STRUCTURAL SIMULATION OF MOLECULAR CLUSTERS AND VAPOR-LIQUID INTERFACE

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Structural simulation of molecular clusters and vapour-liquid interface
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Abstract

The atmosphere is an inhomogeneous system of vapors, and liquid as well as solid particles. The nucleation process is an important source of particles, observed at most sites where particle measurements have been carried out. Sulfuric acid plays an important role in the first steps of particle formation, but a complete picture of process, after several years of research, is still unclear. Computational methods provide valuable information to support experimental observations, and sometimes they are the only way to obtain information about the system. In this thesis, molecular level simulations have been performed for inhomogeneous systems.

The description of surface composition has been connected to the unphysical behavior of classical nucleation theory in the case of a surface-active mixture. Density functional theory for classical fluid has been employed to test three well known phenomenological models for surface composition. Simple models presented by Ebenhart, and Kulmala and Laaksonen who modified Eberhart's model, give good agreement with computed composition.

The quality of molecular dynamic simulations depend on simulation conditions and the interaction potentials used. Indirect nucleation simulations performed for argon indicate that a vapor phase of tens of atoms is large enough to correct predict the density distribution, surface tension and equilibrium cluster size. The repulsive wall of a spherical simulation box disturb only vapor density and temperature distributions. The use of a Nosé-Hoover thermostat simplifies the simulation procedure, and the system properties such as the density profile are indistinguishable from the constant energy simulations. The uncertainty concerning the reliability of molecular dynamic simulation results increases when a chemically active molecular system is simulated. Proton transfer reactions appearing in the sulfuric acid - water system are modelled by simulating bisulfate-oxonium ion pairs instead of neutral molecules. Structural differences between systems including ion pairs and neutral molecules are observed as expected. However, all the observed differences may also be simulation artefacts.

Atmospheric sulfuric acid is mainly formed via oxidation of sulfur dioxcide. Byproducts of the oxidation chain are proposed to participate in nucleation, and dimer formation of sulfur-containing compounds with sulfuric acid, as well as the hydration of these dimer by one water molecule, are studied using quantum chemical calculations. A stability study of dimers and trimers shows that only peroxidisulfuric acid-sulfuric acid dimer is more stable than sulfuric acid dimer Peroxidisulfuric acid ($H_2S_2O_8$) may also replace a sulfuric acid in a sulfuric acid - water cluster, but the second replacement is unfavorable, and thus $H_2S_2O_8$ does not enhance sulfuric acid addition to the cluster.

Keywords: sulfuric acid, nucleation, quantum chemistry, molecular dynamics, density functional theory for classical fluids

Contents

List of publications

I **Martta Salonen**, Jussi Malila, Ismo Napari and Ari Laaksonen: Evaluation of composition of surface active water-alcohol type mixtures: a composition of semi-empirical models, *J. Phys. Chem. B*, 109, 3472–3479, 2005.

II **Martta Salonen**, Ismo Napari and Hanna Vehkamäki: Molecular dynamics simulations of atomic clusters in equilibrium with vapour, *Molecular Simulation*, 33,245–251, 2007.

III **Martta Salonen**, Theo Kurtén, Hanna Vehkamäki, Torsten Berndt and Markku Kulmala: Computational investigation of the possible role of some intermediate products of SO_2 oxidation in sulfuric acid - water nucleation, *Atmos. Res.*, 91:1, 47–52, 2009.

IV **Martta Toivola**, Ismo Napari and Hanna Vehkamäki: Structure of water-sulfuric acid clusters from molecular dynamics simulations, *Boreal Env. Res.*, 14, 654–661, 2009.

V **Martta Toivola**, Theo Kurtén, Ismael K. Ortega, Markku Sundberg, Ville Loukonen, Agílio Pádua, Hanna Vehkamäki: Quantum chemical studies on peroxodisulfuric acid-sulfuric acid-water clusters, *Comp. Theor. Chem.*, 967, 219–225, 2011.

1 Introduction

A group of atoms or molecules stuck together is a cluster. If the cluster is stable and able to grow, and it is surrounded by vapor, the combination of the cluster and vapor is called an aerosol. Aerosol particle sizes range from a few nanometers to hundreds of micrometer, and this definition is not rigorous. However, all these tiny regions of condensed phase have a large surface area (interphase) compared to their volume, which gives them special characteristics.

The air around us is an aerosol. Aerosol particles participate in atmospheric chemistry (Abbatt et al., 2012; Deshler, 2008). Particles enable heterogeneous reactions of gases on the particle surface, and inside the condensed phase (Wayne, 2000; Bianco and Hynes, 2006).

Atmospheric aerosol particles also affect our every day life in several ways, depending on their concentration, chemical composition and size. Low visibility in polluted cities is reported frequently in newspapers, and anthropogenic atmospheric aerosol particles have been linked to increased mortality since at least 1930 (Seinfeld and Pandis, 1998). The Air quality in Europe - 2012 report estimates that over 80% of urban population in EU is exposed to atmospheric particle concentration above the WHO reference levels (European Environment Agency, 2012).

Aerosol particles affect Earth's radiation balance as short lived climate forcers: the lifetimes of long-lived greenhouse gases is measured in years, but for an aerosol particle in the lower troposphere the life time is of the order of one day to one week (Seinfeld and Pandis, 1998). Aerosols can both warm and cool the climate, depending on their nature and location According to current knowledge, the net effect is cooling. The Intergovernmental Panel on the Climate Change has identified particles as the greatest uncertainty in climate change scenarios (IPCC, 2013).

Atmospheric aerosol particles are produced by two different mechanisms. Primary particles like sand, sooth and pollen are emitted from different sources close to the ground. Secondary particles are formed from gaseous molecules. Until the early 90's, secondary particle formation was not believed to happen at all in the atmosphere, but according to current best estimates (Spracklen et al., 2008; Merikanto et al., 2009; Kazil et al., 2010), roughly 20-80% of atmospheric aerosol particles are of secondary origin.

The first step of the secondary particle formation, nucleation, starts from the collision of two molecules. Groups of molecules may then grow molecule by molecule, or via collisions with other molecule groups, clusters, or evaporate back to the vapor phase. A cluster is called a critical cluster, when its growth becomes more probable than evaporation. The main part of freshly formed particles are scavenged to pre-existing large particles, and are finally removed from the atmosphere by deposition onto an available surface.

Both theoretical and experimental studies indicate that sulfuric acid plays a central role in atmospheric nucleation and cluster growth (see e.g. Kerminen et al., 2010, and references therein). According to current knowledge of nucleation, binary nucleation of sulfuric acid

and water may be behind the secondary particle formation in the upper troposphere and stratosphere (Spracklen et al., 2005). In the lower troposphere, either amines, ammonia (Kurtén et al., 2008; Loukonen et al., 2010; Nadykto et al., 2011; Zhao et al., 2011; Almeida et al., 2013), organic compounds (Laaksonen et al., 2008b; Zhang et al., 2004) or ions (Hirsikko et al., 2011; Kirkby et al., 2011) are thought to participate in nucleation together with sulfuric acid and water.

During the last decade, new measurement techniques have been employed to study atmospheric particles. Condensation Particle Counters (CPC) are commonly used to measure number concentrations of aerosol particles. Simplifying, inside the CPC aerosol particles grow first by condensation of a working fluid, and then the particles are optically counted. CPCs are able to measure neutral particles without charging them, but the downside of the technique has been that the detection limit was around 3nm, and early steps of particle formation was thus not measurable. However, new sophisticated technologies have been developed to grow particles to optically detectable sizes (1μm), and sub-2nm particles are now measurable even in atmospheric conditions (Vanhanen et al., 2011). Development of instrumentation was an essential part of the solution of the so-called sulfuric acid mystery: deviation of results of laboratory and field measurement studies on sulfuric acid nucleation motivated several studies, e. g. **Paper III** and **V**, until the work of Sipilä et al. (2010) was published. A closer look into the mystery is given in Chapter 2.

