clusters, and generic ionizing species that can collide with the clusters to change their charging state, but do not attach to them. In the latter case Eq. (3.1) includes also all possible ionization and recombination terms (for more details see **Paper II**). Generic ions can be introduced into the system as source terms, and their concentrations are determined by birth-death equations that include collisions with all clusters that can get charged or neutralized by the ion, recombinations with generic ions of the opposite polarity, and possible external sinks. Charged clusters and/or generic ions of the same polarity are not allowed to collide with each other because of electrostatic repulsion. Figure 2 presents a schematic picture of the processes included in the simulations.

As output, the kinetic simulation yields the time-dependent cluster concentrations and molecular fluxes in the system. The fluxes can be used to determine the formation rate of clusters growing out of the simulated cluster size range (see Section 3.2), and the formation and loss routes of all the clusters. The growth pathways resulting in the outgoing cluster flux can be solved by seeing which collisions lead out of the simulated size range, and tracking the formation routes of the boundary clusters down to monomers (**Paper II**).

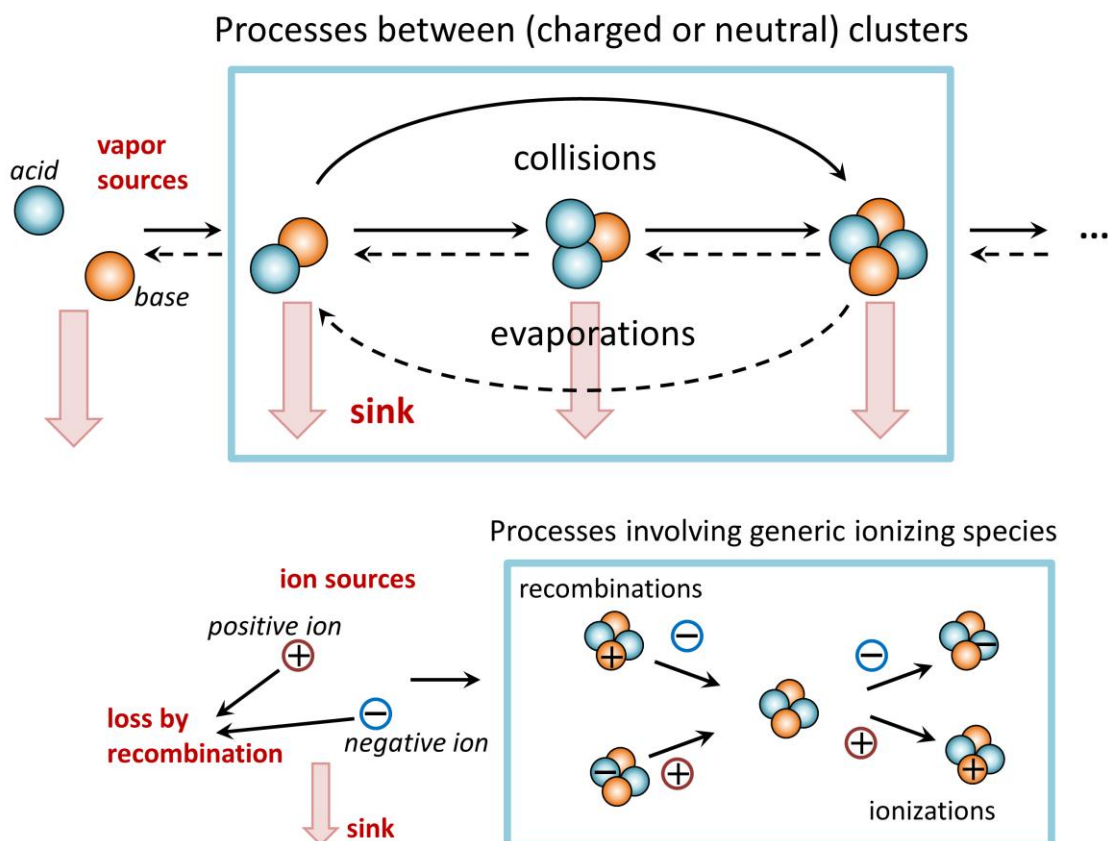


Figure 2: Processes included in the dynamic cluster population simulations. For figure clarity, the processes are presented for a two-component acid–base system, but the model can be applied to arbitrary one- or multicomponent systems.

3.1 Collision and evaporation coefficients determine the rate of processes

In order to solve the birth-death equations, the collision and evaporation rate coefficients must be known. In this thesis, the collision coefficients between two electrically neutral clusters are calculated as hard-sphere collision rates according to kinetic gas theory (Chapman and Cowling, 1952)

$$\beta_{i,j} = \left(\frac{3}{4\pi}\right)^{1/6} \left[6k_{\text{B}}T \left(\frac{1}{m_i} + \frac{1}{m_j}\right)\right]^{1/2} (V_i^{1/3} + V_j^{1/3})^2, \quad (3.2)$$

where m_i and V_i are the mass and volume of cluster i , respectively. Cluster volumes are calculated from the masses and liquid densities of the species assuming ideal mixing. Another option is to calculate the volumes from the average radii of the clusters obtained from quantum chemical cluster structures or molecular dynamics simulations. However, the collision rate is not very sensitive to small changes in the cluster volume (Ortega et al., 2012). For collisions involving a neutral and a charged cluster or molecule, the rate coefficient is calculated according to the parameterization by Su and Bowers (1973; **Papers I and II**) or Su and Chesnavich (1982; **Paper IV**). Both parameterizations consider the masses of the collision partners, and the dipole moment and polarizability of the neutral cluster or molecule. A detailed description of the parameterizations can be found in the study by Kupiainen-Määttä et al. (2013), who also showed that the two parameterizations lead to qualitatively similar results in terms of clustering.

In this thesis, the sticking factor in all collisions is assumed to be unity, that is, all collisions lead to cluster formation. The effective collision rate may be decreased by steric effects or energy barriers related to the collision processes. The former effect may become an issue especially when the colliding species contain a large number of atoms that do not participate in the bonding, which may be the case for organic acids, for instance, but also for alkylamines that contain methyl groups. However, molecular dynamics simulations have shown that steric hindrance is insignificant in head-on collisions between sulfuric acid and dimethylamine molecules (Loukonen et al., 2014a). Kinetic barriers associated to sulfuric acid–ammonia clustering have been proposed based on experimental findings (Bzdek et al., 2013), but at the moment it is not possible to assess their significance in the absence of quantitative estimates for the barrier heights. The formed cluster may also break due to the excess energy before it is thermalized by collisions with inert air molecules. For sulfuric acid–containing clusters it is usually assumed that the clusters have a large enough number of vibrational modes to temporarily accommodate the excess energy (Kurtén et al., 2010).

