From air-sea gas exchange to climate change

Transport of greenhouse and trace gases in sea water and across the organic ocean-surface microlayer

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In Short

- Classical-mechanical molecular dynamics simulations of selected greenhouse and trace gases dissolved in pure water and artificial sea water are performed employing the all-atom CHARMM polarizable force field.
- Additionally, we elucidate the role of the organic ocean micro- and nanolayer in reactive ocean-atmosphere gas exchange.
- Both project lines are complemented by ongoing experimental work of collaborators.
- In the long term, results from these molecular-level experimental/theoretical collaborations will help to improve larger-scale continuum models of air-sea gas exchange, which in turn will provide a solid physico-chemical foundation to better represent such processes in global ocean-atmosphere models.

The transport properties of greenhouse and trace gases are very important for environmental modeling, especially in describing accurately the mass fluxes across the water-air interface. In the case of air-sea gas exchange, the mass transfer becomes diffusion-controlled at overall low wind speeds; hence the diffusion coefficients need to be accurately known. Apart from the main greenhouse gases water, carbon dioxide and methane, the transport properties of many other trace gases, including bromomethane and dimethylsulfide, are of interest.

In their seminal work, Jähne et al. showed that the measured value of the diffusion coefficient of a small gas in artificial seawater can vary more than 20% depending on the experimental method [1]. Obviously, such experiments are still very demanding and therefore there is a pressing need for reliable data [2].

Moreover, it has been shown that, in comparison with pure water, the diffusion coefficients of solutes such as helium and methane are reduced in artificial seawater while the diffusion coefficients of other solutes, such as bromomethane, remain the same [3]. Given that the density of artificial seawater is higher than that of pure water and excluding any specific solute-water interaction, it is expected that the diffusion coefficient of any solute will be reduced. Nevertheless, the findings for bromomethane, among others, contradict this simplistic expectation. The underlying mechanisms of this phenomenon are still not well understood. This lack of physico-chemical understanding also becomes apparent when estimating the diffusion coefficient of a solute using semi-empirical correlations [4]. These estimates increasingly deviate from reference data with decreasing solute size as well as increasing temperature and ionic strength of the solvent [1].

Another important ingredient to a complete picture of air-sea gas exchange is the ocean micro- or nanolayer. The microlayer is a thin layer of organic substances covering the ocean surface, ultimately separating the atmosphere from the underlying bulk water by a nanolayer of surface-active molecules with nanometer thickness. This organic layer is widespread and does not arise from human pollution but simply from normal left-overs of life in the oceans. Due to sea spray aerosols generated from breaking waves, organic material is even transported into the atmosphere. The organic layer forms a barrier for air-sea gas exchange, and in case of reactive gases it can even be a place for intense chemical transformations. Using surface-sensitive laser techniques such as sum-frequency-generation (SFG) spectroscopy, the Friedrichs group gains insight into the processes at such organic-covered interfaces. However, these experiments need computational support to achieve full molecular-level interpretations of the observed surface structure and chemistry.

For all these reasons, we have started to perform classical-mechanical molecular dynamics (MD) simulations with the all-atom CHARMM polarizable force field using the NAMD 2.13 software package to get a deeper insight into the diffusion dynamics of small gases in pure water, in sea water, and into the organic layer. Diffusion simulations are performed at five relevant temperatures, from 5 to 30° C, and for two solvents, (i) for pure water and (ii) for aqueous NaCl solution with a salinity of 3.5%, i.e., a typical salinity of natural sea water. The selected temperature range is representative for seasonal changes of the sea-surface temperature. These data will allow us to quantify the effect of salt concentration and temperature on the transport properties of small gases.

In the first stages of our work along this project line, we have established simulation protocols for reliable, quantitative determination of fundamental related quantities, e.g., the self-diffusion of water (Fig. 1).

