

Structure of water–sulfuric acid clusters from molecular dynamics simulations

Martta Toivola, Ismo Napari and Hanna Vehkamäki

Department of Physics, P.O. Box 64, FI-00014 University of Helsinki, Finland

Received 1 Dec. 2008, accepted 25 Mar. 2009 (Editor in charge of this article: Veli-Matti Kerminen)

Toivola, M., Napari, I. & Vehkamäki, H. 2009: Structure of water–sulfuric acid clusters from molecular dynamics simulations. *Boreal Env. Res.* 14: 654–661.

Molecular dynamics method is applied to study the structure of stable sulfuric acid–water clusters at various compositions. Also a planar liquid–vapor interface is studied. Two different potential models were used. In the simpler model, sulfuric acid (H_2SO_4) remains in an undissociated state. A more realistic scheme requires that in the presence of water (H_2O) H_2SO_4 protonates to form bisulfate (HSO_4^-) and hydronium (H_3O^+) ions. This effect is described by considering a system consisting of HSO_4^- and H_3O^+ ions, and water. The main focus is on the structure of clusters of hundred molecules at different compositions. The results are compared with those for the planar liquid–vapor interface. In the unprotonated system sulfuric acid lies on the cluster surface, if the total mole fraction of H_2SO_4 is smaller than 0.1, whereas at a planar interface such enhanced surface activity is not seen. 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 compositions and the planar interfaces at all compositions.

Introduction

Several studies have shown that sulfuric acid is a key component in the atmospheric aerosol formation (Kulmala 2003, Spracklen *et al.* 2006). A clear correlation between the sulfuric acid concentration and the formation events was observed at several measurement sites (Sihto *et al.* 2006). Yue *et al.* (1994) discovered that sulfuric acid dominates the mass of the aerosol increasing from about 60 mass percentages just above the tropopause to about 86 at 35 km.

Due to its high acidity, sulfuric acid is also a good catalyst for chemical reactions. Heterogeneous reactions are significant part of the atmospheric chemistry. Atmospheric aerosol particles provide both surface and liquid phase reac-

tion sites for heterogeneous chemical reactions (Wayne 2000, Bianco and Hyenes 2005). Since the reaction probability is sensitive to the aerosol composition, the composition is an important parameter worth investigating. Sulfuric acid is fully miscible in water in all compositions.

Computational studies of H_2SO_4 – H_2O clusters have been performed using several computational methods. Simulations provide significant molecular level insight that would be otherwise unattainable, but all the methods have their own downsides. Quantum chemistry provides accurate information about the energetics of the studied system, but the method is restricted to small clusters and it does not provide any information about dynamics. Several groups performed quantum chemistry calculations for sulfuric acid

water clusters (see e.g., Ianni *et al.* 2000, Ding *et al.* 2003a, 2004, Al Natsheh *et al.* 2004). Choe *et al.* (2007) used a so-called first-principle molecular dynamics method to study $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$ system. This method evaluates forces between atoms from the electronic structure calculated using density functional theory. The method is able to treat bond breaking and forming, but it is limited to investigation of dynamics that occur on the time scale of the order of picoseconds (Kusaka *et al.* 1998). Molecular dynamics (MD) or Monte Carlo (MC) simulations use system-specific interaction potentials between the atoms and molecules. The potentials are usually optimized to replicate certain properties such as surface tension. Both methods are suitable when simulations of systems containing hundreds or thousands of molecules are wanted, but there is an inherent difficulty in the treatment of bond breaking and forming. Water-sulfuric acid clusters were simulated, for example, by Kusaka *et al.* (1998), Kathmann and Hale (2001) and Ding *et al.* (2003b). Classical nucleation theory (CNT) provides information about nucleating clusters, such as the composition and radius of the critical nucleus, and nucleation rate. The nucleation rates of $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$ system predicted by CNT are in most cases within experimental errors (Noppel *et al.* 2002). However, the uncertainties are large and CNT is unable to describe the structure of clusters, and system-dependent thermodynamical data is needed.

