Postprint: Molecular Dynamics Study of Ion Effects on Water Vapor Nucleation

Authors: Song Pink 1, Xu Hongfan 1, Liu Chao 2, Fan Jing1, Chen Qicheng1, Li Yong 1

Date: 2017-11-07T00:00:00+00:00

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 reaching equilibrium, the water vapor heat bath is removed, the carrier gas temperature is set to 200 K, which exchanges heat with the water vapor and carries 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 effect on the growth of the largest cluster within the ensemble. According to cluster analysis statistics, when the ensemble contains 20 Na+/Cl-, the nucleation rate is approximately 1.01´1028/(cm3×s), which is of the same order of magnitude as the classical nucleation theory calculated value of 4.89$×1028/(*cm*3×$s).

Full Text

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

Song Fenhong[1], **Xu Hongfan**[1], **Liu Chao**[2], **Fan Jing**[1], **Chen Qicheng**[1], **Li Yong**[1]
[1]College of Energy and Power Engineering, Northeast Electric Power University, Jilin 132012, China
[2]College of Power Engineering, Chongqing University, Key Laboratory of Low-grade Energy Utilization Technologies and Systems of Ministry of Education, Chongqing 400030, China

Abstract

This paper employs molecular dynamics simulation to investigate the influence of ions on water vapor nucleation. The simulation ensemble begins at an initial temperature of 600 K. After reaching equilibrium, the water vapor heat bath is removed, and the carrier gas temperature is rescaled to 200 K to exchange heat with the water vapor and remove the latent heat released during nucleation. The results demonstrate that the presence of ions promotes nucleation, though ion concentration has minimal effect on the growth of the largest cluster within the ensemble. Based on cluster analysis, the nucleation rate in a system containing 20 Na^+/Cl^- ion pairs is approximately 1.01×10^{28} $cm^{-3}s^{-1}$, which is of the same order of magnitude as the value of 4.89×10^{28} $cm^{-3}s^{-1}$ predicted by classical nucleation theory.

Keywords: Ions; Heterogeneous nucleation; Cluster; Molecular dynamics

Introduction

Phase change is a ubiquitous physical phenomenon in nature that plays a crucial role in energy utilization and heat transfer enhancement. 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, as atmospheric aerosols severely impact air quality and pose risks to 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. Concentrations of similarly charged small and large ions vary across marine, rural, and urban environments—small ions are more abundant over oceans, while large ions dominate over cities, with opposite trends in their concentration variations. Positive and negative ion concentrations differ little between land and sea, though positive ions are slightly more prevalent.

Previous experimental work by Winkler et al. investigated heterogeneous nucleation of organic vapors on small clusters and nanoparticles (1–24 nm), comparing results with classical nucleation theory and Kelvin relations, finding that smaller heterogeneous nuclei more effectively trigger nucleation. Inci et al. introduced particles matching nucleating vapor molecules in size as heterogeneous nuclei, varying the interaction forces between nuclei and vapor molecules to examine their effects. Their results showed that when interactions are weak, heterogeneous nuclei minimally affect the formation energy of small cluster embryos; as interaction strength increases, cluster formation free energy decreases. Zhang et al. employed cluster analysis to examine the time evolution of clusters exceeding different thresholds, obtaining nucleation rates for three simulation conditions via least-squares fitting and comparing the effects of differently charged ions. Their findings indicated that divalent positive ions generate stronger electric fields than monovalent ions, exerting greater influence on nucleation. Thus, ions significantly affect water vapor nucleation, yet the microscopic mechanisms underlying the influence of positive/negative ions and their concentrations require further investigation. This study establishes a molecular dynamics simulation model to explore the microscopic mechanisms and physical processes of ion-influenced water vapor nucleation.