High resolution mass spectrometric methods have been employed to measure the elemental composition of atmospheric ions and charged clusters (Ehn et al., 2010b; Junninen et al., 2010; Kirkby et al., 2011). Chemical ionization enables measurements of originally neutral aerosol particles by mass spectrometry (Jokinen et al., 2012). As pointed out by Kurtén et al. (2011) chemical ionization is problematic in two ways: first, all clusters may not, depending on their composition, be ionized, and secondly, the clusters may partly evaporate after ionization, as was shown for sulfuric acid - amine - clusters by high level quantum chemical calculations. However, mass spectrometric methods give unique information on the composition of clusters. Recently, Ehn et al. (2014) demonstrated by mass spectrometric chamber measurements how low-volatility organic vapors enhance the formation and growth of aerosol particles over forested regions, which was earlier reported by model studies.

Experimental studies of aerosol particles yield the time dependence of the particle number and mass distributions, and the elemental composition of (naturally or artificially) charged particles. Even though the experimental methods are rapidly developing, an accurate study of clusters microstructure, including key chemical characteristics such as molecular composition and bonding patterns, is possible only by computational methods. The computational studies of chemical ionization in mass spectrometry are a good example of how simulations may benefit experimental research. In this thesis, various computational and theoretical methods ranging from thermodynamical models to high-level quantum chemistry calculations have been employed to study the properties of inhomogeneous systems. Three different computational methods to study such systems have been applied here: density functional theory for classical fluids, molecular dynamics and quantum chemistry.

It is well known that in macroscopic binary liquids, the component with a lower surface free energy adsorbs at the liquid-vapor interface, causing surface enrichment. Enrichment to the planar or spherical surface of particle affects the interaction between the condensed phase and its surroundings. Water-alcohol mixtures are a convenient choice for the surface enrichment studies because their thermodynamical properties are well-known. Experimental studies of surface composition of water-alcohol mixtures have been performed using several methods (Guggenheim, 1967; Raina et al., 2001; Li et al., 1993), and phenomenological models for surface composition have been presented (Guggenheim, 1967; Eberhart, 1966; Laaksonen and Kulmala, 1991). Density functional theory for classical fluids is a computationally relative fast method for modeling the microscopic properties of liquid-vapor interphases and evaluating the reliability of phenomenological models for surface composition over a wide range of total compositions (**Paper I**).

Even though argon is the third most common substance in the atmosphere, it is not studied because of its atmospheric relevance, but because of the computational simplicity of argon-argon interactions. In studies focusing on molecular dynamic simulation techniques (see e.g. Wedekind et al., 2006, 2007, and **Paper II**), or on complicated phenomena such as nucleation (see e.g. Julin et al., 2008; Lauri et al., 2006), simple model fluids are often used to avoid the unnecessary complexities involved in the interactions of real chemical substances. Molecular dynamics is a versatile method for nucleation studies because it does not assume equilibrium conditions, or pose any geometrical constraints on the nucleating clusters. Even though the processor speed and memory capacity of computers have increased massively over the past decades, the optimization of simulation conditions to avoid unnecessary simulation steps is still necessary. This has been done in **Paper II**.

Quantum chemical calculations on small molecular atmospheric relevant clusters give information for example on their structure, stability (see e.g. Kurtén and Vehkamäki, 2008; Nadykto et al., 2008, and references therein), evaporation rate (see e.g. Ortega et al., 2012) and dipole moment (see e.g. Kupiainen-Määttä et al., 2013). The latter can be then used to calculate ion-molecule collision rates in the absence of kinetic barriers. Quantum chemical methods are restricted to small clusters, and their conventional applications do not provide any information about dynamics. First principles molecular dynamics combine quantum chemistry and molecular dynamics, but only phenomena occurring on picosecond time scale can be studied, even when the cluster size is restricted to just a few molecules (see e.g. Kusaka et al., 1998; Choe et al., 2007; Loukonen et al., 2014).

Quantum chemistry calculations have been performed for several atmospherically relevant compounds and clusters, but before this work (**Papers III** and **V**) clusters of sulfuric acid together with other sulfur-oxygen-hydrogen compounds have not been systematically studied. As mentioned earlier, the experimental studies gave reason to expect that byproducts of SO_2 oxidation might play role in observed atmospheric particle formation. Even though this hypothesis was refuted by later experiments, the computational study increased our understanding of the behavior of sulfur-containing compounds in the atmosphere, and of the O-O-bridge in peroxodisulfuric acid, $H_2S_2O_8$. Peroxysulfuric acid, H_2SO_5, has been observed in negatively charged clusters in chamber experiments (Almeida et al., 2013) and

a large variety of sulfur-oxygen-hydrogen species has been measured from charged clusters in ambient air (Ehn et al., 2010a). Additionally, mass spectrometric measurements indicate that peroxodisulfuric acid is very likely produced in a state of the art calibration setup for condensation particle counters, which generates particles by heating ammonium sulfate (Kangasluoma et al., 2013).

Computational studies of sulfuric acid clusters have been performed using several computational methods. The challenge of classical molecular methods as molecular dynamics and Monte Carlo is to find interaction potentials that are both simple and able to mimic the true interaction. Ding et al. (2003) compared their interaction model to the models presented by Kusaka et al. (1998), and Kathmann and Hale (2001) and find very large differences in the energies of the sulfuric acid - water clusters. In general, only few molecular dynamics (Ding et al., 2003; Matsubara et al., 2009, **Paper IV**) and Monte Carlo calculations (Kusaka et al., 1998; Kathmann and Hale, 2001) for sulfuric acid water clusters exist, even though these are observed to be important components of atmospheric particle formation.
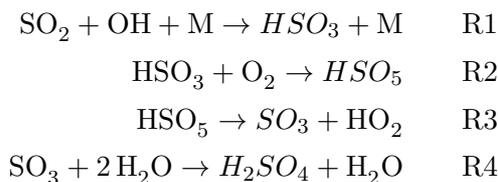
In this thesis I
1. study the local, averaged, and excess quantities of model surface-active fluids using density functional theory of classical fluids, and compare the predictions of different phenomenological models with the classical DFT calculations (**Paper I**).
2. study the effect of simulation conditions such as thermostatting, boundary conditions and system size on the equilibrium cluster size and surface tension of atomistic Lennard-Jones (LJ) fluids in molecular dynamic simulations (**Paper II**).
3. study the formation of dimers and trimers (with water) of sulfuric acid molecules and sulfur -containing compounds that can be formed as a byproduct of sulfuric acid formation (**Papers III** and **V**).
4. study the surface properties of sulfuric acid - water clusters and planar interfaces (**Paper IV**).
5. study properties of the peroxy group, O-O-bridge, in clusters of sulfuric acid, water and peroxodisulfuric acid (**Paper V**).

This thesis consists of an introduction, a short over view of sulfuric acid nucleation studies, presentation of interphase properties and nucleation, a review of the computational methods, and discussion of the main results of the thesis. Details of the results and description of the studies are presented in the articles at the end of the thesis.

2 Atmospheric sulfuric acid

The most important precursor gas for sulfuric acid in the atmosphere is sulfur dioxide, SO_2. The major source of SO_2 is the burning of fossil fuels. The main natural sources are volcanoes, forest fires and dimethyl sulfide emissions from algae in the oceans. In the gas phase, SO_2 is oxidized to sulfuric acid, H_2SO_4, via a series of reactions initiated by the OH radical (Wayne, 2000):

$$SO_2 + OH + M \rightarrow HSO_3 + M \qquad \text{R1}$$
$$HSO_3 + O_2 \rightarrow HSO_5 \qquad \text{R2}$$
$$HSO_5 \rightarrow SO_3 + HO_2 \qquad \text{R3}$$
$$SO_3 + 2\,H_2O \rightarrow H_2SO_4 + H_2O \qquad \text{R4}$$

where M is a third body (typically N_2) removing excess energy. Alternative oxidation products are discussed in **Paper III**.

