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COMPUTER SIMULATION OF WATER NUCLEATION IN THE PRESENCE OF SINGLE IONS AND ION PAIRS

A Dissertation

Submitted to the Graduate Faculty of the Louisiana State University and Agricultural and Mechanical College in partial fulfillment of the requirements for the degree of Doctor of Philosophy

in

The Department of Chemistry

by Samuel Keasler B.S. Iowa State University, 2001 May 2010

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Abstract

Atmospheric aerosol particles play an important role in climate and human health. Despite their importance, the mechanisms of their formation are still poorly understood. Ioninduced nucleation may play a role in the process, but details are lacking about how the nucleation rate depends on the size, charge, and number of ions in the cluster. In order to better understand the role that ions might play in new particle formation, we have performed a series of AVUS-HR simulations of the water nucleation in the presence of both single ions and ion pairs. These simulations have shown that the location of the Gibbs free energy minimum on the free energy profile is a key factor controlling the barrier heights for different ions/pairs. When the minimum is located at larger cluster sizes, there is a smaller loss of gas phase entropy between the Gibbs free energy minimum and the critical cluster size (the cluster sizes contributing to the barrier), and the barrier height is usually lower. The location of the Gibbs free energy minimum is generally controlled by the strength of the ion-water interactions, and how quickly they decay with increasing cluster size. However, it is also possible for small differences between two different ionic clusters to persist over a wide range of cluster sizes, adding up to significant differences in the barrier height even when the minima are at similar sizes. We have also found that ion pairs are not as effective at enhancing nucleation as single ions, largely because the long range ion-water interactions are weaker for the ion pair cases, but can still significantly lower the barrier height for nucleation. Furthermore, they may still make a large contribution to atmospheric nucleation due to the much larger concentrations of potential ion-pair forming species compared to single ions.

Chapter 1 - Introduction

Over a century ago, C.T.R. Wilson performed the first experiments to study condensation in the presence of ionizing radiation.¹⁻³ He found that a visible rain or mist of particles could form much more readily in the presence of ions. Following Wilson's discovery, ion-induced nucleation saw immediate use in the development of cloud chambers to study ionizing radiation. Radiation was passed through a chamber containing a vapor sufficiently supersaturated to condense on ions, but not to form unary nuclei. Clusters of visible size would grow on the ions left in the wake of the radiation, creating tracks that could be observed and photographed.⁴⁻⁵

Since these initial experiments, a tremendous amount of research has been devoted to ionic clusters in the gas phase. These clusters can play a crucial role in the atmospheric electrical system.⁶ Furthermore, the study of gas phase clusters can provide information about ionic solvation that can be much more difficult to obtain in complex bulk systems due to statistical averaging. For example, the solvation of ions or charged functional groups is important in many biological processes including protein folding,⁷⁻⁹ DNA condensation,¹⁰⁻¹¹ and protein-ligand docking.¹²⁻¹⁴ Ion-induced nucleation is also important in instrumentation, where Wilson's use of ion-induced nucleation.¹⁵ Furthermore, methods have been developed to use small ion clusters as "nano-calorimeters".¹⁶⁻¹⁷ Ion-induced nucleation also plays a role in methods using ionization to better control nanoparticle synthesis by chemical vapor deposition.¹⁸

Lately, ion-induced nucleation has received renewed attention for its potential importance in atmospheric aerosol formation. Atmospheric aerosols can play a significant role in climate by absorbing and scattering solar radiation, and by serving as condensation nuclei for cloud formation, though the magnitude of these effects is not well characterized.¹⁹⁻²⁴ Furthermore, heterogeneous chemistry on the surface of aerosol particles can dramatically enhance reaction rates compared to the gas phase or the bulk liquid, altering the concentrations of important atmospheric species.²⁵⁻²⁶ There is also a significant body of evidence tying aerosol particles to increased rates of disease and death.²⁷⁻²⁸ The importance of aerosols to climate and human health has led to an aggressive research campaign to better understand the mechanisms of their formation. However, many of the mechanistic details remain poorly understood.

A strong correlation between new particle formation and sulfuric acid concentration has been observed by a number of researchers.²⁹⁻³⁴ Preliminary calculations using the classical nucleation theory suggested that very low sulfuric acid concentrations could lead to significant nucleation even in the presence of undersaturated water.³⁵ More advanced calculations³⁶⁻⁴¹ and laboratory measurements⁴²⁻⁴⁷ have observed a smaller degree of nucleation enhancement, but still agree that sulfuric acid can significantly increase the rate of water nucleation.

Models based on the available data for binary sulfuric acid/water nucleation are unable to accurately predict the amount of new particle formation in the atmosphere, suggesting that other components or mechanisms must be involved.⁴⁸⁻⁴⁹ Several possibilities have been proposed, including the ternary nucleation of water and sulfuric acid with ammonia or amines,⁵⁰⁻⁵⁷ multi-component nucleation involving organic acids,⁵⁸⁻⁶⁰ the activation of neutral clusters containing sulfuric acid,⁶¹ and the enhancement of nucleation by ions formed from sulfuric acid and water.⁶²⁻⁶⁹ The relative importance of these mechanism is still uncertain and in all likelihood varies from one environment to another.

Ions are primarily formed in the atmosphere through the action of galactic cosmic rays, and the decay of radon.⁷⁰⁻⁷¹ The formation of charged new particles has been observed in a

variety of environments⁷²⁻⁷⁶ and in the exhaust of aircraft.⁷⁷⁻⁸⁰ Several studies have suggested a correlation between cosmic rays and global cloud cover, which could be related to ion-induced nucleation, but this remains controversial.⁸¹⁻⁸⁸ Models employing ion-induced nucleation can explain many instances of global new particle formation.⁶²⁻⁶⁹ However, other studies have found that the contribution of ion-induced nucleation is relatively small compared to nucleation on neutral clusters.⁸⁹⁻⁹² In some cases, different authors analyzing the same data have reached different conclusions about the role of ions.⁶³ In order to clarify some of these discrepancies and better understand how ion-induced nucleation might contribute to aerosol formation, a detailed understanding of how the nucleation process if affected by properties such as the number, type, charge, and structure of the ions is required.

A number of ion-induced nucleation experiments have been performed with the goal of answering some of these questions. Shortly after his discovery of ion-induced nucleation, Wilson performed another experiment in which he used an electric field to sweep ions of one charge from the chamber so that the efficiency of positive and negative ions at enhancing nucleation could be compared. He found that negative ions could produce visible drops at a lower supersaturation than positive ions.⁹³

T.H. Laby performed similar experiments using a variety of organic vapors including alcohols and carboxylic acids and found that they all condensed more efficiently on positive ions.⁹⁴ These experiments were further expanded on by Loeb et al. who confirmed the results of both Wilson and Laby, and attempted to develop a theory for predicting the sign preference.⁹⁵⁻⁹⁶ They argued that the sign preference must be due to a permanent dipole on the condensing monomer and showed that molecules lacking a permanent dipole had no appreciable sign preference. They further suggested that the molecules surrounding ions could be held in rigid

crystalline structure and that one charge or the other created a more favorable surface for impinging molecules to adsorb to.

One feature common to all the experiments studying the sign preference is the application of an electric field to separate the positive from the negative ions. Rabeony et al. argued that the nucleation rate depended strongly on the electric field.⁹⁷ By modifying their experimental setup, they were able to eliminate the electric field in the portion of their chamber where the nucleation was taking place and found that in the absence of such a field, no sign preference could be detected. Similar results were obtained by He et al.⁹⁸ However, a later study by Adachi et al. using a flow tube produced conflicting results, observing a sign preference even at zero electric field.⁹⁹

A potential explanation of this discrepancy was put forth by Katz et al., who argued that the dependence of nucleation rate on the electric field strength actually represented a dependence of the number of nucleation *events* on the field strength.¹⁰⁰ The importance of the field was in changing the amount of time that ions spent in the sensitive portion of the instrument. When they applied a correction for these different residence times, they found no dependence on the electric field strength. They obtained no specific results for the sign preference due to difficulties in measuring nucleation rates for the particular positive ions formed in their experiments.

A problem inherent in nearly all of the previous measurements is that they failed to characterize the exact ionic species involved in the nucleation process, making it impossible to determine for certain how the ionic properties affect the nucleation rate. Katz et al. took steps toward resolving this problem by using laser ionization techniques to ionize specific

4

molecules,¹⁰⁰ and Kane et al. extended this approach further by verifying the identity of the ions using mass spectrometry to characterize the exact ionic species formed.¹⁰¹⁻¹⁰³ They also detected a sign preference in the absence of an electric field, but were only able to unambiguously identify the positive ions.

Other ion-induced nucleation experiments have been performed with the purpose of identifying the relative importance of nucleation on neutral and ionic clusters under atmospheric conditions. Mixtures of $H_2O/SO_2/Air$,¹⁰⁴⁻¹⁰⁵ $H_2O/SO_2/Air/NH_3$,¹⁰⁶ and $H_2O/SO_2/Air/NO_2$ ¹⁰⁷ were exposed to ionizing radiation in a flow tube and the size distributions of neutral and ionic clusters were monitored. Under the conditions of these experiments, ion-induced nucleation was found to be the dominant process, though the importance of neutral nucleation increased with increasing concentrations of SO₂, NO₂, and NO₃. It is difficult to draw conclusions from these experiments about the effectiveness of particular ions at enhancing nucleation because it is likely that multiple different ionic species are formed in their experiments. However, the authors found that the total concentrations of positive ions reaching the particle counter was higher than negative ions, but the concentration of large (nucleated) particles containing negative ions was higher, suggesting that the negative ions were more efficient at promoting nucleation.

Clearly, one of the biggest challenges in ion-induced nucleation experiments is the difficulty of identifying the ions involved. An alternative approach is to use mass spectrometry to probe small ionic clusters. Mass spectrometry methods can be used to obtain equilibrium constants and free energies for clustering reactions and with data from multiple temperatures, enthalpies and entropies can be determined as well. This approach has been employed for a wide variety of systems. Halide ions¹⁰⁸⁻¹¹³ and alkali metal cations¹¹⁴⁻¹¹⁵ have frequently been studied as they provide useful model systems to study the effect of the ionic size and the sign of the

charge. Experiments have also been performed for atmospherically relevant polyatomic ions such as NH_4^+ , H_3O^+ , OH^- , and HSO_4^{-} .¹¹⁶⁻¹²⁸ The advantages of using this approach include the ability to accurately calculate free energies for individual clustering steps, and to unambiguously characterize the ionic species involved.

IR spectroscopy has also become a valuable tool for studying ionic clusters. These methods utilize the fact that ion-water bonding and water-water hydrogen bonding shift the water O-H stretching frequency by an amount dependant on the strength of the interaction. This can be used to provide detailed information about the structure of ionic clusters, and is sometimes combined with *ab initio* calculations to help identify the structures responsible for particular spectral features.¹²⁹⁻¹³⁷ These methods have been used to distinguish between energetically driven structures with a large number of ion-water interactions and more extended, entropically favorable structures.

In order to better understand the process of ion-induced nucleation and resolve some of the discrepancies between different results, theoretical methods can be extremely valuable. One of the most widely used is the Kelvin-Thompson theory.¹³⁸⁻¹³⁹ This theory extends the Kelvin equation describing the free energy of cluster formation from a vapor to include the effect of ions. This theory predicts that the free energy depends on the size of the ion and the magnitude of the charge but not on its sign.

$$\Delta G_n = -nk_B T lnS + 4\pi r_n^2 \sigma - \frac{q_X^2}{2} \left(1 - \frac{1}{\epsilon}\right) \left(\frac{1}{r_X} - \frac{1}{r_n}\right)$$
1-1

 ΔG_n is the free energy change to form a cluster with *n* molecules, k_B is the Boltzmann constant, *T* is the temperature, *S* is the supersaturation, defined as the ratio of the actual vapor pressure to the saturated vapor pressure of the nucleating species, σ is the bulk surface tension, q_X is the charge of the ion, ϵ is the bulk dielectric constant, while r_X and r_n are the radius of the ion, and the radius of a droplet containing the ion and *n* molecules of the nucleating species, respectively.

The Kelvin-Thompson theory suffers from all the deficiencies of the Classical Nucleation Theory (CNT)¹⁴⁰⁻¹⁴⁴ such as using bulk properties to describe small clusters,¹⁴⁵⁻¹⁴⁶ and extends this approach further, using the bulk dielectric constant to describe even small ionic clusters, and assuming that the ion is symmetrically solvated even in clusters containing one solvent molecule. As in the case of CNT, the Kelvin-Thompson equation can predict the behavior for large clusters reasonably well, but errors for the small clusters can accumulate and significantly affect the barrier height.

Several other classical theoretical descriptions of ion-induced nucleation have been formulated to improve on the deficiencies of the Kelvin Thompson equation.¹⁴⁷⁻¹⁵¹ However, these theories are at least partially continuum based and may be unable to describe the molecular effects that can be dominant in clusters. Furthermore, these theoretical approaches tend to assume that the ion will reside on the center of the cluster, but that is frequently found not to be the case, particularly for larger negative ions. A more desirable approach is to use a molecular description of the nucleation process that can provide insight into the cluster structures, and how these different structures affect the nucleation rate.

One such approach is to perform *ab initio* calculations for small ionic clusters. This has the advantage of describing the cluster energetics with a very high degree of accuracy and providing detailed structural information. For alkali metal cations and halide ions, extensive *ab intio* calculations have been performed.^{135-136,152-172} These data can be extremely helpful in identifying and characterizing low energy structures and can also be used to predict the IR spectra for each structure, allowing for easier interpretations of experimental spectra averaged over multiple different conformations. This approach has also been used on ions such as NH_4^+ , H_3O^+ , OH^- , and $HSO_4^{-,122-124,173-183}$ which has been extremely helpful in parameterizing atmospheric models and helping to distinguish between likely nucleation pathways.

The main deficiency of both mass spectrometry methods and *ab initio* calculations for studying nucleation is that they are limited to relatively small clusters. Mass spectrometry can only probe clusters formed in sufficiently large concentrations to detect, while the computation expense of *ab intio* calculations dramatically increases as the cluster size increases. The free energy data for larger clusters is particularly important for ion-induced nucleation. Free energy profiles for ion-induced nucleation show the unusual feature of having a minimum at some small cluster size, as depicted in Figure 1-1. The barrier height is measured as the difference in free energy between the minimum and the critical cluster. This means that ions which strongly promote the clustering of the first few water molecules may actually lead to higher free energy barriers if the free energy minimum is strongly stabilized relative to the critical cluster. Without information about how the free energy changes at larger cluster sizes, it is difficult to draw conclusions regarding the free energy barrier and the nucleation rate.

