Ion Effects on Water Vapor Nucleation: A Molecular Dynamics Study (Postprint)

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Abstract

This study employs molecular dynamics simulation methods to investigate the effect of ion presence on water vapor nucleation processes. The simulation ensemble has an initial temperature of 600 K; after equilibrium is reached, the water vapor thermal bath is removed, and the carrier gas temperature is calibrated to 200 K to exchange heat with the water vapor, carrying away the latent heat of nucleation released during water vapor nucleation. The results indicate that the presence of ions can facilitate nucleation, but ion concentration has a minor influence on the growth of the largest cluster within the ensemble. According to cluster analysis statistics, when the ensemble contains 20 Na+/Cl- ions, the nucleation rate is approximately 1.01 1028/(cm3 s), which is of the same order of magnitude as the calculated value of 4.89×1028/(cm3 s) from classical nucleation theory.

Full Text

Preamble

Molecular Dynamic Study of the Effect of Ions on Water Vapor Nucleation

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Abstract

Molecular dynamics simulation was employed to explore the mechanism of heterogeneous nucleation of water vapor under the effect of ions. After the system reached equilibrium at an initial temperature of 600 K, the temperature of the carrier gas was rescaled to 200 K, which served as a heat sink to remove the latent heat released during water vapor nucleation. The results show that ions promote the nucleation process in its initial stage, while the ion concentration has minimal effect on the growth of the largest cluster within the system. Based on cluster analysis of an ensemble containing 20 Na /Cl ion pairs, the nucleation rate was determined to be approximately 1.01×10^{2} /($\mathrm{cm}^3\cdot\mathrm{s}$), which is of the same order of magnitude as the value of 4.89×10^{2} /($\mathrm{cm}^3\cdot\mathrm{s}$) predicted by classical nucleation theory.

Keywords: Ions; Heterogeneous nucleation; Cluster; Molecular Dynamics

Introduction

Phase change is a fundamental physical phenomenon widely observed in nature and plays a crucial role in energy utilization and heat transfer enhancement [1-2]. In the atmosphere, water vapor condensation leading to cloud formation occurs when relative humidity reaches supersaturation or when sufficient dust particles are present. With economic development and technological advancement, aerosol particle pollution has attracted increasing attention due to its severe impact on air quality and human health. Atmospheric suspended ions are classified into small and large ions. Small ions consist of several neutral molecules clustered around a charged ion, while large ions form when small particles adsorb onto larger neutral aerosol particles. The concentrations of small and large ions of the same sign vary across marine, rural, and urban environments, with more small ions over oceans and more large ions over cities, exhibiting opposite concentration trends. The concentrations of positive and negative ions over land and sea are similar, though positive ions are slightly more abundant [3].

Winkler et al. [4] experimentally investigated heterogeneous nucleation of organic vapor on small clusters and nanoparticles ranging from 1–24 nm, comparing their results with classical nucleation theory and the Kelvin equation. They found that smaller heterogeneous nuclei more effectively trigger nucleation. Inci et al. [5] studied heterogeneous nucleation by introducing particles of the same size as vapor molecules as heterogeneous nuclei, examining how the interaction strength between nuclei and vapor molecules affects nucleation. Their results indicated that when the interaction is weak, heterogeneous nuclei have minimal influence on the formation free energy of small cluster embryos; as the interaction strength increases, the cluster formation free energy decreases. Zhang et al. [6] employed cluster analysis to examine the time evolution of clusters exceeding different size thresholds, obtaining nucleation rates for three simulation conditions through least-squares fitting to compare the effects of ions with different charge states. Their findings revealed that divalent positive ions generate stronger electric fields than monovalent ions, exerting a greater influence on nucleation. Therefore, while ions significantly affect water vapor nucleation, the microscopic mechanisms underlying the influence of positive/negative ions and ion concentration on water vapor nucleation require further investigation. This study establishes a molecular dynamics simulation model to investigate the microscopic mechanisms and physical processes of ion-influenced water vapor nucleation.