The evaporation coefficients connect the cluster energies to kinetic modeling: they are calculated from the collision coefficients and the formation free energies (which can be obtained with the approaches described in Section 2) according to the concept of detailed balance as (see *e.g.* Vehkamäki, 2006)

$$\gamma_{(i+j)\rightarrow i,j} = \beta_{i,j} \frac{P_{\text{ref}}}{k_{\text{B}}T} \exp\left(\frac{\Delta G_{\text{ref},i+j} - \Delta G_{\text{ref},i} - \Delta G_{\text{ref},j}}{k_{\text{B}}T}\right), \quad (3.3)$$

where $\Delta G_{\text{ref},i}$ is the Gibbs free energy of formation of cluster i calculated at the reference pressure P_{ref} (which is usually 1 atm for the quantum chemical calculations; Section 2.3). It must be noted that the evaporation rate is independent of the reference pressure: if all the free energies are converted to another pressure according to Eq. (2.7), the pressure conversion cancels out in Eq. (3.3). In general, the detailed balance approach implies that the evap-

oration rate of a cluster is always that of the equilibrium situation, in other words independent of ambient conditions other than the cluster temperature. Furthermore, it is assumed that the cluster settles to the global minimum-energy configuration immediately when being formed in a collision (Section 2.3). In reality, it may be more likely that an optimal structure is not found instantly after the collision, and the evaporation rate is higher shortly after the cluster is formed compared to the situation where the molecules have rearranged into a more stable configuration. While different approaches have been utilized to determine cluster collision and evaporation rate coefficients, they are generally assumed to be related via detailed balance (Schenter et al., 1999; Kathmann et al., 1999). The dynamics of collision and evaporation processes can be studied more accurately by first-principles molecular dynamics simulations where electronic structure methods are used to determine the forces within the system (Loukonen et al., 2014a and 2014b). However, at present this is computationally far too demanding for clusters of the size studied in this work, and using Eq. (3.3) is the only way to obtain the rate coefficients.

3.1.1 Effect of hydration

As water vapor is ubiquitous in the atmosphere, clusters related to particle formation are likely to contain water molecules. While water is a weak base and thus not capable of stabilizing sulfuric acid clusters as efficiently as stronger bases such as ammonia and amines, its effect on the collision and evaporation rates of growing clusters may be non-negligible. To model sulfuric acid–base initiated cluster formation in tropospheric conditions more comprehensively, water must be included in the simulation. This poses however a problem: the concentration of water and its collision and evaporation frequencies with clusters and molecules are approximately ten orders of magnitude higher than those of the other compounds. Including water explicitly in the simulated system results in an extremely stiff set of birth-death equations, which cannot in practice be solved for systems studied in this work.

Therefore, the effect of water must be taken into account implicitly. This is done by calculating the effective collision and evaporation rates of hydrated clusters, assuming that the clusters are in equilibrium with respect to water (Lovejoy et al., 2004; Paasonen et al., 2012; Almeida et al., 2013; **Paper III**). Because of the extremely high concentration of water compared to the other components, equilibration of the hydrate distributions can be assumed to occur much faster than the other kinetic processes. The equilibrium hydrate distribution of each cluster or molecule at a given temperature and concentration of water vapor is calculated from the formation free energies of the hydrates based on the law of mass action (Jaeger-Voirol et al. 1987; Noppel et al., 2002; **Paper III**). In its most simplified form, the relative concentration $C_m / \sum_n C_n$ of a hydrate containing m water molecules can be written as

$$\frac{C_m}{\sum_{n=0}^{n_{\max}} C_n} = \frac{\left(\frac{P_{\text{water}}}{P_{\text{ref}}}\right)^m \exp\left(-\frac{\Delta G_m}{k_B T}\right)}{\sum_{n=0}^{n_{\max}} \left(\frac{P_{\text{water}}}{P_{\text{ref}}}\right)^n \exp\left(-\frac{\Delta G_n}{k_B T}\right)}, \quad (3.4)$$

where the summation goes over all possible numbers of water molecules from zero to n_{\max} , ΔG_m is the formation free energy of the hydrate with m water molecules, P_{ref} is the pressure at which the formation free energies are calculated, and P_{water} is the partial pressure of water vapor, which is related to the relative humidity RH as $P_{\text{water}} = \text{RH}/100 \times P_{\text{water}}^{\text{eq}}$, where $P_{\text{water}}^{\text{eq}} = P_{\text{water}}^{\text{eq}}(T)$ is the equilibrium vapor pressure of water (for a parameterization, see for example Wexler, 1976).

The effective collision rate of clusters i and j can then be calculated by averaging over the hydrate distributions as

$$\beta_{i,j}^{\text{eff}} = \sum_{n=0}^{n_{\max}} \sum_{m=0}^{m_{\max}} \beta_{i,n;j,m} f_{i,n} f_{j,m}, \quad (3.5)$$

where n and m refer to the number of water molecules in clusters i and j , respectively, $\beta_{i,n;j,m}$ is the collision rate of the n -hydrate of cluster i and the m -hydrate of cluster j , and $f_{i,n}$ is the relative fraction of the n -hydrate of the hydrate distribution of cluster i . The effective evaporation frequency of cluster $i+j$ into clusters i and j is similarly

$$\gamma_{(i+j) \rightarrow i,j}^{\text{eff}} = \sum_{n=0}^{n_{\max}} \sum_{m=0}^{m_{\max}} \gamma_{(i+j,n+m) \rightarrow i,n;j,m} f_{i+j,n+m}. \quad (3.6)$$

In the case that there is an external sink for the clusters and the loss rate depends on cluster size, also the loss coefficient can be averaged over the hydrate distribution of each cluster (**Paper III**).

Another challenge related to including water in the simulations is the computational effort of obtaining the free energies for the hydrates. As multiple water molecules are added to the cluster, both the complexity of the configurational sampling and the time required for the actual quantum chemical calculations increase. The computational burden naturally increases also with the size of the dry cluster. Weak binding of water to the clusters is also challenging to capture accurately with quantum chemical methods. At the moment, there do not exist extensive datasets of hydrate free energies for systems of the sizes studied in this work. For smaller sets of clusters, quantum chemical hydration free energies are available (Henschel et al., 2014; Nadykto et al., 2014) and the effect of water has been studied in dynamic simulations (Paasonen et al., 2012; Almeida et al., 2013; **Paper III**).