An additional difficulty with *ab initio* methods is that they are generally too expensive to perform a complete sampling of the phase space for each cluster size, and instead focus on the minimum energy configurations only. Kathmann et al. have demonstrated the importance of conformational sampling in ion-induced nucleation, showing that the minimum energy structure is often not the structure with the lowest Helmholtz free energy.¹⁸⁴ Furthermore, IR data suggests that not only are higher energy structures important, but that they may even be dominant at non-zero temperatures.¹³¹

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Figure 1.1 The nucleation free energy profile for pure water at 300K and a vapor density of 2.5×10^{-6} molecules/Å³ is shown in black, while the free energy profile for water at the same conditions clustering around an ion is shown in red.

Molecular simulation represents an attractive alternative that overcomes many of the difficulties encountered by the various types of experimental measurements, as well as *ab initio* calculations. Not only can the exact ionic species involved always be precisely characterized, but there is significant flexibility to develop ionic models that can help answer fundamental physical questions about how individual ionic properties affect the cluster structures and the nucleation free energy barrier. Furthermore, the use of less expensive empirical models allows a complete sampling of the relevant phase space for all the cluster sizes of interest, all the way up to the critical cluster.

Some of the earliest calculations for ion-water clusters using empirical models were performed in the 1960's in an attempt to better understand the results of mass spectrometry experiments.¹⁸⁵⁻¹⁹⁴ As these researchers lacked the powerful computers available today, the calculations were limited to energy minimizations for small clusters. However, they were still able to provide some significant insight. For example, Spears demonstrated that the repulsive portion of the potential played a critical role in determining the separation between the ions and the solvent, modifying the magnitude of all the other interactions.¹⁸⁷⁻¹⁸⁸ Mruzik et al. used *ab initio* results to fit an ion-water force field and obtained free energy data for some small clusters using a Monte Carlo simulation.¹⁹⁵

The first computer simulations attempting to calculate free energy profiles for a reasonably wide range of cluster sizes were based on relatively simplistic models. As early as the 1970's, O'Brien et al. obtained nucleation free energy profiles for Lennard-Jones clusters containing an otherwise identical ion.¹⁹⁶ Kusaka et al. used a density functional approach to describe a system containing an ion in a cluster of dipolar spheres. Based on these results, they predicted a sign preference for negative ions, and described some specific interaction types that could lead to such a preference.¹⁹⁷⁻¹⁹⁸ They later performed a simulation of nucleation enhancement by H_3O^+ using a Grand Canonical Monte Carlo approach.¹⁹⁹

Oh et al. used atom-based force fields and a Monte Carlo method to investigate the sign preference for water and methanol.²⁰⁰ The found that water nucleation was more efficient on negative ions, but positive ions were better enhancers for methanol. They argued that the different sign preferences for water and methanol were due to differences in the relative balance between ion-solvent and solvent-solvent interactions. The ion-solvent interactions were more favorable for the anions, but the solvent-solvent interactions favored the cations. However, the

ion-methanol interactions are significantly weaker than the ion-water interactions and the methanol-methanol contribution dominates in that case.

Brodskaya et al. used molecular dynamics to calculate the work of formation for clusters of varying sizes containing monatomic ions, ²⁰¹ as well as H_3O^+ and OH^- .²⁰² For the monatomic ions, they found a lower work of formation for the negative ions than the positive ions, but little change in the difference between the work of formation for clusters containing positive and negative ions as the cluster size was increased. This suggests that the difference in work of formation may not necessarily mean that there is any difference in the barrier heights. On the contrary, for the H_3O^+/OH^- pair, they also found a lower work of formation for OH⁻ at small cluster size, but that the works of formation crossed at larger size and became lower for the positive ions. They were unable to calculate the chemical potential with their approach, preventing them from comparing directly to nucleation free energy data.

Kathmann et al. have applied Dynamical Nucleation Theory²⁰³⁻²⁰⁴ to study ion-induced nucleation and have argued that no conclusions regarding the sign preference can be drawn in the absence of further information about the chemical composition of the ions involved.²⁰⁵ As an example, they showed that clusters containing anions had lower free energies than clusters containing a small cation may have lower free energies than those with a larger anion.

Despite the significant efforts that have been devoted to studying ion-induced nucleation, a number of important questions remain. The origin of the sign preference is still somewhat unclear. Russell suggested that positive and negative ions might favor different orientations of the interfacial molecules. He assumed that the interfacial structure in neutral clusters was the most favorable and the ion cluster leading to the interfacial structure most similar to that in neutral clusters will have the lowest free energy.²⁰⁶ However, simulations have suggested that the water hydrogen bonds point parallel to the interface in neutral clusters rather than into the clusters, contrary to their assumptions.²⁰⁷⁻²⁰⁸ Oh et al. have suggested that the balance between ion-solvent and solvent-solvent interactions leads to different sign preferences for different substances.²⁰⁰ However, this explanation does not consider the influence of entropic differences between clusters containing positive and negative ions.

For the same size ion, the free energies are lower for anionic clusters, while smaller cations have lower free energies than larger anions.²⁰⁵ However, the picture of how the sign preference depends on the ionic size remains incomplete. In particular, as the incremental free energies for different sizes and charges cross each other with increasing cluster size in some cases, it is important to identify how these size and charge effects on the free energy translate into changes in the barrier heights.

A point that may be extremely important, but has received less attention is the potential role of ion pairs in the nucleation process. Some researchers have argued that most atmospheric nucleation takes place on neutral particles.⁸⁹⁻⁹² However, this does not preclude the possibility of nucleation enhancement by ion pairs. In recent years, a number of studies of ion pairs in water clusters have been performed including salts,²⁰⁹⁻²¹⁵ acids,²¹⁶⁻²²⁵ and bases,²²⁶ but there has been little work on the effect of ions pairs on nucleation. As sulfuric acid have been shown using *ab initio* calculation to dissociate in clusters containing 3-6 water molecules,^{216-218,223-224} an accurate characterization of the nucleation free energy profile for clusters containing 2 (or more) ions could be extremely valuable in understanding and modeling atmospheric nucleation events.

In an attempt to better understand the answers to these questions, we have performed a series of ion-induced nucleation simulations using the AVUS-HR approach. This methodology was developed in our group and has been successfully applied to fairly wide range of single and multi-component nucleation phenomenon. Furthermore, we have extended the AVUS-HR approach to more efficiently study ion pair systems. By performing multiple simulations with the ions fixed at different separations, we were able to avoid the sluggish sampling of this coordinate in large water clusters, and a weighted average of the free energy profiles obtained at each separation can be performed to obtain the complete profile.

Our method will be discussed in chapter 2. Our results for the sign preference in Lennard-Jones ions, the effect of ionic polarizability, and the effect of ion pairs on water nucleation will presented in chapters 3, 4, and 5 respectively. Chapter 6 contains some concluding remarks.

Chapter 2 - Methodology

There are a few different approaches used to simulate nucleating systems. In theory, a straightforward molecular dynamics simulation would be most desirable as this would allow direct access to the nucleation rates, and there are a number of methods for calculating nucleation rates from molecular dynamics simulations.²²⁷ However, the time scales for nucleation in both atmospheric and laboratory systems are generally much longer than those accessible to a molecular dynamics simulation. In order to observe nucleation during the simulation time, extremely high supersaturations are required, limiting the applicability of the results.

Monte Carlo simulation provides an extremely useful alternative. Molecular dynamics simulations calculate time averages for the system properties, which requires that the simulation trajectories correspond to the real time evolution of the system. On the other hand, Monte Carlo simulations are used to calculate ensemble averages, allowing special Monte Carlo moves specifically designed to sample the states/processes of interest, such as cluster formation and evaporation in nucleation.

In addition, while the nucleation rates are not directly accessible in Monte Carlo simulation, the kinetics of the nucleation process are well described by the expression²²⁸

$$J = C * exp[-\beta \Delta G^*]$$
 2-1

Where *J* is the nucleation rate, *C* is a kinetic prefactor, $\beta = 1/k_BT$, and ΔG^* is the height of Gibbs free energy barrier to nucleation. Differences in the exponential term frequently dominate differences in the nucleation rate between two systems, allowing a reasonable comparison of the rates without computing them explicitly. Furthermore, for multi-component systems, the free energy profile as a function of the cluster size and composition can be used to identify the dominant nucleation mechanisms and the distribution of compositions in the critical cluster. The simplest way to calculate the free energy profile from a Monte Carlo simulation would be to use the Metropolis Monte Carlo method²²⁹ to study the distribution of cluster sizes in a supersaturated vapor and determine the free energies using²³⁰

$$\Delta G(N) = -k_B T ln \frac{P(N)}{P(1)}$$
 2-2

Where P(N) and P(1) are the concentrations of the *N*-mer and the monomer, respectively $\Delta G(N)$ is the free energy change to form the *N*-mer, k_B is the gas constant, and *T* is the temperature. However, such a method would suffer from the same difficulties as molecular dynamics simulation. The number of Monte Carlo moves required to form a critical cluster would be computationally intractable at any reasonable set of simulation conditions. Therefore, we have developed a more sophisticated algorithm for performing nucleation simulations called AVUS-HR²³¹ which allows for the efficient sampling of nucleation events. This approach combines several advanced simulation techniques including aggregation volume bias Monte Carlo (AVBMC),²³²⁻²³³ umbrella sampling (US),²³⁴ and histogram reweighting (HR).²³⁵⁻²³⁷

A discussion of the Metropolis algorithm and the reasons for its inadequacy in nucleation simulations will be provided in the next section, followed by descriptions of how the AVBMC, US, and HR techniques are used to overcome these difficulties.

2.1 Metropolis Monte Carlo

Classical computer simulation is generally used to compute integrals of the form²³⁸⁻²³⁹

$$\langle X \rangle = \frac{\int d\mathbf{r}^{N} \exp[-\beta E(\mathbf{r}^{N})] X(\mathbf{r}^{N})}{\int d\mathbf{r}^{N} \exp[-\beta E(\mathbf{r}^{N})]}$$
2-3

Where $\langle X \rangle$ is some observable averaged over all the sets of possible coordinates for the N molecules in the system (\mathbf{r}^N) , and $E(\mathbf{r}^N)$ is the energy in state \mathbf{r}^N and

$$\rho(\mathbf{r}^{N}) = \frac{\exp[-\beta E(\mathbf{r}^{N})]}{\int d\mathbf{r}^{N} \exp[-\beta E(\mathbf{r}^{N})]}$$
2-4

is the probability of observing the system in the configuration r^N . In a conventional numerical integration, the values of the two integrands in equation 2-3 would be calculated at a series of discrete points and used to interpret the value for the integral over the entire range. However, the necessary integrals can be extremely difficult to evaluate numerically.

For the vast majority of the possible r^N , one or more pairs of molecules overlap and the value of the Boltzmann factor $(\exp[-\beta E(r^N)])$ is vanishingly small due to the high repulsion energy. Therefore, the value of the integral is determined by a very small subset of the possible points. This makes the numerical integration extremely inefficient as most of the computational effort is spent evaluating $X(r^N)$ at points that do not contribute to the integral. Furthermore, as the integrals are 3N dimensional, even for a fairly small system, the integrand can be computed for only a small fraction of the possible r^N in a reasonable amount of computer time. Unless a more advanced technique is applied to locate the points where the integrand is non-zero, the calculation will be subject to extremely large errors. Metropolis Monte Carlo²²⁹ represents one method to efficiently locate these states and compute a more accurate value for the integrals.

The system is initially set up in a physically reasonable (no molecular overlap, non-zero Boltzmann factor) configuration and new configurations are generated by slightly perturbing the system. Rather than generating points with equal probability in configuration space and weighting them by their Boltzmann factors, the configurations are generated with a probability proportional to their Boltzmann factors and weighted evenly. The Metropolis algorithm is a method for generating points in configuration space with a probability proportional to their Boltzmann factors. This is done using the following procedure.

- 1) Select a particle at random
- 2) Apply a random displacement to this particle to generate a new configuration
- 3) Determine the change in the energy of the system ΔE due to the displacement
- 4) Accept the new configuration with a probability $min[1, exp[-\beta\Delta E]]$
- 5) Whether the new configuration is accepted or not, compute the value of *X* and add it to the average

If the energy is less than zero, the Boltzmann factor is greater than 1 and the new configuration is always accepted. However, the non-zero probability to accept a new configuration that increases the energy allows the system to properly sample higher energy configurations, not just the minima. Using this method, the sampling of configurations with negligible values of the Boltzmann factor is eliminated and all of the computational effort is focused on the small fraction of the configurations that contribute to the integral.

The validity of this approach can be verified by proving that it obeys the "detailed balance" condition. A Monte Carlo simulation involves the calculation of an ensemble average, or an average over a large number of independent systems taken simultaneously. At any given time, the number of systems in a given state should correspond to the equilibrium probability of observing that state. For a Monte Carlo simulation to meet this requirement, any changes in the configurations must leave the number of systems in a particular state constant. This requires that the flux of systems out of a given configuration be equal to the flux from all other configurations into it. This requirement can be expressed using the following equation.

$$\rho(o)\alpha(o \to n)A(o \to n) = \rho(n)\alpha(n \to o)A(n \to o)$$
2-5

Where *o* and *n* refer to the old and new configurations respectively, $\rho(o)$ and $\rho(n)$ refer to the equilibrium probability for the system to be in state *o* or *n*, respectively, $\alpha(o \rightarrow n)$ and $\alpha(n \rightarrow n)$

o) refer to the probabilities of generating the trial configuration n from a system currently in state o, and vice versa, while $A(o \rightarrow n)$ and $A(n \rightarrow o)$ refer to the probabilities of accepting those trial configurations.

For simulations in the canonical ensemble, the probability of observing a particular configuration is proportional to its Boltzmann factor, $e^{-\beta E}$ where *E* is the potential energy and $\beta = 1/k_B T$, as shown in equation 2-4. Furthermore, in the Metropolis algorithm, the α are random translations (or rotations) and movement in opposite directions is equally likely, giving $\alpha(o \rightarrow n) = \alpha(n \rightarrow o)$. The transition probabilities in equation 2-5 cancel, and we have for the acceptance rates

$$\frac{A(o \to n)}{A(n \to o)} = \exp[-\beta(E_n - E_o)]$$
 2-6

Any set of acceptance rates meeting this criterion will yield the correct equilibrium distribution. The choice made by Metropolis et al. is

$$A(o \to n) = min[1, e^{-\beta(E_n - E_o)}]$$
 2-7

where the probability is equal to 1 if the move decreases the potential energy and equal to the Boltzmann factor for the energy change if the move increases the energy.