In order to study the structure of $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$ system, we will use a molecular dynamics simulation method. We will simulate clusters in equilibrium with a vapor and planar vapor-liquid interfaces, with H_2SO_4 mole fraction varying from 0.01 to 0.6. We will concentrate on the structure of the clusters in several compositions and compare our results with the structure of planar interfaces. As mentioned above, molecular dynamics method is not able to treat chemical reactions (dissociation). The quantum chemical calculations show that H_2SO_4 molecules protonate easily in small water clusters (see e.g. Ding *et al.* 2004). However, the second protonation occurs only at 25% of H_2SO_4 molecules in the bulk phase solutions and the percentage is 50 in a small cluster. We will therefore ignore the second protonation for simplicity and simulate two kinds of sys-

tems. Protonation environments are different if we compare the bulk liquid, liquid surface and cluster. The polarity at the surface is reduced as compared with that of the bulk liquid, and in the small cluster there is no clear difference between the surface and the bulk phases. Bianco *et al.* (2005) studied the dissociation at the surface and concluded that acid dissociation is not at all guaranteed in the temperature range 190–300 K and that undissociated, molecular H_2SO_4 may exist at the surface. This is not surprising if we remember that dissociation is only slightly exothermic reaction in the bulk liquid (Bianco *et al.* 2005). However, dissociation occurs in small clusters already when three water molecules are present with one sulfuric acid molecule, or two water molecules with two sulfuric acid molecules (Re *et al.* 1999, Ding *et al.* 2003). One water molecule acts as a proton acceptor, while two water molecules or (in the later case) one water molecule and one sulfuric acid molecule stabilize the newly-formed hydronium ion. We will first simulate a system where we have H_2SO_4 and H_2O molecules, and second, a system consisting of HSO_4^- and H_3O^+ ion pairs and water. The ion pairs are not coupled to each other.

Methods

Computational details

The simulations were performed using GROMACS (Groningen Machine for Chemical Simulations) (Berendsen 1995) molecular dynamic program ver. 4.0.2. We used a potential model for sulfuric acid and water molecules constructed by Ding *et al.* (2003). Two atoms of different molecules interact via the pair potential

$$u(r_{ij}) = A \frac{q_j q_i}{r_{ij}} + \varepsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right], \quad (1)$$

where A is a constant and r_{ij} is the distance between i and j atoms. Charges q_i and q_j , Lennard-Jones energy parameter ε_{ij} , and distance parameter σ_{ij} are the interaction parameters obtained from the parametrization of quantum chemistry calculations. The intramolecular potentials are simple harmonic potentials. For a more detailed information see Ding *et al.* (2003).

The simulations were carried out with periodic boundaries, which necessitates the use of the potential cutoff. In the GROMACS program the cutoff length is restricted to be smaller than half of the box length. We used a cutoff of 3.9 nm for the intermolecular potentials in the cluster simulations and 1.9 nm in the planar vapor-liquid interface simulations. Quite a large cutoff length was needed for a realistic treatment of electrostatic interactions. The GROMACS package does offer more advanced methods for taking long-range forces into account, for example Ewald summation and particle-mesh methods, but they are considerably more time-consuming than the simple cutoff. Also, as the cutoff length is larger than the diameter of the cluster and the vapor density is very low, the contributions beyond the cutoff will not affect the cluster structure noticeably. The smaller cutoff in the simulations of planar interface will affect a property like surface tension somewhat, but the effect on the surface structure is likely to be very small. Jungwirth and Tobias (2006) compared the results of simulations with Ewald summation and cut-off for aqueous NaI solution and they found that the use of cutoff caused only subtle differences in the density profiles of planar interfaces.