Sulfuric acid is fully miscible in bulk water, and the two molecules form H_3O^+-HSO_4^--ion pairs. Proton transfer from H_2SO_4 in small clusters has been studied computationally by several groups (Arstila et al., 1998; Bandy and Ianni, 1998; Re et al., 1999; Ding and Laasonen, 2004; Kurtén et al., 2007b). The latest, highest level, quantum chemical computations have shown that an ion pair is formed if a cluster containing one sulfuric acid has four or more water molecules, depending on temperature (Temelso et al., 2012). A second proton transfer (forming the sulfate ion SO_4^{2-}) is less favorable, but may nevertheless occur in clusters including one sulfuric acid and less than 10 waters (Ding and Laasonen, 2004). H_2SO_4 has a low saturation vapor pressure, and it is eager to condense.

Even though atmospheric observations made at various measurement sites during the last decades suggest that aerosol formation correlates with the sulfuric acid concentration (Weber et al., 1997; Fiedler et al., 2005; Kulmala et al., 2006), the laboratory experiments were not able to reproduce the results until 2010 (Sipilä et al., 2010). The sulfuric acid concentration required to produce a unit nucleation rate, defined as number of clusters (able to grow) formed per unit volume in unit time ($\#\ cm^{-3}\ s^{-1}$), was measured to be much higher in laboratory experiments (Viisanen et al., 1997; Berndt et al., 2005; Brus et al., 2010) than what was observed in the atmosphere.

In addition, Berndt et al. (2005, 2008) reported laboratory experiments where the sulfuric acid was produced in situ and not evaporated from a liquid reservoir. The measured sulfuric acid concentration required for to aerosol particle formation were closer to the atmospheric data than the earlier laboratory experiments, which gave a reason to believe that some other sulfur-containing compounds such as $H_2S_2O_8$ could also be involved in the nucleation process (Laaksonen et al., 2008a; Du and Yu, 2009; Sorokin, 2010, **Papers III** and **V**).

Sipilä et al. (2010) explained the differences between laboratory and atmospheric experiments and why nucleation rates measured by Berndt et al. (2005, 2008) are closer the atmospheric ones than the earlier laboratory experiments. They performed laboratory measurements using new technology enabling the counting of particles down to 1,3nm, and obtained sulfuric acid nucleation at concentrations resembling the atmospheric conditions.

They found out that earlier the measured H_2SO_4 concentrations, and calculations of critical cluster sizes, had been disturbed by size sensitive counting efficiency. Additionally, H_2SO_4 clusters produced from the evaporated liquid exit the growth reactor too fast, and were thus not detectable. This problem was avoided if sulfuric acid was produced in situ. This does not exclude the participation of other sulfur-containing compounds in nucleation, but those were no longer needed to explain the differences between field and laboratory experiment.

These findings support the results of quantum chemical calculations presented in this theses (**Paper III** and **V**): the stability of clusters including sulfuric acid and other reaction products of SO_2 oxidation are studied, and the results show that alternative reaction products are unlikely to enhance nucleation.

Later, Vehkamäki el al. (2012b) have questioned the common way to calculate the critical cluster size from the slope of the log-log plot of the formation rate versus the concentration of the nucleating compounds, without additional information about the prenucleation clusters (the clusters below detection limit). Critical cluster size calculations are based on the assumption that no local minima in the free energy surface of cluster formation exist prior to the maximum at the critical size and clusters of pre-critical size are not lost to larger particles or walls. However, according to the calculation a deep local minima on the free energy surface exist in the case of a system of sulphuric acid, ammonia, dimethylamine, and water (Ortega et al., 2012) and cluster sinks are practically always present which disturbs the slope analysis (Kupiainen-Määttä et al., 2014).

3 Inhomogeneous system

In an inhomogeneous system with several phases, matter is continuously exchanged between the phases. Equilibrium is reached when the flow of matter is equal in both directions. The starting point of the study of phase equilibrium is the second law of thermodynamics: the entropy of an isolated system reaches its maximum value, or the free energy of a system coupled to its environment reaches its minimum value, at equilibrium. In a one-component system this leads to the equilibrium conditions for two phases (in our case: l, liquid and g, gas): thermal equilibrium $T_l=T_g$, mechanical equilibrium $P_l=P_g$ for the flat surface, and chemical equilibrium $\mu_l=\mu_g$.

The vapor at equilibrium is called saturated vapor, and the ratio of the equilibrium vapor pressure (p_{eq}) and the actual vapor pressure (p) is the saturation ratio:

$$S = \frac{p}{p_{eq}}. \tag{1}$$

The saturation ratio tells us how far from equilibrium the system is. For a supersaturated-vapor $S > 1$.

Supersaturated vapor tends to condense spontaneously on pre-existing surfaces. If the lowering energy is not possible by condensation, (e.g. due to the lack of surfaces), the supersaturation may reach values high enough for nucleation to commence. Nucleation processes and theories are discussed in Chapter 3.1.

Thermodynamical phases are homogeneous, and the boundaries between them are sharp. However, real interfaces between liquid and vapor phases are diffuse on the microscopic level. This leads to the question of the location and thickness of a surface. The definition of the location of the surface is especially interesting in the case of small clusters, where the number of atoms at the interphase region may be higher than inside the cluster. The equimolar surface is a sharp surface of a sphere defined as follows. Atoms or molecules of the cluster are assumed to be distributed homogeneously and the volume of the sphere is number of atoms in the cluster divided by the number density equal to the bulk liquid. Another choice for the location is the surface of tension, which is the surface for which the surface tension has the value corresponding to that obtained by mechanical surface tension measurements.

The molecular origin of surface tension is the inhomogeneous surrounding of a surface molecule. Thermodynamical surface tension may be calculated from the free energy of the system. If temperature (T), volume (V) and chemical potential (μ) are kept constant, but surface area (A) changed, the surface tension (γ) is the grand potential energy (Ω) change of the system.

$$\gamma = \left(\frac{\partial \Omega}{\partial A} \right)_{T,V,\mu}. \tag{2}$$

The Laplace equation gives the mechanical equilibrium condition for a spherical surface:

$$P_l = P_g + \frac{\gamma}{r}, \tag{3}$$

where P_l is the liquid pressure, P_g is the equilibrium vapor pressure, γ is the surface tension and r is the radius of the droplet at the surface of tension. Besides the thermodynamical potential or the Laplace equation (Eq. 3), surface tension may be calculated via a mechanical route from the pressure tensors (Thompson et al., 1984, **Paper I**).

Surface tension is closely linked to the surface composition. The mole fraction of compound i in the mixture is $x_i = N_i/N_{tot}$, where N_i is number of molecules of compound i and N_{tot} is total number of molecules. For an ideal mixture, the mole fractions of a compound is equal in all the phases, and for a non-ideal mixture, the mole fractions of the phases are not equal.

In **Paper I**, we study a surface-active system, where one of the components concentrates at the surface layer. Non-ideality can be described by the gas phase activity $A_{iv} = P_{iv}/P_{0iv}$, where P_{iv} is the equilibrium vapor pressure of compound i over the mixture, and P_{0iv} is the equilibrium vapor pressure over the pure liquid.

3.1 Nucleation

When the pressure of vapor increases, a tiny liquid phase, a droplet, is formed in the vapor. A first-order phase transition occurs if the conditions within the initial phase (Phase 1, also known as the metastable phase) become more favorable for another phase (Phase 2), and if no pre-existing stable phase (Phase 2) is available. In this chapter we concentrate on vapor-liquid phase transitions.