This procedure has been widely used since its development and is still incorporated in most Monte Carlo simulations, at least in some capacity. However, nucleation presents a new set of problems requiring the development of more advanced Monte Carlo moves. The AVUS-HR method represents one such approach.

2.2 Aggregation Volume Bias Monte Carlo

Nucleating systems pose a unique set of difficulties for computer simulation. The expression given in equation 2-2 can be evaluated based on the ratio of the partition functions for the vapor and the cluster parts of the system

$$\frac{P(clust)}{P(vap)} = \frac{\int d\mathbf{r}_{clust}^{N} \exp[-\beta E(\mathbf{r}_{clust}^{N})]}{\int d\mathbf{r}_{vap}^{N} \exp[-\beta E(\mathbf{r}_{vap}^{N})]}$$
2-8

To evaluate this expression using Monte Carlo, we simply need to perform the integrations over all the relevant configurations and use some appropriate set of criteria to separate the molecules into the vapor and cluster parts of the system. However, the Metropolis scheme is extremely inefficient for this purpose. This is because the number of states for the vapor part of the system is much larger than the number of states for the cluster, but the Boltzmann factors for the cluster states are much larger, as the molecules are close enough to interact significantly.

This can make calculating the ratio in equation 2-8 extremely difficult. In the vapor phase, a large number of random translational moves are required to locate a clustered configuration. On the other hand, the chance of moving a molecule from the cluster to the vapor phase is very low, because of the loss of favorable interaction energy when a molecule evaporates from a cluster.

The aggregation volume bias Monte Carlo scheme²³²⁻²³³ is used to efficiently hop between the vapor and cluster phases by using an asymmetric transition matrix. The Metropolis scheme uses a symmetric transition matrix which makes the acceptance rates proportional to the equilibrium probabilities only. However, this approach can be easily extended to asymmetric matrices by modifying the acceptance rates. The aggregation volume bias Monte Carlo method employs moves which transfer particles directly from the vapor to the cluster and directly from the cluster to the vapor. The procedure for a cluster formation move in the canonical ensemble is as follows.

- 1) Randomly select a particle i
- 2) Randomly select a target particle $j \neq i$
- Move particle i to a random position inside the bonding volume (a parameter of the simulation) of particle j
- 4) Calculate the energy of particle i in the new configuration
- 5) Accept the move with a probability to be discussed below
- 6) Compute and store the cluster size distribution

The probability of generating a particular trial configuration is given by

$$\alpha(vap \to clust) = \frac{1}{N} \times \frac{1}{(N-1)} \times \frac{1}{V_{in}}$$
 2-9

Where *N* is the number of particles and V_{in} is the bonding volume assigned to the i and j pair. The first term represents the probability of selecting a particular molecule i, the second term is the probability of selecting a particular target molecule j, and the third term gives the probability of selecting a particular position within the bonding volume. The reverse move is performed as follows.

- 1) Randomly select a target molecule j
- 2) Select a random molecule i from within the bonding volume of j
- 3) Transfer molecule i to a random position outside the bonding volume of particle j
- 4) Calculate the energy of i in the new configuration
- 5) Accept the move with a probability to be discussed bleow
- 6) Computer and store the cluster size distribution

In this case, the probability of generating a particular trial configuration is given by

$$\alpha(clust \to vap) = \frac{1}{N} \times \frac{1}{(N_{in} + 1)} \times \frac{1}{V_{out}}$$
 2-10

Where *N* refers to total number of particles, N_{in} refers to the number of molecules in the bonding region of molecule j and V_{out} is equal to the total system volume minus the bonding volume. Using these transition probabilities the detailed balance condition for an insertion move becomes

$$e^{-\beta E_{vap}} \frac{1}{N(N-1)V_{in}} A(vap \to clust) = e^{-\beta E_{clust}} \frac{1}{N(N_{in}+1)V_{out}} A(clust \to vap)$$
2-11

$$\frac{A(vap \to clust)}{A(clust \to vap)} = \frac{(N-1)V_{in}}{(N_{in}+1)V_{out}} e^{-\beta(E_{clust} - E_{vap})}$$
2-12

To satisfy this condition, the acceptance rate for particle insertions is

$$A(vap \rightarrow clust) = \min\left[1, \frac{(N-1)V_{in}}{(N_{in}+1)V_{out}}e^{-\beta(E_{clust}-E_{vap})}\right]$$
2-13

The situation is nearly reversed for the particle deletion moves, except that the deletion is being performed for a molecule with N_{in} neighbors rather than $N_{in} + 1$, giving the acceptance rate

$$A(clust \to vap) = \min\left[1, \frac{N_{in}V_{out}}{(N-1)V_{in}}e^{-\beta(E_{vap}-E_{clust})}\right]$$
2-14

The algorithm enhances the sampling of the nucleation events in two ways. First of all, the chance for two particles to meet and form a cluster is greatly enhanced by the fact that particles are inserted directly into the bonding volume of other particles. In the conventional Metropolis scheme, the probability of a random translation moving a particular particle into the bonding region of another particular particle is related to

$$\alpha(vap \to clust) \propto \frac{1}{N} \times \frac{1}{N-1} \times \frac{V_{in}}{V_{out}}$$
 2-15

Using the AVBMC approach, this becomes

$$\alpha(vap \to clust) \propto \frac{1}{N} \times \frac{1}{N-1}$$
 2-16

This means that the transition probability has been enhanced by a factor of V_{out}/V_{in} which is a significant improvement because $V_{out} \gg V_{in}$. For particle deletions, where the acceptance rates can be extremely low due to the loss of attractive energy, the acceptance rate is enhanced by the same factor.

2.3 Enhancements to Aggregation Volume Bias Monte Carlo

The acceptance rates above were derived for the canonical ensemble, but their extension to other ensembles is straightforward. For example, the AVBMC moves are the same in the isothermal-isobaric ensemble (constant pressure, temperature, and total number of molecules). All that is required is the performance of trial moves to change the system volume. The best choice, due to substantial gains in efficiency, is usually to perform the simulations in the grand canonical ensemble.^{231,240-247} The grand canonical ensemble uses a fixed temperature and volume but allows the number of particles to fluctuate. This is accomplished by coupling the system to a "particle bath" at a specified chemical potential. Nucleating systems readily lend themselves to such an approach.

For most conditions relevant in nucleation simulations, the interactions between the vapor phase molecules and the cluster are relatively small, and the probability of two separate clusters being close enough to interact can also be reasonably neglected. This allows us to explicitly simulate only one single cluster. If the approximation that vapor-cluster and cluster-cluster interactions are negligible is sufficiently accurate (at high temperature and low density), the size distribution for this single cluster is equivalent to the size distribution for the entire system. We then couple this system to a particle bath with a specified chemical potential (which can often be more conveniently expressed as the monomer density) and avoid the need to treat the vapor phase explicitly. In the grand canonical ensemble, the equilibrium probability to observe a state with N particles in the cluster in a configuration denoted by r^N is given by

$$\rho(N, \mathbf{r}^{N}) = \frac{\exp[\beta \mu N] \exp[-\beta E(\mathbf{r}^{N})]}{\sum_{N} \int d\mathbf{r}^{N} \exp[\beta \mu N] \exp[-\beta E(\mathbf{r}^{N})]}$$
2-17

The transition probabilities are slightly different in the grand canonical ensemble. The first step for insertion moves (choosing a vapor phase molecule to be inserted) is no longer necessary because the gas phase particles are not explicitly simulated and it is irrelevant which molecule is selected. The transition probability is now given by

$$\alpha(vap \to clust) = \frac{1}{N} \times \frac{1}{V_{in}}$$
2-18

where N is now the number of particles in the cluster instead of the number of particles in the combined vapor-cluster system. For the reverse move we have

$$\alpha(clust \to vap) = \frac{1}{N+1} \times \frac{1}{N_{in}+1}$$
2-19

Note that the V_{out} term that appeared in the canonical ensemble is not included here. For particle deletions, the probabilities are

$$\alpha(vap \rightarrow clust) = \frac{1}{N-1} \times \frac{1}{V_{in}}$$
 2-20

$$\alpha(clust \to vap) = \frac{1}{N} \times \frac{1}{N_{in}}$$
 2-21

Working out the detailed balance condition using the new probabilities gives

$$A(vap \rightarrow clust) = min\left[1, \frac{e^{\beta\mu} e^{-\beta (E_{clust} - E_{vap})} NV_{in}}{(N+1)(N_{in}+1)}\right]$$
 2-22

$$A(clust \to vap) = min\left[1, \frac{e^{-\beta\mu} e^{-\beta(E_{vap} - E_{clust})} NN_{in}}{(N-1)V_{in}}\right]$$
2-23

In the grand canonical ensemble, as the volume is unspecified, the enhancement factor of V_{out}/V_{in} no longer appears in the acceptance rate for deletions, but this becomes significantly less important when the umbrella sampling technique is used.

There are several other techniques that have been incorporated into the AVBMC approach to make it more efficient, and to extend the range of systems to which it can be applied. One of the most important is the configurational bias Monte Carlo method (CBMC).²⁴⁸⁻²⁵⁰ This approach was developed to allow the insertion of polyatomic molecules into dense fluids. The molecule is grown step-by-step, checking multiple different conformations and orientations to avoid overlap with existing molecules. Furthermore, CBMC focuses the sampling of the internal degrees of freedom on configuration that are reasonably low in energy. This technique increases the acceptance rates for AVBMC swaps, and allows their use for molecules with articulated structures. This is particularly important for longer chain molecules, but can also improve the simulation efficiency for smaller molecules like water by considering multiple different trial orientations of the water molecule to be inserted and selecting a favorable one.

In a similar spirit, a biased selection for particle deletions is also incorporated.²⁴³ The acceptance probability for particle deletions can be low for molecules interacting very favorably with the rest of the cluster. In order to improve the probability of accepting particle deletions, rather than randomly selecting a particle from the bonding region to delete, a particle is selected with a probability

$$P_i^{del} = \frac{e^{\beta E_i}}{\sum_i e^{\beta E_i}}$$
 2-24
where E_i is the interaction energy of particle *i* and the summation in the denominator is over all the molecules in the bonding region of the target molecule. Using this scheme, the transition probability for a particle insertion is unchanged, but for the reverse move

$$\alpha(clust \to vap) = \frac{1}{N+1} \times \frac{P_i^{del}}{\sum_j e^{\beta E_j} + P_i^{del}}$$
2-25

where the summation is over all the molecules in the bonding region of the target molecule except for particle *i*. Similarly, for particle deletions, the forward transition probability is now

$$\alpha(clust \to vap) = \frac{1}{N} \times \frac{\sum_{i} e^{\beta E_{i}}}{P_{i}^{del}}$$
 2-26

which makes the acceptance rates

$$A(vap \to clust) = min\left[1, \frac{e^{\beta\mu} e^{-\beta (E_{clust} - E_{vap})} NV_{in} P_i^{del}}{(N+1)\left(\sum_j e^{\beta E_j} + P_i^{del}\right)}\right]$$
2-27

$$A(clust \to vap) = min\left[1, \frac{e^{-\beta\mu} e^{-\beta(E_{vap} - E_{clust})} N \sum_{i} e^{\beta E_{i}}}{(N-1)V_{in} P_{i}^{del}}\right]$$
2-28

2.4 Umbrella Sampling

AVBMC allows us to circumvent one of the biggest sampling problems in nucleating systems, but by itself is insufficient. The goal of AVBMC is to increase the frequency of cluster growth and destruction events. However, the sampling of clusters near the critical size remains a significant problem. As seen in Figure 1-1, the barrier height for water nucleation at the specified conditions is more than $60k_BT$. This means that the monomer will be sampled on the order of e^{60} times for every time the critical cluster is sampled. A simulation sufficiently long to sample the critical cluster enough to obtain good statistic could not be completed, even on a supercomputer. To alleviate this problem, we apply the umbrella sampling technique.²³⁴

Umbrella sampling involves simulating a biased distribution of states in such a way that the bias can be subsequently removed during the data analysis. In the grand canonical ensemble, the probability of observing a particular state described by the number of particles N and their configuration \mathbf{r}^N in the biased distribution is

$$\rho(N, \mathbf{r}^{N}) = \exp[\beta \mu N] \exp[-\beta E(N, \mathbf{r}^{N}] W(N)$$
 2-29

where W(N) is a biasing potential that is a function of the cluster size N. The acceptance rates for AVBMC swap moves become

$$A(vap \rightarrow clust) = min\left[1, \frac{e^{\beta\mu} e^{-\beta(E_{clust} - E_{vap})} NV_{in}}{(N+1)(N_{in}+1)} \times \frac{W(N+1)}{W(N)}\right]$$
2-30

$$A(clust \to vap) = min\left[1, \frac{e^{-\beta\mu} e^{-\beta(E_{vap} - E_{clust})} NN_{in}}{(N-1)V_{in}} \times \frac{W(N-1)}{W(N)}\right]$$
2-31

Using this sampling scheme, we compute the concentration (probability) of clusters of size N in the biased distribution. The concentration in the unbiased distribution is now given by

$$P(N)_{unbiased} = \frac{P(N)_{biased}}{W(N)}$$
 2-32

In choosing a weighting function, our objective is to obtain a statistically precise estimate of the $P(N)_{biased}$ in the least possible amount of simulation time. One reasonable criteria to obtain good statistics is to have an equal probability to observe each cluster size N, which provides the maximum possible sampling of each size for a given simulation length. One choice of weighting function that satisfies this criterion is

$$W(N) = \frac{1}{P(N)_{unbiased}}$$
2-33

This gives an equal concentration for every cluster size N in the biased distribution. With this choice of the biasing potential, the free energy of formation for a cluster of size N is given by

$$\Delta G_i = -k_B \operatorname{Tln} W(N) - k_B T \ln \left[\frac{P(N)}{P(1)}\right]$$
 2-34

Unfortunately, this choice generates a new problem, as the unbiased probabilities are not known (and their determination is the objective of the simulation). There are a number of ways to obtain the appropriate biasing potential. The most straightforward is to use an iterative, self-consistent procedure. A simulation can be performed using some guess for the biasing potential. For example, no biasing potential could be used initially, or if one is available, the biasing potential from a simulation of a similar system would be preferable. The simulation is performed and the data analyzed to obtain the free energy using the expression in equation 2-34 and the new bias potential is computed as the exponential of the free energy.

