NUCLEATION AND GROWTH PROCESSES OF ATMOSPHERIC AEROSOLS AND CLOUDS

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Objective:

To gain enhanced understanding of the rate of formation and growth of new particles and of cloud droplets as a function of pertinent controlling atmospheric variables, thereby permitting accurate representation of these processes in climate models.


Approach:

Aerosol size distributions are shaped by complex nucleation and growth and mixing processes that are difficult to represent in models. A major difficulty arises from the need to accurately represent the evaporation/growth kinetics for each of the billions of discrete cluster sizes in the growth sequence, ranging from molecular clusters to particles of radius of several tenths of a micrometer or greater. A potentially very powerful means of solving this problem may be given by the method of moments (MOM), which tracks the time dependence of just the lower-order radial moments of the size distribution without requiring knowledge of the distribution itself. In setting up this task, we proposed to examine suitability of the MOM as a tool for describing atmospheric aerosol dynamics. As described below, our findings in this project to date lend strong support to this choice.

The lower-order moments of a particle size distribution may also be available from measurement, even in cases where the measurements are too few, or the measurement uncertainty too large, to yield detailed information about the unknown distribution itself. An important example is the retrieval of aerosol size distribution moments from multiwavelength remote sensing of aerosol extinction or scattering. This suggests the possibility of utilizing remote sensing measurements for estimation of aerosol moments, which can then be directly compared with the results of model calculations.

Status: Work on this task is proceeding as planned.

Results:

We have developed a quadrature-based method for description of atmospheric aerosol dynamics (1) and shown it to be highly accurate in evaluating moments of the evolving aerosol size distribution in comparison with moments evaluated from distributions calculated using a sectional bin model. We have also evaluated the accuracy of calculating aerosol optical properties from size distribution moments (2). Specifically, we have shown that the lower-order
moments are sufficient for estimating the physical properties (e.g. surface area, mass loading) and optical properties of the simulated aerosol, whereas the full aerosol size distribution generally contains much more information than is required for most applications. An efficient algorithm for inverting moment sequences to obtain information about the aerosol size distribution has been developed (3) and test calculations have been presented demonstrating the power of method as a tool for simulating coupled nucleation and growth processes in complex flowfields (4).

Near Term Plans:

- Examination of the accuracy of the MOM in a box model description of sulfuric acid nucleation and growth kinetics.
- Informal collaboration with European Community on the AEROCONTRAIL program scheduled to begin Jan. 1996. Some of our codes developed for binary sulfuric acid-water mixtures (5) will be utilized by P. Mirabel and his group in that program.

Task 2. Heteromolecular and heterogeneous nucleation studies.

This task is being carried out in part in collaboration with Howard Reiss at UCLA through a subcontract.

Approach:

It has been recognized in recent years that homogeneous vapor-liquid nucleation phenomena play a central role in many atmospheric processes including new particle formation in marine aerosols and Arctic haze. Largely as a result of the recognized importance of nucleation in the atmosphere, considerable attention has been paid in the literature to the formulation of phenomenological theories, which try to predict nucleation rates quantitatively starting from macroscopic, measurable properties of fluids. However, at the moment it is not clear that any of these theories is overall more successful than the classical nucleation theory. On the other hand, more fundamental molecular-based approaches that aim to describe the statistical mechanical and microscopic properties of nucleating clusters have been developed along with more sophisticated experimental techniques for measurements of nucleation rate. We recently identified scaling properties for the critical nucleus which are in harmony with novel findings from both experimental and theoretical studies, and which will hopefully help in steering the phenomenological efforts in a more productive direction.
Work to date in this task has examined binary nucleation in sulfuric acid-water mixtures and includes a detailed study of the kinetics and relaxation times for this system. Currently, motivated in part by reports of enhanced new particle formation (McMurry and co-workers), we have begun examining the effects of ammonia on the sulfuric acid-water system. Specifically we are setting out to understand the effect of ammonia on the surface tension of the binary system, both through experimental studies (carried out under subcontract to UCLA) and through theoretical investigations.

**Status:** Work on this task is proceeding as planned.

**Results:**

We completed the first fully binary calculation for the homogeneous nucleation rate and time lag in sulfuric acid-water mixtures (5). This result has been compared with results of models which assume water vapor to be in rapid dynamic equilibrium with the sulfuric acid clusters. That assumption is shown to be suitable under atmospheric conditions, but breaks down under conditions of high water supersaturation, such as in cloud chambers. Work carried out under the subcontract to UCLA has clarified the Kohler theory for cloud droplet activation. Specifically, by providing a general analytic representation of the free energy surface, that study has shown how to characterize fluctuations in drop size that occur at the boundary between stable and unstable Kohler regimes. Finally, as noted above, we recently completed a scaling analysis of the critical nucleus that provides a simple, yet remarkably accurate parameterization of the observed discrepancies between classical nucleation theory and experimental nucleation rate measurements, and between classical and molecular-base nucleation theories (9).

**Near Term Plans:**

- Continued investigation of molecular-based approaches to nucleation particularly in regard to the heteromolecular nucleation studies in progress at UCLA.
- Extension of the UCLA collaboration to examination the ternary ammonia-sulfuric acid-water system.
Publications:

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