In further steps, we will focus on four important gases, namely helium, argon, methane and bromomethane. By analyzing sufficiently long MD trajectories, the dynamic properties of small gases, such as the rotational and translational diffusion coefficient, will be accurately computed. Moreover, the dynamical structure of water and

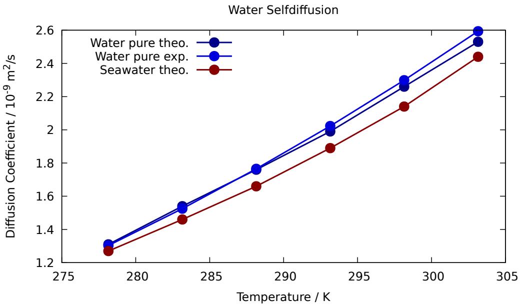

Figure 1: *Experimental and theoretical self-diffusion coefficients of pure and artificial seawater as a function of temperature.*

Na^+/Cl^- ion arrangements close to the dissolved gases will be determined. Insights on the modifications of the hydrogen-bond network and structural order of water in the vicinity of small gases will be obtained. This project line has been motivated by a close collaboration with the research group of Prof. H. Bange at the GEOMAR Helmholtz Centre for Ocean Research in Kiel, within the Cluster of Excellence "Future Ocean". Our findings will directly improve the interpretation of experimental gas exchange data by validating the employed models and simulation methods.

To interpret the SFG experiments on the reactivity of the organic nanolayer, currently performed in the Friedrichs group, our simulations will first provide information on the microlayer structure (cf. Fig. 2), both for different representative organic substances (e.g., oleic acid, petroselinic acid) and for different surface concentrations. Current results indicate good agreement between simulated and preliminary experimental data, as indicated in Fig. 3.

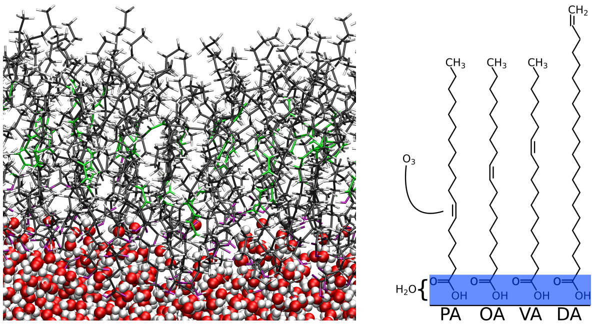

Figure 2: *MD simulation snapshot (left) and schematic drawing (right) of various fatty acids on a water surface.*

As a second step in this project line, we will directly simulate the diffusivity and reactivity of ozone with the carbon-carbon double bonds in the experimentally studied layers of unsaturated fatty acids (cf. right-hand-side of Fig. 2). Preliminary estimates of reaction rates, shown in the table below relative to the rate of oleic acid (OA), indicate good agreement between experimental and theoretical trends:

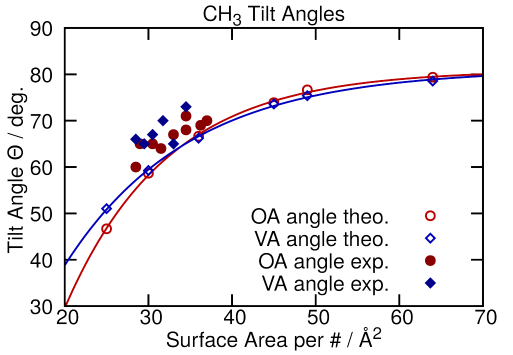

Figure 3: *Comparison of experimental and theoretical tilt angles of the terminal methyl group in nanolayers of oleic and vaccenic acid for varying surface concentrations (i.e., surface areas per molecule).*

fatty acid	PA	OA	VA	DA
theory/exp.	0.7/0.6	1.0/1.0	1.6/1.4	3.5/2.3

Our long-term goal is to integrate these molecular-level simulations of different key aspects into overall, coarse-grained "process models" of air-sea gas exchange, which in turn make further scale upgrades easier, all the way to global-scale climate models. Current models, if at all, contain chemical and physical processes at the molecular level only via highly integrated, empirically fitted parameters. These may work well within a narrow range of situations, however, supporting model development with proper physico-chemical models based on molecular understanding will help to render these large-scale models more robust and reliable for simulating strongly changing scenarios.

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`http://www.phc.uni-kiel.de`

More Information

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Project Partners

Research group of Prof. H. W. Bange at GEOMAR Helmholtz Center for Ocean Research Kiel

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