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# Mass transfer kinetics between gas and particle phase of an aerosol

## Abstract

Mass transfer processes at the interface between the vapor and particle phase of an aerosol are ubiquitous in our environment. This article discusses current experimental challenges and new experimental approaches for kinetic studies of new particle formation from the vapor phase and water accommodation on organic aerosol particles.

## Introduction

An aerosol is a highly dynamic system that reacts very sensitively to changes in environmental conditions, in particular when the aerosol consists of multiple compounds of varying volatility. Among the most important but least understood processes are vapor nucleation, i.e. the very first steps in the formation of new particles from the gas phase, and the accommodation of gas molecules at the surface of an aerosol particle, which governs the condensation and evaporation dynamics of that molecular species. A truly molecular-level understanding of these phenomena, however, is still missing. The research in our group focusses on fundamental laboratory studies of the said phase transitions.

Gas phase nucleation plays a critical role in the formation of new particles in the atmosphere of our and other planets and in various technical processes [1, 2]. Nucleation is exquisitely sensitive to changes in the environmental conditions because it often involves the formation of small, weakly-bound molecular clusters ("nucleating clusters"), which makes experimental studies very challenging. Thus, major experimental issues concern the initiation of nucleation under well-controlled conditions along with the sensitive, and destruction-free detection of nucleating clusters. As a consequence many questions regarding nucleation are still open, such as the influence of the chemical composition of a vapor [3, 4], how nucleation changes as it transitions from a barrier-dominated process to the collisional limit [5], and where the huge discrepancies between experimental results and theoretical predictions arise [6].

The mass transfer of a substance across the gas-particle interface depends on the mass accommodation coefficient  $\alpha_M$ . It indicates the probability of a gas-phase molecule to stick to the surface upon collision. Mass transfer of water is of particular interest because of its widespread abundance and its influence on many processes, from cloud formation to the delivery of pharmaceutical aerosols [7]. Accurate values of  $\alpha_M$  are difficult to determine experimentally, and even for apparently simple cases, such as the accommodation of water vapor on pure water, the values of  $\alpha_M$  vary by orders of magnitude [7-9]. For reliable results, it is important that the studied system stays close to equilibrium during the measurement. This is experimentally challenging to realize since it means that only miniscule mass transfer may occur, necessitating extremely sensitive measurement techniques. The fact that  $\alpha_M$  values are usually required for a range of different temperatures and relative humidities (RH) makes experiments even more demanding.

This article illustrates different aspects of mass transfer for two examples. The first one addresses the role of the volatility of different gas components in the nucleation kinetics. A key result is that highly volatile components can catalyze the nucleation of less volatile components [4]. The second example concerns water accommodation on water-miscible organic aerosol particles. It turns out that the miscibility with water explains both the pronounced inverse temperature-dependence of  $\alpha_M$  and its RH-dependence [7].

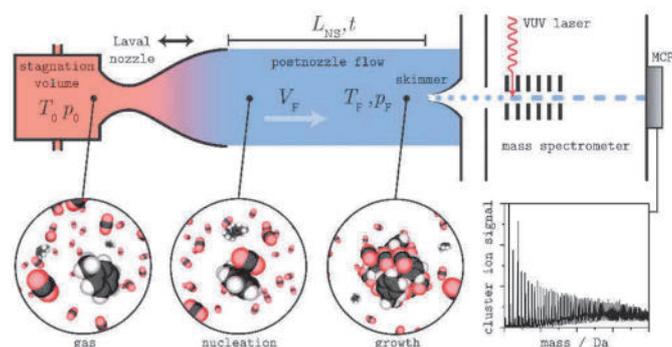
## Gas Phase Nucleation

Nucleation kinetics are very sensitive to the exact conditions, i.e. pressure, temperature and saturation ratio (ratio of the vapor pressure of the condensable substance and its equilibrium vapor pressure). It is thus crucial that nucleation is initiated and observed at constant values of these system parameters. In our experiment (Fig. 1 and [4]), this is achieved by inducing nucleation in the uniform postnozzle flow of a Laval expansion, which acts as a flow reactor without walls where frequent collisions establish equilibrium at constant flow pressure ( $p_F$ ), flow temperature ( $T_F$ ), saturation ratio ( $S$ ) and flow velocity ( $V_F$ ). The molecular clusters that form during nucleation are probed with a mass spectrometer after soft laser ionization, which keeps the cluster largely intact. High ion extraction voltages up to 30kV allow us to detect the cluster ions with high sensitivity. By inducing nucleation under well-defined conditions and detecting the clusters almost destruction-free and with high sensitivity this experimental setup largely overcomes the experimental challenges associated with gas phase nucleation studies.