3.2 Boundary conditions deal with the finite size range

When a collision leads to a cluster that is outside of the simulated size range, the fate of the resulting cluster is determined by *boundary conditions*. In ACDC, boundary conditions are defined via the composition of the outgoing clusters. If the composition can be assumed to be favorable so that the cluster is more likely to grow further than to evaporate back into the simulation system, the cluster is allowed to leave the system. Clusters that are let out are removed from the simulation, and the total outgoing flux of clusters is recorded as the formation rate of clusters larger than the simulated range. In this work, it is assumed that the

removed clusters do not act as an additional scavenging sink for the clusters explicitly included in the simulation. It must be noted that if the evaporation rates of the outgrowing clusters are in reality non-negligible compared to their collision rates with molecules and clusters, the outgoing flux may be somewhat overestimated. Thus it is important to ensure that the system is large enough in the sense that the outgrowing clusters can be assumed to have relatively low evaporation rates (see *e.g.* **Paper II**). If the composition does not satisfy the given boundary conditions, the cluster is brought back into the simulation by monomer evaporations.

In the research of this thesis, the boundary conditions are given in terms of the acid:base ratio of the outgrowing clusters, and are based on trends observed inside the simulation size range and/or experimental cluster data, if available. The conditions depend on the charging state of the clusters. In general, the most stable and abundant electrically neutral acid–base clusters contain approximately equal numbers of acid and base molecules; negatively charged clusters contain more acid than base, and positively charged clusters contain more base than acid. The exact minimum numbers of acid and base species required in the outgrowing clusters depend on the system and compounds (**Paper II**). In the case that the system contains more than one acid or base species, the order in which the excess molecules are evaporated when bringing back clusters that are not allowed to leave the simulated system can be defined based on the relative acid and base strengths. For instance, if a cluster with excess base forms outside the ternary sulfuric acid–ammonia–dimethylamine system, the first evaporating base molecule can be defined to be ammonia, as it is a weaker base than dimethylamine, and binds to sulfuric acid less strongly.

3.3 Comparing modeling results with experimental data

The most straightforward validation of a cluster model against experiments is the comparison of cluster concentrations. In principle, also the formation rate of clusters of a certain size can be obtained by experimental means and compared to the simulated formation rate (Almeida et al., 2013). The experimental formation rate is however derived from measured cluster concentrations, and thus a more direct comparison is that of the concentrations. In the past, instrumental limitations have restricted particle measurements to sizes larger than approximately 2–3 nm in diameter. At present, state-of-the-art techniques enable the detection of sizes down to 1 nm and even smaller. Concentrations of clusters of the sizes simulated in this work can be measured with various instruments, each of which has its strengths and weaknesses.

3.3.1 Charged clusters: possibility for a direct comparison

Electrically charged particles can be detected and counted with ion mobility spectrometers and mass spectrometers. Mobility spectrometers, such as the AIS (Air Ion Spectrometer; Mirme et al., 2007) and the BSMA (Balanced Scanning Mobility Analyzer; Tammet, 2006), are based on classifying charged particles into different size bins according to their electrical

mobility, which is a function of mobility diameter. Mobility spectrometers are able to give particle number concentrations down to a mobility diameter of circa 1 nm with a high accuracy, but, on the other hand, have a relatively low size resolution. In addition, they do not give information on the chemical composition of the particles. The elemental composition of charged molecular clusters can be determined with mass spectrometry, namely the APi-TOF-MS (Atmospheric Pressure Interface Time-Of-Flight Mass Spectrometer; Junninen et al., 2010), a mass spectrometer coupled with a pressure interface which guides the ions from atmospheric pressure into the spectrometer while the gas is pumped away. The APi-TOF gives the ion signal as a function of mass; however, the ion transmission of the instrument is fairly low and depends on the mass of the ion. To convert the ion signals to ion concentrations, the APi-TOF needs to be calibrated using a mobility spectrometer (Ehn et al., 2011).

APi-TOF measurements enable a direct comparison between simulated and experimental concentrations of individual charged clusters (**Paper I**). Nevertheless, a source of uncertainty related to the measurement data is the possible fragmentation processes that clusters may undergo inside the APi-TOF (see *e.g.* Adamov et al., 2013). As cluster ions are accelerated in the electric fields of the ion focusing elements, they experience more energetic collisions with gas molecules than in the ambient atmosphere, and one or more molecules may be lost from the clusters. Based on experiments performed by varying instrument settings, the breaking of clusters in collisions is likely to be most significant for the smallest clusters containing two or three sulfuric acid molecules, with the larger clusters being less affected. Clusters can also lose relatively weakly bound molecules by evaporation in the case that the evaporation is fast enough to occur during the time that the cluster spends inside the low-pressure environment of the instrument before it is detected. An example of such a loosely bound molecule is water, which is normally not detected in the clusters by the APi-TOF, although the clusters are likely to be hydrated before entering the instrument at the ambient relative humidity (see *e.g.* Almeida et al., 2013). Although the fragmentation phenomena are still poorly understood, they are unlikely to have a significant qualitative effect, as shown by comparisons with mobility spectrometers (Ehn et al., 2011) and simulated cluster data (**Paper I**). In the latter study, the most significant difference between measured and simulated distributions of negatively charged sulfuric acid–ammonia clusters was found to be the ammonia content: the number of ammonia molecules in the modeled clusters was on average one or two higher than in the observed clusters. This may be caused by fragmentation processes, since ammonia is generally less strongly bound to the negative clusters than are the acids. On the other hand, the discrepancies may also be related to possible differences in the actual cluster collision and evaporation rate coefficients and those used in the model.

3.3.2 Electrically neutral clusters: challenging to measure

Electrically neutral particles can be observed using CPC (Condensation Particle Counter) techniques (for a review, see *e.g.* Lehtipalo, 2011). The working principle of a CPC is to enlarge particles by condensing vapor, for example water or butanol, to enable their optical

detection. Two-stage condensation particle counters, where very small particles are first magnified by condensing diethylene glycol, after which they can be further enlarged and detected by a regular CPC, are capable of detecting the smallest clusters of a mobility diameter of approximately 1 nm (Vanhanen et al., 2011; Jiang et al., 2011; Wimmer et al., 2013). One type of a diethylene glycol particle counter is the PSM (Particle Size Magnifier; Vanhanen et al., 2011), which can be operated in a scanning mode to divide the particles into size classes. This is done by varying the detection limit of the instrument via the supersaturation of the condensing vapor. The detection efficiency is not, however, a stepwise function of size, and the finite size resolution needs to be taken into account in the size classification (see *e.g.* Lehtipalo et al., 2014). The CPC and the PSM do not in principle yield information on particle composition, although it is possible to indirectly assess the chemical nature of the particles as the instrumental detection efficiency may depend on it (Kangasluoma et al., 2014). Concentrations measured in the smallest observable size classes can thus be compared to simulated total cluster concentrations, but a comparison of distributions with respect to cluster composition is not possible.

