Effect of droplet size and counterions on the spatial distribution of ions - Inferring microscopic properties from nanoscale simulations of charged droplets

Victor Kwan and Styliani Consta*

*Department of Chemistry, The University of Western Ontario, London, Ontario, Canada
N6A 5B7*

E-mail: sconstas@uwo.ca

Abstract

Electrosprayed droplets have emerged as a new environment for accelerating chemical reactions by orders of magnitude relative to their bulk analogues. Nevertheless, the reaction mechanisms are still unknown. Unraveling of the ion spatial distribution is critical as to where charge transfer reactions are likely to take place and as to their effect on the ionic atmosphere of macroions. Here we address the question of how properties of highly charged droplets converge with system size using analytical theory and molecular dynamics. We investigate the ion spatial distributions, surface charge and surface electric field in aqueous droplets with diameter in the range of 5 nm (which is ≈ 1000 H₂O molecules) to 16 nm (which is $\approx 6 \times 10^4$ H₂O molecules) with and without counterions. The charge carriers are Na⁺, Cl⁻, I⁻ ions and model hydronium ions. We find convergence of the ion distribution in droplets of diameter of 16 nm and we present the analytical theory that allows one to extrapolate the ion distribution maximum to larger droplets. We show that approximately 40% of the free ions contribute directly in the droplet's surface charge. The model hydronium ions reside in the very outer layers of water, which is strikingly different from the location of Na⁺, Cl⁻ and I⁻ ions. In the presence of counterions the concentration of the ion

in excess increases in the outer water layers of the droplet, relative to that in a droplet with only one type of ion present and the counterions reside mainly in the droplet interior. We settle a long-standing discussion about the surface charge of a highly charged droplet. The ion distribution convergence allows us to perform simulations in nanoscopic droplets and extrapolate the results to larger sizes, which are still inaccessible to atomistic simulations. For the first time droplet sizes that are accessible to experimental scrutiny are atomistically modeled.

Introduction

In the last one and a half decades there has been a surge in the use of microdrops in many chemistry and industry applications, which include dispersive liquid-liquid micro-extraction,¹ micro-fluidity and acceleration of reactions in electrosprayed droplets.²⁻⁸ Progressive miniaturization of chemistry has led to the use of even smaller volumes in the case of nanofluidics. Even though our ability to carry out chemical reactions on mass-scale in these minute volumes is rapidly growing, the knowledge of the reaction mechanisms of the dissolved species in the droplet environment is still limited. The micro-drops and nano-drops are macroscopic and mesoscopic clusters, respectively.^{7,8}

In this work we present the results of molecular dynamics simulations and analytical theory that demonstrate the convergence of the ion spatial distribution with droplet size in highly charged liquid drops found in aerosol phase. The convergence allows us to perform simulations in nanoscopic droplets and extrapolate the findings to larger droplet sizes, which are still not accessible to atomistic simulations.

This study is significant for several experiments where the droplet chemistry in aerosols plays a central role. These experiments include use of electrosprayed droplets as reaction vessels²⁻⁶ and droplet-based ionization techniques used in native mass spectrometry.⁹ The spatial distribution of ions is also important in droplets found in atmospheric aerosols. Droplets and particulates in atmospheric aerosols are also charged but not as highly as electrosprayed droplets.¹⁰ The ion distribution is the first step for establishing the ion-evaporation mechanism,¹¹⁻¹³ which is a principal disintegration mechanism of charged droplets in atmospheric and electrosprayed aerosols. The effect of the droplet environment in the charge state of a macroion is one of the most debated questions in native mass spectrometry. The spatial variation of the ion concentration in droplets may indicate as to where charge transfer reactions that determine the charge state of proteins and nucleic acids may take place in droplets.

Regardless of their charge, droplets in general combine certain characteristics due to their finite-size. These characteristics are: confinement, existence of a large interface with the surrounding medium, large density gradients due to the interface, break-down of translational invariance and shape fluctuations. Depending on the droplet size certain characteristics are more pronounced in certain sizes than others. Notably, shape fluctuations are more pronounced in nano-drops (mesoscopic clusters) relative to their spherical shape than in clusters of a handful of molecules and in macroscopic clusters. The shapes fluctuations are important to consider because they may couple with the reaction mechanisms.^{7,8} Highly charged droplets have additional features to those of neutral droplets. These features are: distinct ion spatial distribu-

tion, and thus variable ionic strength throughout the droplet volume, fluctuations pertinent to the charged droplets and charge-induced instabilities when the charge exceeds a threshold value for a certain system size.¹⁴⁻¹⁸ All of the aforementioned characteristics with the possible exception of the charge-induced instability are also present in droplets of atmospheric aerosols.

In a highly charged droplet we should define the condition of stability. The stability of a charged conducting droplet¹⁴⁻¹⁸ is determined by the fissility parameter (X) defined as

$$X = \frac{Q^2}{64\pi^2\gamma\epsilon_0 R^3}. \quad (1)$$

where Q is the droplet charge, γ the surface tension, ϵ_0 and R are the permittivity of vacuum and the radius of the droplet, respectively. Energy considerations in combination with volume and charge conservation demonstrate that the division of a charged droplet (mother) into two sub-droplets (daughter) is always favored.¹⁷ For droplets at $X < 1$, the mother droplet and the daughter droplets are separated by a free energy barrier.^{11-13,17} For a droplet at $X > 1$ the droplet fission proceeds spontaneously.¹⁷ The combination of parameters of charge, surface tension and radius for $X = 1$ is defined as the Rayleigh limit.¹⁴⁻¹⁸ Computer simulations of the droplet evaporation-fission process indicate that the Rayleigh fissility parameter stays near 0.9.¹⁹ The majority of the droplets that we study are found at $X > 0.85$ besides droplets of 880 water molecules that are found at $X \approx 0.57$.

A lot of experience has been obtained over a few decades in modeling ions near a planar interface.²⁰⁻²⁴ These systems are overall neutral, thus we cannot expect a direct transfer of these findings to the case of a charged curved interface. A major force that determines the location of the ions in the droplets is their inherent conducting character.

In this article, we present a systematic study of Na^+ spatial distributions in aqueous droplets with diameter in the range of 5 nm (which corresponds to ≈ 1000 H_2O molecules) to 16 nm (which corresponds to $\approx 6 \times 10^4$ H_2O

molecules). We use the Na^+ ions as an example to demonstrate the effect of droplet size, but the results hold for different ions as well. The ion spatial distributions of model hydronium ions in a droplet of ≈ 1000 H_2O molecules, Cl^- and I^- in droplets of ≈ 3500 H_2O molecules are also computed. We examine: (a) the convergence of properties of charged droplets as a function of size. To our knowledge droplets of diameter 16 nm are the largest that have been atomistically modeled thus far and they approach in size those that may be directly emitted by a nano-electrospray source. (b) the ion distribution of negative ions (Cl^- and I^-) and their mixture (c) the distinct features of the distribution of model hydronium ions and (d) the effect of counterions.

The presence of the counterions change the ion spatial distribution considerably relative to that of the one type of ions. The concentration of the ion in excess increases in the outer water layers of the droplet, relative to the droplet analogue with only the ion in excess present. The counterions are found mainly in the droplet interior while they reside mainly in the outer water layers when they are the only charged species present. The model hydronium ions reside in the very outer layers of water, which is strikingly different from the location of Na^+ , Cl^- , and I^- ions. The location of the hydronium ions affects the orientation of the H_2O molecules in the droplet differently from that of the Na^+ ions. Droplets with excess Cl^- ions show similar ion distribution to that of Na^+ ions but the orientation of the water dipoles inverts.

