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INVESTIGATING THE CLIMATE-RELEVANT IMPACTS OF CHEMICAL COMPLEXITY IN MARINE AEROSOLS

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PI: Kimberly Prather[1]
Co-PI: Rommie Amaro[1]

[1]University of California, San Diego

EXECUTIVE SUMMARY

Marine atmospheric aerosols make up a significant portion of the planetary aerosol budget but represent one of the largest sources of uncertainty in current climate models. Aerosols impact climate through cloud seeding and multiphase heterochemistry. However, understanding of the structure and morphology of marine aerosols and the resulting impacts on atmospheric processes is extremely limited. Given the difficulty of experimental single-particle analysis techniques and the high complexity of individual particles, computational methods are used to explore how particle size and chemical composition impact climate-relevant physical and chemical properties of marine aerosols. Model sea spray aerosols are generated based on experimentally determined aerosol lipidomic and proteomic information, then simulated using Blue Waters, with the goal of understanding how chemical complexity modulates aerosol dynamics.

RESEARCH CHALLENGE

Marine aerosols impact the climate by interacting with incoming solar radiation, serving as nuclei for cloud formation and providing interfaces for heterogeneous and multiphase atmospheric chemistry. Individual aerosols vary widely in their size, chemical profile, and internal mixing states; however, current single-particle analysis techniques in the laboratory are not able to access the nanosecond to millisecond timescale dynamics within these aerosols, which ultimately guide their climate-relevant properties. These simulations allow the researchers to understand how aerosol chemistry ultimately impacts the dynamics and interactions within aerosols at the microscale, including protein and lipid partitioning, diffusion, and water transport across the interface, allowing the team to make predictions about macroscale aerosol behavior. The variation in lipid, protein, and saccharide (carbohydrates such as simple sugars or polymers) concentration—strongly modulated by the biochemistry at the ocean surface—allows the research team to connect ocean microbiology to aerosol properties. Integrating computational methods with experimental techniques advances the capacity to accurately model marine aerosols, inching scientists closer to unraveling the complexity of marine aerosol chemistry and how it shapes our climate.

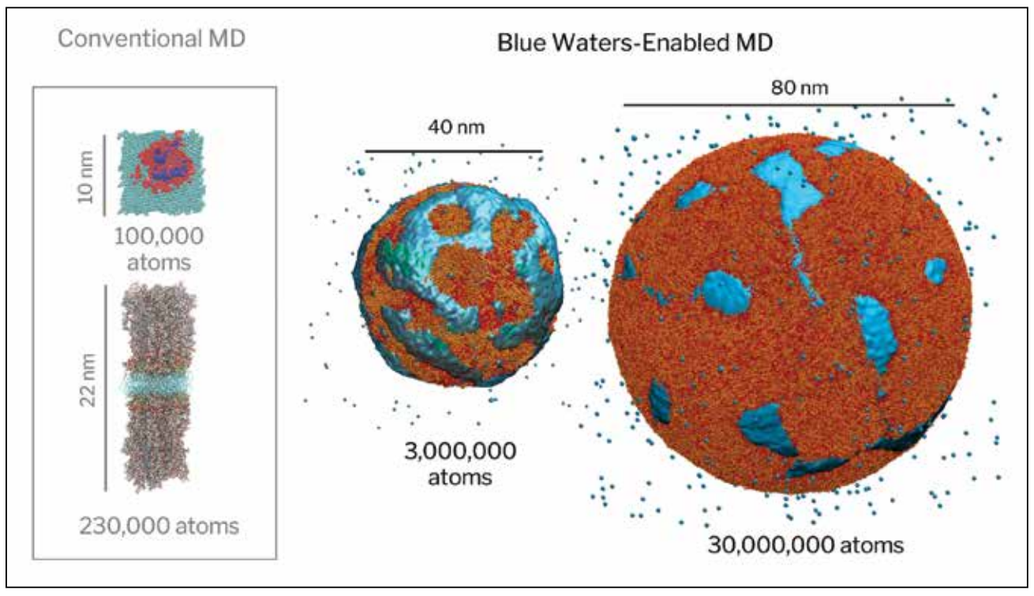

Figure 1: Blue Waters enables the simulation of much larger systems than would be feasible on conventional supercomputers or workstations. Left: Model systems of a protein embedded in a lipid monolayer (top) and a lipopolysaccharide (LPS) bilayer (bottom) with dimensions labeled. Right: 40-nanometer (nm) aerosol particle and 80-nm aerosol particle after approximately 25 nanoseconds of simulation. Lipids are colored orange and water is colored blue.

METHODS & CODES

While marine aerosols have yet to be fully characterized in terms of their chemical composition and structural morphology, and though they exhibit a wide variety of types and variation based on relative humidity, ocean conditions, geographic origin, etc., the team based their aerosol models on the recipe derived by Bertram *et al.* [1] for submicron particles at 70% relative humidity. The researchers' models were constructed with PACKMOL [2] and parameterized using the CHARMM36 [3] force field and TIP3P [4] water. All simulations were carried out with GPU-accelerated NAMD [5].

To investigate the impacts of chemical complexity on nanoaerosol molecular dynamics, the team simulated three aerosol systems and increased the number of components at each step. The three aerosol systems were simulated in triplicate for up to 500 nanoseconds each. System I contains a base level of complexity, and includes four fatty acids at experimentally determined ratios, protein (*Burkholderia cepacia* lipase), and sodium chloride. In system II, the team added lipopolysaccharides from *E. coli* and increased the diversity of cation types to include magnesium, calcium, and potassium in addition to sodium. System III is the most chemically complex and includes a neutral polysaccharide (laminarin) as well as glucose monomers.

RESULTS & IMPACT

Although work only began in early 2019, the team hopes the results will lend a more complete understanding of nascent sea spray aerosol morphology. Microscopy data show that sea spray adopt a morphology where the organics separate to the surface of the particle, leaving a salty aqueous core in the particle center. Preliminary results from this project suggest that at nanometer particle sizes, the organic and aqueous fractions within the particle do not phase separate as expected. Rather, the organic and aqueous components are distributed throughout the particle and are stabilized as an emulsion. If verified, the research team's work will challenge the current understanding of marine aerosol morphology, and could have impacts on how scientists model multiphase atmospheric aerosol chemistry.

WHY BLUE WATERS

The Blue Waters system has enabled the research team to explore molecular dynamics on systems of real physical and chemical relevance to the climate, which includes simulating particle sizes up to 100 nanometers in diameter, containing many millions of atoms, for microsecond timescales. The Blue Waters staff has been integral to the success of this work. Their expertise in GPU-accelerated NAMD has allowed the team to get their simulations up and running quickly, with minimal setbacks.