Another option is to charge naturally neutral particles and detect them with ion spectrometers. Mobility spectrometers can again be utilized to obtain particle number concentrations; the NAIS (Neutral Cluster and Air Ion Spectrometer; Manninen et al., 2009), which is basically an AIS combined with a charger, can detect neutral particles through corona charging down to the size of approximately 2 nm. However, from the modeling point of view, the essential benefit in charging neutral clusters is that it enables their chemical characterization by mass spectrometry. The CI-APi-TOF-MS (Chemical Ionization Atmospheric Pressure Interface Time-Of-Flight Mass Spectrometer; Jokinen et al., 2012; Almeida et al., 2013) is an APi-TOF combined with a chemical ionization unit where an electrically neutral sample is first ionized before it enters the APi-TOF. For the present, the CI-technique has been used to ionize sulfuric acid –containing clusters with nitrate ions to produce negatively charged clusters.

Nevertheless, there is a catch related to the charging procedure: it changes the composition of the clusters. Being a Lewis base, the bisulfate ion in a negatively charged cluster stabilizes the cluster. Thus the most stable negative clusters with a certain number of sulfuric acid molecules (including the ion) generally contain fewer neutral base molecules than their electrically neutral counterparts (Ortega et al., 2014). Similarly for positively charged clusters, the protonated base molecule acts as a Lewis acid, and therefore positive clusters contain less acid than neutral clusters with the same number of base molecules. Therefore, when, for instance, a neutral cluster is charged negatively, it is likely to evaporate one or more neutral base molecules almost instantaneously to reach a more stable composition (Ortega et al., 2014). This needs to be considered when comparing simulation results for neutral clusters to CI-APi-TOF data. Moreover, the charger ion may remain attached to the cluster and stabilize it, in which case the base evaporation may not occur (Kupiainen-Määttä et al., 2013). A comprehensive comparison of theoretical results with CI-APi-TOF measurements thus requires modeling also the charging process. This can be done by a two-step simulation,

where the neutral cluster population is first modeled in ambient conditions to solve the distribution before the sample is charged. The result is then used as input for a simulation in conditions corresponding to the chemical ionization chamber where the charger ion is included as additional species (Kupiainen-Määttä et al., 2013). The distribution after the simulated ionization is directly comparable to measurements; yet, this type of simulation is restricted by computational resources. Similarly to obtaining hydration free energies (Section 3.1.1), including the charging ligands in the clusters requires vast computational efforts, and currently such free energy datasets are not available.

4 Growth of small clusters

The question of how molecular clusters that initiate particle formation from condensable vapors are *formed* is obviously relevant, but in view of the climatic effects of atmospheric particles, a question of equal or even greater importance is how the clusters *grow*. Due to their high mobility, freshly formed clusters are relatively easily scavenged by pre-existing larger particles and other surfaces. The probability that the clusters reach larger, climatically relevant sizes depends on the rate at which they grow compared to the rate at which they are scavenged (Weber et al., 1997; Kuang et al., 2010). Therefore, in addition to the *formation rate* of clusters or particles of a certain size, another parameter used to characterize particle formation events is the particle *growth rate*. These two quantities, together with the scavenging sinks, determine the total flux of particles surviving to larger sizes.

Traditionally, the formation and growth of molecular clusters has been assumed to occur via collisions with vapor monomers; collisions involving two clusters, *i.e.* self-coagulation, have often been neglected based on the assumption that cluster concentrations are negligible compared to vapor concentrations. For larger particles, the effect of self-coagulation has been studied by *e.g.* Leppä et al. (2011). Cluster fission has also been often omitted, assuming that cluster decay happens by monomer evaporations. The clustering process has thus been modeled via molecular fluxes between subsequent cluster sizes, starting from individual vapor molecules and proceeding to larger, more stable clusters. This approach, called the Szilárd-Farkas scheme, is the concept for example in the widely used classical nucleation theory. These simplified assumptions may, however, not be valid for real atmospheric multicomponent systems, and the dynamic processes involved in cluster formation may be more complex.

4.1 Growth pathways of sulfuric acid–base clusters

Experimental studies have shown that both ammonia and dimethylamine increase sulfuric acid driven particle formation, with the enhancing effect of dimethylamine being much stronger than that of ammonia (Kirkby et al., 2011; Almeida et al., 2013). Theoretical results obtained with the ACDC model using quantum chemical formation free energies agree with this finding (Almeida et al., 2013). Now the natural question is: what are the clustering mechanisms behind these phenomena? The only way to look for detailed answers is by studying the dynamics of the cluster population. Experimentally, the growth steps can be indirectly assessed based on the composition as a function of cluster size (Schobesberger et al., 2015), but this does not yield information on the actual growth dynamics. On the other hand, a kinetic model gives the absolute molecular fluxes between all clusters of the simulated system, from which the formation routes of all clusters can be obtained (for the given collision and evaporation rates). Since ACDC is capable of reproducing observations of sulfuric acid–base cluster formation, the logical modeling follow-up is to examine the growth pathways of these clusters (**Paper II**).

4.1.1 Growth mechanisms depend on the identity of the base

In **Paper II**, the principal growth routes of sulfuric acid–ammonia and sulfuric acid–dimethylamine clusters were tracked by following the main cluster fluxes through the system. The systems were studied both in the absence and presence of charged clusters originating from natural ionization. The results, summarized in Figure 3, revealed a very different behavior for these two systems. In the system with ammonia, cluster growth proceeds via monomer additions, as assumed in many traditional theories, but for dimethylamine, the contribution of cluster-cluster collisions is non-negligible. Moreover, in conditions relevant to atmospheric particle formation, ions do not play a significant role in the case of dimethylamine. For ammonia, ions participate in cluster formation both by growing through the system as charged clusters, and by forming neutral clusters via recombination of smaller cluster ions of different polarities. The essential explanation is rather simple: being a stronger base than ammonia, dimethylamine is capable of stabilizing sulfuric acid clusters more efficiently, and binding strongly even to a single acid molecule. Further, as electrically neutral acid–dimethylamine clusters are extremely stable, the stabilizing potential of ions is less significant.