Thermodynamically, nucleation starts from density fluctuations of the metastable phase, in this case supersaturated vapor. Metastable vapor is stable for small fluctuations, because even though the new phase would lower the energy, the formation of new surface costs energy. Larger fluctuations lead to a transition to a liquid droplet. Cluster growth is unfavorable until the cluster size reaches a critical size, which corresponds to the top of the energy barrier where the thermodynamic advantage of the phase change starts to dominate over the surface formation energy. Due to the energy cost of surface formation, nucleation on pre-existing surfaces is energetically favorable compared to homogeneous nucleation. This process is called heterogeneous nucleation.

The free energy of cluster formation in a one component case is

$$\Delta G = -nk_B T \ln S + 4\pi r^2 \gamma \qquad (4)$$

where n is the number of molecules in the cluster, T is the temperature, S is the saturation ratio, r is the radius of the cluster, and γ is the surface tension. The critical cluster size denoted by *, may be solved by taking the derivative of ΔG with respect to cluster size (n) and setting it to zero.

The nucleation rate, i.e. cluster formation per unit time and volume, can be expressed as

$$J = K e^{\left(\frac{-\Delta G^*}{k_B T}\right)}, \qquad (5)$$

where K is a kinetic prefactor.

Classical nucleation theory (CNT) was introduced by Becker and Döring in 1939, and it is still widely in use. The advantage of CNT is that only measurable bulk parameters are needed, but naturally the macroscopic theory can not fully describe the microscopic phenomena of nucleation. The following assumptions are made in CNT: the vapor is an ideal gas, the liquid is incompressable, the surface of tension is equal to the equimolar surface, and the surface tension of a cluster is equal to the surface tension of a planar surface. The last

assumption is called the capillary approximation, and it fails when we consider small nanoclusters (Merikanto et al., 2007). In the case of argon clusters, the capillary approximation is reasonable for clusters with more than 150 atoms (Julin et al., 2010).

A simplified picture of nucleation kinetics includes monomer collisions to the cluster and monomer evaporations from the cluster. However, if small stable precritical clusters exist in the atmosphere, non-monomer collisions may be important (Vehkamäki and Riipinen, 2012a). More sophisticated kinetic models account for cluster-cluster collisions as well as cluster fissions; clusters breaking up into two smaller clusters (McGrath et al., 2012). The birth-death equation for a certain cluster size describes how the concentration of that type of cluster changes with time. A set of coupled equations for all cluster sizes governs the time evolution of the cluster size distribution. Collision coefficients between clusters are usually taken from the kinetic gas theory. Through detailed balance, evaporation rates then depend exponentially on the formation free energies. Earlier, free energies were usually obtained from classical thermodynamics, but now energy values for a limited number of small systems are provided by quantum chemistry calculations (Kupiainen et al., 2012; McGrath et al., 2012; Ortega et al., 2012).

4   Molecular modeling

Molecular -level studies can be roughly divided into classical and a quantum mechanical (QM) approaches depending on how the atomic interactions are treated. Widely used classical methods are molecular dynamics (MD), Monte-Carlo (MC) methods and density functional theory for classical fluids (DFT). The basic idea of classical methods is that the atoms appear in a limited number of different chemical environments, and the potential energy as a function of system configuration (e.g. interatomic distances, angles and dihedral angles) can thus be parametrized. The interaction parameters are always optimized to reproduce certain properties of the system, like surface tension or density of the liquid, and they can be based on experimental or quantum chemical data or both. Molecular dynamics and density functional theory for classical fluids are be discussed in Chapters 4.3 and 4.4. In Monte-Carlo methods based on statistical mechanics, stochastic sampling of configuration space is performed to study the averages of system properties. The advantage of classical methods is that they are relative fast compared to QM and larger systems can be studied. The downside is that the parametrization is always optimized for certain atom pairs in a certain environment, and atoms may behave unphysically if the limits of the paramerization are exceeded.

The problem of classical treatment can be overcome by computing interactions using quantum mechanical methods (**Paper III** and **V**). QM methods are based on the approximate solution of the Schrödinger equation, and a brief description of the most common methods is given in Chapter 4.2. The downside of these methods is that they are computational demanding, and only a limited number of atoms can be studied. In this work, QM is applied to find the minimum energy structures of clusters. First principle MD and MC calculate interactions from quantum chemistry, and these simulations are not limited by parametrizations.

The computation time increases strongly with accuracy and system size. For this reason, classical and quantum mechanical methods are sometimes combined to describe one part of the system more accurately by QM and interactions of less interesting surrounding molecules are parametrized by classical potentials (Warshel and Levitt, 1976; Sloth et al., 2003).

4.1 Classical interactions

Molecular mechanics, force field methods, and classical methods, all refer to the same principle for calculating the potential energy of the studied system. Interactions of atoms and molecules are parametrized using experimental or high level computational data. Electrons are not treated explicitly. Instead, attractive and repulsive forces are descibed by a set of functions. The potential energy of a classically interacting molecular system are usually expressed as:

$$E = E_{\text{vdW}} + E_{\text{Coulomb}} + E_{\text{stretching}} + E_{\text{bending}} + E_{\text{torsion}} + E_{\text{cross}}, \tag{6}$$

where E_{vdW} and E_{Coulomb} are associated with interactions of nonbonding atoms. $E_{\text{stretching}}$ and E_{bending} are potentials arising from stretching and bending of a chemical bond. Both the bond distances and the bond angles are usually approximated to oscillate harmonically, or set to constant values (frozen). In the case of large molecules, intramolecular rotations become significant, and torsion potentials are needed to handle the torsional degrees of freedom (E_{torsion}). E_{cross} couples two or more potentials in cases where one interaction affects the equilibrium parameter used for another potential (Jensen, 2007).

The van der Waals interaction, E_{vdW}, is very often parametrized as a pair potential where the interaction between two atoms is not affected by surrounding atoms, and the total force field affecting an atom is the sum of the pair interactions. The Lennard-Jones potential is one of the most widely used interaction potentials describing the van der Waals interaction between two neutral atoms (**Papers I** and **II** and **IV**):

$$E_{ij}^{LJ}(r) = 4\epsilon_{ij}[(\frac{\sigma_{ij}}{r})^{12} - (\frac{\sigma_{ij}}{r})^6], \tag{7}$$

where r is the distance between interacting particles i and j, and σ_{ij} and ϵ_{ij} are the optimized length and energy parameters. The first term inside parenthesis in Eq. 7 is the repusive interaction arising from the Pauli exclusion principle, while the second, attractive, part of the Lennard-Jones potential can be considered to represent the attraction between two induced dipole moments.

More flexible Morse and Buckingham potentials would give a better description of interactions for small systems, where accurate parametrization are available (Jensen, 2007), but the downside of this flexibility is that more parameters are needed, and they all need to be fitted to achieve optimal reproduction of experimental data. The LJ-potential requires only two parameter whereas three are needed for the Morse and Buckingham potentials.

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Energy and length parameters ϵ_i and σ_i are associated with each atom type i. In this work, the interaction between atoms of type i and j are parametrized using standard Lorentz-Berthlot mixing rules:

$$\epsilon_{ij} = \sqrt{\epsilon_i \epsilon_j} \qquad (8)$$

$$\sigma_{ij} = \frac{1}{2}(\sigma_i + \sigma_j) \qquad (9)$$

The potential energy for the interaction of two charged particles is the well-known Coulomb potential, E_{Coulomb}:

$$E_{\mathrm{Coulomb}}^{ij}(r) = \frac{Q_i Q_j}{\varepsilon r} \qquad (10)$$

where the interaction energy depends on the atomic charges (Q_i and Q_j) and the distance, r, between the atoms. ε is the dielectric constant of the medium. In the case of charged atoms, LJ-potentials are combined with the Coulomb interaction.

For molecules, a combination of several LJ and Couloumb potentials is used. The interaction sites of molecules are typically placed on the atoms. Due to the spherical symmetry of the potentials, additional interaction sites may need to be placed between the atoms in the molecule.