Systems and Simulation Methods

We performed equilibrium molecular dynamics (MD) simulations of charged aqueous droplets with Na^+ , model hydronium ions, Cl^- and I^- ions. A typical snapshot of a system comprised H_2O molecules, Cl^- and I^- ions is shown in Fig. 1. The simulations were performed by using the software NAMD version 2.12.²⁵ The Newton’s equation of motion for each atomic site was integrated using the velocity-Verlet

algorithm with a time step of 1.0 fs. The trajectories were analyzed using VMD 1.9.2.²⁶ The water molecules were modeled with the TIP3P (transferable intermolecular potential with 3 points)²⁷ -CHARMM and the TIP4P/2005²⁸ and the ions with the CHARMM36m^{29,30} and OPLS (Optimized Potentials for Liquid Simulations),^{31,32} respectively. The TIP3P-CHARMM is a m(odified)TIP3P, which is the original TIP3P with Lennard-Jones potential on the hydrogen sites. Hereafter we will use the notation TIP3P for this water model. The parameters of the force fields are presented in Table S1 in the SI.

All the forces were computed directly without any cut-offs. Equilibrium simulations in NAMD were set by placing the droplet in a spherical cavity of radius 20.0 nm by using spherical boundary condition. The cavity was sufficiently large to accommodate the shape fluctuation of the droplet. The droplet will eventually reach vapor pressure equilibrium. The systems were thermalized with Langevin thermostat with the damping coefficient set to 1/ps. The Rayleigh limit of the droplet (Eq. 1) was calculated with the surface tension values of the water model used at the simulation temperature.³³ Specifically, for TIP3P at $T = 300$ K the value of surface tension is taken to be 0.0523 N/m and at $T = 350$ K to be 0.0432 N/m. For TIP4P/2005 at $T = 350$ K is taken to be 0.0619 N/m.

The system that were examined are shown in Table 1. The production runs of the 2×10^4 and 3×10^4 H_2O -molecule drops were for 40 ns, following a 10 ns equilibration time and that of 1000 and 3500 H_2O -molecule clusters for 150 ns and 50 ns, respectively. The production run for the 6×10^4 H_2O -molecule drop was 8.5 ns.

A question that may arise concerns the effect of the force field on the ion distributions. The details of the force field lead to different values of macroscopic properties of the solvent (e.g. surface tension, dielectric constant), that enter the general macroscopic models relevant to ion-droplet interactions. First of all, the surface tension, that depends on the water model, enters Eq. 1, and hence the Rayleigh limit. Since the stability of a droplet depends on the charge-squared to surface tension ratio (considering

Table 1: Systems studied, radii and charge of the droplets. $n_{\text{H}_2\text{O}}$ denotes number of water molecules in the droplet and n_{I} denotes the number of ions in the aqueous droplet in the production run. R_e [nm] is the radius of the equimolecular dividing surface (computed by using density of the TIP3P model at 350 K to be 0.9539 g/cm³ and that of the TIP4P/2005 model²⁸ at 350 K to be 0.9713 g/cm³. Q_{est} (in units of elementary charge e) is the charge estimated at the Rayleigh limit, considering radius R_e . R_r is the Rayleigh radius estimated considering the total droplet charge in the simulations. R_{sim} [nm] is the distance found from the concentration profiles in Fig. 5 at which the density becomes 5×10^{-4} g/cm³. R_{max} [nm] is the distance from the droplet COM to the maximum of the ion concentration profile. X is the fissility parameter, calculated by taking the square of the ratio between the charge of the droplet and Q_{est} . R_c [nm] is the distance measured from the droplet COM at which the surface charge starts to build up. “—” indicates that we have not computed the charge distribution profiles in these systems. In all the systems the temperature is set at $T = 350$ K, besides those marked with an asterisk, which are found at $T = 300$ K. The simulations were performed using the TIP3P water model, besides those marked with a dagger, where the TIP4P/2005 model was used.

System	$n_{\text{H}_2\text{O}}$	n_{I}	R_e	Q_{est}	R_r	R_{sim}	R_{max}	X	R_c
1	880	6Na ⁺	1.88	7.9	1.56	2.6	0.90-0.95	0.57	1.2
2	980*	8Na ⁺	1.91	8.7	1.81	2.9	0.95-1.00	0.84	—
3	5880	19Na ⁺	3.65	20.6	3.37	4.4	2.65-2.70	0.85	2.9
4	2×10^4	36Na ⁺	5.31	37.6	5.16	6.1	4.30-4.35	0.92	4.4
5	3×10^4	44Na ⁺	6.08	46.0	5.90	6.8	5.10-5.15	0.91	5.1
6	3×10^4	44Na ⁺ + 23 NaCl	6.08	46.0	5.90	6.8	5.10-5.15	0.91	5.1
7	3×10^4	44Cl ⁻	6.08	46.0	5.90	6.8	5.05-5.10	0.91	5.1
8	3×10^4	44Cl ⁻ + 23 NaCl	6.08	46.0	5.90	6.8	5.10-5.15	0.91	5.1
9	6×10^4	63Na ⁺	7.66	65.1	7.50	8.3	6.90-6.95	0.94	—
10	880	6H ₃ O ⁺	1.88	7.9	1.56	2.6	1.60-1.65	0.57	—
11	980*	8H ₃ O ⁺	1.92	8.2	1.92	2.6	1.80-1.85	0.95	—
12	880	6Cl ⁻	1.88	7.9	1.56	2.6	1.05-1.10	0.57	—
13	980*	8Cl ⁻	1.92	8.2	1.92	2.6	1.15-1.20	0.95	—
13	3500 [†]	15I ⁻	2.95	18.4	3.04	3.5	2.45-2.50	0.65	—
14	3500 [†]	16Cl ⁻	2.95	18.4	3.04	3.5	2.20-2.25	0.75	—
15	3500 [†]	8Cl ⁻ + 8I ⁻	2.95	18.4	3.04	3.5	2.15-2.20 2.55-2.60	0.65	—

Figure 1: Typical snapshot of a droplet that comprises ≈ 3500 TIP3P molecules (red oxygen site, white hydrogen site) and 8 Cl^- ions (green spheres) and 8 I^- ions (magenta spheres).

volume constant), the surface tension for the specific water model will regulate the amount of charge a droplet can support. Thus, fundamental questions, which include the validity of the Rayleigh limit in droplets, and the factors that determine the ion spatial distribution should not be affected by the surface tension of the specific water model. Another important parameter that enters the ion distribution is the system’s dielectric constant. On the one hand, the dielectric constant that enters Eq. 1 is that of the medium (vapor in our studies) surrounding the droplet because the Rayleigh model deals with a conducting droplet. On the other hand, the dielectric constant of the droplet determines the solvation energy of the ions, for instance it enters the Born’s solvation model and the Debye length.³⁴ The dielectric constant also enters the ion-evaporation mechanism. Thus, the ion distribution may be affected by the dielectric constant of the water model. We expect that the majority of the ions will be found in the outer water shells of the droplets, thus they are subject to shape fluctuations and large density gradients. The shape fluctuations are coupled to the ion distribution. The distinct environment of the surface and the presence of ions will reduce the value of the dielectric constant considerably.³⁵ We think that

any water model will yield a lower dielectric constant on the droplet surface, thus it will be able to provide the trends in the spatial distribution of ions with the droplet size and the effect of counterions in the outer droplet layers. In bulk solution TIP3P predicts a closer value to the experimental dielectric constant than the TIP4P/2005.