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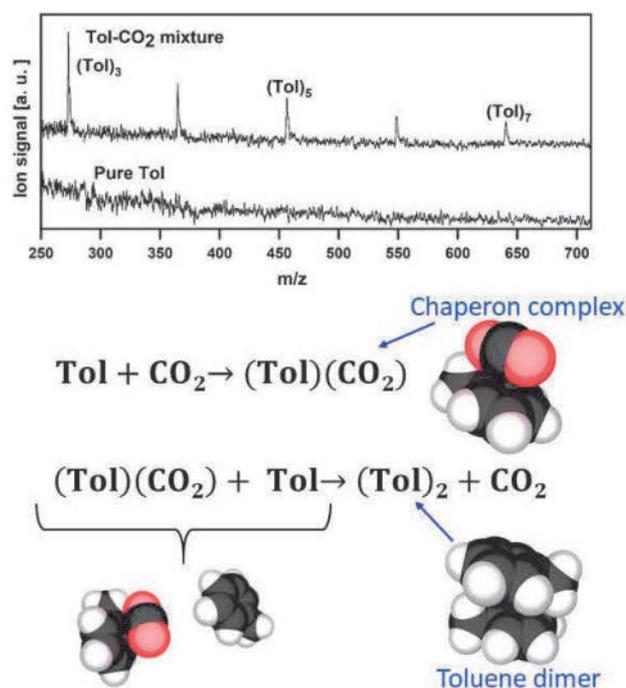
Systematically changing the nozzle-to-skimmer distance  $L_{NS}$  allows for the collection of mass spectra as a function of the nucleation time  $t$ . These mass spectra contain information on a variety of time-dependent cluster properties, such as the mass, the chemical composition and absolute number concentrations of clusters. The analysis of these time-dependent cluster data yields information about onset conditions for nucleation, critical cluster sizes and compositions, nucleation rates and mechanisms.



**Fig. 1:** Vapors of condensable substances along with a carrier gas (rare gases or nitrogen) are supplied to the stagnation volume of the Laval nozzle with stagnation pressure  $p_0$  and stagnation temperature  $T_0$ . Expansion of the gas mixture through the nozzle results in a large temperature drop, leading to supersaturation ( $S > 1$ ) and thus nucleation after the nozzle exit in the first part of the postnozzle flow (constant flow pressure ( $p_F$ ), flow temperature ( $T_F$ ), saturation ratio ( $S$ ) and flow velocity  $V_F$ ). Part of the postnozzle flow enters the home-built time-of-flight mass spectrometer through a skimmer. The clusters are ionized by a home-built low-fluence vacuum ultraviolet (VUV) laser and detected at a microchannel plate detector (MCP), resulting in mass spectra (lower right) as a function of the nucleation time  $t$  (or nozzle-to-skimmer distance  $L_{NS}$ ). Reprinted from Fig. 1 of ref. [4], which is licensed under a Creative Commons Attribution NonCommercial License 4.0 (CC BY-NC). <https://creativecommons.org/licenses/by-nc/4.0/>.

In natural settings, nucleating vapors usually consist of multiple components of different volatility, which all can affect the nucleation behavior. The question is, how? While previous experiments could identify comparatively strongly-bound constituents in nucleating clusters [3], our recent investigation on nucleation in binary vapors was the first experimental study to elucidate the role of weakly-bound constituents in nucleating clusters [4]. Different  $\text{CO}_2$ -containing binary vapors were investigated with toluene (Tol), water, propanol, hexane and butane as the second component. Nucleation in such  $\text{CO}_2$ -containing vapors is, for example, relevant to natural gas separation processes and to cloud formation in the Martian atmosphere. The study shows that the presence of more volatile gaseous components (here  $\text{CO}_2$ ) can enhance the nucleation of less volatile components by the formation of transient, hetero-molecular clusters. The comparison of the mass spectra for a Tol- $\text{CO}_2$  mixture (upper trace in the upper panel in Fig. 2) and for pure Tol gas (lower trace) illustrate this enhancement effect (see ref. [4] for details). While nucleating clusters are clearly visible in the mass spectra of the Tol- $\text{CO}_2$  mixture, pure Tol gas does not nucleate (no nucleating clusters) under the very same conditions. Evidently, the presence of  $\text{CO}_2$  greatly enhances the nucleation of Tol. That only homo-molecular Tol clusters are present but no mixed Tol- $\text{CO}_2$  clusters seems surprising at first sight given that hetero-molecular Tol- $\text{CO}_2$  clusters must be involved in the nucleation mechanism. The reason is the transient character of the mixed clusters. At a  $T_F$  of 55K, their lifetime is simply too short