2. Simulation Model and Computational Details

Na^+ and Cl^- ions are used to represent positive and negative particles for studying their effects on water vapor nucleation. Figure 1 illustrates the simulation system for water vapor nucleation in the presence of charged ions. Five thousand SPC/E water molecules are uniformly distributed in a 29\$×29×29*nm*^{3}\$ simulation box, with 5,000 argon vapor molecules serving as carrier gas (not shown). After system equilibration, the carrier gas temperature is controlled to remove both sensible and latent heat released during water vapor nucleation. For clarity, water molecules are depicted as points while Na^+ and Cl^- ions are represented by enlarged spheres.

Argon-argon interactions employ the classical Lennard-Jones (12-6) potential. The SPC/E model is selected for water molecules, with the potential function given by [EQUATION]. Due to the small mass of hydrogen atoms, the L-J term in equation (1) calculates only oxygen-oxygen interactions, where σ and represent the length scale and potential well depth for oxygen-oxygen interactions, respectively. The second term computes electrostatic forces between charged atoms, with q and q being the charges on atoms i and j, r their separation distance, and $_0$ the vacuum permittivity. Water-argon interactions are calculated using a modified L-J potential, while water-ion interaction potentials are taken from literature [7]. Energy and length parameters for interactions with water oxygen atoms are determined via the Lorentz-Berthelot mixing rules. Table 1 lists the potential function parameters and atomic charges.

The simulation uses a 3 fs time step, 1.5 nm cutoff radius, and PPPM method for long-range electrostatic corrections. Periodic boundary conditions and a Velocity Nose-Hoover thermostat are applied. The system is simulated for 300 ps to reach equilibrium at 600 K, after which the thermostat is removed and the carrier gas temperature is rescaled to 200 K. Nucleation is then simulated for 2000 ps for statistical analysis.

3. Results and Discussion

3.1 Thermodynamic Parameters of the Nucleation Process

To examine ion concentration effects, 20, 50, 100, and 200 Na^+/Cl^- ion pairs are introduced into the ensemble. Figure 2 presents the kinetic and potential energy evolution of water vapor for different ion concentrations. After equilibration, the thermostat is removed and the carrier gas temperature is set to 200 K. Under carrier gas cooling, water vapor temperature decreases to the nucleation equilibrium temperature. Figure 2(a) shows that during early nucleation, systems with lower ion concentrations nucleate more slowly, releasing less latent heat and cooling slightly faster. Conversely, higher ion concentration systems exhibit more vigorous nucleation, where released latent heat cannot be promptly removed, resulting in slower temperature decrease. As nucleation progresses, temperatures converge to equilibrium values, with ion concentration having minimal impact on the equilibrium temperature, which stabilizes at 372-375 K. Nucleation is a potential energy reduction process; ionic attraction decreases intermolecular distances, causing systems with higher ion concentrations to exhibit correspondingly lower potential energies.

3.2 Analysis of the Nucleation Process

The short-range van der Waals forces between Na^+/Cl^- ions and water molecules are relatively weak compared to their dominant long-range Coulombic interactions. Figure 3 depicts the dynamic nucleation process with 100 Na^+/Cl^- ion pairs, while Figure 4 shows the corresponding cluster size distribution at various times. After 300 ps of equilibration at 600 K, water molecules are uniformly distributed with no stable clusters. Upon thermostat removal and carrier gas rescaling to 200 K, heat exchange between carrier gas and water vapor removes sensible heat, lowering the system temperature. Nucleation is a metastable process where strong ion-water molecule interactions act as perturbations that trigger nucleation. When temperature drops to the nucleation point, water molecules surrounding ions nucleate 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 separation. At t = 500 ps (Figure 3), numerous small clusters form (Figure 4, t = 500 ps), with unstable clusters breaking apart while stable ones continue growing. By t = 1300 ps, small clusters begin coalescing into larger ones, with the largest cluster containing approximately 500 water molecules. Some small, unstable clusters persist, continuously breaking and reforming as water vapor supersaturation decreases. By t = 2000 ps, nucleation reaches dynamic equilibrium with several large clusters stably existing—the largest containing about 700 water molecules—and monomeric water molecules uniformly distributed. Extending the simulation to 2300 ps yields minimal change in cluster size distribution, confirming that the system has achieved dynamic equilibrium between nucleation and evaporation.