In classical force field simulations, the bonding pattern between the atoms (i.e. which atoms are bonded to each other) as well as the types of interactions in the system, are defined at the beginning of the simulation. For this reason, chemical reactions can not usually be modeled - only structural and conformational changes are possible. In this thesis, we have studied the sulfuric acid and water system, where a proton transfer reaction is expected to happen (**Paper IV**). This reaction is taken into account by simulating two kinds of sulfuric acid and water molecular pairs: neutral molecules, and the bisulfate-oxonium ion pair. This means in practice four different molecular configuration and interaction parameter sets (Ding et al., 2003). Another option would be to allow changes in molecular bonds and interaction parameters during the simulation if certain conditions (atom distance etc.) are fulfilled. A combination of dynamic simulations with quantum chemistry (first principle MD or MC) would represent the most accurate treatment of chemistry.

4.2   Quantum chemistry

This chapter gives a brief overview of different quantum chemistry methods and the challenges related to studies of molecular clusters. Quantum chemistry calculations are computationally very demanding, and in this thesis the calculations are performed using well tested and optimised program suites: TURBOMOLE (Ahlrichs et al., 1989), Gaussian (Frisch et al.,

2004) and SIESTA (Spanish Initiative for Electronic Simulations with Thousands of Atoms) (Soler et al., 2002). The quantum chemistry calculations in this thesis are used to study the stability of the small molecular clusters. In practice, a geometry optimization procedure is used to find the configuration corresponding to the lowest electronic energy.

The quantum chemical calculations presented in this work are based on the solution of the time-independent and non-relativistic Schöringer equation,

$$H\psi(r, R) = E\psi(r, R), \tag{11}$$

where H is the Hamiltonian operator, E is the energy and the wavefunction ψ fully describes the state of the molecular system. The hamiltonian operator may be divided into kinetic and potential energy terms:

$$H_{\text{tot}} = T_{\text{n}} + T_{\text{e}} + V_{\text{ne}} + V_{\text{ee}} + V_{\text{nn}}, \tag{12}$$

where T_{n} and T_{e} are the kinetic energy operators of nuclei and electrons, and V_{ne}, V_{ee}, and V_{nn} are the potential energy operators for nuclei-electron, electron-electron and nuclei-nuclei interactions, respectively.

Equation 11 is an eigenvalue equation, and the solutions (ψ) correspond to different stationary states of the system. However, a solution to the Schrödinger equation can not be found without various approximations for both the Hamiltonian operator and the wavefunction. The main approximations are described below.

All systems of atoms or molecules consists of electrons and nuclei. Due to the fact that the mass of the nuclei are at least thousands times greater than mass of an electron, the movement of the nuclei is so much slower that the electrons are almost instantaneously adapted to the new geometry. From the point-of-view of the electrons, the nuclei look fixed. The Born-Oppenheimer Approximation (BO) separates the motion of nuclei and electrons, and the electronic wavefunction is solved separately for each nuclear configuration.

The starting point for the so-called wave function base methods is Hartree-Fock theory. The true many body wavefunction (ψ) is replaced by a set of one-electron spin orbitals, combined via a Slater determinant which ensures that the Pauli exclusion principle is obeyed. The Hartree-Fock method is called mean field approximation because the electron-electron interactions are replaced by an average interaction. In other words, the Hartree-Fock method neglects the correlation between electrons of opposite spin, because the wavefunction is expressed as a single Slater determinant. The one-electron orbitals are further described as a linear combination of basis functions, a basis set (Jensen, 2007). This is called the basis-set approximation.

The variation principle states that a trial wave function inserted into the Schrödinger equation yields an energy above or equal to the exact energy. An iterative procedure can thus be used

to find the wave function that gives the lowest energy within the restrictions of the used approximation (BO, single Slater determinant, basis set, etc.).

Commonly used basis set functions are nuclei centered Slater and Gaussian functions (Jensen, 2007). Slater functions describe the real atomic orbitals better, but Gaussian type functions are computationally more efficient, and with the same computational effort many more of them can be used. A minimum basis set contains only one basis function per atomic orbital. However, the electron distribution at chemical bonds is asymmetric and more flexible functions, or sets of functions, are needed to describe molecular orbitals. Basis sets are classified by how many basis functions are used per atomic orbital. In this work (**Papers III** and **V**) Double-ζ polarized (DZP) type basis which contains two basis functions per atomic orbital, aug-cc-pV(T+d)Z, which contains three basis functions for each valence orbital, and a QZVPP type basis which contains four basis functions per valence orbital are used. In addition, all these basis sets contain extra polarization functions (corresponding to higher values of the angular momentum) and diffuse functions (corresponding to smaller values of the exponents). These improve the description of chemical interactions.

For many chemical systems, Hartree-Fock theory gives an absolute electronic energy which is 99% (Jensen, 2007) of total energy. However, the remaining percent is important for chemical bonding, and especially for the comparison of different structures of molecular systems. The absolute values of electronic energies are rarely interesting while the relative energies, as formation energies of the clusters, tell more about the studied system. Therefore, electron correlation must be accounted for if accurate results are required. The most common electron correlations methods are Configuration Interaction (CI), Möller-Plesset perturbation theory (MP), and Coupled cluster theory. They all use Hartree-Fock result as a starting point. Möller-Plesset perturbation theory, to be precise the MP2-theory (Möller and Plesset, 1934), is used in **Papers III** and **V**. According to Jensen (2007), MP2 usually accounts 80-90% of the correlation energy and a single-point calculations on the atmospheric relevant, $H_2SO_4 \cdot (H_2O)$, cluster shows that MP2 calculations reproduce well the higher level, couple cluster, energies (Kurtén et al., 2006).

Beside wavefunction-based methods, the other main branch of quantum chemistry is density functional theory (DFT), where electron correlation is modelled as a function of electron density. W. Kohn and L. J. Sham showed that the ground state electronic energy of a system can be written as a sum of terms of classical energy of charged particles plus an exchange-correlation term, E_{xc}:

$$E = E_{kin} + E_{ne} + E_{ee} + E_{xc}, \tag{13}$$

where E_{kin} is the kinetic energy of electrons, E_{ne} is the energy of nuclear-nuclear attraction and nuclear-electron attraction, and E_{ee} is the energy of electron-electron repulsion. The accuracy of DFT methods depend on the approximation of E_{xc}. DFT methods are generally computationally less demanding than even the cheapest correlated wave function method, MP2.

The choice of method involves a trade-off between computational cost and accuracy. Wavefunction-based methods convergence slower than DFT with respect to the basis set size, and very large basis sets are often needed for sufficient accuracy. The drawback of DFT is the inability to systematically improve the results. For calculations on atmospheric relevant clusters, the main problem is that the traditional DFT methods, such as the B3LYP (Becke, 1988) functional used in this study, poorly describe the weak interactions due to dispersion forces. Compared to the high-level coupled-cluster methods the B3LYP density functional underestimates the binding energy of sulfuric acid–water clusters (A. Al Natsheh, 2004; Kurtén et al., 2007c; Nadykto and Yu, 2007). During the last years, the dispersion problem of DFT has been is overcome by including a few global fit parameters (Grimme, 2011). A recent study by Leverentz et al. (2013) compared methods to find the best balance between computational cost and energetic accuracy for small atmospherically relevant clusters. As conclusion they recommended the dispersion-corrected PW6B95-D3 density functional with the MG3S basis set.

The solution of the electronic Schöringer equation yields a single point energy, in the other words the energy of a given nuclear configuration. A geometry optimization procedure is then needed to find stable molecular or cluster configurations corresponding to minima on the potential energy surface. The potential energy surface illustrates how the electronic energy of system varies with small changes in its structure. First derivatives of energies are used to move atoms toward the minimum energy configuration. Optimization procedures of quantum chemical program suite locate the minima closest to the initial guess geometry. For large systems, several initial geometries are therefore needed to find the global minima of the potential energy surface. At the end of this chapter we discuss this configuration sampling.