2. Simulation Model and Computational Details

Na and Cl ions were used to represent positive and negative particles for studying their effects on water vapor nucleation. Figure 1 [Figure 1: see original paper] shows a schematic of the water vapor nucleation simulation system with charged ions. Five thousand SPC/E water molecules were uniformly distributed in a simulation box of 29×29×29 nm^3, with 5,000 argon vapor molecules serving as carrier gas (not shown). After system equilibration, the carrier gas temperature was controlled to remove both sensible and latent heat released during water vapor nucleation. For clarity, water molecules are represented as points while Na and Cl ions are shown as enlarged spheres.

Argon-argon interactions were modeled using the classical Lennard-Jones (12-6) potential function. The SPC/E model was adopted for water molecules, with the potential function given by [equation reference]. Due to the small mass of hydrogen atoms, the L-J term in equation (1) calculates only oxygen-oxygen interactions, where   and   represent the length scale parameter and potential well depth for oxygen-oxygen interactions, respectively. The second term computes electrostatic forces between charged atoms, where q and q are the charges on atoms i and j, r is the interatomic distance, and   is the vacuum permittivity. Water-argon interactions were calculated using a modified L-J potential, while water-ion interaction potentials for Na and Cl were taken from literature [7]. Energy and length parameters for interactions with water oxygen atoms were determined using the Lorentz-Berthelot mixing rules. Table 1 provides the potential function parameters and atomic charges.

The simulation employed a time step of 3 fs, a cutoff radius of 1.5 nm, and the PPPM method for long-range electrostatic corrections. Periodic boundary conditions were applied, and the Velocity Verlet algorithm was used to integrate the equations of motion. Initially, a Nose-Hoover thermostat was applied for 300 ps to equilibrate the system at 600 K. The thermostat was then removed, and the carrier gas temperature was rescaled to 200 K. Subsequently, a 2000 ps simulation was performed to analyze nucleation statistics.

3. Results and Discussion

3.1 Thermodynamic Parameters of the Nucleation Process

To investigate the effect of ion concentration on water vapor nucleation, ensembles containing 20, 50, 100, and 200 Na /Cl ion pairs were simulated. Figure 2 [Figure 2: see original paper] presents the evolution of kinetic and potential energies for different ion concentrations. After equilibration, the thermostat was removed and the carrier gas temperature was rescaled to 200 K. Through heat exchange with the carrier gas, the water vapor temperature decreased to the nucleation equilibrium temperature. As shown in Figure 2(a), during the initial nucleation stage, systems with lower ion concentrations exhibited slower nucleation, releasing less latent heat and thus cooling slightly faster. Conversely, systems with higher ion concentrations showed more vigorous nucleation, where the released latent heat could not be promptly removed, resulting in slower temperature decrease. As nucleation progressed, all systems approached equilibrium temperatures of 372–375 K, with minimal influence from ion concentration. Since nucleation is a potential energy reduction process, stronger ion attraction in higher-concentration systems led to lower potential energies.

3.2 Nucleation Process Analysis

The short-range van der Waals forces between Na /Cl ions and water molecules are relatively weak compared to the dominant long-range Coulombic forces. Figure 3 [Figure 3: see original paper] illustrates the dynamic process of water vapor nucleation in an ensemble containing 100 Na /Cl ion pairs, with Figure 4 [Figure 4: see original paper] showing the corresponding cluster size distributions at various times. After 300 ps of equilibration at 600 K, water molecules were uniformly distributed with no stable clusters present. Upon thermostat removal and carrier gas rescaling to 200 K, heat exchange removed sensible heat and lowered the system temperature. Nucleation is a metastable process, and the strong ion-water interactions act as perturbations that trigger nucleation. When the temperature dropped to the nucleation point, water molecules surrounding the ions nucleated with the ions serving as nucleation centers. Since atomic interactions weaken with distance, the influence of charged ions on water molecule nucleation also varies with radial distance. At t = 500 ps, numerous small clusters formed, as shown in Figure 3, with the corresponding size distribution in Figure 4. Unstable small clusters continuously broke apart and reformed, while stable clusters continued growing. By t = 1300 ps, small clusters began coalescing into larger ones, with the largest cluster containing approximately 500 water molecules. At t = 2000 ps, the system reached dynamic equilibrium with several large stable clusters present, the largest containing about 700 water molecules, while monomeric water molecules remained uniformly distributed. Continuing the simulation to 2300 ps showed minimal change in cluster size distribution, confirming that the system had achieved a dynamic balance between nucleation and evaporation.