Unless the initial guess is extremely good, some cluster sizes of interest will not be well sampled. However, the new bias potential will provide a better guess, producing better statistics for the subsequent run. Typically within a few iterations, a bias potential will be obtained that leads to roughly equal (within a factor of 10) sampling of all cluster sizes. This approach can be accelerated somewhat by obtaining accurate free energies at small cluster size and extrapolating the data to larger size. This can be done using the classical nucleation theory (CNT), or for ion-induced nucleation, the Kelvin-Thompson equation. Both of these theories are inaccurate at small cluster size, but can provide reasonably accurate estimates of the incremental free energies at larger sizes.

2.5 Histogram Reweighting

Histogram reweighting²³⁵⁻²³⁷ is a technique that allows us to take free energy data obtained at one set of temperature and pressure conditions and interpolate it to nearby state points without performing any additional simulations. This is done by taking advantage of the

independence of the microcanonical density of states to the simulation conditions. This density of states can be obtained from our simulations without any additional computational expense as the energy is calculated for each Monte Carlo move anyway, and can then be reweighted to different sets of simulation conditions. The microcanonical density of states for the *N*-mer is given by

$$\Omega_N(E) = P_N(E) \exp[\beta(-N\mu + E)]$$
2-35

where $\Omega_N(E)$ is the density of states with energy *E* for the *N*-mer, $P_N(E)$ is the concentration of N-mers with energy *E*, $\beta = 1/k_BT$ and μ is the chemical potential. It should be noted that this approach can only be applied over a limited range of temperature differences. In the limit of an infinite number of configurations, equation 2-35 is rigorously correct for temperature, but during a finite computer simulation, poor statistics will be obtained for energy states that are unlikely to be sampled. If these states make a significant contribution at the new temperature, the statistical error of the interpolation will be very large. This density of states can be computed at the simulation temperature and chemical potential. Then, at a different temperature and/or chemical potential, the concentration of N-mers with energy *E*, $P'_N(E)$ can be computed using

$$P'_{N}(E) = \Omega_{N}(E) \exp[(N\mu' - E)/k_{B}T']$$
 2-36

where μ' and T' are the new chemical potential and temperature respectively. The total concentration of N-mers can then be determined by integrating over all values of the energy

$$P'_{N} = \int \Omega_{N}(E) \exp[(N\mu' - E)/k_{B}T'] dE \qquad 2-37$$

and the free energy is

$$\Delta G'_n = -k_B T ln \int \Omega_N(E) \exp[(N\mu' - E)/k_B T'] dE \qquad 2-38$$

2.6 Extension to Ion Pairs

The simulation of nucleation enhancement by ions pairs poses some unique difficulties. Specifically, ions may form both contact and solvent separated pairs in solution.²⁵¹⁻²⁵⁵ The accurate sampling of these different configurations can require extremely long simulation times, as transitions between them can be very slow. Not only do the ions have to change separation, but the solvent shells must reorganize to accommodate them. If the equilibrium distribution of contact and solvent separated states is not accurately simulated, the nucleation free energy profile could be significantly affected.

In order to alleviate some of these sampling problems, we have slightly modified our approach. Rather than attempting to compute the free energy profile in a single simulation, we perform multiple simulations with the ion pair fixed at a given separation. This allows us to sidestep the sampling of the ionic separation coordinate. We have previously demonstrated that this method can be used to accurately calculate the bulk potential of mean force for ion pairs, provided that the cluster size is sufficiently large.²⁵⁵ This approach has a several advantages for ion-induced nucleation. Obviously, it allows for a more complete sampling of the ionic separation, ensuring that the free energy profile is accurately averaged over this coordinate. In addition, by separately simulating the different ionic separations, we can gain insight into how the nucleation free energy is affected by this variable. This may be helpful in identifying ion pairs that will be good nucleation enhancers based on their propensity of form contact or solvent separated pairs.

This method is implemented for ion pair-induced nucleation by performing multiple simulations with the ions fixed at a given separation. The average free energy profile can then be obtained using

$$\Delta G_{total}(N) = -k_B T ln \frac{\sum_r \exp\left[-\beta \Delta G_{gas}(r)\right] \exp\left[-\beta \Delta G_{nucleation}(N,r)\right] 4\pi r^2}{\sum_r \exp\left[-\beta \Delta G_{gas}(r)\right] 4\pi r^2} \qquad 2-39$$

where $\Delta G_{gas}(r)$ is the free energy to increase the ionic separation from the contact pair to a separation r in the gas phase, $\Delta G_{nucleation}$ (N, r) is the nucleation free energy obtained with the ions fixed at a separation r, and the $4\pi r^2$ term accounts for the greater accessible surface area of the ions at longer separations. $\Delta G_{total}(N)$ gives the free energy profile averaged over all the separations. For all the cases considered here where the ions are monatomic, the gas phase free energy contribution is considered to be equal to the energetic contribution. To be extended to polyatomic ions, this term needs to be averaged over the different relative orientations of the two ions.

Chapter 3 - Sign Preference in Ion-Induced Nucleation by Lennard-Jones ions

While a few molecular simulations have been performed to study ion-induced nucleation for Lennard-Jones ions, a picture of how the ionic size and the sign of the charge influence the process remains somewhat incomplete. The simulations of Oh et al.²⁰⁰ and Kathmann et al.^{184,205} both probed similar systems to the ones considered here. Oh et al performed simulations for a wide variety of different model systems, but they generally vary in more than one parameter from one another, making it difficult to draw conclusions about the effect of individual ionic properties. On the other hand, the simulations of Kathmann et al. used a consistent set of parameters to determine the free energy, but considered only two extremely different ionic sizes and provide no comparisons of the Gibbs free energy barriers.

Furthermore, while there has been significant progress made in understanding the origin of the sign preference, many of the details remain unclear. In particular, while the work of Oh et al. highlighted the importance of the balance between ion-solvent and solvent-solvent interactions, there has been little consideration of the role of entropy, which may be significantly different for positive and negative ions. Furthermore, they did not consider how these quantities varied between the Gibbs free energy minimum and the critical cluster size, which determines their contribution to the free energy barrier.

In an attempt to expand on the previous computer simulation studies and provide a more comprehensive picture of how the sign preference depends on the ionic size and other properties of the ionic force field, we have performed a series of AVUS-HR simulations of the ion-induced nucleation of water for Lennard-Jones ions with both positive and negative charges, a wide variety of ionic sizes, and different values for the Lennard-Jones ε parameter.

3.1 Simulation Details

We performed simulations for both positive and negative Lennard-Jones ions with a variety of different sizes, characterized by σ parameters of 3, 4, 5, and 6Å. Furthermore, in order to gauge the sensitivity of the simulation results to other force field parameters, we have considered ions with $\varepsilon = 1$ and 50k_BK. These particular values are of similar magnitude to the values used by Oh et al. and Kathmann et al., respectively. The water was modeled with TIP3P.²⁵⁶ Monte Carlo moves were performed only on water molecules and were divided evenly between insertions, deletions, translations, and rotations.

Throughout the simulations, a Stillinger-type,²⁵⁷ energy based cluster criterion was enforced where each molecule is required to have at least one neighbor in the cluster with which it satisfies the criterion. These cutoffs were set to -260 k_BK for both the ion-water, and waterwater interactions. This value is close to the available thermal energy and significantly less than the typical hydrogen bond energies. The simulation results have been shown to be relatively insensitive to the choice of the cluster criterion.^{231,242}

3.2 Results and Discussion

Plots of the Gibbs free energy profiles are shown in Figure 3.1. For all the ions considered, the free energy barriers increase with increasing ionic size, which is to be expected, because favorable ion-water interactions are reduced with increasing separation of water from the ion. For the same size ion, the free energy barriers are lower for the ions with $\varepsilon = 1k_BK$ than for those with $\varepsilon = 50k_BK$. The repulsive interactions are weaker when $\varepsilon = 1k_BK$ and water can approach the ions more closely, leading to more favorable coulomb interactions.



Figure 3.1 Free energy profiles for ions with $\varepsilon = 1$ and $50k_BK$ are shown in panels a) and b), respectively. Ions with $\sigma = 3, 4, 5$, and 6Å are shown in black, red, blue, and green, respectively. Negative ions are shown as solid lines, while positive ions are shown as circles.

To illustrate this point, the radial density profiles for the oxygen atom of water with respect to the center of the ion are plotted in Figure 3.2. The first solvation shell is located much closer to the ion than the combined σ for the ion and water. It is also closer to the ions with $\varepsilon = 1k_BK$ than for those with $\varepsilon = 50k_BK$ and is generally closer to the negative ions than positive ions except for the smallest ion with $\varepsilon = 1k_BK$, where the positive ion has the closer first solvation shell. This is likely caused by repulsions between hydrogen atoms for the negative ion case due to the extremely close approach of water to this ion. Clearly, the σ parameter alone is insufficient to describe the ionic size. This is an important point to note when using empirical ionic models. As the coulombic interactions dominate the potential energy, the separation between the ions and the nucleating species can depend strongly on all of σ , ε , and q.

Regarding the sign preference, a number of important trends emerge. The Gibbs free energy barriers are lower for the negative ions than the positive ions for the same size and model parameters in all the cases considered here. In addition, the difference in free energy barriers between the negative and positive ions decreases with increasing ionic size. The preference for anions is generally larger for ions with $\varepsilon = 1k_BK$ than with $\varepsilon = 50k_BK$. As the water is much closer to the ions in these cases, electrostatic effects on the sign preference are magnified. In general, it appears that the main difference between the ions with $\varepsilon = 1k_BK$ and $\varepsilon = 50k_BK$ is the smaller effective sizes of the ions with $\varepsilon = 1k_BK$. There are no qualitative differences between the two sets of ions if these differences in size are taken into consideration.



Figure 3.2 Radial density profiles showing the average oxygen density as a function of distance from the ion for clusters containing 100 water molecules. Ions with $\sigma = 3$, 4, 5, and 6Å are shown in panels a), b), c), and d), respectively. Negative and positive ions are shown in black and red, respectively while ions with $\varepsilon = 1$ and $50k_BK$ are shown as solid lines and circles with dotted lines, respectively.

The preference for negative ions is consistent with previous simulations^{200,205} and agrees with much of the experimental work,^{93-94,96,104-107} though the relevance of this agreement is

somewhat unclear due to open questions about the exact ions involved. These results disagree with the conclusions of Nadykto et al. who have argued that due to quantum effects, cations are more effective nucleation enhancers than anions. Using DFT calculations, they have found that small H_3O^+ clusters have lower free energies than OH^- clusters.¹⁷⁴ They have also observed lower free energies for cations in a few other systems.²⁵⁸⁻²⁵⁹

It has been shown that some degree of charge transfer occurs between ions and water in small clusters.²⁶⁰⁻²⁶² These behaviors (and other quantum mechanical phenomenon) are not explicitly modeled here and could play some role in the discrepancies. However, it is less clear what effect this might have on the free energy changes when the cluster size is larger and water is being added further from the ion. As the free energy profile has a minimum at small cluster size, the cluster size at which this minimum is observed, and the free energy changes over an intermediate cluster size range are of paramount importance.²⁶³ In the absence of *ab initio* free energy data for larger clusters, it is somewhat unclear whether empirical and *ab initio* models would yield qualitatively different results for the barrier height or for the sign preference. In any case, a better understanding of the different contributions to the free energy profile in a simple system like this one can provide valuable insight into the origin of the sign preference and other trends in the rate of ion-induced nucleation.

3.2.1 Ion-Water Potential Energies

The differences in ion water-potential energy between the positive and negative ions are plotted in Figure 3.3. In agreement with Oh et al.,²⁰⁰ these potential energies are more favorable for the negative ions for the same ionic size and model. The potential energy differences decrease as the ionic size increases. One reason for this is that the hydrogen atoms are closer to the negative ions than oxygen atoms to the positive ions. The ion-water separation for the

positive and negative ions changes by a roughly equal amount with increasing ionic size and therefore the loss of electrostatic interactions is more rapid for the negative ions because the hydrogens are moving in a steeper portion of the coulomb potential.



Figure 3.3 Differences between the ion-water potential energy of positive and negative ion clusters (positive – negative) for ions with $\varepsilon = 1$ and $50k_BK$ are shown in panels a) and b), respectively. Ions with $\sigma = 3$, 4, 5, and 6Å are shown as black, red, blue, and green lines, respectively.

However, a more important factor may be the different preferences of the anions and cations for the cluster surface. The radial density profiles for the ion are plotted in Figure 3.4. When the ionic size is small, the ions prefer to be on the cluster interior. However, for larger ions there is a significant chance for the ion to be at the interface, with a greater probability for the anions than the cations. When the ions are on the cluster surface, they have fewer first shell neighbors and the ion-water interactions are decreased. As the anions are more likely to be on the surface, the loss of ion-water interactions is larger, which leads in part to the decreased ion-water potential energy differences between the positive and negative ions with increasing ionic size.



Figure 3.4 The average densities of the ion as a function of distance from the center of mass of the water molecules for 100 water molecule clusters containing ions with $\varepsilon = 1$ and $50k_BK$ are shown in panels a) and b), respectively. Ions with $\sigma = 3$, 4, 5, and 6Å are shown in black, red, blue, and green, respectively. Negative ions are shown as solid lines, while positive ions are shown as circles. The radial density profile for the oxygen atom of water is shown as a dashed cyan line. The water oxygen profile is purely intended as a guide to help locate the interface and has been scaled to fit more conveniently on the plot.

For small ions, the loss of ion-water interactions would be too large for surface solvation to be favorable. As the ionic size increases, the loss of ion-water interactions associated with moving to the interface is smaller, increasing their preference for the surface. The surface solvation of some ions has been well known for some time.²⁶⁴⁻²⁷² In agreement with our results, for the same size ion, negative ions have a greater chance to be found at the interface than cations and the propensity of ions for the surface increases with their size. This behavior has been associated with polarization, which certainly plays a very significant role, but recent data has shown that the disruption of the water structure caused by creating a large cavity in the solvent can serve as a sufficient driving force to move large ions to the interface.²⁷³⁻²⁷⁴

The potential energy differences converge to a fairly constant value by a cluster size of around 25 molecules. This suggests that water is able to interact more favorably with negative

ions even beyond the first solvation shell. It is interesting to note that the decrease in the potential energy difference with increasing size seems to mirror the trend of decreasing barrier height difference. This contribution of the ion-water interactions to the barrier height will be discussed in more detail in section 3.2.4.