The temperature of the system was fixed at 260 K throughout the present study. The system was coupled to a Nosé-Hoover thermostat (Hoover 1985). The mass-like parameter of the thermostat was $1.65 \times 10^{-24} \text{ s}^2 \text{ K}$. The simulation time step was 0.5 fs. We used Stillinger definition to distinguish between the vapor and the cluster atoms: a molecule is a part of the cluster if it has another molecule inside the Stillinger radius. The Stillinger radius we used was 0.495 nm. This refers to the O–O distance in interactions between H_2O molecules (or H_3O^+ ions), S–S distance between H_2SO_4 molecules (or HSO_4^- ions), and O–S distance otherwise. Wedekind and Reguera (2007) showed for the argon system that the Stillinger cluster definition overestimates the number of molecules in small clusters but the variation of the Stillinger radius alone is not sufficient to reach a more realistic cluster description. However, the overestimation is small when the cluster is larger than a couple of tens of molecules (Julin *et al.* 2008).

Fortunately, the issue of cluster definition is of minor importance in our study, because we base our analysis on density profiles and the cluster definition is only used to distinguish the moment when the final state with a large equilibrium cluster is achieved and to calculate the location of the center of the cluster.

Initial configurations

First we simulated a system containing water and unprotonated sulfuric acid molecules. The total amount of the molecules was 100. The mole fraction of sulfuric acid was varied from 0.01 to 0.6. At the beginning of the simulations all the molecules were in the vapor phase. During the equilibration period, some small clusters were formed via nucleation. Coagulation of clusters and condensation of free molecules led the system to a state, where we had only one cluster surrounded by a vapor phase. After the equilibration period, the cluster-vapor system was simulated for data collection. Structure analysis was done only for the equilibrium cluster.

In the planar interface simulations, 2000 molecules were initially randomly placed in a liquid slab that covered half of the simulation box with the end parts of the box left empty. Equilibration time was 300 ps, during which a vapor phase was formed on the both sides of the liquid slab. Data were then collected from 300 ps to 1 ns. As in the cluster simulations, the mole fraction of sulfuric acid was varied from 0.01 to 0.6.

We simulated the protonated sulfuric acid water system at bisulfate mole fractions 0.01–0.10. At the beginning of simulations all the molecules were in the vapor phase. We ran simulations until all the nucleated clusters were coagulated together. A structure analysis was done for the system containing only one cluster having bisulfate ions. We performed only some separate simulations of the planar vapor-liquid interface for the reasons explained below.

Structure analysis

We studied the structures of $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$ systems by analyzing the density profiles. The clusters

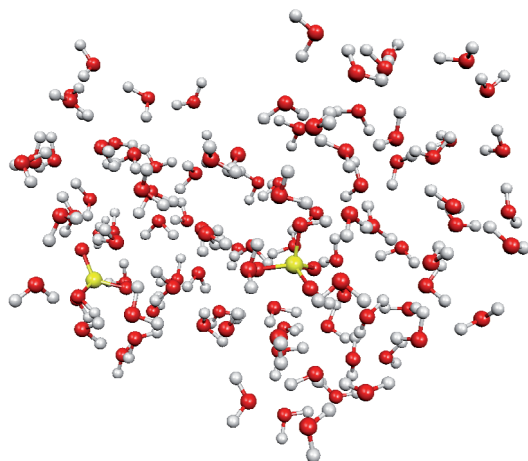


Fig. 1. A cluster of the equilibrated system containing H_2SO_4 and H_2O molecules. Mole fraction of H_2SO_4 is 0.02 and the simulation time is 2 ns. Color coding: white = hydrogen, red = oxygen and yellow = sulfur. The cluster is not spherical all the time.

were sampled for the density profile every 50 fs (every 100 steps). In order to simplify the density profile calculations, we only considered sulfur atom in H_2SO_4 and HSO_4^- molecules and oxygen in H_2O and H_3O^+ molecules. To calculate the density profiles, the systems were divided into thin planar layers (planar interface) of spherical shells (clusters) and data on the number of particles in each layer were collected. We considered the center of the cluster as a positional average of the cluster molecules and we assumed that the cluster is spherical when we calculated the density profile. The density profile of the planar liquid–vapor interface is the average of the densities of both sides of the liquid phase. From the density profiles we calculated the mole fraction of the interfacial surface layer and the central (bulk) part of the condensed phase. We defined the surface as a 0.6-nm-thick layer located around the point where the total density had half the value of the density in the middle of the condensed phase. The thickness of the surface layer is of about the diameter of a sulfuric acid molecule. In the systems containing protonated sulfuric acid, we also calculated the distances between the sulfur atom in HSO_4^- and the oxygen atom in H_3O^+ .