to be detected – the  $\text{CO}_2$  is lost or evaporates before the clusters are detected. The increasing amounts of mixed clusters observed in experiments at lower  $T_F$  confirm this explanation (see ref. [4]). The temperature acts as a sensitive control for the nucleation mechanism, turning on and off different pathways. At lower temperatures, less excess energy from collisions must be dissipated upon cluster formation while collisional deactivation by the carrier gas might become more effective. Further insight into the nucleation mechanism was obtained by varying the  $\text{CO}_2$ :Tol ratio between  $\sim 10$  and 50 [4]. The increase of the nucleation rate both with increasing  $\text{CO}_2$  and with increasing Tol concentration, together with the above observations provided the basis for the kinetic scheme shown in the lower panel in Fig. 2. The first step postulates a transient Tol- $\text{CO}_2$  dimer, which we refer to as a chaperon complex. This complex precedes the formation of a Tol dimer (second equation), and eventually the formation of larger clusters. The two consecutive reactions in Fig. 2 represent a  $\text{CO}_2$ -catalyzed toluene dimerization. Interestingly, this mechanism is to some extent analogous to the chaperon or radical-complex mechanism for radical recombination [10].

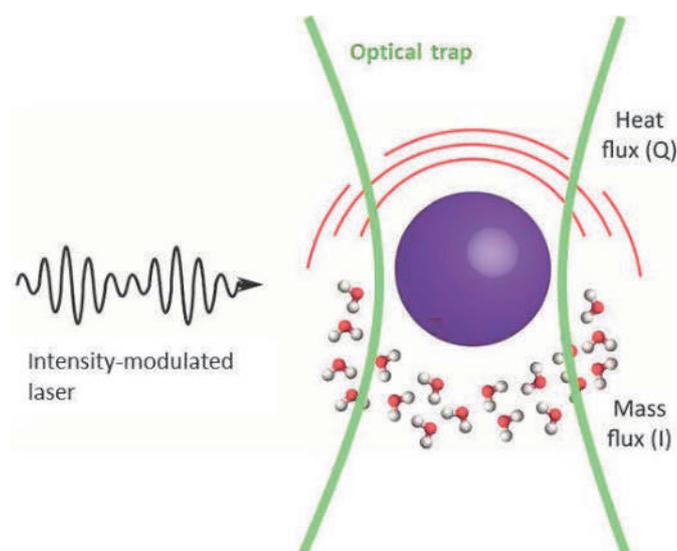


**Fig. 2:** Upper panel: Mass spectra of nucleating clusters for a binary toluene- $\text{CO}_2$  vapor showing the region from the trimer to the heptamer (upper trace) and a pure toluene vapor (lower trace).  $m/z$  is the mass-to-charge ratio. The data have previously been published in ref. [4]. Lower panel: chaperon mechanism proposed for the nucleation of toluene from binary  $\text{CO}_2$ -toluene vapors.

### Mass Accommodation

To minimize experimental biases associated with the determination of mass accommodation coefficients  $\alpha_M$ , we have recently proposed a new technique, which we refer to as Photo-thermal Single-Particle Spectroscopy (PSPS) [7, 11]. It allows us to determine  $\alpha_M$  from simultaneous photoacoustic (PA) and modulated Mie light scattering (MMS) measurements on a single optically-trapped aerosol particle (Fig. 3). The absorption of an intensity-modulated laser induces small temperature oscillations

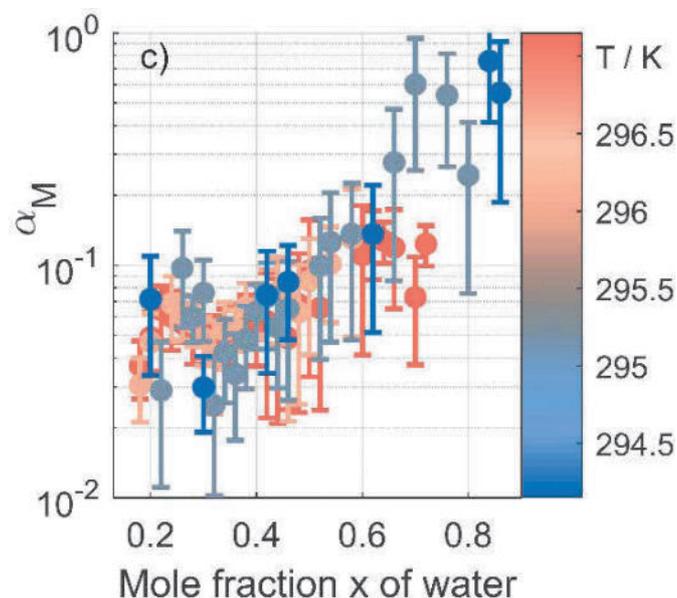
lations in the particle in the sub-Kelvin to Kelvin range, resulting in periodic heat and mass transfer between the particle and the surrounding gas phase. This periodic energy transfer gives rise to photoacoustic signals (photoacoustic amplitude (PAA) and phase (PAP)), which are monitored with a microphone, and to a periodic change in the droplet size, which is monitored by MMS [7, 11]. Through the mass flux contribution, PAA, PAP and MMS depend on  $\alpha_M$ , which can be retrieved from the respective signals by combining Mie theory with a kinetic model that describes heat and mass flux by Fourier's law of thermal conduction and Fick's first law of diffusion, respectively [7, 11]. PSPS has the following advantages for the determination of  $\alpha_M$ : i) The single-droplet approach allows precise control over droplet size and environmental conditions by avoiding ensemble averaging effects. ii) The high sensitivity of PA and MMS measurements allows us to detect minute perturbations of the droplet induced by the modulated laser so that  $\alpha_M$  can be retrieved under close-to-equilibrium conditions. iii) By minimizing potential biases associated with each individual method, the simultaneous determination of  $\alpha_M$  from three independent measurements (PAA, PAP, and MMS) makes the retrieval of  $\alpha_M$  very robust.



