Researchers find intermolecular forces stabilize clusters, promote aerosol production

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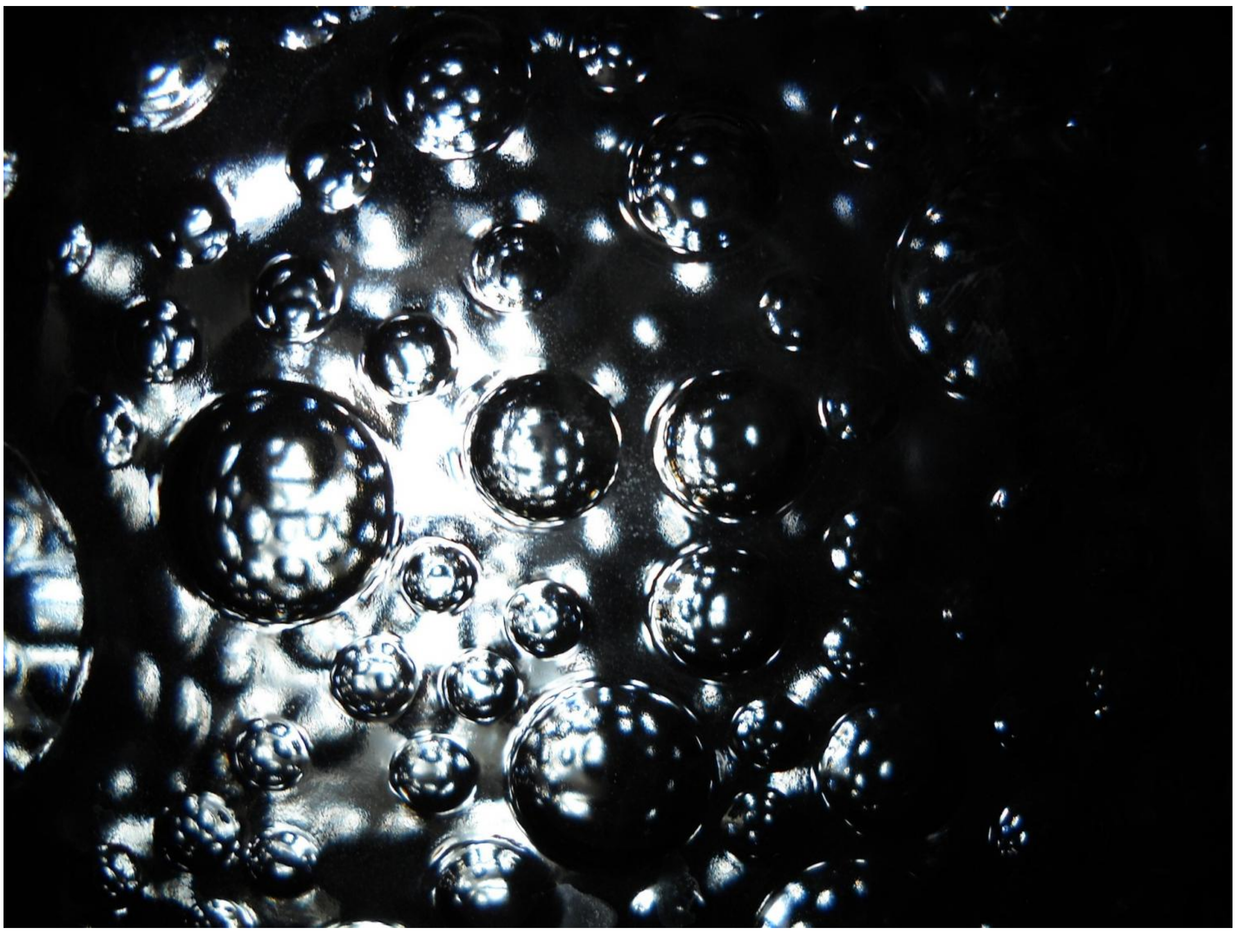

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One enigma that has perplexed scientists is how new particles form in the atmosphere. They know how aerosols can grow into sizes large enough to seed cloud droplets, but those same theories fail to explain how the initial particle core develops. Researchers have chipped away at the nucleation mystery – far enough to identify small clusters of certain types of molecules as the key step. Yet, the underlying mechanism for why some oxidized organic molecules formed clusters with bisulfate over others remained unclear. To improve nucleation predictability in models, researchers need a fundamental understanding of what's happening at the molecular level.