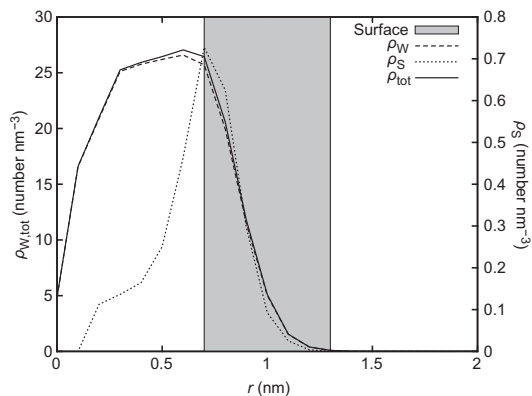


Fig. 2. A density profile of sulfuric acid–water cluster with unprotonated sulfuric acid molecules. The total number of molecules is 100 and the sulfuric acid mole fraction of the system is $x_{\text{tot}} = 0.02$. ρ_W , ρ_S and ρ_{tot} refer to the densities of water and sulfuric acid molecules and the total density of the system, respectively. The gray area in the figure shows the position of the surface layer.

Results and discussion

Sulfuric acid–water system

The binary nucleation of H_2SO_4 and H_2O molecules occurred immediately in the vapor phase during the simulations in systems containing unprotonated sulfuric acid. At all compositions (the total mole fraction of H_2SO_4 (x_{tot}) varying from 0.01 to 0.6) the nucleated clusters coagulated and formed one large cluster during the first 2 ns (Fig. 1). Data were collected for 2 to 4 ns.

We present the radial dependence of sulfuric acid and water densities for two compositions as examples of cluster densities. The total mole fractions of sulfuric acid molecules is 0.02 (Fig. 2) and 0.20 (Fig. 3). For the small clusters, like the represented ones, the surface layer of the cluster is a major part of the volume of the cluster. If the mole fraction of the system is as small as 0.02, the total density of the system is close to the density of water molecules. It is evident that sulfuric acid molecules are located on the cluster surface for $x_{\text{tot}} = 0.02$ (Fig. 2). However, if the mole fraction of sulfuric acid is increased, the sulfuric acid molecules distribute more evenly and concentrate slightly in the center (Fig. 3). Note that the sudden decrease of densities close to the center of

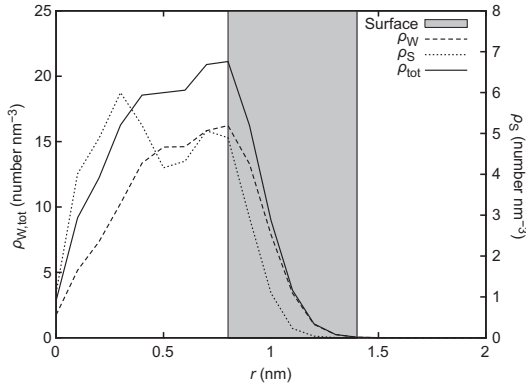


Fig. 3. Same as Fig. 2 but the sulfuric acid mole fraction of the system is $x_{\text{tot}} = 0.20$.

the cluster is an artifact: the density derived from the count of molecules in spherical shell is underestimated near the origin. However, the effect on the mole fraction is very small due to the small volume of the centermost part.

Examples of the density profiles of the planar-liquid interfaces are shown in Figs. 4 and 5. If the sulfuric acid mole fraction is 0.02, density of sulfuric acid peaks at 1.3 nm, indicating slightly increased concentration of H_2SO_4 molecules immediately beneath the topmost surface layer, but otherwise densities are uniform in the liquid phase and no H_2SO_4 molecules appear in the vapor phase (Fig. 4). If we increase the mole fraction of sulfuric acid to 0.2, the water molecules concentrate on the surface (Fig. 5).