Figure 5 [Figure 5: see original paper] examines the effect of ion concentration on nucleation by analyzing the time evolution of the largest cluster size under different ion concentrations. During the initial nucleation stage, ions promoted rapid cluster growth, with stepwise increases corresponding to coalescence events where small clusters merged into the largest cluster. As nucleation progressed and the system approached equilibrium, the largest cluster contained approximately 700 water molecules across all ion concentrations, indicating that ion concentration has minimal effect on the final maximum cluster size.

3.3 Nucleation Rate Calculation

The nucleation rate is defined as the number of activated nuclei (stable, growing molecular clusters) produced per unit time per unit volume. Using the ensemble containing 20 Na /Cl ions as an example, the nucleation rate was determined through both classical nucleation theory prediction and cluster distribution statistical analysis. The nucleation system had a saturation ratio of approximately 2.9, and the dynamic equilibrium temperature was about 375 K. At this temperature, the saturated vapor and liquid densities were 6.27×10 g·cm^{3} and 0.9165 g·cm^{3}, respectively, with a reference surface tension of 36.94 N·m^{1}. Since the charged ions were treated as point charges without finite size, the homogeneous nucleation rate formula was applied, yielding a theoretical nucleation rate of 4.89×10^{2} /(cm^{3}·s).

Additionally, the nucleation rate was obtained from cluster analysis based on its definition. Figure 6 [Figure 6: see original paper] shows the evolution of cluster numbers exceeding various threshold sizes (10, 20, 30, 40, and 50 molecules). For a threshold of 10 molecules, the cluster number initially increased rapidly before decreasing, showing unstable behavior. For thresholds greater than 20 molecules, the slopes of cluster number increase were essentially identical, enabling nucleation rate determination from these linear regions. The dashed lines in Figure 6 represent linear fits during the cluster growth stage, yielding a nucleation rate of approximately 1.01×10^{2} /(cm^{3}·s) for the system with 20 Na /Cl ions. This value is consistent with the classical nucleation theory prediction and higher than the homogeneous nucleation rate of 2.8×10^{2} /(cm^{3}·s) reported in literature [8], confirming that ions promote water vapor nucleation. Similar analyses for systems containing 50, 100, and 200 Na /Cl ion pairs yielded nucleation rates of 1.54×10^{2} /(cm^{3}·s), 2.27×10^{2} /(cm^{3}·s), and 4.52×10^{2} /(cm^{3}·s), respectively, showing a nonlinear increase with ion concentration.

Conclusion

This study established a molecular dynamics model for water vapor nucleation in the presence of Na /Cl ions to investigate the effects of ions and ion concentration on the nucleation process. The evolution of temperature and potential energy was analyzed, and nucleation rates were determined through cluster analysis and classical nucleation theory predictions. The results demonstrate that while ions promote nucleation during the initial stage, ion concentration has minimal influence on the maximum cluster size at dynamic equilibrium. For the system containing 20 Na /Cl ions, the nucleation rate determined from cluster analysis was approximately 1.01×10^2 /($\mathrm{cm}^3\cdot\mathrm{s}$), which is higher than that of homogeneous nucleation systems and of the same order of magnitude as the classical nucleation theory prediction of 4.89×10^2 /($\mathrm{cm}^3\cdot\mathrm{s}$).

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Note: Figure translations are in progress. See original paper for figures.