Test of a model hydronium force field

The large number of studies on the Eigen³⁶ and Zundel³⁷ complexes of water with hydronium ion in small clusters are indicative of the challenges in modeling and experiments.^{38–57} Because of the large droplets that we study, we model the hydronium ions by a simple empirical model, where the parameters were taken from.⁵⁸ We address the following questions: (i) Is there enough space on the droplet surface to accommodate the Eigen “pyramids”. (ii) Does the particular structure of the Eigen complex, differentiate its location in a droplet relative to that of Na^+ ions?

To test the Eigen structure of the model we used,⁵⁸ we carried out classical MD simulations on the protonated water cluster $(\text{H}_2\text{O})_{30}\text{H}_3\text{O}^+$. The structures were compare with those by Ufimtsev et. al⁵⁹ generated by ab initio MD (AIMD) performed at $T = 300$ K. As there are multiple local energy minima (at finite T), a conventional simulation of the canonical ensemble (NVT) will not capture the structural isomers. Instead, simulated annealing were used to explore the complex energy landscape more reliably.

The simulation protocol is as follows: The system is heated by setting the temperature of the Langevin thermostat to 200 K for 0.5 ns, then it is quenched by setting the temperature of the thermostat to 100 K for 0.5 ns. The heating-cooling cycle is repeated 20 times and we observed distinct configurations between the cycles. We discard the trajectory where the temperature is 200 K and only use the 100 K trajectory for analysis.

At $T = 100$ K, the hydronium ion forms

an Eigen complex and reside on the surface of the cluster. We compare the hydronium-water O–O radial distribution function (RDF) shown in Fig. 2 with that of Ufimtsev et. al.⁵⁹ The model hydronium model reproduces well the oxygen-oxygen distance of an Eigen complex (2.6 Å). In the RDF we observe a small shoulder centered at 2.9 Å that is absent in the AIMD. The shoulder correspond to an oxygen that is 'colinear' with the hydrogen at the base of the H_9O_4^+ pyramid. The wide band from $\sim 4 - 4.8\text{Å}$ in our simulation is slightly shifted outwards compared to the AIMD simulation.

Figure 2: The O–O radial distribution function between the hydronium ion and water molecules.

Results and Discussion

Spatial distribution of Na^+ ions in aqueous droplets

Initially, we analyze the ion spatial distribution and surface charge for a droplet of 3×10^4 H_2O molecules-44 Na^+ ions at $T = 350$ K and then we examine the ion distributions of several droplet sizes in order to examine their convergence.

Droplet of 3×10^4 H_2O molecules-44 Na^+ ions Fig. 3 (a) shows the oxygen-TIP3P density profile (O-DP) and the Na^+ concentration profile (CP) for two droplet sizes comprised (a)

Figure 3: (a) Water density profiles (blue lines) and Na^+ concentration profiles (red lines) vs distance from the droplet COM for droplets comprised 2×10^4 TIP3P H_2O -36 Na^+ ions and 3×10^4 TIP3P H_2O -44 Na^+ ions at $T = 350$ K. The blurry region shows the error bars. The standard deviation is calculated by using 5 blocks of raw data, where every block has 4×10^4 configurations. (b) Cumulative probability of the systems in (a). (c) Charge distribution profile for 3×10^4 H_2O -44 Na^+ ions at $T = 350$ K (bin size 2.0 Å). The black line is for the water molecules only in the 3×10^4 H_2O -44 Na^+ ions system, and the blue line is for the water molecules and the ions.

2×10^4 TIP3P H_2O -36 Na^+ ions and (b) 3×10^4 TIP3P H_2O -44 Na^+ ions. The profiles have been normalized by dividing with the volume

(a)

(b)

Figure 4: (a) Charge distribution of a droplet comprised 3×10^4 H_2O molecules and 44 Na^+ ions vs distance from the droplet COM (bin size $2.0 \text{ \AA}$). Blue line is the Na^+ ion distribution and the black line the distribution of the total charge (ions, oxygen and hydrogen sites). The semi-circular region is taken from simulations of the system. (b) Colored shells centered at the droplet COM: yellow colored $0 \text{ \AA} < r < 50.0 \text{ \AA}$, green colored $50.0 \text{ \AA} < r < 56.0 \text{ \AA}$, grey colored $56.0 \text{ \AA} < r < 62.0 \text{ \AA}$, red colored $r > 62.0 \text{ \AA}$.

element of a spherical shell ($\frac{4}{3}\pi[(r + dr)^3 - r^3]$ where r is the droplet radius). The Na^+ -CP shows a broad maximum at $\approx 4.3 \text{ nm}$ and $\approx 5.3 \text{ nm}$ in the droplets of 2×10^4 and 3×10^4 TIP3P H_2O molecule, respectively. In droplets sizes that we examined, the highest concentration of Na^+ ions is found in the outer H_2O layers, where the density of H_2O is still high (but still slightly lower than that at the droplet center). As shown in Table 1 the density in droplet sizes of a few tens of thousands of molecules dies-off to $5 \times 10^{-4} \text{ g/cm}^3$ at approximately

(a)

(b)

Figure 5: (a) Na^+ concentration profiles vs distance from the droplet COM for aqueous droplets of various sizes at $T = 350 \text{ K}$. Error bars are sparsely shown for clarity purpose. The error bars are shown in figures in the SI. (b) Scaled plots of (a). The x-axis is scaled by R_r for the specific droplet charge state (Q) and the y-axis by Q/R_r^3 (data presented in Table 1).

1.7 nm from the Na^+ concentration maximum. In the droplet comprised 6×10^4 H_2O molecules the distance is shorter, 1.4 nm . As we are going to discuss in the next section, the shorter distance arises from the smaller shape fluctuations of the larger droplet relative to its spherical shape. In this 1.7 nm layer the water density decreases rapidly. Considering that the diameter of a TIP3P H_2O molecule is $3.15 \text{ \AA}$ and the radius of a Na^+ is $1.4 \text{ \AA}$, the 1.7 nm layer would correspond approximately to five aqueous shells. The outer three shells are not complete and are characterized by roughness (islands of water) and short dangling water

chains (see mainly the grey and red shells in Fig. 4 (b)).

Fig. 3 (b) shows the cumulative probability profiles (CPP) that result from the integration of Na^+ -CP (Fig. 3 (a)). The CPPs show three regions of different increase rates: (i) near the droplet COM the slope of the profiles is close to zero, (ii) in an intermediate distance from the droplet COM there is a rapid growth and (iii) near the droplet surface there is slower growth that leads to a plateau of the CPP. Specifically, for the droplet of 3×10^4 TIP3P H_2O we find $\approx 15 \text{ Na}^+$ ions in a spherical volume with radius 4.1 nm from the droplet COM. For radius greater than 4.1 nm the CPP increases rapidly up to ≈ 5.6 nm and that is followed by a slower saturation that reaches the value of 44 Na^+ ions at 6.5 nm. The profile of the droplet of 2×10^4 , 880 and 6000 TIP3P H_2O found in the SI (Fig. S1 (a), (b), (c)) show the same trend as that of the 3×10^4 TIP3P droplet. In the 2×10^4 TIP3P droplet, the majority of the ions are found in a radius of 3.8 nm - 4.8 nm (1.0 nm thickness). In the 3×10^4 TIP3P the majority of the ions are in the spherical shell with radius 4.5 nm - 5.8 nm (1.3 nm thickness). Overall, we find that in the sizes of droplets we have studied $\approx 23\% - 38\%$ of the Na^+ ions are found in the region (i) of the CPP.