The above examples suggest that at low H_2SO_4 mole fractions (Figs. 2 and 3), H_2SO_4 molecules concentrate on the cluster surface. Also there are noticeable differences between the cluster and planar interfaces when $x_{\text{tot}} = 0.02$, whereas at $x_{\text{tot}} = 0.20$ the surfaces are more alike (compare Figs. 2 and 4, and Figs. 3 and 5). Our simulations for the entire range of x_{tot} (0.01–0.6) indicate that the surface mole fraction of the clusters is higher than the total mole fraction if the total mole fraction is smaller than 0.1. In other words, sulfuric acid molecules tend to be on the surface if the total mole fraction is below 0.1. For higher mole fractions, the surface mole fraction is lower than the total mole fraction. For the planar vapor-liquid interface the surface mole fraction is lower than the total mole fraction at all x_{tot} except at 0.01 and 0.02. The

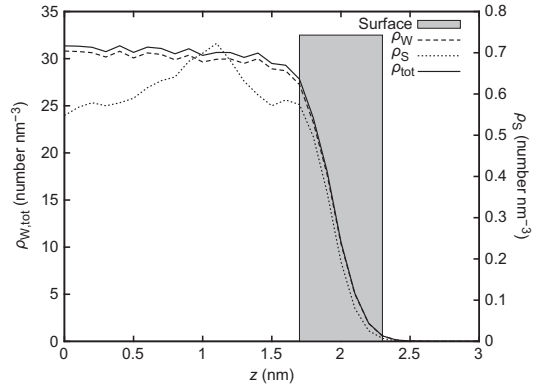


Fig. 4. Density profile of planar a vapor-liquid interface in sulfuric acid-water system with unprotonated sulfuric acid molecules. Total number of molecules is 2000 and the sulfuric acid mole fraction of system is $x_{\text{tot}} = 0.02$. ρ_W and ρ_S and ρ_{tot} refer to densities of water and sulfuric acid molecules and the total density of the system, respectively. The gray area in the figure shows the position of the surface layer.

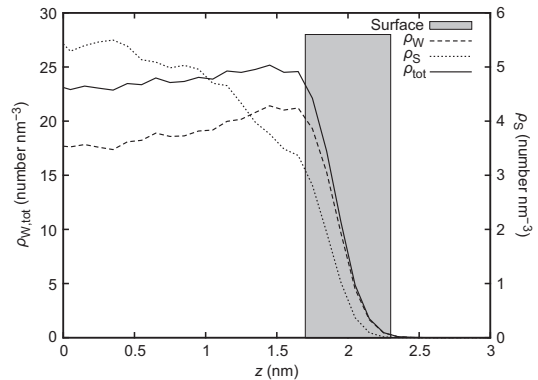


Fig. 5. Same as Fig. 4 but the sulfuric acid mole fraction of the system is $x_{\text{tot}} = 0.20$.

composition data is collected in Fig. 6. Note that due to the limited number of molecules in the clusters, and to some extent even in the liquid layers, the mole fraction at the center (“bulk” mole fraction) is not completely independent of the mole fraction at the surface.

Ion pair-water system

Due to the proton transfer we had three kinds of molecules in our simulation box: H_2O molecules, HSO_4^- ions, and H_3O^+ ions. We aimed to simulate similar clusters and planar vapor-liquid

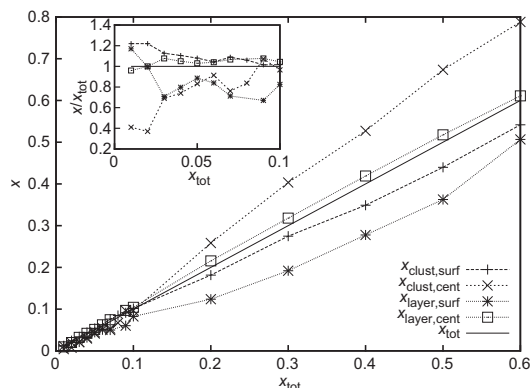


Fig. 6. Sulfuric acid mole fraction of surface and bulk liquid in clusters and planar liquid–vapor interfaces.

interfaces as in the unprotonated $\text{H}_2\text{SO}_4\text{--H}_2\text{O}$ system.