3.2.2 Water-Water Potential Energies

The differences in water-water potential energy between the positive and negative ions are plotted in Figure 3.5.



Figure 3.5 Differences between the water-water potential energy of positive and negative ion clusters (positive – negative) for ions with $\varepsilon = 1$ and $50k_BK$ are shown in panels a) and b), respectively. Ions with $\sigma = 3$, 4, 5, and 6Å are shown as black, red, blue, and green lines, respectively.

There are several important points to note about these plots. First, the water-water interactions are more favorable for the positive ions for all the ionic cases considered here, when the cluster size is greater than 10. For the smallest cluster sizes, negative ions can form one hydrogen bond to the ion, while the other hydrogen is free to form a hydrogen bond with an adjacent water molecule. On the other hand, water molecules in the first solvation shell of

positive ions form few water-water hydrogen bonds. This leads to the more favorable waterwater interactions at small cluster sizes for some negative ions. However, as the cluster size increases the water-water potential energy becomes more favorable for the cations.

One reason for this is that the water molecules (and particularly the hydrogen atoms) approach the negative ions more closely and the repulsion between water molecules is larger. Another important reason for the less favorable water-water interactions is the more restricted water structure around negative ions. If the water molecules are held in a very rigid orientation near the ion, this could significantly hamper their ability to form hydrogen bonds with other water molecules. The probability distributions for the angle between the oxygen-hydrogen bond vectors and the oxygen-ion vectors are plotted in Figure 3.6.

For the negative ions, the distribution is peaked very sharply at a cosine of 1, indicating that one hydrogen is pointed directly at the ion, with the second peak simply corresponding to the H-O-H angle in water. For the positive ions, the preferred orientation has the dipole moment vector pointed directly away from the ion. However, the distribution is not nearly as sharp as for the negative ions. This indicates that the positive ions have more flexibility to form hydrogen bonds with water molecules in the second solvation shell.

While the water-water potential energies are always more favorable for the positive ions, the difference tends to be less for the largest ions. As was the case for the ion-water interactions, the main reason for this trend is the different preferences of anions and cations for the cluster surface. A surface solvated ion perturbs the water structure much less than one on the interior (which is an important driving force for surface solvation). When the negative ions have a greater chance of being on the surface, the difference in water-water interactions becomes significantly smaller.



Figure 3.6 Probability distributions for the angle between the oxygen-hydrogen bond vector in water and the oxygen-ion vector are shown for negative ions with $\varepsilon = 1$ and $50k_BK$ and positive ions with $\varepsilon = 1$ and $50k_BK$ in panels a), b), c), and d), respectively. Ions with $\sigma = 3$, 4, 5, and 6Å are shown as black, red, blue and green lines, respectively.

Another interesting feature of the water-water potential energy differences from Figure 3.5 is that the magnitude of the difference initially increases sharply with increasing cluster size but then decreases gradually, not reaching a constant value even for clusters containing 200 water molecules. These results suggest that in addition to the more obvious ion-water interactions, ions can significantly perturb the water-water interactions even in very large clusters. This could be significant, as the ions are still changing the water-water interactions

differently for positive and negative ions in the cluster size range contributing to the free energy barrier. In contrast to the ion-water interactions, the trends in the water-water interactions are generally opposite to the trends in the free energy barrier heights, being more favorable for cationic clusters but by an amount that decreases with increasing ionic size.

3.2.3 Entropies

An additional factor that has not been discussed is the entropic contribution to the free energy. The fact that water binds more tightly to the negative ions suggests that these clusters may be lower in entropy than their positive ion counterparts and that this difference could make a significant contribution to the free energies. In order to assess this possibility, the differences in entropy between the positive and negative ion clusters are plotted in Figure 3.7.

In general, the negative ion clusters are lower in entropy, though the magnitude of the entropy difference tends to decrease with increasing ionic size. The preference of negative ions for the cluster surface is likely a major factor in this trend as well as the larger, surface solvated anions do not create such a strongly ordered solvent environment in the vicinity of the ion. In particular, for the largest ions with $\varepsilon = 50k_BK$ (where the preference for the cluster surface is the greatest), the entropy is actually lower for the negative ions at small cluster size. As with the water-water potential energies, the differences do not converge to a constant value, even for clusters as large as 200 water molecules.

The difference in entropy between the positive and negative ions makes a relatively small contribution to the differences in the free energy compared to the ion-water potential energy and makes a slightly larger contribution than the water-water potential energy. Both of these contributions are more favorable for the cationic clusters. However, the differences in ion-water potential energy dominate the total free energy difference and are more favorable for the anionic clusters.



Figure 3.7 Differences between the cluster formation entropy of positive and negative ion clusters (positive – negative) for ions with $\varepsilon = 1$ and $50k_BK$ are shown in panels a) and b) respectively. Ions with $\sigma = 3$, 4, 5, and 6Å are shown as black, red, blue, and green lines, respectively.

3.2.4 Contributions to the Barrier Height

While the data in sections 3.2.1 - 3.2.3 can provide significant insight into the important interactions in these clusters, in order to determine their importance to the sign preference, it is essential to know how they change between the Gibbs free energy minimum and maximum, as this determines the contribution they make to the barrier height. The different contributions discussed above, as well as the total enthalpy, are shown in Table 3.1.

The ion-water potential energy contribution to the barrier height is the smallest of the three discussed above, despite the large potential energy differences in Figure 3.3, and actually favors lower barrier heights for the positive ions in some cases, even though the anionic clusters always have lower ion-water potential energies. In contrast, the water-water potential energy and the entropy are more similar for positive and negative ions at the same cluster size as shown

in Figures 3.5 and 3.7, but make large contributions to the difference in barrier height. For the same cluster size, both are generally less favorable for the negative ions. However, while the water-water potential energy contribution to the barrier height is still much more favorable for cations, the entropic contribution is much more favorable for the anions, leading to the observed sign preference.

Table 3.1 The differences between the enthalpy, entropy, ion-water potential energy and waterwater potential energy of the Gibbs free energy minimum and the critical cluster. All quantites are expressed in units of k_BT .

	ΔH^*	T∆S*	ΔE_{IW}^*	ΔE^*_{WW}	ΔH^*	T∆S*	ΔE_{IW}^*	ΔE^*_{WW}
	$\varepsilon = 1 k_{\rm B} K$ (Negative)				$\varepsilon = 1 k_{\rm B} K$ (Positive)			
$\sigma = 3\text{\AA}$	-1814	-1826	-39.2	-1775	-1915	-1933	-49.5	-1865
$\sigma = 4 \text{\AA}$	-1785	-1797	-38.5	-1747	-1944	-1962	-45.2	-1898
$\sigma = 5 \text{\AA}$	-1769	-1782	-47.5	-1722	-1985	-2004	-49.8	-1935
σ=6Å	-1909	-1926	-59.5	-1849	-2040	-2061	-54.2	-1985
	$\varepsilon = 50 \text{ k}_{\text{B}} \text{K}$ (Negative)				$\epsilon = 50 \text{ k}_{\text{B}} \text{K}$ (Negative)			
$\sigma = 3\text{\AA}$	-1711	-1723	-38.4	-1674	-1931	-1948	-45.5	-1885
σ=4Å	-1771	-1783	-44.7	-1727	-1934	-1951	-44.5	-1889
$\sigma = 5 \text{\AA}$	-1925	-1941	-62.8	-1862	-2000	-2019	-59.3	-1941
σ=6Å	-2039	-2062	-71.9	-1966	-2046	-2070	-67.7	-1978

An explanation for these behaviors can be found from a closer examination of the free energy profiles in Figure 3.1. For small ionic sizes, the Gibbs free energy minimum is located at a larger cluster size for the negative ions than for the positive ions. Fewer water molecules are removed from the gas phase over the cluster size range contributing to the barrier height for negative ions, lead to a smaller loss of entropy. It is this fact, rather than the more subtle differences between the positive and negative ions over the range of cluster sizes contributing to the barrier height, that leads to the sign preference. Furthermore, as the ionic size increases, the difference in ion-water potential energy decreases and the minima are located at more similar cluster sizes. This leads to the decreased preference for anions with increasing ionic size.

To further illustrate this point, the different contributions to the barrier height are plotted in Figure 8 as a function of the difference in cluster size between the critical cluster and the Gibbs free energy minimum. All of the different contributions depend strongly on the number of molecules between the free energy minimum and maximum. The agreement is equally good for the positive and negative ions.

The source of these features can be qualitatively understood by referring to the classical Kelvin-Thompson equation¹³⁸⁻¹³⁹ (see equation 1-1) The first term is due to the bulk free energy difference between the vapor and liquid phases, the second term is the free energy penalty to form the interface, and the third term accounts for the coulomb interactions between the ion and the nucleating vapor. The first term is directly related to the number of molecules transferred from the vapor to the cluster and scales with n. The second term depends on the area of the cluster and assuming a perfectly spherical shape, scales with $n^{2/3}$. The last term depends on the reciprocal of the cluster radius, or $n^{-1/3}$.

This is of crucial importance, because the entropy and water-water potential energy terms dominate the total free energy, but vary only slightly between positive and negative ions. The weaker ion-water interactions for the positive ions result in the free energy minimum at smaller size, and a less favorable entropic contribution to the barrier height. This is what leads to the lower barriers for negative ion clusters. As the ionic size increases and the ion-water potential energy differences between the positive and negative ions become smaller, the locations of the free energy minima become more similar and the barrier height differences decrease.



Figure 3.8 The contributions of the enthalpy, entropy, ion-water potential energy, and waterwater potential energy to the Gibbs free energy barrier are shown as function of the number of water molecules between the critical cluster and the free energy minimum. Negative ions are shown in black and positive ions are shown in red. Ions with $\varepsilon = 1$ and $50k_BK$ are shown as circles and triangles respectively. A linear fit to the data is shown as a green line.

3.2.5 Sign Preference for Ions of Different Sizes

Reconsidering the Gibbs free energy profiles in Figure 3.1, another interesting trend emerges. Negative ions with σ as large as 6Å when $\varepsilon = 1k_BK$ and 5Å when $\varepsilon = 50k_BK$ still have lower barrier heights than the corresponding cations with $\sigma = 3$ Å. This is somewhat surprising considering the available experimental data for alkali metal cations and halide anions in small clusters, which suggests that if the cation is smaller, the free energies will generally be lower for those clusters.^{108,114} In order to explain this apparent discrepancy, the Helmholtz free energy differences between cations with $\sigma = 3$ and 4Å and larger anions are shown in Figure 3.9.



Figure 3.9 The Helmholtz free energies of larger negative ions relative to the 3Å positive ions are shown panels a) and c) for the ions with $\varepsilon = 1$ and $50k_BK$, respectively, while those relative to the 4Å positive ions are shown in panels b) and d), respectively. The 4, 5, and 6Å negative ions are shown in black, red, and blue, respectively. The cluster sizes of the Gibbs free energy minima and maxima are shown as triangles and circles for the anions and cations, respectively.

For all but one of the free energy differences shown, the smaller cations have lower free energies at all cluster sizes. However, the free energy difference peaks at a small cluster size and gradually decreases as the cluster grows. This results in a smaller difference for the critical clusters than for the free energy minima. Therefore, even though the free energy is generally lower for the smaller cations over the whole range of cluster sizes, by as much as $80 k_B T$ in some cases, the free energy barriers are still lower for the anions.

The reason for this behavior can be understood from an examination of the coordination numbers plotted in Figure 3.10. For the first few water molecules, the free energies of the cations are significantly lower as the solvent can approach the smaller ion much more closely. However, as the cluster size increases, more water molecules are able to solvate the larger negative ions which decreases this effect somewhat, leading the decreasing free energy differences observed in Figure 3.9. On the other hand, when the larger anions show a significant tendency to be on the cluster surface, the smaller cations have more neighbors and distinct peaks in the Helmholtz free energy differences are not observed.



Figure 3.10 Integrated number of water molecules as a function of distance from the ion for ions with $\varepsilon = 1$ and 50 k_BK are shown in panels a) and b), respectively. The profiles for the cations with $\sigma = 3$ Å, and anions with $\sigma = 4$, 5, and 6Å are shown as black, red, blue, and green lines, respectively.

In addition to the gradual trends with increasing cluster size, the location of the Gibbs free energy minimum is important here as well. The extra first and second shell neighbors for the negative ions allow the ion-water interactions to dominate the surface free energy over a wider range of cluster sizes, despite the fact that the total ion-water potential energy may be lower for the small cationic clusters. A similar trend is not observed in the case of large cations and smaller anions. As shown in section 3.2.1, the ion-water interactions are generally weaker for cations. Therefore, while large cations may still have more neighbors than smaller anions, the additional interactions are not sufficient to balance the strong hydrogen bonds between water and the anions.

These trends may at least partially account for the differences between free energy data for small clusters from both theory and experiment and simulated nucleation free energy barriers from other researchers using empirical models. While quantum effects are certainly important (and could potentially lead to different results than those observed here), as suggested by Nadykto et al.,¹⁷⁴ our results indicate that these data are not necessarily inconsistent because small cationic clusters can have lower free energies but still lead to higher barriers.

3.3 Conclusions

We have performed a series of ion-induced nucleation simulations using the AVUS-HR method. These simulations have shown, in agreement with Kathmann et al., that the sign preference can depend strongly on other ionic properties, including σ , and ε . Furthermore, we have shown that the location of the Gibbs free energy minimum can be a dominant factor in the sign preference for anions. When the minimum is at a larger size for anions, there is less gas phase entropy loss between the minimum and the critical cluster size. The reason the Gibbs free energy minimum occurs at larger cluster sizes for the anions is that the stronger ion-water

interactions can overcome the surface effect over a wider cluster size range. As the ionic size increases, the difference in ion-water interactions becomes less significant, and the minima are located at about the same size, leading to similar barrier heights.

We have also shown that while the total free energies tend to be lower for small cations than large anions, the barrier heights are often still lower for the anions. This effect is most important for cases where the anion is on the cluster interior and the larger anions tend to have more neighbors than the smaller cations. These results provide a potential explanation for the fact that empirical nucleation simulations predict a lower free energy barriers for a fairly wide range of anions, despite the fact that mass spectrometry data and *ab initio* calculations for small clusters seem to show a preference for smaller cations. This underscores the need to consider the full free energy profile, rather than just data for the smallest clusters. These simulations use fairly simple models and verification using more sophisticated modeling approaches could go a long way towards clarifying the role the behaviors observed here might play in more realistic systems.