Figure 3 (c) and Fig. 4 present the layering of the charge for a $\approx 3 \times 10^4$ H_2O molecule droplet, as a function of the droplet radius (measured from the COM). For comparison purpose, first of all, we will discuss the pure water case: If we plot the charge layering in pure water (presented in Fig. S2 in SI), we will find a wavy function in the outer water shells similar to that shown in Figure 3 (c) and Fig. 4. The wavy portion appears when the water density sharply declines. Modelling that we performed using TIP3P and TIP4P/2005 at $T = 300 \text{ K}$, 350K for pristine water droplet comprised $\approx 6000 \text{ H}_2\text{O}$ molecules, showed that in both models the charge minimum appears at 3.2 nm and the maximum at 3.6 nm (which is equal to the R_e). The charge variation starts to build up, not on the layers that are exposed to vapor but at $\approx 30 \text{ \AA}$, where the density starts to decline slightly relative to the bulk. In the presence of

ions for the $\approx 6000 \text{ H}_2\text{O}$ -molecule droplet, the charge starts to build up at about $2.0 \text{ \AA}$ before that in the pure H_2O and dies off at a distance of $\approx 4.0 \text{ \AA}$ longer than that of pure H_2O (presented in Fig. S2 in SI). Thus, in the presence of ions the charge starts to build up from the water layers where the water density is still high, thus this water layer is not exposed to vacuum (vapor). Figure 3 (c) and Fig. 4 show the charge layering for a droplet comprised $\approx 3 \times 10^4 \text{ H}_2\text{O}$ molecules and 44 Na^+ ions. The onset of the building up is found at $\approx 5.1 \text{ nm}$, which is in the green colored region shown in Fig. 4 (b).

We note several interesting features: (a) the H_2O polarization appears in the droplet interior. The presence of the free ions lead to an average zero value of charge in the droplet interior. (b) In the outer water layers, there is a wavy form of the charge profile as it also appears in the pristine water droplet. However, *the wavy portion of the charge profile is determined by both the free charge (ions) and the solvent polarization (which is already present to a certain extent in pristine water droplets)*. As expected, the integral from 5.1 nm to infinity yields the total charge of the droplet. The amount of free charge in this region is $\approx 42\%$ of the total number of Na^+ ions in the droplet. The integral over the positive portion of the profile only yields a much larger number, which is $\approx 53e$. In the presence of counterions the total and water charge profiles are identical to those of the one ion only.

We emphasize here the size of the standard deviation - one sigma - (shown in Fig. S2-S4 in SI). The size of the standard deviation indicates that there are large charge fluctuations in the outer droplet layers, which may lead to release of solvated single ions or charge transfer processes to macroions (when macroions are present).

It is in order to compare our findings with prevailing theories⁶⁰ in the literature concerning the surface charge of highly charged droplets. It has been widely accepted⁶⁰ in the literature that: All the excess charge (that of the ions since the water molecules are neutral) is transferred on the surface layer that is found at the extreme outer layers of water and that the carri-

ers of the charge are solely the “half dipoles” of water. Ahadi⁶⁰ et al. have supported their finding by simulating a droplet of approximately 1248 H₂O molecules with 10 Na⁺ or 10 X⁻ ions in vacuo at $T = 320$ K. The authors conclude that “droplets containing 10Na⁺ carry all their excess charge in a surface layer located ca. 26 Å from the droplet center. . . . Figure 7 illustrates how the charge layer generated in this way at the water/vapor interface can be thought of as unpaired half-dipoles. This layer has exactly the same timeaveraged magnitude as the buried ionic charge Q (Figure 6).”

The authors also support that “Buried Na⁺ ions cause large-scale dipole ordering that extends all the way to the droplet periphery. Here, the positive ends of water dipoles preferentially point into the vapor phase. *These half-dipoles in the outermost droplet layers assume the role of surface charge, while solvation effectively neutralizes Na⁺ ions in the interior.*”

In the same article⁶⁰ for the negative ions the location of the surface charge layer is placed at 21 Å from the droplet center. Figure 3 in the same article⁶⁰ shows that the 21 Å and 26 Å are where the H₂O density has diminished considerably (it is beyond the sharp decrease of the water density, where the density start to level off).

Our studies do not support these findings. Below we present the explanation: Let us consider as an example the data in Fig. 3 (of this manuscript) for a droplet of 3×10^4 H₂O molecules and 44 Na⁺ ions. The corresponding distance to the 26 Å reported by Ahadi et al. (for the droplet of ≈ 1248 H₂O molecules) is at ≈ 65 Å in the droplet of 3×10^4 H₂O molecules. The integral of charge of water (see Fig. 3 (c)) for > 64 Å yields $+25e$, which is much less than the droplet’s charge, which is $+44e$. If we integrate starting from shorter distances, for > 61 Å we get $+42e$ and for > 60 Å we get $+52e$. Since the water molecules are polarized in the droplet surface due to the total charge of the droplet⁶¹ and at the same time the very great majority of these molecules are exposed to the vacuo, it is natural that the integration from some distance outward may yield exactly the number of $+44e$, which is the num-

ber of 44 Na⁺ ions in the droplet. Slight variations away from the position that yields the exact number of droplet charge ($+44e$ in our example) yields considerably different values for the integral of charge. We note that pristine water droplets also show positive charge on the very outer surface,^{62,63} thus one can also define an amount of positive charge on their surface. This outer charge is also carried by “half-dipoles”. These features do not differentiate the positively charged from the pristine droplets. *Thus, this approach to define the surface charge is completely arbitrary.* The same findings as those that we presented for a droplet of 3×10^4 H₂O molecules and 44 Na⁺ ions hold for all the droplet sizes we have studied.

We show that the overall charge on the surface in a highly charged droplet is determined differently. Plots similar to that in Fig. 3 (c) may indicate the surface charge. If one integrates the wavy part of the total charge, one recovers the total charge of the droplet. This is the shell of the droplet that carries the total charge. This shell includes the green+grey+red regions in Fig. 4 (b) and it starts at the maximum of the ion distribution. The location of the shell in relation to the water density is shown in Fig. 3 (a). We emphasize the size of the charge fluctuations in the droplet shells. In the article by Ahadi et al.⁶⁰ error bars and the charge fluctuations in the surface charge have been neglected. Here, we showed the size of the fluctuations and the fact that they are larger than the average values. These large charge fluctuations may cause charge transfer reactions and ejection of ions. *Hence, the overall droplet charge is found in a thick outer layer and it is determined by a combination of free charge (ions) and polarization charge of the solvent (Fig. 4).*

In the exterior of the droplet, where Ahadi et al. locate the surface charge the polarization of the solvent is caused by the total droplet charge⁶¹ and not by each individual ion as Ahadi et al. have supported “Buried Na⁺ ions cause large-scale dipole ordering that extends all the way to the droplet periphery.”⁶⁰ . Our view is supported by the Na-O radial distribution functions (RDF) shown in Fig. S5 in SI, which shows that the spatial correlation in the

Na-O positions has diminished at $\approx 7 \text{ \AA}$ - $8 \text{ \AA}$. In Fig. 4 by Ahadi et al.,⁶⁰ the spatial correlation in the Na and O or H positions is diminished at $\approx 6 \text{ \AA}$. Considering that in Fig. 4 in Ref.⁶⁰ the ions are located between $10 \text{ \AA} - 15 \text{ \AA}$, then the ordering of the water molecules due to the individual ions cannot be extended at distances of $26 \text{ \AA}$, because the correlation in the position has been lost. Based on our arguments at this longer distance it is the overall droplet charge that polarizes the solvent as it is discussed by Kwan et al.⁶¹