First, we simulated a system of 100 molecules containing 1 to 10 ion pairs, that is the sulfuric acid mole fraction ranged from 0.01 to 0.1. The total simulation time was 12 ns. An extended simulation time was needed, because it took very long before the system reached an equilibrium state where there was only one cluster and few water molecules in the vapor phase. In fact, systems with a sulfuric acid mole fraction higher than 0.03 did not reach an equilibrium state during 12 ns. We made a couple of test calculations at a lower temperature. Even if the clusters nucleated at the lower temperature and coagulated to one large cluster, they broke down if we increased the temperature to 260 K.

A cluster of the equilibrated system after 8 ns of simulation time is shown in Fig. 7.

Second, we simulated a vapor–liquid interface containing 2000 molecules. At all compositions, the molecules formed an unstable condensed phase and the system could not be divided into distinctive vapor and liquid phases. The difficulties in simulating the liquid phase are probably related to the parameters of the interaction potentials. The potential model was originally developed for cluster simulations at low concentrations (Ding *et al.* 2003) and it seems to fail if we have several HSO_4^- ions in the condensed phase. Due to the electric charge of the molecules there are strong repulsive interactions at liquid densities, which destabilize the system.

The cluster density profile for a system with the HSO_4^- mole fraction 0.02 (two HSO_4^- – H_3O^+

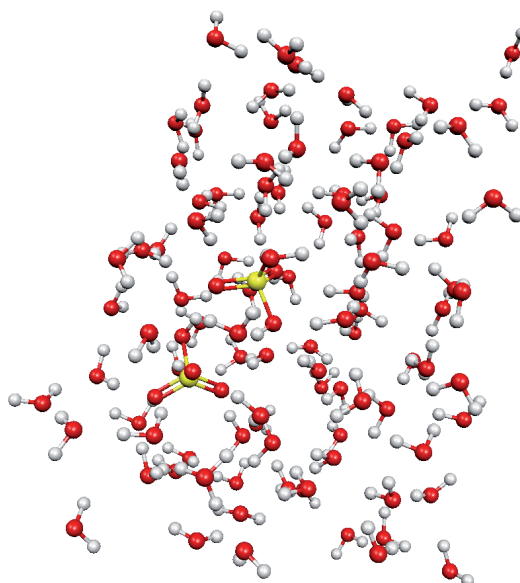


Fig. 7. A cluster of the equilibrated system containing an HSO_4^- – H_3O^+ ion pair and H_2O molecules. The mole fraction of HSO_4^- is 0.02 and the simulation time is 8 ns. Color coding: white = hydrogen, red = oxygen and yellow = sulfur.

ion pairs and 96 water molecules) is shown in Fig. 8. It is evident that HSO_4^- ions tend to be at the center of the cluster and the water molecules are concentrated on the surface. Hydronium ions are distributed rather evenly. The structure is totally different as compared with that presented in Fig. 1: the sulfuric acid molecules tend to lie on the surface, whereas the protonated sulfuric acid molecules (HSO_4^- ions) are in the middle of the cluster. The density profiles at $x_{\text{tot}} = 0.01$ and 0.03 are qualitatively similar to those shown in Fig. 6.