**Fig. 3:** Sketch of the processes involved in a PSPS measurement. A single droplet is immobilized in air by an optical trap (green beam). The absorption of light from an intensity-modulated laser (arrow) by the droplet results in heat (Q) and mass (I) flux between droplet and surrounding gas phase and in a change in the droplet size (not shown). See [7, 11, 12] for details. Figure adapted from Fig. 1 of ref. [12] with permission from the PCCP Owner Societies.

Interfacial mass transfer of water between the gas phase and a condensed phase containing organic compounds determines the fate of organic aerosols in the atmosphere as well as during the delivery of pharmaceutical sprays. Despite its importance, comparatively few data exist for  $\alpha_M$  values of such systems, with even fewer information on temperature and concentration dependence (see e.g. Table 1 in ref. [7]). We have recently studied interfacial water transfer for aqueous tetraethylene glycol (TEG) aerosol droplets as a proxy for mass accommodation processes on water miscible organics [7, 11, 12]. The concentration (RH) and temperature dependence (selected data) is summarized in Fig. 4. For water mole fractions,  $x$ , below  $\sim 0.5$ ,  $\alpha_M$  is essentially independent of  $x$  as the surface mainly consists of TEG with negligible water content. For  $x > 0.5$ , the water

content at the surface increases and so does the frequency of collision between gas phase and surface water molecules leading to a pronounced concentration-dependence of  $\alpha_M$ . The systematic increase of  $\alpha_M$  with  $x$  reflects the higher value of  $\alpha_M$  for water on water compared with water on TEG (The relative frequency of collisions between water molecules increases from about every 10<sup>th</sup> collision at  $x=0.5$  to every 3<sup>rd</sup> collision at  $x=0.85$ ). Furthermore, the analysis of the temperature dependence reveals a pronounced decrease of  $\alpha_M$  by about a factor of six with increasing temperature between 296 K and 309 K. This inverse temperature dependence follows an Arrhenius behavior (Fig. 8 in ref. [7], [12]), which can be explained by a barrier that is entropic in nature, likely a result of the loss of unbound degrees of freedom (translations and rotations) upon accommodation of a vapor molecule in the liquid phase.



**Fig. 4:** Mass accommodation coefficient  $\alpha_M$  for aqueous tetraethylene glycol (TEG) aerosol droplets as a function of the water mole fraction  $x$  in the droplet and the temperature  $T$  (color scheme) measured with PSPS. Reprinted from Fig. 9c of ref. [7] © The authors, Creative Commons Licence CC BY-NC-ND 4.0.

## Summary

It turns out that the nucleation enhancement by highly volatile gas components follows a mechanism with analogies to the chaperon radical-complex mechanism for radical recombination. This enhancement effect seems much more general in new particle formation than previously anticipated. The strong temperature and relative humidity dependence of the mass accommodation coefficient for water on water-miscible organic aerosols implies that depending on the actual conditions the water uptake kinetics can change from accommodation-limited to diffusion-limited. In the atmosphere, for example, the specific kinetics influences the cloud activation potential of aerosols.

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## Data

Data sharing is not applicable to this article as no new data were created or analyzed for this article.

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Ruth Signorell received her MSc and PhD degrees in the field of molecular spectroscopy from the Swiss Federal Institute of Technology (ETH Zurich). She started working with aerosol particles and molecular clusters in 2002 as an Assistant Professor at the Georg-August University Goettingen, Germany. In 2005 she accepted a tenured position as Associate Professor at the University of British Columbia, Vancouver (Canada), where she was promoted to Full Professor in 2009. In 2012, she returned to Switzerland to take up a position as a Full Professor for Physical Chemistry in the Department of Chemistry and Applied Biosciences at ETH Zurich.