There is another point to note here. It has been supported that “These half-dipoles in the outermost droplet layers assume the role of surface charge, while solvation effectively neutralizes Na^+ ions in the interior.” Differently, our data show that the ions cancel the polarization charge of the solvent in the droplet interior. An aqueous droplet with free charges is a conductor, thus as continuum electrostatics predicts, the charge will be on the surface. One has to distinguish between continuum electrostatic theory and atomistic level electrostatics. At the molecular level the free charge is not exactly on the surface as it has been explained in the classic textbook of D. Jackson⁶⁴ and has been discussed in detail in our previous work.⁶¹ Indeed, simulations and analytical theory⁶¹ have shown that a large portion of the free charge is on the surface (defining the surface as a thicker layer and not in the continuum electrostatics sense) but because of the Boltzmann distribution, the ion distribution will have a width. The ion (free) charge (as a whole) polarizes the solvent (water in our study) molecules. The polarization is directed towards the interior of the droplet and towards the exterior. The ions that are in the interior polarize the solvent locally, but since the solvent polarization is symmetric around a single ion, it is difficult to isolate the role of each individual ion in the overall polarization. The polarization of the water molecules is manifested in plots of the dipole orientation and plots of the charge distribution (black solid line in Fig. 3 (c)). Comparison of the pristine and charged droplets (Fig. S2 in SI) suggest that toward the interior the *ions cancel the polarization charge of the solvent molecules* in

contrast to the argument that the “solvation effectively neutralizes Na^+ ions in the interior.” The exact polarization of the water molecules needs further study and we examine it in a future article.

In summary, we presented how to determine the surface charge of a highly charged droplet and that the surface charge is composed of a portion of the free ions and the solvent polarization charge. We quantified the amount of the free charge that contributes directly into the surface charge. We emphasize the significance of the charge fluctuations in the droplet shells.

Convergence of droplet properties with size

Figure 5 (a) shows the ion distributions for five droplet sizes, which are summarized in Table 1. The largest droplet comprises 6×10^4 H_2O molecules and 63 Na^+ ions. The profiles have been normalized by dividing with the volume element of a spherical shell ($\frac{4}{3}\pi[(r+dr)^3 - r^3]$ where r is the droplet radius).

We can recast Eq. 1 into the following form

$$\frac{1}{(4\pi\epsilon_0)^2} \frac{Q^2}{R^4} R = |E|^2 R = 4\epsilon_0 \gamma X \quad (2)$$

where $|E|$ is the magnitude of the electric field of a spherical conductor and the rest of the terms have the same meaning as in Eq. 1. Equation 2 shows that the surface charge density, denoted hereafter by σ , (which is proportional to $|E|$)⁶⁴ is proportional to $1/\sqrt{R}$. The surface charge density is computed by integrating the ion molarity $n(r)$

$$\sigma = \frac{1}{4\pi R_r} \int_0^\infty dr 4\pi r^2 n(r) \quad (3)$$

where the charge density is computed in units of $[\text{mol}]/[\text{m}]^2$. Another related quantity is the charge molarity on the surface of the droplet $n(R_r)$. For large droplets we may find a relation between the surface charge density and the charge molarity on the surface using the solution of the nonlinear Poisson-Boltzmann equation⁶¹

$$\sigma = \lambda_{DH} n(R_r) \quad (4)$$

where λ_{DH} is the Debye length⁶¹ of electrolyte with the ion molar concentration $n(R_r)$. Using the relation between the concentration and the Debye length we arrive at the scaling for the maximum ionic concentration $n(R_r) \sim 1/R_r$. The simulation data agree with the theoretical prediction (Eq. 2) that the surface charge density σ decreases with the increase of the droplet radius as shown in Fig. 5 (a). Figure 5 (b) shows the scaled distributions, where the distance (x axis) in Fig. 5 (a) has been scaled by the Rayleigh radius shown in Table 1. The scaled ion distributions reveal an interesting behavior that it is not obvious in the non-scaled data (Figure 5 (a)). The distributions of all droplet sizes besides that of 880 H₂O molecules are very similar. In long distance, the smaller the droplet, the slower the ion distribution dies-off. This behavior arises from the size of the relative shape fluctuations. The large relative shape fluctuations of the smallest droplet are partly due to its higher charge density relative to the other droplets and partly due to its inherent smaller size. In the largest droplets of 6×10^4 H₂O molecules the ion distribution decays faster than all the rest. The fastest decay leads to an increase of the ion distribution maximum. The larger relative shape fluctuations of the smallest droplets give rise to some other features in the ion concentration profile. Firstly, the concentration profile of 880 H₂O molecules-6Na⁺ ions appears to be much broader than those for the larger droplets. The broadness is revealed in the scaled coordinates but in the non-scaled coordinates the distribution appears to follow the same trend as the larger droplets. Secondly, the maximum of the Na⁺ spatial distribution from the droplet very outer surface where the density of water is 5×10^{-4} g/cm³ (Table 1) becomes shorter as the droplet size increases. This distance is ≈ 1.7 nm for the smallest droplet and ≈ 1.4 nm for the largest droplet. The difference (absolute value) between the R_e and the maximum of the Na⁺ distribution follows the same trend: it is ≈ 1.0 nm for the smallest droplet and ≈ 0.74 nm for the largest droplet. The relative shape fluctuations affect these distances. In microscopic droplets the distance of the maximum of the ion distribution

to R_e (data presented in Table 1) may become even shorter because of the reduced relative shape fluctuations. We estimated that the ratio of R_{max}/R_r changes from 0.59 for droplets of 880 H₂O molecules to 0.92 for droplets of 6×10^4 H₂O molecules. The ratio of R_{max}/R_r vs R_r is shown in Fig. S7 in SI. Extrapolation of the data led us to the intriguing observation that $R_{max}/R_r = 1$ when $R_r \approx 10$ nm. At this point we make a connection to the ion-evaporation mechanism (IEM) for the disintegration of charged droplets. It has been found that the IEM^{11,12} dominates over the Rayleigh fission mechanism¹⁴ for droplet radius less than ≈ 10 nm. We think that the coincidence in the droplet Rayleigh radius is not fortuitous. It suggests that the fluctuations in charge density or shape found in the droplets with radius less than 10 nm will lead to a faster droplet disintegration by solvated ion release than the Rayleigh fission mechanism. The specifics of the fluctuations deserve a separate study in future work.

In summary Fig. 5 that supports the relation $n(R_r) \sim 1/R_r$ shows that we can infer the maximum of the ion spatial distribution in droplets that are much larger than those that we can model atomistically thus far. In droplets with diameter > 16 nm the ion spatial distribution is not affected significantly by the shape fluctuations relative to droplets of diameter of ≈ 5 nm. The R_{max} of the ion distribution equal R_r at $R_r \approx 10$ nm. This value coincides with the experimental finding^{11,12} that for droplets with larger radius than 10 nm, Rayleigh fission is the dominant mechanism for charged droplet disintegration.