The impacts of these results on cluster growth modeling are diverse. Neglecting the contribution of small clusters may lead to considerable errors if these clusters are in reality abundant enough to have a role in the growth dynamics. The effect of cluster-cluster processes on the flux through the boundary of a very non-linear system is not necessarily intuitive: while collisions of clusters naturally increase the growth rate and thus also the outgoing flux, they also, on the other hand, decrease cluster concentrations which has a decreasing effect on the flux (**Paper IV**). The same can be said about the role of charged clusters: the effect of ions on the formation flux at a certain size depends on the identity of the base, *i.e.* the relative stability of neutral clusters. Furthermore, the contribution of recombination processes to the formation of neutral clusters may be prominent (Figure 3). While the fraction of recombination products has been indirectly assessed based on measured particle distributions for larger size classes (Kontkanen et al., 2013), there is no way to directly observe their role in molecular cluster formation. The effects of different processes on formation rates and growth pathways of neutral and/or charged clusters cannot be predicted without actually testing them by simulations.

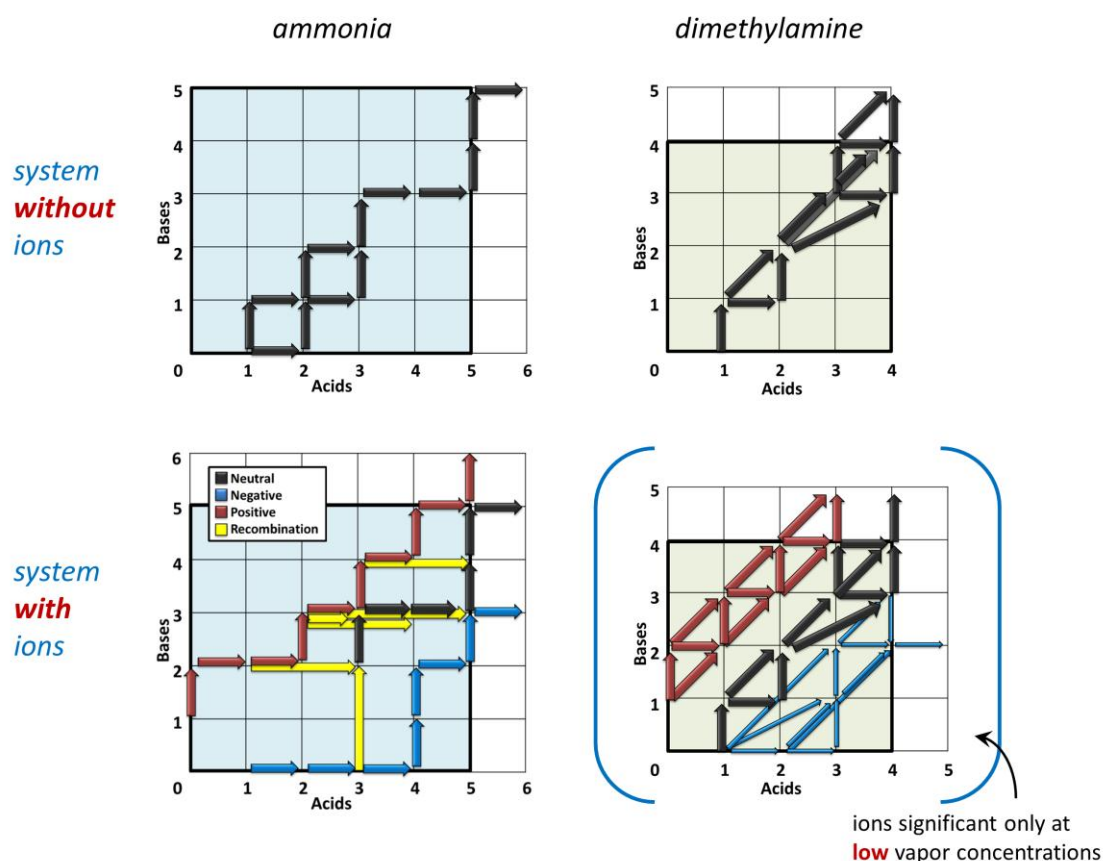


Figure 3: Main growth routes in simulated sulfuric acid–ammonia and sulfuric acid–dimethylamine systems in atmospherically relevant conditions (for detailed information, see **Paper II**).

4.1.2 Free energy profile of cluster growth may differ from traditional assumptions

Tracking the clustering pathways provides a means to examine the growth energetics, and to identify the critical cluster in the case that the growth involves energy barriers. Figure 4 shows the formation free energy along the main growth routes in sulfuric acid–ammonia and sulfuric acid–dimethylamine systems in representative atmospheric conditions (Figure 3), converted to the monomer vapor pressures by Eq. (2.8). Figure 4 demonstrates that free energy curves related to the growth of atmospheric acid–base clusters may differ from the traditional view originating from the droplet model. Instead of one global free energy maximum, there may be several energy barriers, as is the case here for ammonia, or no barrier at all, and thus no critical cluster, as for dimethylamine. Also the qualitative evaporation profile along the growth pathways may be different than that determined by bulk thermodynamics (Ortega et al., 2012).

The fact that atmospheric systems may not behave as has been traditionally assumed may affect the validity of earlier derived analysis methods, such as the nucleation theorem given by Eq. (2.2). This widely used form of the theorem is derived assuming that cluster growth

occurs solely by monomer additions, and that there is only one growth pathway that exhibits a single free energy maximum. Now, in the case of dimethylamine, the former assumption is not valid, and the theorem is not applicable at all (Vehkamäki et al., 2012; **Paper IV**). For ammonia, the theorem works reasonably well for a system of neutral clusters. However, in the presence of ions the assumptions of a single pathway and growth by only monomers do not hold, and the theorem cannot be applied. Moreover, the theorem also assumes that there are no external sinks for the clusters –this is probably the worst of all the assumptions, since external losses are likely to be present in all real situations. It turns out that the loss terms have a significant effect on the slope $\partial (\log J) / \partial (\log C_i)$ in Eq. (2.2) at vapor concentrations relevant to atmospheric particle formation, and application of the theorem in the presence of sinks is likely to lead to erroneous conclusions of a critical size (Ehrhart and Curtius, 2013; Malila et al., 2015; **Paper IV**).

