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151464**Final Technical Report:****NASA Innovative Research Program
(Grant Number NAGW-3054)****Project Title:****ATMOSPHERIC CONDENSATIONAL PROPERTIES OF ULTRAFINE CHAIN
AND FRACTAL AEROSOL PARTICLES**

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Summary of Results

The purpose for the research sponsored by this grant was to lay the foundations for qualitative understanding and quantitative description of the equilibrium vapor pressure of water vapor over the irregularly shaped, carbonaceous particles that are present in the atmosphere (Reference 1). This work apparently was the first systematic treatment of the subject. Research was conducted in two complementary components:

1. Calculations were performed of the equilibrium vapor pressure of water over particles comprised of aggregates of spheres in the 50-200 nm radius range. The purposes of this work were two-fold. First, since no systematic treatment of this subject had previously been conducted, its availability would be directly useful for quantitative treatment for a limited range of atmospheric aerosols. Second, it would provide qualitative indications of the effects of highly irregular particle shape on equilibrium vapor pressure of aggregates comprised of smaller spheres. Reference 5 contains a complete description of these studies.

The first phase of this work extended previous results on the water vapor pressure over a pair of spheres, as well as over a single sphere, to the complex case in which a fixed quantity of H_2SO_4 (representative of an electrolyte) was present on the single sphere or in the interstitial region between the paired spheres. The interfacial curvatures between the surface electrolyte solution and the air was calculated for increasing masses of water and used with tabulated water activity data and modeled surface tensions to calculate the equilibrium vapor pressure of water relative to a planar interface. According to the results of this part of the study, the presence of the electrolyte generally did not enable the sphere to become activated to unlimited condensational growth at supersaturation levels found in clouds and generally contributed little to the overall

condensational growth of single spheres. In contrast for the adhering pair of spheres, the electrolyte contributed in some cases to the continuous growth of the pair due to water condensation below full saturation and in most cases the paired spheres were capable of activation at the modest levels of supersaturation typically found in tropospheric clouds. This phase of the work is described in Reference 7.

The second phase of these calculations was undertaken to facilitate estimation of the equilibrium vapor pressure of water (and total water content in the absence of electrolyte) over aggregates of large numbers of spheres, often termed "fractal aggregates." In aggregates, the critical, elementary units for analyses are three or four adhering spheres which may occupy any possible relative orientation with respect to each other. By assembling these units along with a pair of spheres, any possible shape of aggregate can be constructed. If the equilibrium distributions of water are found for the two-, three-, and four-particle units, then, the overall distribution of water on the aggregate can be treated. These calculations were conducted on the three- and four-unit spheres in a range of relative orientations by use of a code for finding the minimal-energy surface of a liquid in contact with a surface with fixed boundary conditions and the complete results are described in Reference 5, 10, and 11.

2. In the first component of this project, described above and in References 5, 7, 10, and 11, the treatments of all quantities were strictly macroscopic and continuum. This approach is appropriate for spheres larger than 50 nm radius and employs data that can be measured on the laboratory scale, such as the contact angle and surface tension. For aggregate particles comprised of primary spheres that are smaller, these macroscopic descriptions become increasingly questionable with decreasing size of the host substrate for condensate deposition. To develop a picture of the equilibrium vapor pressure of water over aggregates of spheres in the 1 – 50 nm range, the interaction energy of condensate molecule with substrate particle must be amenable to calculation for physical adsorption interactions. The intermolecular van der Waals interaction potential is the appropriate energy for this relatively weak sorption process (i.e. compared with chemisorption). With this potential plus the condensate-condensate potential available, a thermodynamically correct picture of condensate equilibrium with nanostructured aggregates can then be developed.

This project has advanced the calculational methodology for the molecular van der Waals interaction to permit an accurate computation of the energy in the vicinity of, and at the minimum separation for a molecule interacting with a surface. Heretofore, the magnitude of this energy at this critical distance was only qualitatively estimated and its functional form was unavailable. These developments are described in References 2, 3, 6, and 8. In addition, this work was extended to the analytic description of the interaction energy for close approach of two condensed bodies in Reference 4 and applied to describe particle aggregations in Reference 9.