We computed the radial distribution function ($g(r)$) between the Na⁺ ions (Fig. S7 in SI). We computed the potential of mean force (PMF) shown in Fig. 6 directly from the $g(r)$. The Na-Na radial distribution function shows two significant peaks, at ~ 3.7 Å and ~ 6.1 Å. The peaks correspond to contact ion pairs (CIP) and solvent separated ion pair (SSIP) respectively. The location and ratio of the two peaks corresponding to the CIP and the SSIP agrees with earlier result obtained from bulk simulation of 0.3 M NaCl in TIP3P water.⁶⁵ As the size of the

Figure 6: Potential of mean force (PMF) as a function of the distance between any pair of Na^+ ions in droplets of various sizes. The blurry regions show the error bars.

droplet shrinks, the ion concentration needed to maintain the total charge of the droplet close to the Rayleigh limit increases. Savelyev et al. suggested that “in more dilute solutions the repulsion between like charged ions is stronger because they are less screened electrostatically by ions of the opposite charge”. The same trend holds in highly charged droplets without the presence of counterions, where the ions prefer to be in the SSIP form.

Surface charge and electric field

Figure 7: Size dependence of normalized charge distribution (ρ) in aqueous droplets with Na^+ ions.

The normalized charge distribution for different droplet sizes is shown in Fig. 7. The wavy portion is not unique in the charged droplets, it also appears in a pristine water droplet^{62,63} In-

terestingly, in the presence of Cl^- there is only one trough in the charge distribution and not a wavy segment (Fig. S3 in SI).

It is interesting to examine the electric field and potential on the droplet surface. The continual motion of the water molecules and the shape fluctuations prevent a direct computation of the electrostatic potential and electric field on the droplet surface because of the large statistical errors.^{61,66} We use an approach that we have developed to reconstruct the droplet surface (Fig. 9 (a)) and then compute the electric potential by using a multipole expansion. The method is described in detail in Ref.⁶¹

The electric field for a droplet composed of 2×10^4 H_2O molecules and 36 Na^+ ions is shown in Fig. 8 (b) and the fluctuations in Fig. 9. Comparison with the findings by Kwan et al.⁶¹ for a droplet of 6000 H_2O molecules - 19 Na^+ ions we find that the droplet electric field in the larger droplet decreases. Moreover, the fluctuations of the electric field on the droplet surface decrease, which may explain the prevalence of the ion-evaporation mechanism in charged droplets with radius less than 10 nm.^{11–13}

Effect of counterions

Figure 11 shows the spatial ion distribution of a droplet comprised $\approx 3 \times 10^4$ H_2O molecules, 44 Na^+ ions and 23 NaCl pairs. The distributions in the same size droplet but for excess Cl^- ions are shown in Fig. S10 in the SI. A main feature in Fig. 11 (a) is that in a droplet with counterions the excess ions, Na^+ form an outer shell of higher concentration. The Cl^- ions are depleted from the region where the Na^+ concentration is the highest. The Cl^- concentration gradually increases toward the droplet center, where the Na^+ concentration is the lowest. In Figs S19, S20 in SI is shown that in aqueous droplets with Cl^- only the Cl^- show a clear propensity to be found near the surface. The fact that the Cl^- are restricted in the droplet interior in the presence of the excess Na^+ is the result of the conducting character of the droplet, which dictates that the excess charge accumulates on the surface.

If we scale the Na^+ concentration in the pres-

(a)

(b)

Figure 8: (a) Reconstruction of the droplet surface using the spherical harmonics amplitudes as discussed in Ref.⁶¹ The droplet comprises 2×10^4 H_2O molecules and 36 Na^+ ions. (b) Interpolated electric field of the molecular surface of the droplet. The arrows represent the direction and the magnitude of the electric field on the surface. The arrows are color coded according to the value of the electric potential from red (8.5V) of the extruded domains of the droplet to blue (11.5V) on the areas of the surface that are closer to the droplet center.

ence of Cl^- ions the two concentrations with and without counterions coincide. In the presence of counterions, the Na^+ concentration (not scaled) appear to extend more toward the outer H_2O layers and to have higher concentration in the interior. This behavior is attributed to the fact that in the presence of counterions the concentration of Na^+ is higher in order to keep the overall charge of the droplet the same as with-

Figure 9: Distribution of the normal component of the electric field on the molecular surface (details are presented in Ref.⁶¹) of a droplet comprised 2×10^4 water molecules and 36 Na^+ ions. The average electric field on the surface is 0.187 [V/Å] , however, on 2% of the total area of the droplets used in the analysis the electric field magnitude is twice the average value.

Figure 10: Average radial potential of a droplet comprising 2×10^4 H_2O molecules and 36 Na^+ ions. Contribution from all the point charges is considered. For large r the potential coincides with that of a point charge with $Q = 36e$. Inside the droplet the potential can be well approximated by a constant value, which is the potential on the surface of the droplet.

out counterions.

Figure 11 (b) shows that the cumulative probability saturates at 6.2 Å for Na^+ ions in droplet

Figure 11: (a) Same as Fig. 3 (a) but for a droplet comprised $\approx 3 \times 10^4$ H₂O molecules, 44 Na⁺ ions and 23 NaCl pairs at $T = 350$ K. The blurry region shows the error bars. The standard deviation is calculated by using 5 blocks of raw data, where every block has 4×10^4 configurations, separated by 0.2 ps. (b) Same as Fig. 3 (b) but for the droplet in (a). (c) Cumulative probability profiles of the net charge in droplets comprised $\approx 3 \times 10^4$ H₂O molecules - 44 Na⁺ only and the same droplet with additional 23 NaCl pairs.

with and without Cl⁻ counterions. The saturation point has been reached earlier for the Cl⁻ ions than that of the Na⁺ ions. Figure 11 (c) shows that the net charge in the interior, estimated by subtracting the number of Cl⁻ ions from that of Na⁺ ions is lower in the droplets with counterions. This finding shows, that there is a higher concentration of Na⁺ ions on

the surface due to the presence of NaCl. The increased concentration of Na⁺ ion in the surface indicates that the surface is not saturated with charge with free charge when only Na⁺ ions are present.

Solvent structure induced by the Na⁺ ions

Figure 12: $\cos(\phi)$ distribution of the water electric dipole orientation in representative spherical shells of radius r (shown in the legend) in a droplet comprised $\approx 3 \times 10^4$ H₂O molecules and 44 excess Na⁺ ions. ϕ is defined in the text. The thickness of the spherical shell is 0.5 Å.

As expected the presence of the ions affect the solvent structure relative to that of the droplets without ions. In order to study the orientation of the water electric dipoles within the droplet, we compute $\cos(\phi)$, where ϕ is the angle between the H₂O dipole moment (which is found along the HOH bisector, and starts at the oxygen site) and the vector that starts from the droplet center of mass (COM) and points to the oxygen site of a water molecule. Figure 12 shows the $\cos(\phi)$ distribution at representative spherical shells with center at the droplet COM. We focus in the region where the Na⁺-CP shows its maximum (48 Å - 54 Å) and beyond ($r > 54$ Å). We find that in the outer water shells there is an overall shift toward the positive $\cos(\phi)$ values. At $48\text{\AA} < r < 54\text{\AA}$ (which is the range of the maximum Na⁺-CP)

the range $-0.25 < \cos(\phi) < 1.0$ is preferred. The $\cos(\phi)$ distribution in the r values of the maximum of the Na^+ -CP is to be contrasted with that of droplets of 1000 and 6000 H_2O discussed by Kwan et al.⁶¹ In the smaller droplets the preference for positive $\cos(\phi)$ values is more pronounced. This difference in the cosine distribution is attributed to the fact that the larger the droplet the lower the surface charge density. At $r > 54\text{\AA}$ the preference for the positive $\cos(\phi)$ becomes more pronounced. At the very outer water shells ($r \approx 72\text{\AA}$) the water molecules often form short dangling chains. The dangling water molecules are strongly oriented by the overall charge of the droplet. The distribution of $\cos(\phi)$ and of the orientation of the water molecule planes for 2×10^4 water molecules - 36 Na^+ ions is shown in Fig. S15 in the SI. Similar orientation of the H_2O dipoles in droplets of 3×10^4 - 44 Na^+ ions to that of 2×10^4 - 36 Na^+ ions are also observed.