Chapter 4 – The Importance of Ionic Polarizability

Due to the large computational expense associated with polarizable models, most of the previous molecular simulations of ion-induced nucleation did not consider the effect of polarizability. However, polarization of both the ion and the solvent can play a key role in determining an ion's propensity for the interior or surface of clusters.²⁷¹ This behavior could be extremely important in ion-induced nucleation, and cannot be modeled by theoretical treatments that constrain the ion to the center of the cluster.

The work of Oh et al.²⁰⁰ included data using a polarizable force field. However, as completely different sets of parameters were used for the non-polarizable ions, no quantitative comparisons can be made. Furthermore, a comparison of the effects of polarizability for smaller, interior solvated ions and larger, more polarizable ions could prove useful. We have performed a series of AVUS-HR simulations of ion-induced nucleation using both polarizable and non-polarizable ionic models with different sizes and charges. These simulations should help to paint a comprehensive picture of how ionic polarizability affects ion-induced nucleation.

4.1 Simulation Details

The explicit treatment of solvent polarizability is certainly important, but would incur a considerable computational expense. On the contrary, the treatment of a single polarizable ion adds a very small amount to the cost while still playing a very important role in the propensity of ions for the interface. In order to explicitly quantify the effects of ionic polarizability, the simulations were performed for otherwise identical polarizable and non-polarizable models. The ions were treated using both positive and negative hard spheres with diameters (σ) = 3, 4, and 5Å. In contrast to our simulations using Lennard-Jones ions in Chapter 3, the use of hard spheres allows us to closely control the actual size of the ions. For Lennard-Jones ions, the

effective sizes of ions with the same value of σ can be quite different, while hard sphere parameters allow us to clearly define the size as the minimum separation between the ion and water.

Polarization was accounted for through an induced dipole located at the center of the ion with an associated isotropic polarizability. These polarizabilities were determined by making a plot (not shown) of polarizability $(\alpha)^{275}$ vs. ionic volume (V), calculated from ionic radii²⁷⁶ for alkali metal cations and halide anions. These plots lead to the following equations for the polarizabilities of the anions and cations:

$$\alpha_{\text{cations}} = 0.1460V - 0.4567$$
 4-1

$$\alpha_{\text{anions}} = 0.1673V - 0.7608$$
 4-2

In order to help gauge how the details of the water model affect the nucleation process, simulations were preformed for clusters of up to 200 water molecules using the TIP3P²⁵⁶ and TIP4P²⁵⁶ water models, and for clusters containing up to 100 water molecules using the TIP5P²⁷⁷ water model. All other simulation parameters are identical to those used in the simulations of Lennard-Jones ions.

4.2 Results and Discussion

Plots of the nucleation free energy profiles using the TIP3P water model are shown in Figure 4.1. For all the ions examined, the nucleation free energy barrier increases with increasing ionic size and the anions have lower barrier heights than the cations. These findings are consistent with our previous simulations for Lennard-Jones ions. The negative ions have lower barrier heights than the positive ions, primarily because the free energy minima are located at a larger clusters size for the negative ions, due to the strong ion-water interactions in those clusters. The magnitude of the preference for negative ions decreases with increasing ionic size as the ion-water interactions become more similar and the free energy minima move closer together.



Figure 4.1 Gibbs free energy profiles for negative and positive ions using TIP3P water are shown in panels a) and b), respectively. The non-polarizable ions are shown as solid lines while the polarizable ions are shown as circles. Ions with diameters of 3, 4, and 5Å are shown in black, red, and blue, respectively. Plots are at a vapor phase density of 2.5×10^{-6} molecules/Å³.

The free energy profiles calculated using the TIP4P and TIP5P water models are plotted in Figure 4.2. The free energies for these models are higher and the profiles are plotted at higher vapor densities in order to visualize the barrier heights. The TIP5P free energies in particular, are considerably higher than either of the other two models. While the TIP5P model is the most expensive to implement and reproduces a number of bulk phase quantities more accurately than either of the other two models, it may be the most problematic at small cluster size as the deviation from quantum mechanical calculations of the water dimer energy is largest for TIP5P.²⁷⁷



Figure 4.2 Gibbs free energy profiles for negative and positive ion clusters using TIP4P water are shown in panels a) and b), respectively while the profiles obtained with TIP5P water are shown in panels c) and d), respectively. The non-polarizable ions are shown as solid lines while the polarizable ions are shown as circles. Ions with diameters of 3, 4, and 5Å are shown in black, red, and blue, respectively. Profiles for TIP4P are plotted at a density of 2.6×10^{-6} molecules/Å³ while those for TIP5P are plotted at 1.65×10^{-5} molecules/Å³.

4.2.1 Comparison of Polarizable and Non-polarizable Ions

Comparing the results for polarizable and non-polarizable models with the same size and charge reveals a somewhat surprising trend. Polarizability adds a term to the potential energy that is purely attractive. This seems to imply that the nucleation barrier height should be lower for polarizable ions than non-polarizable ions. However, for all the cases considered here, the barrier heights are farily similar for the polarizable and non-polarizable ions, and for the smaller ionic sizes, the polarizable ions actually have slightly higher barriers.

The differences in Helmholtz free energy between the polarizable and non-polarizable ions, along with the polarization energies are plotted in Figure 4.3.



Figure 4.3 The Helmholtz free energy differences between the non-polarizable and polarizable ions (non-polarizable – polarizable) are shown in panels a) and b) for negative and positive ions, respectively. The corresponding polarization energies are shown in panels c) and d), respectively. Ions with diameters of 3, 4, and 5Å are shown in black, red, and blue, respectively. The positions of the Gibbs free energy minima and maxima from Figure 4.1 are indicated with circles.

The Helmholtz free energies are particularly illuminating here as they do not depend on the vapor density. For all ionic sizes and charges, most of the change in the Helmholtz free energy

difference is contained in the smallest cluster sizes. For cases where the non-polarizable ion has the higher barrier, the Helmholtz free energy difference has a peak at small cluster size, eventually decreasing, and mostly leveling off at larger size.

This peak at small cluster size suggests that polarization stabilizes clusters near the Gibbs free energy minimum by a larger amount than clusters near the critical size. This trend is similar to the one observed when comparing positive and negative Lennard-Jones ions of different sizes. In this case, the free energy minima are generally located at the same cluster size for the polarizable and non-polarizable ions (never more than ± 1) so differences in barrier height cannot arise due to differences in the location of the minimum. Rather, the relatively small differences in barrier heights observed here are due to small, subtle effects that persist over a wider range cluster sizes, adding up to the observed differences in the barrier height.

4.2.2 Effect of Supersaturation

For all the ions considered here, but particularly for cases where the relative Helmholtz free energies show distinct features like those in the top panels of Figure 4.3, the relative Gibbs free energy barriers depend on the supersaturation. The position of the Gibbs free energy minimum and the critical cluster size are marked on the Helmholtz free energy plots. If the position of these points, particularly the minima, were shifted by changing the vapor density, the magnitude and sign of the barrier height difference could be altered. With increasing supersaturation, the critical cluster size decreases and the Gibbs free energy minimum shifts to a larger cluster size. However, as the bulk contribution to of the free energy (which contains the effects of supersaturation) is small at small cluster sizes, the critical cluster size is much more sensitive to this parameter. At a very low supersaturation, the barriers could be significantly lower for the polarizable ions as the free energy minimum would be pushed back to a smaller cluster size than the peaks in Figure 4.3, where the polarization energy is small. The critical cluster size would be significantly larger (beyond the sizes considered here), but this would have a fairly small effect on the relative free energy barriers as the incremental free energies (ΔA_i - ΔA_{i-1}) approach each other at large cluster size, as shown in Figure 4.4. By a cluster size of 35-40 molecules, the incremental free energies for all the ions are essentially identical.



Figure 4.4 The incremental free energies for the negative and positive ion clusters are plotted in panels a) and b), respectively. The non-polarizable and polarizable ions are shown as solid lines and circles, respectively. Ions with diameters of 3, 4, and 5Å are shown in black, red, and blue, respectively.

With increasing supersaturation, the free energy minimum would shift to larger cluster sizes, making the barriers for the non-polarizable ions lower relative to the polarizable ions near the simulation conditions considered here. With any further increase in supersaturation, the barriers for the non-polarizable ions will now increase compared to the polarizable ions as the free energy minimum will move past the peaks in Figure 4.3 and the critical cluster size will

begin to decrease to clusters where the solvation is more asymmetric. With further increase in supersaturation, the barrier will eventually vanish entirely for all the ions.

The Helmholtz free energy differences are also plotted for the TIP4P and TIP5P water models in Figure 4.5.



Figure 4.5 The Helmholtz free energy differences between the non-polarizable and polarizable ion clusters using TIP4P water are shown in panels a) and b) for negative and positive ions, respectively while the profiles obtained with TIP5P water are shown in panels c) and d), respectively. Ions with diameters of 3, 4, and 5Å are shown in black, red, and blue, respectively.

4.2.3 The Importance of Surface Solvation

The origin of these features in the Helmholtz free energy differences clearly correlates with the polarization energies, which are plotted in the bottom panels of Figure 4.3. For the cases considered here, the polarization energy matches the shape of the Helmholtz free energy difference plot very closely. The reason that some ions show large peaks and others do not is related to the different affinities of the ions for the cluster surface.

The radial density profiles for the ions with respect to the center of mass of the water molecules are plotted in Figure 4.6. In agreement with our studies for Lennard-Jones ions, larger ions have a greater tendency to lie on the surface than smaller ions, and for the same size ion, anions are more likely to be surface solvated than cations. In addition, adding polarization moves all the ions toward the interface.



Figure 4.6 The average densities of the ion as a function of distance from the center of mass of the 100 water molecules clusters for negative and positive ions are shown in panels a) and b), respectively. The non-polarizable ions are shown as solid lines while the polarizable ions are shown as circles. Ions with diameters of 3, 4, and 5Å are shown in black, red, and blue, respectively. The density profile for the oxygen atom of water is shown as a green dashed line. This profile is purely intended as a guide to help locate the interface and was scaled to fit more conveniently on the plot.

Polarizability has been found to play a crucial role in this effect,²⁶⁸⁻²⁷¹ as also shown here. As polarizability increases with increasing ionic size, this could explain the greater preference of larger ions for the interface but more recent studies, as well as the present results, show that ionic size alone can also serve as a sufficient driving force to move the ion to the interface due to the free energy penalty associated with forming a large cavity in the solvent.²⁷³⁻²⁷⁴ Results for Cl⁻ have shown that if the sign of the charge is changed (giving an ion similar to Cs⁺), the ion moves to the cluster interior,²⁶⁵ in agreement with our finding that for the same size ion, anions show a greater preference for the interface. However, our results indicate that cations show a similar trend to anions, moving to the cluster surface with increasing ionic size or with the addition of polarization, but that this behavior requires significantly larger ionic sizes for cations. More significantly for our purposes, in all the cases where the Helmholtz free energy differences show a large peak, the ion has significant density on the cluster interior in Figure 4.6.

This explains the large trough in the polarization energy for these ions. For larger clusters the ion is symmetrically solvated and the polarization is small. At smaller size the solvation is far from being symmetrical because there are not enough solvent molecules to form a full solvation shell. This behavior is not observed for ions lying on the cluster surface. The ion is solvated asymmetrically at all cluster sizes and as more water is added, the asymmetry becomes larger resulting in similar or greater polarization for larger cluster sizes than small ones.

To verify this explanation, the 3Å polarizable ion cluster systems are oriented such that the vector connecting the ion with the center of mass of the water molecules is along the z-axis with the ion at the origin. The number of water molecules with a given z-coordinate is plotted in Figure 4.7, and representative snapshots of some important clusters are shown in Figure 4.8.²⁷⁸

For the negative 3Å ion, the first 4-5 water molecules tend to form a loose ring structure with one hydrogen bond to the ion, and one to another water molecule. This ring forms mostly on one side of the ion. Starting with 5-6 water molecules, it starts to become favorable to add

water on the other side of the ion. While there is some chance of the 5th and 6th water molecules being added on the same side as the other water molecules, in a second solvation shell, the probability of more symmetric solvation is significantly greater.



Figure 4.7 The number of water molecules is plotted as a function of z-coordinate where the system is oriented such that the vector linking the ion with the center of mass of the water molecules is along the z-axis with the ion at the origin. Polarizable negative and positive ions are shown in panels a) and b), respectively. Clusters containing 2, 4, 5, and 6 water molecules are shown in black, red, blue, and green, respectively.

For the positive 3Å ion, a maximum is seen in the Helmholtz free energy differences at 2 water molecules, followed by a shoulder over range of 4-8 water molecules. The first 2 water molecules both form oxygen-ion contacts on the same side of the ion but do not interact favorably with each other. When two more water molecules are added, they orient more symmetrically about the ion, resulting in the increased number of water molecules in the negative z direction, as shown in panel b) of Figure 4.7. This behavior is distinct from that observed for the negative ion because there are no water-water hydrogen bonds to hold the water molecules close together on one side. This more symmetric solvation is why the peak in the Helmholtz free energy difference is located at smaller cluster size for the positive ions. While
the fifth water molecule may be added to the first solvation shell, in general, additional water molecules beyond 4 are in a second solvation shell. The shoulder in the 5-8 molecule range may correspond to the addition of an asymmetric second solvation shell.



Figure 4.8 Snapshots of some important clusters containing polarizable ions are shown with the ion in cyan, oxygen in red, and hydrogen in white.

4.2.4 The Effect of Increased Polarizability

Our results indicate that the majority of the polarization effects are contained in the smallest clusters and because of this, polarization makes a fairly small contribution to the nucleation free energy barrier. However, if the ion were more polarizable, the change in the barrier could be significant. Considering the approximate way in which polarizabilities were assigned, we have assessed the impact of larger ionic polarizabilities by performing additional simulations with the TIP3P water model and the polarizability of all the ions increased by a factor of two. The Gibbs free energy profiles are plotted in Figure 4.9. The trends remain

consistent, with the barrier height increasing for the 3 and 4Å ions and decreasing for the 5Å ions. However, the magnitude of these effects is increased somewhat, raising the free energy barrier by up to about $1k_BT$ for the smaller ions, and decreasing the barrier for the 5Å negative ion case by more than $5k_BT$. With the exception of the largest negative ion, the change in the barrier height still represents a fairly small perturbation, but clearly some caution should be exercised when dealing with highly polarizable ions.