Semi-empirical methods reduce the computational cost by neclecting some interaction terms, and/or replacing them with parameters derived from experimental data. The semiempirical methods, as RM1 and AM1 (Rocha et al., 2006; Dewar et al., 1985), are commonly used to create guess geometries for the higher level quantum chemistry calculations (Nadykto et al., 2011; Herb et al., 2013; DePalma et al., 2012, **Paper III**). Semiempirical methods are developed to study the ground state properties of large, simple, organic molecules and their description of hydrogen bonding and transition state structures are poor. They are also highly dependent on the quality of parametrizations (Foresman and Frisch, 1996).

The Gibbs free energy is the thermodynamic potential of a system at constant temperature and pressure, and to describes the state of a real system and the energy difference between two states or systems better than the pure electronic energy. It can be written as a function of entalphy (H) and entropy (S)

$$G = H - TS, \tag{14}$$

where T is temperature.

Thermodynamical functions such as internal energy, entalphy and entropy depend on the

derivatives of the partition function. The partition function q of a system is a sum of exponential terms of all possible energy states of the system, ε_n:

$$q = \sum_{n=0}^{\infty} e^{\varepsilon_n/k_B T}, \tag{15}$$

where k_B is the Boltzmann constant and T is the temperature. For an isolated molecule, the energy term ε_n may be approximated to be a sum of electronic, translational, rotational and vibrational energies, and the partition function can be expressed as a product of different degrees of freedom. Enthalpy and entropy terms then become a sum of transitional, rotational, vibrational and electronic degrees of freedom.

Due to the size of molecular clusters studied in this thesis, thermal contributions to the Gibbs free energy are computed using the ideal gas, rigid rotor and harmonic oscillator approximations. The partition function for translation degrees of freedom is a function of the energy of standing wave, in other words the molecule is considered as "a particle in a box". The system specific variable s are pressure, temperature and the total molecular mass. Within the rigid rotor approximation, the rotating molecule or cluster is assumed to have a fixed internal geometry. The rotational partition function of a polyatomic molecule then becomes a function of moments of inertia about the principal axes, and the rotational symmetry number. Information on atomic masses and positions are needed to calculate the rotational partition function. The vibrational degrees of freedom are computational by the most demanding, even if vibrations are approximated to be harmonic. Calculation of vibrational partition functions requires calculation of the second derivative of the energy respect to atom coordinates. In practice this is done as a separate step once the minimum-energy geometries have been optimized. Harmonic frequencies are also less sensitive to the accuracy of the method than electronic energies, and may be calculated at the lower level.

Kurtén et al. (2007a; 2007d) noted that quantitatively accurate formation free energies would require the computation of anharmonic vibrational frequencies. However, this would be prohibitively expensive for the larger cluster types studied in this thesis. Our study is focused on comparing formation free energies of different clusters to each other, and the errors due to anharmonicity are mostly cancelled out.

Besides the local anharmonics related to the vibrations of intra- or intermolecular bonds, Kathmann et al. (2007) raised the question of global anharmonicity related to different configurations of the system. Temelso et al. (2012) calculated effective energies of small sulfuric acid-water clusters by weighting energies of local minimum-energy configurations by a Boltzmann distribution function. They found that the effect of averaging was relative small.

Recently, Partanen et al. (2013) calculated accurate thermochemical parameters for a single sulfuric acid molecule. Besides the anharmonic treatment of vibrational frequencies, the contributions of the two stable conformers of sulfuric acid was taken into account in calculating of the thermal energy. They concluded that inclusion of both conformers has a significant

effect on the vibrational partition function of the sulfuric acid molecule. Unfortunately, even small clusters have too many degrees of freedom to be treated at this level of theory.

The size of the system limits the accuracy of the quantum chemical calculations, but the biggest challenge is to find good initial guess geometries. For a cluster of a couple of molecules, the minimum energy geometry can be roughly estimated using basic rules for molecular bonding, but the number of possible geometries increases rapidly with the number of molecules in the cluster. In this work, we have also used molecular dynamic simulated annealing (see e.g. Loukonen et al., 2010; Temelso et al., 2012)) and semiempirical methods to generate initial guess geometries. Initial geometries are then typically pre-optimized by quantum chemistry using a lower level of theory and/or small basis set. Finally, the optimized geometry depends on the optimization procedure of the quantum chemistry program and the level of theory. However, the geometry is less sensitive to the level of computational accuracy than the electronic energy of the system. Multi level methods, as used in **Paper V**, take advantage of this and optimize the geometry at a lower level, then do a single point energy calculation at one or more higher levels (see e.g. Ortega et al., 2008, 2009; Montgomery Jr. and Petersson, 1999, 2000).

In this thesis, quantum chemistry methods are used to study the stability and structure of clusters containing one sulfuric acid and one other sulfur-containing compound formed in SO_2 oxidation (**Paper III**). In **Paper V**, hydration of the clusters is taken account by adding a water molecule. The calculated parameters are electronic energies (ΔE), Gibbs free energies (ΔG), entalphies (ΔH), and entropies (ΔS). Additionally, in paper **Paper V** the Quantum Theory-Atoms-in-Molecules (QTAIM) is used to study the O-O-bridge in the peroxodisulfuric acid molecules. The QTAIM method analyzes the electron density distribution, and yields information about the strength and nature of bonds between atoms through the properties of the so-called bond critical points (e.g. the values of the electron density and its laplacian at these points).

4.3   Molecular dynamics

Molecular dynamics (MD) simulate the real motion of atoms and molecules in a certain environment using classical mechanics. Contrary to the other two computational methods presented here, the simulated microscopic behavior of a system is time-dependent. Molecular dynamics methods are widely used in both material and biosciences, and several commercial programs for these purposes are available (see e.g. Case et al., 2012; Brooks et al., 2009; Phillips et al., 2005). The simulations discussed in this thesis are performed using the GROMACS (Groningen Machine for Chemical Simulations, Berendsen et al., 1995) molecular dynamic program version 4.0.2 (**Paper IV**) and a code developed in-house (**Paper II**).

In the MD simulations, Newton's equation (16) of motion are solved for each atom between short intervals.

$$F_i = m_i a_i = m_i \frac{dv_i}{dt} = m_i \frac{d^2 r_i}{d^2 t}, \qquad (16)$$

where F_i denotes the force on the particle i, m_i the mass of the particle, a_i the acceleration, v_i the velocity of i and t the time. As mentioned earlier (Chapter 4.1), interactions between atoms can be calculated using quantum mechanics (first principle MD) or classical force fields. The real time required for the simulation depends on the system size, the interaction potentials, the time step and the modeled phenomena.

A critical parameter in the molecular dynamic simulation is the time step, in other words the time interval between the interaction potential update. Too long time steps may lead to unphysical behavior, for example the total energy may not be conserved in a microcanonical system. Too short time steps make the simulation slow. The interaction potential that varies most strongly as a function of location determines the length of time step. A suitable time step for an argon interacting via LJ-potential is roughly ten times longer than for a vibrating water molecule (**Paper II**, **Paper IV**). One possibility to avoid short time steps and long simulation times is to apply the multistep method RESPA (Tuckerman et al., 1990) where different time steps are used for the intermolecular and intramolecular forces.

Depending on the studied phenomena, atomic coordinates at the beginning of the simulations are either given random values, or the atoms are placed in a specific configuration. In an indirect nucleation simulation, the starting configuration is a cluster in equilibrium with a surrounding vapor (**Paper II** and e.g. Toxvaerd, 2001). If we want to follow stochastic dynamical processes like nucleation, atoms are placed randomly into the simulation box to form a supersaturated vapor (**Paper IV**). This is called a direct nucleation simulation (e.g. Napari et al., 2009).

Periodic boundary conditions of a simulation box permit the modeling of very large systems. Atoms near the simulation box border interact with the images of the atoms on the other side of the simulation box. However, periodic boundaries introduce a level of periodicity that is not necessarily present in nature. This need to be taken account when the size of the simulation box and the interaction potential are chosen.