The first application of this new interaction potential to the description of water on the surfaces of 1 to 2 nm radius particles has been made and it showed that the water-substrate attractive energy is distinctly lower for these small particles than it is for a planar substrate. This study is presented in Reference 8.

References: Bibliography of Publications and Technical Papers

In the following listing, published works are given according to their complete literature citations. Papers which have been accepted or are in earlier prepublication stages of preparation are given according to tentative titles and abstracts.

1. Marlow, William H. 1993. Atmospheric condensational properties of ultrafine chain and irregular aerosol particles. *Remote Sensing Reviews* **8**, 255-260.
2. Lu, J. X., W. H. Marlow 1995. Universal non-singular van der Waals potentials. *Physical Review Letters*. **74**, 1724-1727.
3. Lu, J. X., W. H. Marlow 1995. Non-singular van der Waals potentials. *Physical Review A*: **52**, 2141-2154.
4. Lu, J. X., W. H. Marlow, V. Arunachalam 1996. Nonsingular van der Waals potentials for non-conducting condensed bodies. *Journal of Colloid and Interface Science*: **181**, 429 – 442.
5. Xie, Jianyong 1996. *Equilibrium Vapor Pressure of Water over Multiple Aerosol Particles*. Dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, Physics. Texas A&M University. Degree granted December, 1996.
6. Lu, J. X., W. H. Marlow 1997. Nonsingular multipole dispersion forces. *Physics Letters, A* (in press)
7. Xie, Jianyong, William H. Marlow 1997 Water vapor pressure over complex particles, I: Sulfuric acid solution effect. *Aerosol Science and Technology*. (accepted for publication)

Abstract

The equilibrium vapor pressures of water are calculated for two different geometric configurations: a liquid cap formed on a single substrate sphere and a liquid pendular ring formed about the contact point of a pair of adhering, identical spheres. The substrate is a structureless, macroscopic (i.e. radius $R = 50\text{nm}$), relatively hydrophobic sphere. For each configuration, pure water and sulfuric acid solution are used separately as the interface liquid. In addition to the available surface tension measurements of sulfuric acid solution against air, our calculations utilize the tabulated data of activity of water over the sulfuric acid solution and the solution density. The substrate's interfacial tension against air is treated as a parameter in these calculations. Then, by using Young's equation as a constraint in our calculation, we can determine the contact angle of the surface liquid residing on substrate spheres for both configurations. We

apply Kelvin's equation in combination with both water activity of sulfuric acid solution and combining relations (semiquantitative relations describing molecular forces) to perform the calculations in the macroscopic picture. The calculations show, for example, that the equilibrium water vapor pressure over a pendular ring containing relatively dilute sulfuric acid solution (e.g. 0.5%-10%) is always less than the equilibrium vapor pressure over the same configuration with only pure water when both sphere radii are 100 (nm) and contact angle is around 20°. The results also show that if all conditions are the same, except geometric configuration, the pendular ring of condensation has a lower equilibrium vapor pressure than the cap of condensation does. Even more significantly, the graph of equilibrium vapor pressure vs. volume of condensed water for the pendular ring configuration indicates unconstrained condensational growth at subsaturation relative humidity. In contrast, in the cap configuration, condensational growth is usually limited for any subsaturation relative humidity.

8. Fang, J. X., W. H. Marlow, J.X. Lu, R. R. Lucchese, Monte Carlo studies of effects of substrate size on the water structure and water-substrate interaction energy. (submitted for publication with revision in progress, 1997)

Abstract

Heterogeneous systems consisting of water in equilibrium with a planar substrate and with spherical substrates of radii $r = 10, 15, \text{ and } 20 \text{ \AA}$ are studied at temperatures of 200, 240, 270, and 290 K by Monte Carlo simulations. The Single Point Charge (SPC) model, an empirical pair potential, for the water-water interaction and the nonsingular van der Waals potential plus the Born-type repulsive potential for the water-substrate interaction are used to obtain the average water-water potential energy and the average water-substrate interaction energy. Computing efforts are focused on the effect of substrate size on the water-substrate interaction energy and the structure of the surface-associated water. Water-substrate interaction energy is shown to be sensitive to substrate size. The expected layering is found by the simulations for water molecules on the planar substrate, but it is less obvious for water molecules on the spherical substrates. However, there is a clear tendency for the shape of the density profile of water molecules on a spherical substrate to approach that found for water molecules on the planar substrate as the spherical substrate size increases. Monte Carlo simulations show that the substrate size must be taken into account when substrate size is in the range of nanometers.

