Determining the mass accommodation coefficient of dicarboxylic acids using molecular dynamics simulations

Jan Julin[1] and Ilona Riipinen[1]

[1]Department of Applied Environmental Science and Bert Bolin Centre for Climate Research, SE-10691 Stockholm, Stockholm University, Sweden.

Keywords: mass accommodation, fundamental aerosol physics, adipic acid, molecular dynamics.

Presenting author email: jan.julin@itm.su.se

The ability of an atmospheric aerosol particle to uptake gas phase molecules arriving on the aerosol surface will limit the rate of the condensational growth of the particles, and thus control their growth from the nanoscale to climate-relevant sizes. The fraction of the incoming molecules that remain with the condensed phase is given by the mass accommodation coefficient α_m. This coefficient can be defined either as a surface accommodation coefficient, where any molecule that is not directly scattered back to the gas phase is counted as accommodated, or as a bulk accommodation coefficient, where it is necessary for a molecule to cross the surface into the bulk before it is considered accommodated (Kolb *et al.* 2010). Experiments have suggested that the mass accommodation coefficients of various dicarboxylic acids on surfaces consisting of the same species are far from unity (Saleh *et al.* 2012). Technically these experimental values are evaporation coefficients, but the value of the evaporation coefficient is in general assumed to be identical with the condensation, or mass accommodation, coefficient. In this work we have performed molecular dynamics (MD) simulations of the mass accommodation of adipic acid, as well as other dicarboxylic acids, on solid surfaces corresponding to the experimental conditions.

The MD simulations were performed using the GROMACS software (Hess *et al*. 2008), and the OPLS-AA potential (Kaminski *et al.* 2001) was used to model the acid molecules. The simulation setup consists of a slab of 1000 acid molecules, located in the middle of an elongated simulation box, and incoming molecules that are "shot" toward the surface (close-up seen in Fig. 1). The simulation temperature was T=313.15 K, which corresponds to the thermodenuder temperature in the experiments of Saleh *et al.* (2012).

To create the slab, the molecules were initially placed in a cubic simulation box at a higher temperature (i.e. a liquid temperature). After initial equilibration, the system was cooled through simulated annealing to the desired temperature. Finally, following a short constant pressure simulation at the lower temperature, the system was allowed to equilibrate for several nanoseconds. Only after this step the simulation box was elongated in the *z*-direction.

The mass accommodation simulations consisted of creating incoming molecules at both sides of the slab, with the starting configurations for the slab taken at fixed intervals from slab-only simulations. The incoming molecules were added to the box so that the atom closest to the surface was approximately 1.5 nm away from the surface. The molecules were placed at random *x*,*y*-coordinates, with various orientations. Their initial velocities were assigned from the Maxwell-Boltzmann distribution corresponding to the desired temperature, but always pointing at the center of the surface. The mass accommodation coefficient is determined by classifying the fates of the incoming molecules when they arrive at the surface.

Preliminary results for adipic acid show that when treating α_m as a surface accommodation coefficient we have $\alpha_m \approx 1$, that is, we find that the vast majority of incoming molecules do not scatter. On the other hand, the bulk accommodation coefficient determined from the data is going to differ from unity quite noticeably, as the solid state of the slab efficiently hinders the incoming molecules from crossing the surface into the bulk within the simulation time.

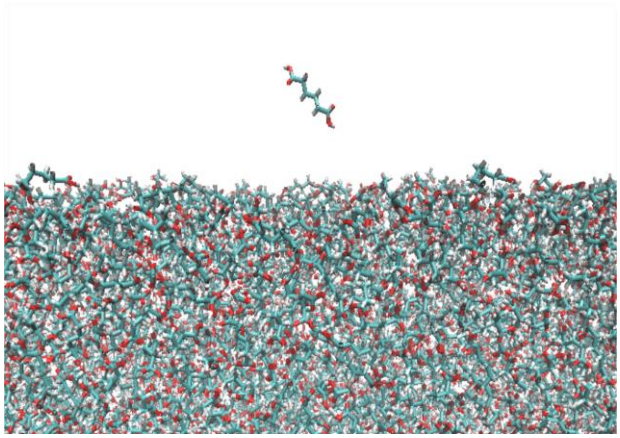

Figure 1. A snapshot of an adipic acid molecule arriving at an adipic acid surface.

This work was supported by the European Research Council grant ATMOGAIN (No. 278277). Computational resources were provided by PDC Center for high performance computing.

Kolb, C. E. *et al.* (2010). *Atm. Chem. Phys.* **10**, 10561-10605.

Saleh, R., Khlystov, A., and Shihadeh, A. (2012). *Aerosol Sci. Tech.* **46**, 22.

Hess, B., Kutzner, C., van der Spoel, D., and Lindahl, E. (2008). *J. Chem. Theory Comp.* **4**, 435-477.

Kaminski, G. A., Friesner, R. A., Tirado-Rives, J., and Jorgensen W. L. (2001). *J. Phys. Chem. B* **105**, 6474.