Figure 5 examines the effect of ion concentration on nucleation by analyzing the time evolution of the largest cluster size under different ion concentrations. During early nucleation, ions promote nucleation and accelerate cluster growth; the stepwise increases in the curves represent coalescence events where small clusters merge into larger ones. As nucleation proceeds, small clusters aggregate and the system reaches a new equilibrium state with the largest cluster containing approximately 700 water molecules. At equilibrium, the maximum cluster size is essentially identical across different ion concentrations, indicating minimal influence of ion concentration.

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 system containing 20 $\mathrm{Na}^+/\mathrm{Cl}^-$ ion pairs as an example, nucleation rates are determined via both classical nucleation theory prediction and cluster distribution statistics. The nucleation system has a supersaturation ratio of approximately 2.9. The dynamic equilibrium temperature for ion-mediated water vapor nucleation is about 375 K, at which the saturated vapor and liquid densities are 6.27$×10^{-4}$ $\mathrm{g \cdot cm}^{-3}$ and 0.9165 $\mathrm{g \cdot cm}^{-3}$, respectively, with a reference surface tension of 36.94 $\mathrm{N \cdot m}^{-1}$. Since the charged ions in this study are treated as point charges, the homogeneous nucleation rate formula is applied:

*12hom2exp()cllBGJmkT

This yields a nucleation rate of 4.89$×10^{28}$ $\mathrm{cm}^{-3}\mathrm{s}^{-1}$. Additionally, the nucleation rate can be obtained from cluster analysis based on its definition. Figure 6 shows the evolution of cluster numbers exceeding various threshold sizes (10, 20, 30, 40, 50 molecules) for the system with 20 $\mathrm{Na}^+/\mathrm{Cl}^-$ ion pairs. For a threshold of 10, cluster numbers increase rapidly then decrease unstably. For thresholds exceeding 20, the slopes of cluster number increase are similar, enabling nucleation rate determination from these slopes. The dashed lines represent linear fits during the cluster growth stage, yielding a nucleation rate of approximately 1.01$×10^{28}$ $\mathrm{cm}^{-3}\mathrm{s}^{-1}$ for the 20 $\mathrm{Na}^+/\mathrm{Cl}^-$ ion system. This value is of the same order of magnitude as the classical nucleation theory prediction and higher than the homogeneous nucleation rate of 2.8$×10^{27}$ $\mathrm{cm}^{-3}\mathrm{s}^{-1}$ reported in literature [8], confirming that ions promote water vapor nucleation. Applying the same method to systems with 50, 100, and 200 $\mathrm{Na}^+/\mathrm{Cl}^-$ ion pairs yields nucleation rates of 1.54$×10^{{28}, 2.27×10}{28}, and4.52×10^{28}$ $\mathrm{cm}^{-3}\mathrm{s}^{-1}$, respectively, showing a nonlinear increase with ion concentration.

Conclusion

This study establishes a molecular dynamics model for water vapor nucleation in the presence of $\mathrm{Na}^+/\mathrm{Cl}^-$ ions to investigate the effects of ions and their concentration on nucleation. The analysis of temperature and potential energy evolution reveals that while ions promote nucleation during the initial stage, ion concentration has minimal influence on the size of the largest cluster at dynamic equilibrium. For the system containing 20 $\mathrm{Na}^+/\mathrm{Cl}^-$ ion pairs, cluster analysis yields a nucleation rate of approximately 1.01$×10^{28}$ $\mathrm{cm}^{-3}\mathrm{s}^{-1}$, which exceeds that of homogeneous nucleation and is of the same order of magnitude as the classical nucleation theory prediction of 4.89$×10^{28}$ $\mathrm{cm}^{-3}\mathrm{s}^{-1}$.

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