Figure 4.9 Free energy profiles using TIP3P water are plotted for ionic polarizabilities twice as large as those used in Figure 4.1. The panels, coloring and line styles are the same as in Figure 4.1.

4.3 Conclusions

We have performed simulations of water nucleation in the presence of various polarizable and non-polarizable hard sphere ions. These simulations have shown that the nucleation free energy barrier increases with ionic size and is lower for negative ions of the same size, in agreement with previous simulation results. We have further shown that for non-polarizable ions, over the size range considered here, anions are more likely to be found on the surface than cations. Polarizable ions show a similar trend but for the 5Å ions both the anion and the cation exist almost exclusively at the interface for the cluster sizes considered here.

We have also found that adding polarizability may significantly reduce the free energy but usually has a much smaller effect on the nucleation free energy barrier, and can actually cause the barrier height to increase. Polarizable ions that tend to reside on the cluster interior are more polarized at small cluster size where the solvation is asymmetric than at large cluster size where the solvation is more uniform. These changes in solvation behavior can produce unexpected results such as the higher barriers for polarizable ions. These findings suggest that great care should be taken in comparing free energies from small cluster sizes when polarizability is taken into account as they may not accurately reflect the differences in barrier height. This is particularly important when comparing ions with different affinities for the These results also emphasize the importance of a molecular treatment of cluster surface. polarization effects in ion-induced nucleation. Finally, although the structures predicted by the non-polarizable models are markedly different, the barrier heights yielded by such models are surprisingly close to those calculated using polarizable ionic models provided that the polarizability is not too large. This is because much of the effect of adding ionic polarizability is contained in cluster sizes that do not contribute to the barrier.

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Chapter 5 – The Enhancement of Water Nucleation by Ion Pairs

While there have been extensive studies of ion-induced nucleation, data about how ion pairs affect the nucleation process is somewhat scarce. There have been a number of studies of ion pair forming species (acids, bases, salts, etc.) in small clusters. However, the primary goal in most of these studies was to identify the cluster size at which the ion pair becomes stable and little information was provided about how the ion pair affects the thermodynamics of nucleation. Zidi et al. have performed a grand canonical ensemble Monte Carlo simulation that considered the equilibrium of water vapor with a salt molecule,²¹⁰ but their simulations were limited to clusters near the most stable size and therefore, could not be used to calculate the free energy barrier.

It is quite likely that ion pairs are involved in the nucleation process because of the importance of sulfuric acid, which can transfer a proton to water even in fairly small clusters. Several of the proposed nucleation mechanisms suggest that ion pair formation could play a role. For example, ammonia has been found to enhance particle formation in the sulfuric acid-water system. If ion pair formation is an important part of the nucleation mechanism, ammonia could potentially act a proton acceptor, stabilizing the ion pairs. Anderson et al. have preformed *ab initio* molecular dynamics simulations to study how the inclusion of different bases or a second sulfuric acid molecule in the cluster could affect the proton transfer.²⁷⁹ Their data have indicated that the presence of ammonia (and other bases) influences the likelihood of a proton transfer event, which could be indicative of the role played by ammonia in enhancing nucleation. Furthermore, the addition of a second sulfuric acid molecule also enhances the proton transfer. It has been suggested that critical clusters at atmospheric conditions contain 2 sulfuric acid molecules.²⁸⁰ If ion pairs are important in the nucleation process, this would provide a

convenient explanation. However, in the absence of any information regarding the effect of ion pairs on nucleation, such conclusions are purely speculative. A better understanding of how ion pairs can affect the nucleation process could be a big step towards clarifying the importance of different potential mechanisms, and provide further detail into the important factors involved.

5.1 Simulation Details

Simulations were performed for 4 different hard sphere ion pairs consisting of both "small" ions with $\sigma = 3$ Å, and "big" ions with $\sigma = 5$ Å. The sizes were chose because the small ions were located on the cluster interior based on the data in Chapter 4, while the larger ions were on the surface, allowing us to consider how the ionic size and the preference of the ions for the surface or interior of the cluster might influence the nucleation process for ion pairs. The four ion pairs include a small anion with a small cation (SASC), a small anion with a big cation (SABC), a big anion with a small cation (BASC), and a big anion with a big cation (BABC). The TIP3P model was used for water.²⁵⁶

The ions were kept fixed at a given separation throughout each simulation. For each ion pair, 65 simulations were performed, starting with the contact pair and increasing the separation by 0.25Å for each subsequent simulation, terminating at a separation 16Å longer than the separation for the contact pair. This wide range of separations allows us to obtain a fairly complete set of data around the contact and solvent separated pairs, which are the most likely to be important, but also allows us to ensure that longer separations make no significant contribution. As we have not explicitly considered them, it remains possible that very long separations make a contribution to the combined free energy profile, but as will be discussed below, the data indicate that this is highly unlikely. The other simulation details are unchanged from the previous chapters.

5.2 Results and Discussion

The combined free energy profiles for the four different ion pair cases are shown in Figure 5.1, along with the individual free energy profiles for the contact pairs, the longest separation considered for each pair, the infinitely separated pairs, and the individual ions making up each pair.



Figure 5.1 Free energy profiles are shown for clusters containing the SASC, BABC, SABC, and BASC ion pairs in panels a), b), c), and d), respectively. The combined profile for the ion pair is shown as a black line while profiles for the contact pairs, the longest separations considered (contact+16Å), and the infinitely separated pairs are shown as magenta crosses, cyan lines, and red lines respectively. The single ion-induced nucleation free energy profiles for the anion and the cation making up each pair are shown as green and blue circles, respectively.

The combined free energy profiles for the ion pair cases are very close to the profiles for the contact pairs, completely overlaying them in some cases. The reason for this is that the contact pair is much more likely to be observed than any of the other separations. This is shown in the potentials of mean force (PMF) plotted in Figure 5.2. While all of the ion pair cases have a solvent separated minimum (or at least a shoulder) at longer separations, these are at least $4k_BT$ less stable than the contact minimum, making a small contribution to the combined profile. Adding additional solvent molecules significantly stabilizes the longer ionic separations. However, any contribution to the combined free energy profile from the longest separations is extremely unlikely for these ions as they are 10-40 k_BT higher in free energy in the gas phase.



Figure 5.2 Potentials of mean force for the ion pairs at cluster size of 50 and 150 water molecules are shown in panels a) and b), respectively. The SASC, BABC, SABC, and BASC cases are shown in black, red, blue, and green respectively.

5.2.1 Ion-Water Potential Energies

While the contact ion pair (and the combined profile) always leads to a higher free energy barrier than either of the constituent ions alone, the longest separation considered leads to a very small free energy barrier that is close to zero at the conditions simulated here. The reason for this shift can be understood by considering the ion-water potential energies, plotted in Figure 5.3 as a function of the ionic separation, along with the ion-water potential energy for the infinitely separated ion pair and the constituent ions. The results for the infinitely separated ion pair were obtained by performing a weighted average of the ion-water potential energies for the single ion cases. This average is taken over all the possible distributions of water between the two ions for each cluster size, weighted by the probability to form the different single ion clusters making up the infinitely separated pair.



Figure 5.3 The ion-water potential energies for clusters containing 150 water molecules are plotted as a function of the ionic separation. The SASC, BABC, SABC, and BASC cases are shown in black, red, blue, and green respectively. The SASC and BABC pairs (panel a) have been separated from the SABC and BASC pairs (panel b), to improve the clarity of the plot. The ion-water potential energy for the infinitely separated pair is shown as a dashed line while the anion and the cation making up the pair are shown as dotted and dot-dashed lines, respectively.

At short separations, the ion-water potential energies are less favorable than for the infinitely separated pair and even some of the single ion clusters. When the ions are close together, few or no water molecules can fit between them, reducing the number of accessible positions for water to bind. Furthermore, the presence of an oppositely charged ion nearby can

disrupt the hydrogen bonds that are formed with the other ion. When the ionic separation increases, water molecules can fit in between the ions and the ion-water potential energy becomes more favorable for the ion pair than the single ions. As the separation is increased further, lots of water molecules can fit in between the ions where they can be favorably oriented with respect to both ions. Furthermore, any disruption of the ion-water interactions due to the presence of an oppositely charged ion is minimized when the separation becomes large. This decreases (more negative) the ion-water potential energy below that of the infinitely separated ion pair, where no water molecules can interact with both ions.

5.2.2 Water-Water Potential Energies

Strong ion-water bonding tends to significantly perturb the solvation structure near the ion, increasing the water-water potential energies. These are plotted in Figure 5.4.



Figure 5.4 The water-water potential energy for clusters containing 150 molecules is plotted as a function of the ionic separation. The SASC, BABC, SABC, and BASC cases are shown in black, red, blue, and green respectively. The water-water potential energy for the infinitely separated pair is shown as a dashed line while the anion and the cation making up the pair are shown as dotted and dot-dashed lines, respectively.

For the contact ion pair, the water-water interactions are similar, or even more favorable than they are for clusters containing single ions and for the infinitely separated pair. The reasons for the trends in the water-water potential energy mirror the reasons for the trends in the ionwater potential energy. When the ions are close together, there is not as much room around the ions to form favorable contacts and the contacts that are made are disrupted by the presence of the other ion, allowing greater flexibility to form favorable water-water hydrogen bonds. As the ionic separation increases, not only do both ions have a full complement of neighbors (which can't hydrogen bond as favorably), but a large number of water molecules can fit in between the ions where the ions can act in concert to restrict the water structure.

The water-water potential energies for the single ion cases are significantly more favorable than for the ion pairs at longer separation because there is only a single ion to disrupt the water structure. Comparing the ion pair results to the infinitely separated pair is more difficult because the cluster has split completely in two and there are different numbers of water molecules in each cluster for the different ion pairs, which is likely the main factor influencing the water-water potential energy of the infinitely separated pairs.

5.2.3 Total Potential Energies

The total potential energies are plotted in Figure 5.5. The potential energy for the ion pair clusters decreases with increasing ionic separation because the decrease in ion-water potential energy is sufficient to overcome the increase in water-water potential energy. The ion-water potential energy makes the largest contribution to the total difference in the potential energy, between ion pairs at different separations. While we have not explicitly calculated the entropic contributions here, they likely make the largest contribution to the free energy differences as well, based on our results for the single ions.

However, the ion-water potential energy contributions generally decay fairly quickly with cluster size as the water molecules are being added further and further from the ions. Therefore, strictly speaking, they make little contribution to the difference in barrier heights between ion pairs with different separations. For ion-induced nucleation, the ion-water interactions still play a crucial role in the height of the free energy barrier because of their importance in determining the cluster size of the free energy minimum. This appears to be the case here as well, as the trends in the cluster size of the free energy minimum match well with the trends in the ion-water potential energies.



Figure 5.5 The total potential energies for clusters containing 150 molecules are plotted as a function of the ionic separation. The SASC, BABC, SABC, and BASC cases are shown in black, red, blue, and green respectively. The potential energy for the infinitely separated pair is shown as a dashed line while the anion and the cation making up the pair are shown as dotted and dot-dashed lines, respectively.

When the ionic separation is small, the ion-water interactions are not so favorable and the free energy minimum is located at cluster size of less than 20 water molecules, leading to a higher free energy barrier. As the ionic separation increases, the favorable ion-water interactions

increase dramatically. This leads to free energy minima at cluster sizes over 50 molecules and extremely low barriers for widely separated ions.

5.2.4 Incremental Ion-Water Potential Energies

While the total ion-water potential energy seems to be closely related to the trend in the barrier heights with increasing ionic separation, it would appear that this is insufficient to explain the differences between the single ion cases and the ion pairs. The ion-water and total potential energies in Figure 5.3 are higher for the contact pairs than for any other separation but they are actually nearly equal to or even lower than the ion-water potential energies for some of the single ion cases. Even so, the barrier heights are significantly higher for the ion pair cases. There are two reasons for this. First of all, the location of the Gibbs free energy minimum does not depend on the total ion-water potential energy, but rather the contribution of the ion-water potential energy to the incremental free energies at cluster sizes around the free energy minimum. To put it another way, the rate at which the ion-water potential energy decays to zero with increasing cluster size is the main factor controlling the location of the Gibbs free energy minimum. It is fairly likely that the ion-water potential energies will approach zero more quickly when the total ion-water potential energy is smaller, but as was observed when comparing the barrier heights for positive and negative Lennard-Jones ions of different sizes, this is not always the case.

The incremental ion-water potential energies plotted in Figure 5.6. At small cluster size, the incremental ion-water potential energy is more favorable for some of the ion pairs. Even though water molecules can't fit directly in between the ions, the first few water molecules can still interact reasonably well with both ions, and these cluster sizes can make a large contribution to the total ion-water potential energy. However, as the cluster size increases, the factors

discussed above lead to less favorable ion-water potential energies for all the ion pairs, and these decay to near zero more quickly than the ion-water potential energies for the single ions.

Furthermore, as the cluster size increases beyond the free energy minimum, water is added further from the ion and at these separations, the ion pair can be reasonably approximated as a point dipole and hydrogen bonding is no longer important. The interactions between water and the ion at these separations can be reasonably described as dipole-dipole. As these interactions decay more rapidly than the ion-dipole interactions that are important at large cluster sizes in ion-induced nucleation, the incremental ion-water potential energies continue to be slightly different even at large cluster sizes. These differences, added up over the entire range of cluster sizes contributing to the barrier, can lead to significant differences in the barrier heights for single ions and ion pairs. When the ion pair is widely separated, the approximation that the ion pair can be treated as a dipole is likely to be poor. At these separations the pair behaves more like to separate ions, which may play a significant role in the lower heights for those cases.



Figure 5.6 The incremental ion-water potential energies $(E_i^{\text{ion-water}} - E_{i-1}^{\text{ion-water}})$ are plotted as a function of the cluster size. The SASC, BABC, SABC, and BASC cases are shown in black, red, blue, and green respectively. The incremental potential energies for the the anion and the cation making up the pair are shown as dotted and dot-dashed lines, respectively.

This can be observed in several of the free energy profiles in Figure 1. For example, for the BABC ion pair, the free energy minima for both of the single ions making up the pair are at smaller cluster size than the minimum for the pair. However, the barrier heights are still significantly lower for the single ions. Therefore, while the location of the free energy minimum is a major factor in the differences in barrier height between ions of different sizes and charges, as well for different ion pairs, it is less important when comparing single ions to ion pairs, as the long range interactions are different for these two cases and seem to be the most important factor leading to lower barrier heights for the single ions.

