

## From air-sea gas exchange to climate change

### Diffusion of greenhouse and trace gases in bulk 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 will be performed employing the all-atom CHARMM polarizable force field.
- Additionally, we will elucidate the role of the organic ocean microlayer in ocean-atmosphere gas exchange and reactivity.
- Both project lines will be performed in close collaboration with ongoing experiments on these two topics.
- In the long term, results from these molecular-level experimental/theoretical collaborations will be integrated into 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 in environmental modeling, especially in describing accurately the mass fluxes through 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 such as water, methane and carbon dioxide, the transport properties of trace gases such as bromomethane and dimethylsulfide are also important.

In their seminal work, Jähne et al. showed that the measured value of the diffusion coefficient of a small gas in artificial seawater could vary more than 20% between two experimental methods [1], although determined under the same conditions. Thus, the experimental determination of the diffusion coefficient is still not unambiguous and there is a pressing need for reliable data [2].

Moreover, it has been shown that 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 mechanism of this phenomenon as well as the conditions under which it takes place are still not well understood.

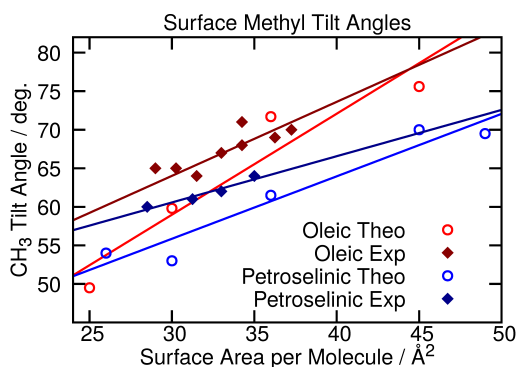
If there are no reliable data available, the diffusion coefficient of a solute can be estimated using semi-empirical correlations [4]. The deviations of these estimates from reference data increase with decreasing solute size as well as with increasing temperature and ionic strength of the solvent [1].

Another important ingredient to a complete picture of air-sea gas exchange is the organic ocean microlayer.[5] This is a thin layer of organic substances prevalent on ocean surfaces everywhere. It does not arise from human pollution but simply as normal left-overs from life in the oceans. Due to sea spray generated from breaking waves, it is even transported onto water-based aerosols. In any case, this organic microlayer obviously forms a barrier to water-atmosphere gas exchange, and in case of reactive gases it can even induce chemical transformations. These roles of the organic microlayer are investigated experimentally in the Friedrichs group, using surface-sensitive laser techniques such as sum-frequency-generation (SFG) spectroscopy. Despite their useful surface sensitivity, these experiments need computational support to achieve full molecular-level interpretations.

For all these reasons, we will perform classical-mechanical molecular dynamics (MD) simulations with the all-atom CHARMM polarizable force field [6,7] using the LAMMPS software package [8] to get a deeper insight into the diffusion dynamics of small gases in pure water and in sea water, and into the organic surface microlayer. Diffusion simulations will be performed at five relevant temperatures, from 5 to 30° C, and will employ two solvents: (i) pure water and (ii) aqueous NaCl solution with a salinity of 3.5%, i.e., with the same salinity as sea water. The selected temperature range is representative of the seasonal changes of the sea-surface temperature. Thus, we will be able to quantify the effect of salt concentration and temperature on the transport properties of small gases. We will focus on five important gases, namely helium, argon, methane, bromomethane and dimethylsulfide. 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 Na<sup>+</sup>/Cl<sup>-</sup> 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 will be carried out in 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 be compared to on-going experiments providing a validation of the employed models and simulation methods.

To interpret the SFG experiments on the organic microlayer in the Friedrichs group, our simulations will first provide information on the microlayer structure, for different representative organic substances (e.g., oleic acid, petroselinic acid) and for different surface concentrations. Preliminary results indicate good agreement between simulated and experimental data, as indicated in Fig. 1.



**Figure 1:** Comparison of experimental and theoretical tilt angles of the terminal methyl group in organic water-surface microlayers of oleic acid and petroselinic acid, respectively. The varying surface areas per fatty-acid molecule correspond to varying surface concentrations.

As second step in this project line, we will simulate the diffusivity and reactivity of ozone, impinging on the organic microlayer from the gas phase and reacting with the carbon-carbon double bonds in these fatty acids. This will provide explanatory aid to the corresponding experimental data that are so far not fully understood.

Our long-term goal is to integrate these molecular-level simulations of different key aspects into an overall, coarse-grained “process modell” of air-sea gas exchange. This will in turn serve as stepping stone to further scale upgrades, in order to ultimately make contact to global-scale climate models. These currently contain chemical and physical processes at the molecular level only via highly integrated, empirically fitted parameters, which can be suspected to work well only within a narrow range of situations. Hence, the upgrading of these models with proper

physico-chemical models based on molecular understanding will serve to render these large-scale and global models more robust when strongly changing scenarios are to be simulated.

#### WWW

<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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