9. Arunachalam, V., W. H. Marlow, J. X. Lu. Development of a picture of the van der Waals interaction energy between clusters of nanometer-range spherical particles. (to be submitted, 1997)

Abstract

The role of the long-range van der Waals interaction energy in spherical, ultrafine aerosol particle collision rates is well known. However, its effects on the collisions of nanometer spheres with aggregated particles comprised of similarly-sized primary spheres has never been examined. As part of a study of this question, an approach based on Lifshitz theory of the van der Waals interaction is developed to compute the interaction energy between condensed bodies. In the first part of this study, the iterated sum over dipole interactions between pairs of approximately-spherical molecular clusters are compared with the Lifshitz energy and Lifshitz-Hamaker energy for equivalent spheres. The Lifshitz energy is shown to converge to the iterated dipolar energy for the clusters for sufficiently large separations while the energy calculated by using the Lifshitz-Hamaker approach does not converge. Next, the interaction energies between a contacting pair of these molecular clusters and a third cluster in different relative positions are calculated first by coupling all molecules in the three-cluster system and secondly by ignoring the interactions between the molecules of the adhering clusters. The error shown by this omission is calculated to be negligible, and is an indication of the error in computing the long-range interaction energy between a pair of interacting spheres and a third sphere as a simple sum over the Lifshitz energy between individual, condensed matter spheres.

This Lifshitz energy calculation is then combined with the short-separation, non-singular van der Waals energy calculation of Lu, Marlow, and Arunachalam to provide an integrated picture of the van der Waals energy from large separations up to contact.

10. Xie, Jianyong, William H. Marlow. Surface Evolver program and its usage for calculations of cap and pendular ring formation. (to be submitted, 1997)

Abstract

One of the fundamental problems in atmospheric aerosol studies is determination of equilibrium vapor pressures over insoluble aerosol particles. The key to solve this problem is to find the condensational surface's mean curvature, and then use its characteristics in Kelvin's equation, assuming the problems studied are in the continuous regime.

In this study we focus on the same problems dealt by Xie and Marlow (1997) and Orr et al. (1975) by using the Evolver program. The geometries for those problems are, respectively, a cap formed on a single spherical substrate, a pendular ring formed on paired adhering spheres, and a liquid bridge between a sphere and a plane. The Surface Evolver program is an interactive program for the study of surfaces minimizing

some energy subject to constraints, e.g. surface tension and other energies.

From this study we find that the results generated from Evolver yield the same values as showed in Xie's and Orr's articles, and we conclude that Evolver is a powerful and reliable tool in dealing with the problems of condensational growth over aerosol particles, especially in the continuous regime, providing comparable geometrical scales are involved in the simulated structures. It provides us another approach in solving some problems for which conventional analytical methods have limitations.

11. Xie, Jianyong, William H. Marlow. Water vapor pressure over complex particles, II: 3 and 4 adhering spheres. (to be submitted, 1997)

Abstract

Numerous studies have been conducted on soot aggregates. In this study we use the Evolver program to study the equilibrium water vapor pressure over those configurations formed by three or four insoluble spherical particles (the basic units of aggregate particles), and to investigate how the configuration geometry of aerosol particles can affect the capacity of those aerosol particles to serve as initial nuclei for cloud condensation, which usually occurs at relative humidities $< 102\%$.

We investigate ten different kinds of configurations formed by two, three and four substrate spheres because those are the basis of complex aerosol particle configurations. For the same mass aerosol particles, our calculations indicate that geometrical configurations play an important role on condensational growth over aggregate aerosol particles. Formations formed on four substrate spheres are more favorable for condensation than the pendular ring formed by two spheres and other formations by three spheres.