The distance between the sulfur atom in the HSO_4^- ion and oxygen atom in the H_3O^+ ion increase with the increasing number of ion pairs. The average distances between the oxygen atom in the H_3O^+ ion and sulfur atom in the nearest HSO_4^- ion are 0.37 nm, 0.48 nm and 0.57 nm for the clusters with one, two and three ion pairs, respectively. Due to the coulombic interaction, ion pairs are not so tightly bound in a cluster with several ion pairs as in a cluster with one ion pair. The average distances we calculated are shorter than the distance reported by Ding *et al.* (2003b). We used the same interaction potential parameterization, but our system was twice the

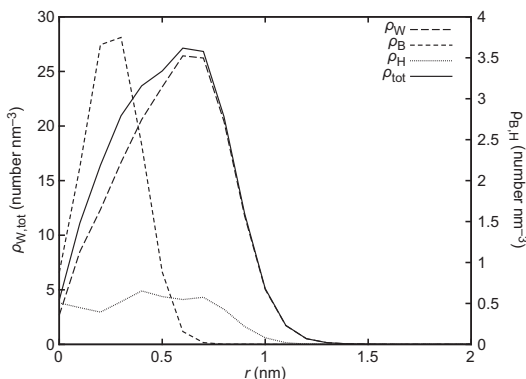


Fig. 8. A density profile of a cluster containing dissociated sulfuric acid molecules in water. The total number of molecules is 100 and sulfuric acid mole fraction of system is $x_{\text{tot}} = 0.02$. ρ_W , ρ_B , ρ_H , and ρ_{tot} refer to densities of water, bisulfate and hydronium molecules and the total density of the system, respectively.

size of theirs and they calculated the distance only for a system containing one ion pair.

Conclusions

The molecular dynamics method was used to study sulfuric acid–water clusters. Due to the protonation of sulfuric acid molecules in presence of water molecules, the system was modeled by two different sets of molecules. We simplified the effect of the protonation by simulating a system containing unprotonated sulfuric acid and water molecules, and a system where all the sulfuric acid molecules were protonated to bisulfate ions and the corresponding number of water molecules reduced to hydronium ions. We studied the structure of clusters in a vapor phase and compared the results with those for the planar vapor–liquid interface.

Our calculations indicate that in the unprotonated system the sulfuric acid molecules in a water cluster lie on the surface if the sulfuric acid mole fraction is smaller than 0.1. On the other hand, sulfuric acid tends to avoid the immediate surface region of a planar interface, and the surface mole fraction is lower than the surface mole fraction of cluster at all compositions. Whether these differences are real or caused by the simple unprotonated model is unclear. If they are real, one can expect considerable differences between

planar interface and clusters in strongly surface-dependent properties, for example surface tension or evaporation rate.

The cluster structure in the systems with protonated sulfuric acid is drastically different from the unprotonated case: bisulfate ions are found to reside inside the cluster and hydronium ions lie on the surface. Unfortunately, we were only able to simulate clusters with low sulfuric acid content. At higher concentrations, a stable cluster was never found and a similar instability afflicted the simulations of planar interface, making the comparison of the cluster and planar surfaces impossible. These problems may be related to the potential model, which was developed on the basis of ab initio simulation data of small clusters. To fully resolve the issues concerning the differences between the cluster and planar interfaces and the stability of the liquid phase, modeling of classic potentials from quantum chemical calculations at higher sulfuric acid compositions and systems sizes is needed along with a more complete investigation of the molecular dynamic simulation methodology.

This study highlights the complications of realistic molecular-level simulations of the atmospherically important water–sulfuric acid system: the conclusions are drastically different if the protonation is neglected or taken into account. The partial second protonation may change the picture even further.

Acknowledgments: This work was supported by the Academy of Finland Centre of Excellence program (project nos. 211483, 211484 and 1118615). We thank the Centre for Scientific Computing for computer time.

References

- Al Natsheh A., Nadykto A.B., Mikkelsen K.V., Fangqun Y. & Ruuskanen J. 2004. Sulfuric acid and sulfuric acid hydrates in the gas phase: a DFT investigation. *J. Phys. Chem. A* 108: 8914–8929
- Berendsen H.J.C., van der Spoel D. & van Drunen R. 1995. GROMACS — a message-passing parallel molecular-dynamics implementation, *Comp. Phys. Comm.* 91: 43–56.
- Bianco R. & Hyenes J.T. 2005. Heterogeneous reactions important in atmospheric ozone depletion: a theoretical perspective. *Acc. Chem. Res.* 39: 159–165.
- Choe Y.-K., Tsuchida E. & Ikeshoji T. 2007. First-principles molecular dynamics study on aqueous sulfuric acid solu-