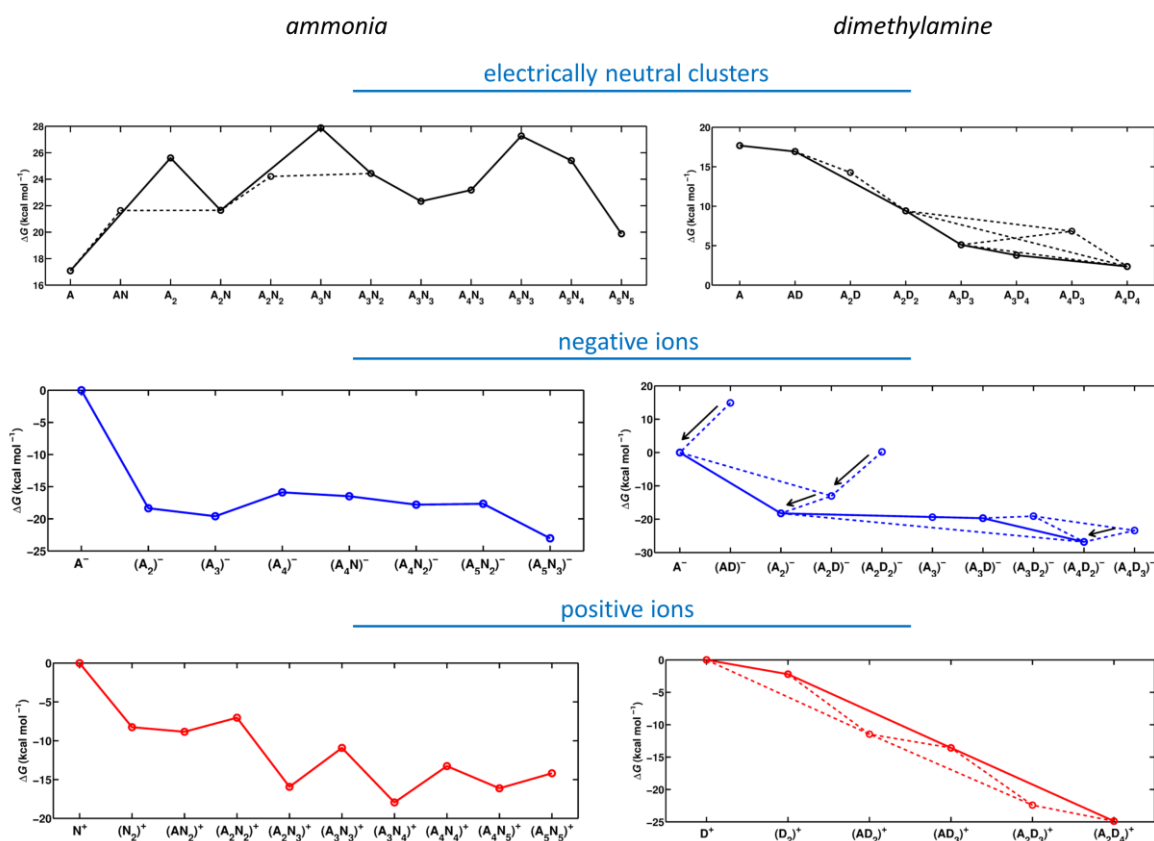


Figure 4: Gibbs free energy of formation as a function of growth step along the main growth routes in simulated sulfuric acid–ammonia and sulfuric acid–dimethylamine systems in atmospherically relevant conditions (for detailed information, see **Paper II**). Abbreviations A, N and D refer to acid, ammonia and dimethylamine, respectively, a plus sign denotes an additional positive hydrogen H⁺, and a minus sign denotes a removed H⁺. Solid and dashed lines correspond to major and minor routes, respectively, and arrows depict evaporation.

4.2 Determining the cluster growth rate

In general, the growth rate characterizes the frequency at which particles of a certain size move to a larger size. The quantity is normally given as the change of particle diameter per unit time (most often in nm h^{-1}), and is used in equations describing the concentrations of different particle size classes. The time derivative of the concentration of particles in a size class with a mean particle diameter D_p is

$$\frac{dC_{D_p}}{dt} = J_{D_p} - J_{D_p+\Delta D_p} - S_{D_p} C_{D_p} = \frac{\text{GR}_{D_p-\Delta D_p}}{\Delta D_p} C_{D_p-\Delta D_p} - \frac{\text{GR}_{D_p}}{\Delta D_p} C_{D_p} - S_{D_p} C_{D_p}, \quad (4.1)$$

where C_{D_p} is the concentration, J_{D_p} is the formation rate, S_{D_p} is the loss rate due to the external sink, and GR_{D_p} is the growth rate, all corresponding to the size D_p , and ΔD_p is the width of the size classes. Eq. (4.1) is naturally analogous to the discrete cluster birth-death equation given by Eq. (3.1). If particle concentrations can be measured, and growth rates and sinks derived from measurements or calculations, Eq. (4.1) can be used to assess the formation rates of particles of different sizes.

Growth rates of particles of a few nanometers are normally extracted from measured particle distributions, or calculated from the concentrations of condensable vapors (for a review, see Yli-Juuti, 2013 and references therein). For very small molecular clusters below approximately 2–3 nm, growth rates have been deduced experimentally with the appearance time method (Kulmala et al., 2013; Schobesberger et al., 2013; Lehtipalo et al., 2014). In this method, the time evolution of the cluster concentrations is measured to determine the appearance time of each cluster size or size class. The appearance time is defined as the time at which the concentration reaches 50% of its maximum value, or sometimes 50% of the total increase in the case of non-zero initial concentration. The cluster size is then presented as a function of appearance time, and the growth rate is determined as the slope of a linear fit to the data.

Theoretically, the growth rate of a cluster can be derived from the molecular flux onto it. This is usually done by calculating the volume change rate of a spherical particle taking into account condensation and possibly also evaporation of vapor molecules. Considering a one-component substance and assuming that only monomer collisions and evaporations are relevant, the diameter change rate of a cluster of i molecules and a diameter of $D_{p,i}$ can be calculated from the volume change rate as (Fuchs and Sutugin, 1970)

$$\frac{dD_{p,i}}{dt} = \frac{dD_{p,i}}{dV_i} \frac{dV_i}{dt} = \frac{2}{\pi D_{p,i}^2} \frac{m_1}{\rho} (\beta_{i,1} C_1 - \gamma_{i \rightarrow i-1}), \quad (4.2)$$

where m_1 the monomer mass, ρ is the density of the substance, $\beta_{i,1}$ and $\gamma_{i \rightarrow i-1}$ are the monomer collision and evaporation rate coefficients, respectively, and C_1 is the monomer concentration. Sometimes also the assumption of negligible evaporation flux has been made, leading to an upper limit estimation for condensational growth (Riccobono et al., 2012).