The comparison of the orientation of the water dipoles in the systems that we have studied (Table 1) revealed certain common features: (a) Within the vicinity of the maximal value of the Na^+ -CP, the distribution of the $\cos(\phi)$ values increases almost linearly, with preference in the positive $\cos \phi$ values. The smaller the droplet, the larger the probability towards the $\cos(\phi) = 1.0$ end. For a droplet of ≈ 880 H_2O - 6 Na^+ ions, the preferred orientation is for $0.25 < \cos(\phi) < 1.0$, for a droplet of ≈ 6000 H_2O - 6 Na^+ is for $0.5 < \cos(\phi) < 1.0$ and for droplets of a few tens of thousand of molecules the distribution becomes more uniform but with a small preference for $\cos(\phi) > 0.0$. (b) In the following water spherical shells of thickness of ≈ 4.5 $\text{\AA}$ (1.5 H_2O diameters), the distribution of $\cos(\phi)$ is an inverted parabola with maximum at approximately $\cos(\phi) = 0.25$. The maximum is not representative of the majority of the dipole orientations. We have to consider the vicinity of the maximum. The dominant part of the $\cos(\phi)$ distribution spreads from the positive range up to the negative range. For the ≈ 6000 H_2O - 6 Na^+ the dominant part is in the range of $-0.25 < \cos \theta < 0.75$ and for droplets of a few tens of thousand of molecules is $-0.5 < \cos \phi < 1$. The larger the droplet, the

less pronounced the parabola is, and a larger range of $\cos(\phi)$ values is preferred. (c) In the very outer shell, there is formation of short dangling H_2O strings that show elastic motion. The H_2O molecules in these strings are strongly oriented by the overall droplet electric field.

Figure S16 in the SI shows the distribution of $\cos(\phi)$ for the droplets of 3×10^4 H_2O - 44 Na^+ ions - 23 NaCl pairs. The distributions of Fig. S16 and Fig. 12 are identical, which reinforces our argument that it is the overall charge of the droplet that determines the orientation of the H_2O and not the specific ions.

Figure 13: $\cos(\theta)$ distribution in representative spherical shells of radius r (shown in the legend) in a droplet comprised $\approx 2 \times 10^4$ H_2O molecules and 36 excess Na^+ ions. θ is defined in the text. The thickness of the spherical shell is 0.5 $\text{\AA}$.

In order to characterize further the orientation of the water molecules, we also compute the planar angle θ , defined as the angle between the normal vector of the plane of the water molecule and the vector that starts from the droplet center of mass (COM) and points to the oxygen site of a water molecule. The possible range of $\cos(\theta)$ is dependent on $\cos(\phi)$, where $\cos^2(\phi) + \cos^2(\theta) < 1$. In addition, since the sign of the normal vector is arbitrary and using the trigonometric identity:

$$\cos(\theta) = \frac{\mathbf{a} \cdot \mathbf{b}}{|\mathbf{a}||\mathbf{b}|} = \cos(-\theta) = \frac{\mathbf{a} \cdot (-\mathbf{b})}{|\mathbf{a}||\mathbf{b}|} \quad (5)$$

We can limit the range of $\cos(\theta)$ to $[0, 1]$.

However, it is possible that the shift to positive of the dipole angle θ leads to the shift of the plane angle to positive. For a droplet of 2×10^4 H_2O - 36 Na^+ ions the maximum of the ion distribution is approximately in the range of $4.0 \text{ nm} < r < 4.8 \text{ nm}$. In the interior of a charged droplet (up to $46 \text{ \AA}$), the distribution of $\cos(\theta)$ is uniform, which indicates that all the plane orientations are equally likely. In the next aqueous shells, up to approximate the Rayleigh radius (5.2 nm – 5.4 nm) the $\cos(\theta)$ shows a propensity for $\cos(\theta) > 0.5$, which indicates that the water plane is tilted on the spherical surface. Further away, the $\cos(\theta)$ distribution becomes uniform once more and in the dangling water $\cos(\theta)$ shows a propensity for values close to zero.

Spatial distribution of hydronium ions

Figure 9 (a) shows the distribution of “hydronium” ions in a droplet of ≈ 1000 H_2O molecules and 8 ions. The general features of the distribution are the same as that of the Na^+ ions but the hydronium reside much more in the outer water shells of the droplet than the Na^+ ions. Even though the hydronium model omits important quantum effects it demonstrates that certain positively charged ions may found in the region of low water density on the surface. In general we expect that very small ions such as Li^+ and large ions will be found further out than Na^+ . Small ions like Li^+ are surrounded by a rigidly bound first solvation that makes them similar to a large ion like Cs^+ . The charge distributions in aqueous droplets with H_3O^+ ions and Na^+ ions are shown in Fig. 15. The outer location of the H_3O^+ ions relative to that of the Na^+ ions is reflected in the charge distributions, where the wavy portion of the profile is in longer distance than that of the Na^+ ions. The orientation of the water dipoles and of the planes in the presence of H_3O^+ ions are shown in Fig. 16.

Figure 14: (a) Droplet density and hydronium ion concentrations. Equilibrated ion distribution in a drop comprised ≈ 1000 H_2O molecules and 8 H_3O^+ ions at $T = 300 \text{ K}$. The blurry region shows the error bars. The production run is for 40 ns. The standard deviation was calculated by using 5 blocks of raw data, each of 40000 frames. (b) Cumulative probability function that arises from the integral of (a).

Conclusion

We examined the convergence of the ion spatial distributions and surface charge with droplet size. We conclude that: (a) For droplets that range in size between several hundreds to several tens of thousands of water molecules the location of maximum of the Na^+ spatial distribution from the droplet surface changes. This depth is $\approx 1.7 \text{ nm}$ from the point that the water density becomes $5 \times 10^{-4} \text{ g/cm}^3$ for the smallest droplet to $\approx 1.4 \text{ nm}$ for the largest droplet. The difference between the R_e and the maximum of the Na^+ distribution is approximately 1.0 nm for the smallest droplet to 0.74 nm for the largest droplet. For droplets larger than 6×10^4 H_2O molecules (diameter $\approx 16 \text{ nm}$) we expect the ion depth from the surface to reduce slightly relative to the changes that we found for 880 H_2O to 6×10^4 H_2O molecules. (b) Scal-

Figure 15: Charge distribution profiles (not normalized) for 880 H_2O -6 H_3O^+ ions at $T = 350$ K (bin size $2.0 \text{ \AA}$). For comparison the Na^+ ions data have been included. (a) Charge distribution profiles for the water only. (b) Charge distribution profiles for the total charge (water and ions).