Another option is to use a container with repulsive walls. The wall potential is the repulsive part of the LJ-potential, including an additional term that shifts the potential minimum to zero. The spherical form of the container used in the **Paper II** is beneficial because of the spherical symmetry of the studied system (cluster and vapor). The repulsive wall disturbs the system close to the wall, and for that reason the simulation box needs to be large enough that the interesting part of the system is not affected.

The use of an interaction potential cut-off is essential if the simulations are carried out with periodic boundary conditions. The potential is cut and shifted so that the potential is zero at the cut-off distance. In the case of large systems, the use of cut-off decrease the number of interacting atoms, and speeds up the simulation. Attractive van der Waals interactions described by LJ- potential decrease proportional to r^{-6}, but for the electrostatic Coulomb

interaction exponent is -2. For that reason, the Coulomb interaction is called a long range interaction, and simulation programs like GROMACS offer advanced methods for taking long-range forces into account, for example Ewald summation (Darden et al., 1993). The choice between a simple cut-off and these advanced methods depends on which properties of the system we are interested in (Jungwirth and Tobias, 2006).

Depending on the studied phenomena MD simulations are usually performed in microcanonical (NVE), canonical (NVT) or isothermal-isobaric (NTP) ensembles. First two are used in **Paper II** and the simulations in **Paper IV** are canonical.The most natural way for temperature control in a canonical ensemble would be using thermalized carrier gas atoms. However, the use of inert carrier gas is time-consuming, because it increases the number of interacting atoms, and the number of carrier gas atoms needs to outnumber the studied atoms for effective thermalization. Another method to control temperature is to couple the system to an artificial thermostat. A thermostat modifies, by some sophisticated way, the velocities of the atoms. The most simple one is velocity scaling, where the velocities of the atoms are scaled so that the total kinetic energy is equal to the energy of the target temperature. The Andersen thermostat gives new velocities for all or some of the molecules according to the Maxwell-Boltzmann distribution (Andersen, 1980). The most advanced thermostat used in this work was Nosé-Hoover thermostat (Martyna et al., 1992; Tuckerman et al., 2001, **Papers II and IV**). The Nosé-Hoover algorithm introduces an additional degree of freedom into the equation of the motion.

In this thesis, molecular dynamic methods are used to study the simulation parameter dependence of argon systems (**Paper II**) and the properties of sulfuric acid-water systems (**Paper IV**). Indirect nucleation simulations are performed for argon clusters for five different system sizes, ranging from 54 to 500 atoms in microcanonical (NVE) and canonical (NVT) ensembles. The temperature, density and pressure distributions, as well as surface tension and cluster size, are evaluated, and the results are then compared between different system sizes and simulation ensembles. In **Paper IV**, the structure of sulfuric acid - water clusters are studied and compared to the results for the planar vapor-liquid interface. The mole fractions of the interfacial surface layer and the central (bulk) part of the condensed phase are calculated from the density profiles of the systems. The mole fraction of sulfuric acid in the whole system of condensed phase and vapor is varied from 0.01 to 0.6.

4.4 Density functional theory for classical fluids

Density functional theory (DFT) is traditionally used in material physics to calculate the electron density, as we discussed in Chapter 4.2. However, density functional theory can also be applied to a classical fluid to calculate the free energy of the system, taking into account the the microscopic molecular interactions. Density functional theory is based on the expression of the free energy of an inhomogeneous system as functional of atomic or molecular density. The free energy functional is minimized, and the density distribution is solved, by iterative methods. DFT is most suitable for simple model substances which have spherical

or cylinderical symmetry (Oxtoby and Evans, 1988; Zeng and Oxtoby, 1991; Laaksonen and Oxtoby, 1995; Napari and Laaksonen, 1999, **Paper I**). However, more complicated molecular systems may also be modelled (Sweatman, 2003; Cherepanova and Stekolnikov, 1994; Seok and Oxtoby, 1998; Hughes et al., 2013). The basics of the used method are described below.

The Helmholtz free energy of a spatially inhomogeneous system is written as a function of the Helmholtz free energy per molecule $f(r)$,

$$F(\rho) = \int d\mathbf{r} f(\mathbf{r}) \rho(\mathbf{r}) \tag{17}$$

The hard sphere approximation introduced by Oxtoby and Evans (1988) is one way to construct a physically reasonable and accurate density functional. Another approximation used in nucleation studies is the gradient approximation. It was introduced by Cahn and Hilliard (Cahn and Hilliard, 1958; Davis, 1996). The hard sphere approximation is based on the van der Waals approximation, where the free energy is divided into a reference system (F_R) and a perturbation part (F_A) corresponding to the attractive interactions.

$$F = F_R + F_A, \tag{18}$$

The free energy of the reference system is a sum of the free energy of an ideal gas F_i and the contribution of the repulsive interactions of the particles to the free energy of the system. The hard sphere approximation applies local density approximation (Henderson, D., 1992) and the equation of state for hard spheres, developed by Carnahan and Starling (Hansen and McDonald, 1986), to calculate the contribution of repulsive interactions to the Helmholtz free energy.

The local density approximation simplifies the the free energy to be a functional of local values of the density. The approximation does not properly take into account the short distance correlations of repulsive interactions, and it is not able to describe the fluids close to a repulsive wall. However, these problems do not significantly affect systems of vapor and liquid phases. Another widely used approximation is the weighted density approximation (Tarazona, 1984), where the free energy is evaluated using a weighted density averaged over the near surroundings. A comparison of approximations to the results in the gas-liquid and liquid-liquid interfaces has been made for example by Napari and Laaksonen (1999). A more recent approximation is Rosenfeld's fundamental measure theory, where the weighted densities are the convolutions of the local densities by geometrical weight functions (Löwen, 2002).

Using the random phase approximation (Andersen and Chandler, 1970), the free energy related to the attractive interactions reduces to

$$F_A = \int \int d\mathbf{r} d\mathbf{r}' u_{i,j}(\mathbf{r} - \mathbf{r}') \rho(\mathbf{r}) \rho(\mathbf{r}') \tag{19}$$

where $u_{i,j}$ is the attractive pair potential between particles i and j, and $\rho(r)$ and $\rho(r')$ are local number densities of particles. The division of the interaction potential, $u_{i,j}$, into repulsive, $\phi_{i,j}^R$, and attractive, $\phi_{i,j}^A$, parts is arbitrary. In this thesis we have followed Weeks, Chandler and Andersen procedure (Weeks et al., 1971) and divided the potential at the minimum. The LJ-potential (Chapter 4.1) reaches its minimum at r=$2^{1/6}\sigma$.

In this thesis, the system under consideration is in contact with a heat and particle reservoir, specified by a temperature and chemical potential μ. The grand potential is obtained by a Legendre transformation from the Helmholtz potential.

$$\Omega = F + \sum_i \mu_i \int dr \rho_i(r), \tag{20}$$

where μ_i is the chemical potential and ρ_i is the density of component i. The equilibrium densities can be determined from

$$\frac{\delta\Omega(\rho)}{\delta\rho_i(r)} = 0. \tag{21}$$

The density profile is solved by an iterative process, starting from a step profile for the liquid-vapor interface. The value of the surface tension is used as a convergence criterion.

In this thesis (**Paper I**), DFT is used to test phenomenological models of surface composition for a binary system, a mixture of monomers and dimers. Monomers were single hard spheres and dimers consisted of two hard spheres. The attractive interactions, LJ-potential parameters, are adjusted so that the dimers are concentrated on the surface, and orientated perpendicular to it – imitating the water-alcohol system. Three tested models are the Guggenheim model (Guggenheim, 1967), the Eberhart model (Eberhart, 1966) and the modified Eberhart model presented by Laaksonen and Kulmala (1991).