- tions. *J. Chem. Phys.* 126, 154510.
- Ding C.-G. & Laasonen K. 2004. Partially and fully deprotonated sulfuric acid in $\text{H}_2\text{SO}_4(\text{H}_2\text{O})_n$ ($n = 6-9$). *Chem. Phys. Lett.* 390: 307-313.
- Ding C.-G., Laasonen K. & Laaksonen A. 2003. Two sulfuric acids in small water clusters. *J. Phys. Chem. A* 107: 8648-8658.
- Ding C.-G., Taskila T., Laasonen K. & Laaksonen A. 2003. Reliable potential for small sulfuric acid-water clusters. *Chem. Phys.* 287: 7-19.
- Hoover W.G. 1985. Canonical dynamics: equilibrium phase-space distributions. *Phys. Rev. A* 31: 1695-1697.
- Ianni J.C. & Bandy R.A. 2000. A theoretical study of the hydrates of $(\text{H}_2\text{SO}_4)_2$ and its implications for the formation of new atmospheric particles. *J. Mol. Struct.* 497: 19-37.
- Jungwirth P. & Tobias D.J. 2006. Specific ion at the air/water interface. *Chem. Rev.* 106: 1259-1281.
- Julin J., Napari I. & Vehkamäki H. 2008. Equilibrium sizes and formation energies of small and large Lennard-Jones clusters from molecular dynamics. A consistent comparison to Monte Carlo simulations and density functional theories. *J. Chem. Phys.* 129: 234508.
- Kathmann S.M. & Hale B.N. 2001. Monte Carlo simulations of small sulfuric acid-water clusters. *J. Phys. Chem. B* 105: 11719-11728.
- Kulmala M. 2003. How particles nucleate and grow. *Science* 302: 1000-1001.
- Kusaka I., Wang Z.-G. & Seinfeld J.H. 1998. Binary nucleation of sulfuric acid-water: Monte Carlo simulation. *J. Chem. Phys.* 108: 6829-6848.
- Noppel M., Vehkamäki H. & Kulmala M. 2002. An improved model for hydrate formation in sulfuric acid-water nucleation. *J. Chem. Phys.* 116: 218-228.
- Re S., Osamura Y. & Morokuma K. 1999. Coexistence of neutral and ion-pair clusters of hydrated sulfuric acid $\text{H}_2\text{SO}_4(\text{H}_2\text{O})_n$ ($n = 1-5$) — a molecular orbital study. *J. Chem. Phys.* 103: 3535-3547.
- Sihto S.-L., Kulmala M., Kerminen, V.-M., Dal Maso M., Petäjä T., Riipinen I., Korhonen H., Arnold F., Janson R., Boy M., Laaksonen A. & Lehtinen K.E.J. 2006. Atmospheric sulphuric acid and aerosol formation: implications from atmospheric measurements for nucleation and early growth mechanisms. *Atmos. Chem. Phys.* 6: 4079-4091.
- Spracklen D.V., Carslaw K.S., Kulmala M., Kerminen V.-M., Mann G.W. & Sihto S.-L. 2006. The contribution of boundary layer nucleation events to total particle concentrations on regional and global scales. *Atmos. Chem. Phys.* 6: 5631-5648.
- Wayne R.P. 2000. *Chemistry of atmospheres: an introduction to the chemistry of the atmospheres of earth, the planets and their satellites*. Oxford University Press, Oxford.
- Wedekind J. & Reguera D. 2007. What is the best definition of a liquid cluster at the molecular scale? *J. Chem. Phys.* 127, 154516.
- Yue G.K., Poole L.R., Wang P.-H. & Chiou E.W. 1994. Stratospheric aerosol acidity, density, and refractive index deduced from SAGE II and NMC temperature data. *J. Geophys. Res.* 99: 3727-3738.