5.2.5 The Importance of Surface Solvation

A closer examination of the free energy profiles in Figure 1 reveals an interesting feature. All of the ion pair free energy profiles for the SASC pair closely resemble those of the SABC pair. On the other hand, the BABC and BASC pairs also match closely. This suggests that for the ions considered here, the anion is the main controlling factor in the barrier height. This seems to be caused by the preferences of the different ion pairs for the cluster surface.

Radial density profiles have been calculated showing the density of the center of mass for the ion pair as a function of its distance from the center of mass for the water cluster and are plotted in Figure 5.7. When the ionic separation is large or the cluster size small, this analysis may be insufficient to distinguish between surface and interior states as the vast majority of the water molecules will be in between the two ions. However, as the most important configuration is the contact pair, for sufficiently large cluster sizes, these plots should be adequate to determine whether the ion pairs are on the interior or surface of the cluster.

For both of the ion pairs involving larger negative ions, the ion pair has some probability to be on the cluster surface. For the ion pairs containing the smaller anion, interior structures are preferable. Larger anions generally show a considerably stronger preference for the interface than similarly sized cations, based on our results for single ions. Therefore, for the ion pairs considered here, the strong tendency for the anion to be on the interface is sufficient to pull the small cation to the surface as well. On the contrary, while the large cation also prefers the interface in single ion clusters, this preference is weaker and insufficient to move the small anion to the interface. There is a slight shift towards the center of the cluster when the ionic separation is increased, but the two ion pairs containing large anions still have some density on the surface, while the ion pairs containing small anions are almost exclusively on the interior.



Figure 5.7 The radial density profile for the center of mass of the ion pair with respect to the center of mass of the water molecules for clusters containing 150 water molecules are shown for the contact ion pairs and the ion pairs separated by an additional 4Å in panels a) and b) respectively. The SASC, BABC, SABC, and BASC cases are shown in black, red, blue, and green respectively. The profile for the oxygen atom of water is shown as a cyan dot-dashed line. This profile is purely intended as a guide to help locate the interface and is scaled to fit more conveniently on the plot.

The incremental Helmholtz free energies for the ion pairs are plotted in Figure 5.8. These plots show a fairly clear distinction between the interior and surface solvated ion pairs as well. The incremental free energies for all the ion pairs are essentially equal beyond a cluster size of 50 water molecules. However, the free energies for ion pair clusters containing either a large or small anion are quite similar for clusters 10 molecules or larger and essentially overlap for clusters larger than 30 molecules. This is likely a product of their similar preferences for the interface. By the time the cluster size reaches about 10 molecules, the formation of a first solvation shell around both ions is complete. Subsequent water molecules will be added further from the ions and the interactions are significantly weaker. However, both the interactions with the ion from beyond the first shell, and disruptions of the water structure by the ions can lead to different free energies for the surface and interior cases up until a cluster size of about 50. These subtle differences over an intermediate cluster size range result in free energy minima at different cluster sizes and different free energy barriers for the surface and interior ion pairs.



Figure 5.8 The incremental free energies $(\Delta A_i - \Delta A_{i-1})$ for clusters containing a contact ion pair and an ion pair separated by the contact minimum+4Å are shown in panels a) and b) respectively. The SASC, BABC, SABC, and BASC cases are shown in black, red, blue, and green respectively.

5.2.6 Implications for Atmospheric Nucleation

Despite the higher barriers for ion pair-induced nucleation compared to ion-induced nucleation, the former could potentially make a large contribution to nucleation in the atmosphere. With ionization rates less than 10 ion pairs/cm³s, and ion-ion recombination limiting the lifetime of isolated ions in the atmosphere, ion concentrations are fairly low, generally less than 100 ions/cm³.²⁸¹⁻²⁸² On the other hand, any salt or acid molecule in the atmosphere can be a potential ion pair source. Typical sulfuric acid concentrations are on the order of 10^6 molecules/cm³.^{33,283}

As sulfuric acid can potentially deprotonate in small clusters, it seems likely that most of the sulfuric acid containing clusters nucleating in the atmosphere contain at least one ion pair. Furthermore, our results indicate that once the ion pair is formed, the free energy profile exhibits a stable minimum at cluster sizes greater than 10 molecules for the conditions considered here. At these cluster sizes, the ion pair should be fairly stable. If the behavior observed for our simple model ions is characteristic of the behavior in sulfuric acid/water clusters, this implies that once a sulfuric acid molecule deprotonates, it may form a relatively large, stable ion pair cluster. Simulations are currently being performed to probe these effects in the sulfuric acid/water system.

5.3 Conclusion

We have performed AVUS-HR simulations of water nucleation enhanced by the presence of ion pairs. The ion pairs lead to free energy profiles with a minimum at small cluster size as is observed for ion-induced nucleation. However, for all the cases considered here, the free energy barrier is higher for the ion pairs than for either of their constituent ions. The reason for this is that the contact pair almost completely dominates the free energy profile. For the contact pair, the ion-water interactions are relatively weak because the oppositely charged ions occupy space around each ion that cannot be used to bind solvent and can interfere with the ion-water contacts that are formed. This causes the ion-water interactions to die off fairly quickly with increasing cluster size, leading to a relatively high barrier.

On the other hand, when the ions are widely separated, the barrier height is significantly lower. As is the case for ion-induced nucleation, the location of the Gibbs free energy minimum seems to be an important controlling factor. This depends very strongly on the strength of the ion-water interactions near the free energy minimum, which are more much favorable for the widely separated ions, leading to lower barriers. The results indicate that while none of the ions here were sufficiently stable beyond the contact pair to make a significant contribution to the combined free energy profile, ion pairs that form very stable solvent separated pairs could lead to low free energy barriers. Similarly, any other factors that stabilize solvent separated pairs could lead to favorable conditions for nucleation. This is of some interest for sulfuric acid/water nucleation. Several authors have developed empirical models and used them to study clusters containing those hydronium and bisulfate ion pairs.²⁸⁴⁻²⁸⁶ Based on the results of those simulations, there may be a very small (less than 10%) chance to observe the contact pair.²⁸⁶

Finally, we found that the size of the anion had a stronger effect on the free energy barriers than the size of the cation. The reason for this seems to be the greater role played by the anion in determining the preference of the ion pair for the surface or interior of the cluster. Large anions are sufficiently attracted to the cluster interface to move the ion pair to the surface even with a small cation. On the other hand, as the large cation is less likely to be on the interface, the ion pair with the small anion prefers the cluster interior.

These data can provide some insights into the physics of nucleation in the presence of ion pairs. However, a complete picture of how ion pairs are involved in real systems will require an accurate treatment of proton transfer so that the relative contributions of the neutral and proton transferred forms can be assessed. Studies of these behaviors could be extremely useful in clarifying the importance of different atmospheric nucleation mechanisms.

Chapter 6 – Summary and Conclusions

We have performed computer simulations of ion-induced nucleation for a wide variety of ions. Furthermore, we have extended our simulation approach to efficiently calculate the free energy profile for nucleation in the presence of ions pairs. These simulations have allowed us to draw a number of conclusions about ion-induced (and ion pair-induced) nucleation.

The unique shape of the ion-induced nucleation free energy profile is of key importance. Even the earliest theoretical treatments of ion-induced nucleation predict a local Gibbs free energy minimum at small cluster size.¹³⁸⁻¹³⁹ The fact that the free energy barrier for ion-induced nucleation is computed as the difference between this Gibbs free energy minimum and maximum makes it difficult to predict how subtle changes in the ionic properties affect the barrier height, and consequently, the nucleation rate. The trends observed in the free energies from small cluster sizes may vary distinctly from trends in the barrier height.

The sign preference in ion-induced nucleation is an excellent example. Stronger ionwater interactions for the negative ions lead to a free energy minimum at larger cluster size. The location of this Gibbs free energy minimum is governed by the balance between the ion-water interactions and the surface free energy, with a smaller contribution from the bulk free energy. Therefore, the location of the Gibbs free energy minimum is fairly sensitive to the nature of the ion. For conditions where the nucleation free energy barrier does not vanish, the critical cluster is usually at a much larger size than the Gibbs free energy minimum. At these cluster sizes, the contribution from the ion-solvent interactions is small and the critical cluster size is largely governed by the surface and bulk contributions, which are less sensitive to the ionic properties. Therefore, the location of the Gibbs free energy minimum is of paramount importance as it is the most important factor in determining the range of cluster sizes between the free energy minimum and maximum. The smaller decrease in entropy for the negative ions between the Gibbs free energy minimum and maximum is the only contribution favoring lower barriers for negative ions. However, the reason for this is that the stronger ion-water interactions dominate the surface free energy over a wider range of cluster size, leading to a Gibbs free energy minimum at larger size.

A similar behavior is observed when comparing positive and negative ions of different sizes. Initially, water can approach the small cations much more closely than the larger anions. This leads to incremental free energies that are much lower for the positive ions. However, as the cluster size increases slightly, provided that the anion is located on the cluster interior, the larger anions contain more water molecules in the first (and subsequent) solvation shells. These extra first shell molecules are sufficient to compensate for the smaller size of the cation and the incremental free energies become more favorable for the anions. As the location of the Gibbs free energy minimum in mostly determined by the relative contributions of the ion-water interactions and the surface free energy to the incremental free energies (rather than the total free energies), the free energy minimum is located at a larger size for the negative ions because the ion-water interactions are significant over a wider range of cluster sizes due to the extra water molecules close to the ion.

An additional factor in the lower free energy barriers for large anions compared to smaller cations is the gradually decreasing free energy difference with increasing cluster size. In the previous discussion the subtle changes in stability between the Gibbs free energy minimum and maximum were of relatively small importance compared to the location of the Gibbs free energy minimum. This is a case where the differences between the incremental free energies display a constant, small trend over a fairly wide range of cluster sizes, which can be enough to significantly impact the total barriers. In this case, the addition of more solvent molecules around larger anions gradually leads to more favorable free energies for the anions.

The comparison of non-polarizable and polarizable ions is another case where a small, consistent trend in the incremental free energies can lead to unexpected behavior in the barrier heights. The free energy minima were generally located at the same cluster size for the polarizable and non-polarizable ions, so this was not a factor in the difference in barrier height. When polarization is factored into the simulations, the potential energy of all the clusters decreases but the free energy barrier sometimes increases. This is because the solvation gradually becomes more symmetric with increasing cluster size for interior solvated ions. The polarization energy still makes a favorable contribution to the free energy for all cluster sizes. However, this favorable contribution gradually, continuously decreases as the cluster size increases, lowering the free energy maximum by less than the minimum, and raising the barrier. When the ion is on the surface, the polarization gradually increases with increasing cluster size. These small, combined differences in the incremental free energies can add up to significant differences in the barrier height in these cases.

While the free energy minima were generally located at essentially the same cluster size for non-polarizable and polarizable ions, the cluster size at which both free energy minima occurs can still play a role in the relative barrier heights. While the location of the Gibbs free energy minimum is not extremely sensitive to the vapor density, because the polarization energy can be sharply peaked at small cluster size, a small change in the cluster size of the minimum could produce a noticeable change in the effect of polarization on the free energy barrier. In order to expand our investigation of ion-induced nucleation to include clusters containing an ion pair, we have applied an approach similar to the one used previously to calculate PMFs for ion pairs in water clusters to calculate the nucleation free energy profile for ion-induced nucleation using multiple simulations instead of one. This approach insures the complete sampling of the ionic separation and can provide useful insights into the process. We have found that the contact pair makes a dominant contribution to the free energy profile for all the ion pairs considered here. For the contact pair, the ion-water interactions are reduced somewhat because potential binding positions around each ion are either inaccessible or less favorable due to the presence of the other ion. This leads a free energy barrier that is higher than the barrier to for more widely separated pairs. As the ionic separation increases, water molecules are able to interact quite favorably with both ions, leading to very favorable ion-water interactions. This is another case where the location of the Gibbs free energy minimum is important.

As was seen for the single ion-induced nucleation studies, one of the biggest factors controlling the barrier height is the strength of the ion-water interactions and how quickly they decay with increasing cluster size. Even though the total ion-water potential energy is similar to, or even lower for the contact ion pair than for some of the single ions, it decays more rapidly with increasing cluster size for the ion pairs. This occurs both because of the limited number of favorable binding positions around the ion, but also because the long range interactions between water and the ion pair decay more rapidly than the interactions between water and a single ion. In some cases this leads to minima at smaller sizes for the ion pairs, but the differences in long range behavior are the most important in this case, leading to significantly lower barriers for the single ions even when the free energy minima are at similar or larger sizes for those ions. The combined results of these studies have provided a fairly unified picture of water nucleation in the presence of both single ions and pairs. The location of the Gibbs free energy minimum is a crucial factor controlling the free energy barrier. In general, the cluster size at which the free energy minimum is located is strongly related to the strength of the ion-water interactions, and the rate at which they decay to zero. However, the free energy minimum is not the only important factor. Small differences between two different ionic clusters that persist over a wide range of cluster sizes can add up to significant differences in the barrier heights.

The results for the ion pairs could have some important implications for the interpretation of atmospheric nucleation events. Our results indicate that if an ion pair is formed in a small water cluster, a small, stable, neutral cluster containing an ion pair and more than 10 water molecules can be formed as the ion pair is likely to be stable in a cluster of that size. From this stable cluster, the nucleation free energy barrier is still significantly lowered compared to pure water. This could allow ion pairs to play a key role in atmospheric nucleation.

Despite the fact that our results show that nucleation on single ions is more efficient than nucleation enhancement by ion pairs, ion pair-induced nucleation could potentially make a larger contribution to aerosol formation than ion-induced nucleation. The concentration of acid and salt molecules in the atmosphere at any time is orders of magnitude higher than the concentration of ions. The ion-induced nucleation mechanism is also hampered by loss due to ion-ion recombination (creating an ion pair cluster). Finally, while our results here indicate that the contact pair makes a dominant contribution to the free energy profile, there may be different ions where longer separations make a greater contribution, decreasing the free energy barrier. Ultimately, a quantitative calculation of the relative importance of nucleation on single ions and ion pairs requires an accurate treatment of the ionization process and any potential equilibrium between the neutral and ion pair forms of the solute. However, such simulations could be extremely valuable in identifying the important particle formation mechanisms in the atmosphere.

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