The Guggenheim model is based on the Gibbs adsorption equation, and information on the area occupied by each molecular species on the surface.

$$\frac{\delta\gamma}{\delta x_b} = \Gamma_1 \frac{\delta\mu_1}{\delta x_b} + \Gamma_2 \frac{\delta\mu_2}{\delta x_b}, \tag{22}$$

where γ is the surface tension of planar interface, x_b is the mole fraction of component 2 in bulk liquid, Γ_i is the number of molecules i (i=1,2) at the surface per unit area, and μ_i is the chemical potential of component i (i=1,2). Additionally, the model assumes that all molecules of component i (i=1,2) occupy the same area at the surface, and $A_1\Gamma_1 + A_2\Gamma_2 = 1$.

In the Eberhart model, the surface tension of a mixture, $\gamma(x_b)$, is expressed as a linear combination of the surface tensions of the pure components γ_1 and γ_2

$$\gamma(x_b) = (1 - x_s)\gamma_1 + x_s\gamma_2, \tag{23}$$

where x_s is the mole fraction of component 2 in the surface phase.

Laaksonen and Kulmala (1991) modified the Eberhart model by weighing the surface mole fractions with the partial molecular volumes of pure components v_1 and v_2:

$$\gamma(x_b) = \frac{(1 - x_s)v_1\gamma_1 + x_s v_2\gamma_2}{(1 - x_s)v_1 + x_s v_2}. \tag{24}$$

Thermodynamical properties of the studied system are then easily obtained via thermodynamical relations from the free energy functional.

5   Review of papers

This thesis consists of five articles published in peer-reviewed journals. All the articles study the structure of non-uniform matter: flat surfaces and clusters. As the size of the studied object becomes smaller, the methods become more accurate. Density functional theory for classical fluids is used on **Paper I** to study the composition of a flat surface. Molecular dynamics is used in **Paper II** and **IV** to study clusters of some hundreds of atoms and molecules. Clusters of less than ten molecules are studied using quantum chemistry in **Papers III** and **V**.

Paper I compares the results of surface phase composition models to the surface phase composition of surface active binary mixture of simple model substances calculated using density functional theory for classical fluids and the surface phase compositions of water-alcohol mixtures (water-methanol, water-ethanol, and water-n-propanol). The models were originally presented by Guggenheim (1967), Eberhart (1966), and Laaksonen and Kulmala (1991). The studied system is a planar liquid-vapor interface. The model of Laaksonen and Kulmala is in best agreement with the classical DFT calculations. The surface mole fraction of the solute component from the Guggenheim model exceeds one for a mixture with high surface activity. The failure of the Guggenheim model is also evident in the calculations for water-alcohol mixtures.

Paper II explores the effects of thermostatting, boundary conditions and system size on the cluster-vapor equilibrium in molecular dynamic simulations. The studied system consists of a cluster of Lennard-Jones argon atoms and the vapor phase around the cluster. Simulations are carried out both using periodic boundary conditions and a spherical boundary with a repulsive wall. The interaction between the repulsive wall and vapor atoms disturbs both the density and the temperature distributions of the vapor. The equilibrium cluster size, and the thermodynamical properties such as surface tension, can quite accurately be predicted using a small system with a limited number of vapor atoms. We found that particle exchange between the cluster and vapor phase is not able to equalize the temperature in constant-energy simulations, but the Nosé-Hoover thermostat performs the temperature regulation quite well.

Paper III is a study of the initial step of sulfuric acid nucleation. Quantum chemical calculations are used to investigate whether or not some SO_2 oxidation intermediates or alternative reaction products could take part in nucleation along with sulfuric acid. The calculations indicate that the only dimer cluster that is more strongly bound than $H_2SO_4 \cdot H_2SO_4$ is $H_2S_2O_8 \cdot H_2SO_4$. Hydration as modeled by the addition of one water molecule to the cluster does not change the situation.

Paper IV investigates the structure of stable sulfuric acid-water clusters and planar liquid-vapor interfaces at various compositions using molecular dynamics methods. Due to the fast protonation of H_2SO_4 in the presence of water, two different potential models are used for sulfuric acid: undissociated H_2SO_4, and the dissociated bisulfate hydronium ion pair (HSO_3^- – H_3O^+). If the total mole fraction of H_2SO_4 is smaller than 0.1, the unprotonated sulfuric acids lie on the cluster surface. Similar surface activity was not seen at the planar interface. In the protonated system, the bisulfates are at the center of the cluster, and the hydronium ions on the surface, when the sulfuric acid concentration is small. The presence of ions is found to destabilize the clusters at higher sulfuric acid concentrations and the planar interfaces at all compositions.

Paper V is a continuation of **Paper III**, studying the properties of peroxodisulfuric acid. A multistep quantum chemistry method is used to study the formation energetics and binding patterns of sulfuric acid-peroxodisulfuric acid-water clusters, with special focus on the O-O bridge. The O-O bridge of the $H_2S_2O_8$ molecule is affected by cluster formation, and the length of the O-O bridge correlates linearly with the average length of S-O bonds next to it. The presence of $H_2S_2O_8$ does not enhance the addition of sulfuric acid to the clusters, but the clustering of peroxodisulfuric acid with sulfuric acid and water is thermodynamically favorable, as is the replacement of one of the sulfuric acid molecules by peroxodisulfuric acid in a sulfuric acid-water cluster.

6   Author's contributions

I am solely responsible for the summary part if this thesis. **Paper I** is combination of two separate lines of work: density functional theory calculations for model fluids, and phenomenological surface model calculations of real binary mixture. I was responsible for all the DFT calculations and the comparison of these results with the phenomenological surface model, and I participated in writing the results. In **Paper II**, I performed all the molecular dynamic simulations and wrote majority part of all the sections of the paper except the introduction. In **Papers III** and **V**, I did all the quantum chemistry calculations and participated in writing all parts of the article. In **Paper IV**, I made all the molecular dynamics calculations and wrote the majority part of the article.

7 Conclusions

This thesis is a contribution to the understanding of composition and structure of sulfur - containing systems and validity of surface composition models. Technical simulation challenges and the effects of changes in simulation condition are pointed out for molecular dynamic simulations.

For surface active substances, the surface tension of the planar binary mixture can be expressed as a linear combination of the surface tensions of the pure components. Surface tensions are weighted by surface mole fractions (Eberhart model) or product of mole fraction and partial molecular volumes of pure components (modified Eberhart model). According to our density functional calculations for classical fluids, the later model gives slightly better results for the the studied systems, but the down side of that model is the need for data for molecular volumes. The Guggenheim model studied in this thesis is not recommended for use.

When performing molecular dynamic simulations of argon-like Lennard Jones fluid at the spherical shell with a repulsive wall, both the density and temperature distribution of vapors are disturbed, while the clusters fixed to the centre of simulation box are not affected. If spatial uniformity of temperature is achieved, the cluster-vapor properties such as density profile and surface tension in a NVE system are virtually indistinguishable from those obtained from a NVT simulation. Simulation times can be reduced by using limited number of vapor molecules. The density distribution, surface tension and equilibrium cluster size can be predicted even if the total number of atoms is 54 instead of 500.

Due to the chemical activity of sulfuric acid, it is challenging to simulate by classical methods. Structural differences between $H_2SO_4 \cdot (H_2O)_n$ and $HSO_4^- \cdot H_3O^+ \cdot (H_2O)_{n-1}$ clusters are expected, but it cannot be determined if the differences are caused by the the nature of the system or by simulation restrictions. Use of first principle simulation methods should be considered to resolve this issue.

The main oxidation product of SO_2 in the atmosphere is H_2SO_4. Apart from peroxidisulfuric acid, side products of the SO_2 oxidation chain do not form more stable dimers with H_2SO_4 than $(H_2SO_4)_2$. Peroxidisulfuric acid may also replace a sulfuric acid in a sulfuric acid - water cluster, but the second replacement reaction is unfavorable. If peroxidisulfuric acid appears in the atmosphere, it will participate in nucleation, but $H_2S_2O_8$ does not enhance sulfuric acid addition to the cluster and thus does not significantly affect the nucleation rate.

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