The growth rate given by Eq. (4.2) is derived via a so-called Lagrangian approach, which is used for following the growth of a specific cluster. However, looking at Eqs. (3.1) and (4.1), it can be seen that the growth rate corresponding to the flux $I_{i \rightarrow i+1}$ to the subsequent cluster size is (**Paper V**)

$$\frac{dD_{p,i}}{dt} = \Delta D_{p,i \rightarrow i+1} \frac{I_{i \rightarrow i+1}}{C_i} = (D_{p,i+1} - D_{p,i}) \left(\beta_{i,1} C_1 - \gamma_{i+1 \rightarrow i} \frac{C_{i+1}}{C_i} \right), \quad (4.3)$$

where C_i is the concentration of a cluster of i molecules. The benefit of Eq. (4.2) is that only the monomer concentration must be known, and no information on cluster concentrations is needed. Yet, the quantity given by Eq. (4.3) is the one that should be used when examining the fluxes between different sizes as in Eq. (4.1).

Kinetic simulations provide a means to obtain the flux-equivalent cluster growth rate given by Eq. (4.3). In fact, the simulations yield the actual particle flux, which is often the main quantity of interest, and is normally calculated from an assumed growth rate as in Eq. (4.1). On the other hand, the growth rate is also a relevant quantity, as it is a widely established concept used to characterize particle formation events and applied, for example, in parameterizations for particle survival probability (Weber et al., 1997; Kerminen and Kulmala, 2002). The flux-equivalent growth rate does not necessarily coincide with the appearance time –based growth rate that can be obtained from measurements, as these two quantities depend on the cluster concentrations in different ways. The appearance time method gives exactly one value for the growth rate of a specific cluster size; the flux between clusters, on the other hand, and consequently the growth rate derived from it, evolve as a function of time, and eventually reach a steady-state value in the case of constant vapor sources. By extracting also the growth rate based on the appearance time from the simulations, the dynamic model can be used to compare the “real” and “measurable” growth rates (**Paper V**). Even for the simplified case of **Paper V** where only monomer collisions and evaporations are considered, the growth rates determined with the two approaches may differ significantly, both quantitatively and qualitatively, with the differences depending on cluster size and ambient conditions. For the studied model substance, the differences were found to be the largest for the smallest clusters with the highest evaporation rates, and to decrease with increasing cluster size and decreasing evaporation rate.

Determining the flux-equivalent growth rate is straightforward for the case where only monomer processes are relevant, but becomes more complex when the contribution of cluster-cluster processes is non-negligible. In fact, the definition of growth rate is not unambiguous when a cluster can grow into several different sizes by collisions with different sized smaller clusters. From the modeling point of view, it is in this case probably more reasonable to study the net flux crossing a specific cluster size, instead of aiming to define the diameter or mass change rate of that size; the flux is anyhow the eventual quantity of interest with respect to the atmospheric relevance of the freshly formed clusters. This applies also to multicomponent systems where a cluster can grow into larger clusters of different compositions due to additions of different compounds. Using a cluster population model to study the effects of these types of phenomena will be a topic of future work.

5 Review of papers and the author's contribution

Overview and the author's contribution to the research articles of this thesis are given below, with the key results of each study summarized in the boxes. The author is solely responsible for the introductory part of the thesis.

Paper I presents a comparison of simulated and experimental distributions of negatively charged sulfuric acid–ammonia clusters. The APi-TOF mass spectrometer measurements were carried out in the CLOUD chamber at CERN, and the dynamic simulations were performed in conditions corresponding to the experimental setup, including both electrically neutral and positively and negatively charged clusters. Cluster evaporation rates were computed from formation free energies obtained from quantum chemical calculations. The author performed the simulations, analysed the simulation data, participated in interpreting the results of the comparison, and wrote most of the paper.

The comparison shows a good agreement between modeled and measured distributions and their trends related to varying acid and ammonia concentrations. Discrepancies are mostly related to the absolute ammonia content of ionic clusters containing four and five acid molecules, and may be due to uncertainties in the rate coefficients used in the model, or fragmentation inside the mass spectrometer. It is also briefly demonstrated that for the same setup, simulations can be used to give information on the distribution of electrically neutral clusters that cannot be directly measured.

Paper II applies ACDC and quantum chemical cluster stability data to study clustering pathways and free energy profiles along the growth routes in two-component sulfuric acid–base systems, where the base is either ammonia or dimethylamine. The systems are studied both with and without charged clusters. The author participated in the initial planning, implemented the growth pathway tracking, performed the simulations, analysed the data, and wrote the paper.

The clustering processes are very different for the two bases: for ammonia, the growth proceeds via monomer additions and involves several energy barriers. In the presence of ions, clustering occurs simultaneously through electrically neutral and negatively and positively charged pathways, with neutral clusters forming also in recombination of small charged clusters. For dimethylamine, collisions with small clusters contribute significantly to the growth, and every growth step along the main pathway is energetically favorable. Thus the clustering is not in fact nucleation, but instead a barrierless process. In atmospherically relevant conditions, the main growth occurs through electrically neutral pathways also in the presence of ions.

Paper III explores uncertainties related to an experimental setup to measure the equilibrium constants of electrically neutral sulfuric acid mono- and dihydrates. Quantum chemical data from the literature, calculated at different levels of theory, and dynamic simulations corresponding to a flow tube measurement were implemented to assess the effect of larger hydrates and base molecules on the measurement result. The author participated in planning the simulations and data analysis methods, performed the simulations, interpreted the data, and wrote the paper.

According to all used quantum chemical data sets, larger hydrates, that are not considered in the original method to deduce the equilibrium constants of the small hydrates, are likely to be present and affect the results. Contaminant base molecules may also have an effect, the magnitude and direction of which depends on the identity of the base. The study also demonstrates the importance of considering the analysis methods of measured data when comparing theoretical and experimental results.

Paper IV examines the validity of the first nucleation theorem in conditions relevant to atmospheric particle formation, considering both the assumptions related to the derivation of the theorem, and the effect of experimental data analysis methods. The author participated in the initial planning of the research idea, contributed to performing and analysing the ACDC simulations, and wrote a large fraction of the paper.

Kinetic simulations show that the slope $\partial (\log J) / \partial (\log C_i)$ of the formation rate J with respect to vapor concentrations C_i is affected by a number of non-idealities, and does not correspond to the number of molecules of type i in the critical cluster in many realistic situations. Therefore the nucleation theorem cannot in practice be applied to obtain reliable information on the existence or composition of a critical cluster.

Paper V compares cluster growth rates determined from the appearance times and from the net fluxes between subsequent cluster sizes in the case where growth occurs solely by monomer additions. For simplicity, the simulations are performed using a one-component model substance with an evaporation profile corresponding to Gibbs free energies from the classical droplet model. The author is responsible for some of the original ideas, designed and performed the simulations, implemented the growth rate calculations, interpreted the data, and wrote the paper.