Scientists know gaseous molecules combine to create new particles. At this nucleation stage, the particles, which are less than two nanometers in size, are too small for individual measurement using commercially-available instruments, according to Xue-Bin Wang, a physical chemist at Pacific Northwest National Laboratory. This size limitation is where Wang figured his team could contribute.

In a paper recently published in *Communications Chemistry* titled "Direct Observation of Hierarchic Molecular Interactions Critical to Biogenic Aerosol Formation," Wang described how he and his coauthors studied the mechanics of aerosol nucleation using custom photoelectron spectroscopy and quantum chemical calculations. Based on previous work, they carefully chose their surrogate clusters of one bisulfate molecule and one oxidized organic compound to represent the varying properties of many organic species found in the atmosphere. By examining the chemical structures and physical properties of the clusters in detail, they sought to understand what the critical forces in forming a new particle might be from their basic molecular interactions.

From their work, the researchers discovered an important finding: the functional groups – those specific groups of atoms on a molecule that tend to have the same characteristics regardless of what molecule they are found on – of the organic compound matter.

Atmospheric aerosols can affect the Earth's radiative balance in multiple ways, but they are complex and therefore challenging to model. Having a better understanding of how a new aerosol forms will guide the models and reduce uncertainty in climate change predictions.

Given the small size of these new particles, determining what the driving forces are at the molecular level is essential. Researchers want to know how to determine the likelihood of a specific organic molecule forming a stable cluster with a bisulfate molecule.

"In the atmospheric chemistry field, people normally use the oxidation state or the carbon-to-oxygen ratio to describe it, but that's not sufficient," said Wang. Based on the new findings, "functional groups is the more precise language to describe it."

If the functional groups can indicate how stable a cluster will be, researchers can determine how long it can survive in the air as a cluster and thereby its probability of forming a particle. This information can be paired with the known concentrations of the cluster-forming organic molecules to predict particle numbers for modeling.

If scientists can better understand why new particles form, they can develop new guidelines for models that use aerosol impacts in their estimations. In the early stages, these new, tiny particles don't follow the same growth theories as larger particles do, so researchers need to figure out what rules they do follow. To do so, Wang and his team studied the fundamental chemical parameters on a molecular scale.

Past research in the field and laboratory identified small clusters made of one bisulfate molecule and one or two organic molecules. These studies suggested that the formation of these clusters is the rate-limiting step in new particle nucleation. To determine whether a cluster with one specific organic molecule is favored over a cluster with another, researchers have relied on the properties of the carbon backbone of each molecule—such as the oxidation state of carbon or the ratio of carbon to oxygen atoms. Yet, these parameters cannot predict every case.

Wang's team decided that thoroughly investigating cluster properties, such as their structures, energetics, and thermodynamics, using spectroscopy and theoretical calculations could shed some light. They chose to study a range of oxidized organic molecules derived from α-pinene, one of the most abundant plant, or biogenic, emissions.

The Communications Chemistry paper titled "Direct Observation of Hierarchic Molecular Interactions Critical to Biogenic Aerosol Formation" describes the unique investigation in detail. The process included generating the clusters with electrospray ionization and characterizing them by cryogenic negative ion photoelectron spectroscopy. On the theoretical side, the researchers used quantum chemical calculations and molecular dynamics simulations to quantify how the clusters are stabilized.

The team found that intermolecular forces from the functional groups are what stabilize the clusters. The hydrogen bonds give the embryo clusters a low enough evaporation rate that they remain in the atmosphere long enough to interact with other molecules and grow larger. The team also determined that the functional groups fall into a hierarchy; for example, the carboxylic group has a stronger interaction with the bisulfate molecule than does the hydroxyl group. This fundamental discovery provides a clearer understanding of new particle formation.

Because this work is a fundamental study, the researchers want to verify that their findings hold true in the atmosphere. Given water's abundance in the atmosphere, Wang anticipates adding water molecules to the cluster measurements as one of the next steps. He also expects to collaborate with his fellow leading scientists at the W. R. Wiley Environmental Molecular Sciences Laboratory at PNNL to determine how his team's predictions can be tested in physical experiments. Such confirmations can strengthen the confidence in models that consider functional groups in evaluating which organic molecules are important for new particle formation.

More information: Gao-Lei Hou et al. Direct Observation of Hierarchic Molecular Interactions Critical to Biogenic Aerosol Formation, *Communications Chemistry* (2018). DOI: 10.1038/s42004-018-0038-7

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