Even in the case of a simple classical substance, the growth rates determined with the two approaches may differ significantly, especially for the smallest clusters that have the highest evaporation rates. Both quantities are also qualitatively affected by ambient conditions, including the magnitude of external sinks and the time evolution of the vapor monomer concentration. Moreover, the critical size cannot be deduced from the size-dependent growth rates in realistic conditions.

The general conclusions of the thesis can be formulated as:

- A dynamic cluster population model with cluster evaporation rates derived from quantum chemical cluster free energies is capable of reproducing observed trends in the formation rates of sulfuric acid–base clusters and in the distributions of charged clusters.
- Cluster population modeling provides information on the cluster formation mechanisms that cannot be directly obtained from measurements, such as the cluster growth pathways. In this work it is demonstrated that in binary sulfuric acid–base systems, the growth mechanisms depend on the identity of the base. As opposed to a system with ammonia, which is a relatively weak base, in a system with dimethylamine, small clusters are abundant enough to contribute to cluster growth, and the role of ions is minor due to the high stability of the electrically neutral clusters.
- In a non-linear system of interacting clusters, variations in ambient conditions, for instance, vapor concentrations and external sinks, may have diverse effects on quantities that can be derived from measured cluster concentrations, such as the formation and growth rates. Thus, comparing observations with modeling results requires considering both the clustering compounds and the parameters related to the environment, as well as the methods used to measure and analyze the experimental data.

6 State of the art and future perspectives

Theoretical approaches to study atmospheric particle formation phenomena include a wide palette of methods ranging from macroscopic thermodynamics to energy calculations based on electronic structures of molecular clusters. The formation pathways of the initial molecular clusters have often been assessed via cluster stability that is characterized by the formation free energy of the cluster. For the free energy calculations, electronic structure methods are by far the most accurate available approach; macroscopic theories do not give reliable results for clusters consisting of a few molecules. On the other hand, while quantum chemical calculations yield energies for static structures given the used approximations, the structures of real-world clusters are all but static. Clustering processes are affected by molecular movement from the initial collision dynamics and rearrangement to the continuous evolution of the structure of the resulting complex and the possible fragmentation of the formed cluster. Probably the most promising tool to explore these effects is first-principles molecular dynamics simulations, the implementation of which in atmospheric studies has just started (Loukonen et al., 2014a and 2014b). In this approach, the classical equations of motion of the atomic nuclei are solved using forces obtained from the electronic structure of the complex.

The measurable quantity for observing particle formation processes is in practice particle or cluster concentrations. From a theoretical point of view, this requires modeling large sets of interacting clusters, which is not currently possible without a simplified treatment of agglomeration and decay processes. The principle of cluster population modeling is rather simple: one only needs to know the rate coefficient of each kinetic process to solve the time evolution of the concentrations. Data regarding free energies can be incorporated in the kinetic framework by converting the energies to evaporation rates assuming detailed balance –this is actually the only way to obtain cluster evaporation rates at the moment. Cluster free energies are directly connected to concentrations in equilibrium conditions, but an equilibrium distribution is not a realistic approximation in a particle formation situation. While the treatment of collision and evaporation processes in cluster population simulations is not as rigorous as in molecular dynamics approaches, the approximations appear justified. Results from cluster population simulations with first-principles quantum chemical data used as input compare very well with experiments: the model captures general trends in sulfuric acid–ammonia and sulfuric acid–dimethylamine cluster formation, and produces the best quantitative agreement thus far (Almeida et al., 2013; **Paper I**). Cluster dynamics simulations of atmospherically relevant molecular clusters can thus in principle provide input of the formation rates or concentrations of small stable clusters for regional and global climate models. In practice, this would be done by parameterizing the simulation results over a range of conditions relevant to atmospheric particle formation.

With respect to basic understanding, probably the most advantageous feature in cluster population modeling is the explicit treatment of individual clusters, which enables the exami-

nation of clustering pathways. In addition to predicting how different factors affect, for example, the cluster formation rate at a specific size, the model can be used to study where this effect originates from through monitoring of concentrations and fluxes. This applies to studying the role of different species in multicomponent systems using high-level cluster free energy data, as well as testing the effects of ambient conditions using simplified model substances.

One of the recurring motifs in this work is the idea of a critical cluster. The assumption that the first steps of atmospheric particle formation proceed via a critical size, corresponding to a maximum in cluster free energy has very often been made –but this assumption cannot in practice be verified. The work presented here suggests that depending on the participating species, there may or may not be energy barriers in atmospheric clustering. Moreover, in the case that barriers exist, the critical size cannot be reliably determined from observations with commonly used approaches. These results also give rise to a very general sidenote: assumptions that may seem intuitively solid should still not be taken for granted. More importantly, it can be argued that while the existence of barriers and the location of the free energy maximum give general information on the energetics of a clustering process, this information may be of little practical value. The quantities of interest related to particle formation include the formation rate of clusters that are stable enough not to decay immediately, and its trends with respect to concentrations of different vapors and other ambient conditions. These are not directly determined by the energy profiles, but rather by the absolute cluster evaporation rates –which may or may not be connected to the energies via detailed balance–, collision rates and cluster concentrations, as well as the time-dependent vapor sources and cluster sinks.

Formation and growth of secondary aerosol particles have often been studied as separate processes: first, stable small particles are formed, and then these particles start growing by condensable vapors. The two processes are commonly characterized by what has often been called the nucleation rate, typically defined as the formation rate of particles of approximately 1.5–2 nm in diameter, and the growth rate, defined as the diameter change per unit time. On the other hand, it can be argued that there is actually no reason for this kind of division: the whole process can be seen as continuous growth that starts from the formation of the initial molecular dimer, and continues with the agglomerate accumulating more and more molecules. Thus, the process can be characterized by the formation rate (*i.e.* the flux of particles to a certain size class) or the equivalent growth rate as a function of size from the smallest sub-1nm clusters to stable larger particles without the separation to nucleation and growth.

The evolution of experimental techniques has been proceeding hand in hand with theoretical progress. Recent advances in mass spectrometer and condensation particle counter applications are bringing the focus to the molecular-level first steps of particle formation phenomena. Theoretical approaches, whether they be quantum chemical minimum-energy calculations and incorporation of their results to cluster population models, first-principles molecular dynamics simulations probing the life of individual clusters, or something else, are essential tools in understanding and interpreting the experimental findings. Probably one of

the most interesting fields in the near future is combining theoretical understanding and measurements of very small electrically neutral clusters, which have recently become observable with the development of chemical ionization and particle size magnifier techniques. As comparing modeling and measurement results requires considering not only the factors affecting clustering in the atmosphere or in a laboratory environment, but also the effects of measurement and data analysis methods, diverse challenges are constantly being provided to the ongoing development of improved modeling tools.

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