Figure 16: Dipole orientation and plane orientation in droplets comprised 1000 TIP3P water molecules and 8 H_3O^+ ions.

ing of the x-axis of the ion distributions by the Rayleigh radius of the droplet, reveals that for droplets with diameter, 7 nm (which is $\approx 6 \times 10^3$

H_2O molecules) to 16 nm the ion distribution profiles almost coincide. For the droplet of diameter 5 nm ($\approx 1000 \text{ H}_2\text{O}$ molecules) the Na^+ scaled concentration profile is broader than the other sizes. The profile for the smallest droplet is determined by the relative large shape fluctuations. (c) The presence of counterions plays a dramatic role in the manner that the ions are distributed. The ions in excess are situated in the exterior while the counterions reside in the droplet interior. The arrangement of the ions is reminiscent of that of a spherical capacitor. (d) The nature of the ions plays a very significant role in its location in droplet as indicate by comparing the distribution of the Na^+ , Cl^- , I^- and that of a model hydronium ion. (e) We presented how to define the surface charge of a highly charged droplet. Different from prevailing views we found that the surface charge comprises of a significant portion of the free ions and the solvent polarization charge. We quantified that amount of the free charge that contributes directly in the surface charge. We emphasize the significance of the electric field fluctuations in the droplet surface. These fluctuations underlie the ion-evaporation mechanism. We found that the normalized charge distributions converge with increasing droplet radius.

Finally, our analysis indicates that at droplet radius ≈ 10 nm the difference in values between R_{max} , R_r and droplet radius becomes negligible. Interestingly, this limit coincides with the droplet radius below which the ion evaporation mechanism dominates over the Rayleigh fission for droplet disintegration. We think that this coincidence is not fortuitous and requires further investigation. The present work prepares the background to shed light into one of the most important mechanisms for the disintegration of highly charged droplets.

Another question is the location of a macroion in a droplet in the presence of counterions.⁶⁷ It is expected that negative ions will condense on a positive charged macroion. A possible location of the macroion in the outer layers will affect its reactivity because of the different ionic strength on droplet outer layers vs the interior. This effect is expected to emerge in larger droplets where there is enough volume so as the

macroion is solvated and there is a large number of counterions. We suggest that large droplets of at least 20 nm in diameter have to be simulated in order for this effect to emerge.

Supplementary Material

See supplementary material of (a) Details of the force field parameters; (b) Comparison of Na^+ , Cl^- , I^- distribution profiles; Na^+-Na^+ radial distribution profiles.

Acknowledgement S.C. greatly thanks Prof. D. Frenkel, Department of Chemistry, University of Cambridge, UK, Prof. S. S. Xantheas, Pacific Northwest National Laboratory and Dr. Anatoly Malevanets, University of Western Ontario for discussions on the stability of charged systems. S.C. acknowledges an NSERC-Discovery grant (Canada) for funding this research. Sci-Net, SHARCNET and Compute Canada are acknowledged for providing the computing facilities.

References

- (1) Rezaee, M.; Assadi, Y.; Hosseini, M.-R. M.; Aghaee, E.; Ahmadi, F.; Berijani, S. Determination of organic compounds in water using dispersive liquid-liquid microextraction. *J. Chromatogr. A* **2006**, *1116*, 1–9.
- (2) Bain, R. M.; Pulliam, C. J.; Cooks, R. G. Accelerated Hantzsch electrospray synthesis with temporal control of reaction intermediates. *Chem. Sci.* **2015**, *6*, 397–401.
- (3) Chen, X.; Cooks, R. G. Accelerated reactions in field desorption mass spectrometry. *J. Mass Spectrom.* **2018**, *53*, 942–946.
- (4) Schrader, R. L.; Fedick, P. W.; Mehari, T. F.; Cooks, R. G. Accelerated Chemical Synthesis: Three Ways of Performing the Katritzky Transamination Reaction. *J. Chem. Educ.* **2019**,
- (5) Lee, J. K.; Banerjee, S.; Nam, H. G.; Zare, R. N. Acceleration of reaction in charged microdroplets. *Q. Rev. Biophys.* **2015**, *48*, 437–444.
- (6) Ingram, A. J.; Boeser, C. L.; Zare, R. N. Going beyond electrospray: mass spectrometric studies of chemical reactions in and on liquids. *Chem. Sci.* **2016**, *7*, 39–55.
- (7) Consta, S.; Kapral, R. Dynamics of proton transfer in mesoscopic clusters. *J. Chem. Phys.* **1996**, *104*, 4581–4590.
- (8) Consta, S.; Kapral, R. Proton transfer in mesoscopic, molecular clusters. *J. Chem. Phys.* **1994**, *101*, 10908–10914.
- (9) Wilm, M. Principles of electrospray ionization. *Mol. Cell. Proteomics* **2011**, *10*, M111–009407.
- (10) Mather, T.; Harrison, R. Electrification of volcanic plumes. *Surv. Geophys.* **2006**, *27*, 387–432.
- (11) Iribarne, J. V.; Thomson, B. A. On the evaporation of small ions from charged droplets. *J. Chem. Phys.* **1976**, *64*, 2287–2294.
- (12) Thomson, B.; Iribarne, J. Field induced ion evaporation from liquid surfaces at atmospheric pressure. *J. Chem. Phys.* **1979**, *71*, 4451–4463.
- (13) Consta, S.; Mainer, K. R.; Novak, W. Fragmentation mechanisms of aqueous clusters charged with ions. *J. Chem. Phys.* **2003**, *119*, 10125–10132.
- (14) Rayleigh, L. XX. On the equilibrium of liquid conducting masses charged with electricity. *Philos. Mag.* **1882**, *14*, 184–186.
- (15) Hendricks, C.; Schneider, J. Stability of a conducting droplet under the influence of surface tension and electrostatic forces. *Am. J. Phys.* **1963**, *31*, 450–453.
- (16) Peters, J. Rayleigh’s electrified water drops. *Eur. J. Phys.* **1980**, *1*, 143.

- (17) Consta, S.; Malevanets, A. Disintegration mechanisms of charged nanodroplets: novel systems for applying methods of activated processes. *Mol. Simul.* **2015**, *41*, 73–85.
- (18) Oh, M. I.; Malevanets, A.; Paliy, M.; Frenkel, D.; Consta, S. When droplets become stars: charged dielectric droplets beyond the Rayleigh limit. *Soft Matter* **2017**, *13*, 8781–8795.
- (19) Consta, S.; Oh, M. I.; Malevanets, A. New mechanisms of macroion-induced disintegration of charged droplets. *Chem. Phys. Lett.* **2016**, *663*, 1–12.
- (20) Jungwirth, P.; Tobias, D. J. Specific ion effects at the air/water interface. *Chem. Rev.* **2006**, *106*, 1259–1281.
- (21) Dang, L. X.; Schenter, G. K. Rate theory of ion pairing at the water liquid–vapor interface: A case of sodium iodide. *J. Chem. Phys.* **2018**, *148*, 222820.
- (22) Nguyen, M.; Rick, S. W. The influence of polarizability and charge transfer on specific ion effects in the dynamics of aqueous salt solutions. *J. Chem. Phys.* **2018**, *148*, 222803.
- (23) Smith, J.; Rick, S. W. Ion clustering in aqueous salt solutions near the liquid/vapor interface. *arXiv preprint arXiv:1603.07106* **2016**,
- (24) Petersen, P. B.; Saykally, R. J. On the nature of ions at the liquid water surface. *Annu. Rev. Phys. Chem.* **2006**, *57*, 333–364.
- (25) Phillips, J. C.; Braun, R.; Wang, W.; Gumbart, J.; Tajkhorshid, E.; Villa, E.; Chipot, C.; Skeel, R. D.; Kalé, L.; Schulten, K. Scalable molecular dynamics with NAMD. *J. Comput. Chem.* **2005**, *26*, 1781–1802.
- (26) Humphrey, W.; Dalke, A.; Schulten, K. VMD: Visual Molecular Dynamics. *J. Mol. Graphics* **1996**, *14*, 33–38.
- (27) Jorgensen, W. L.; Jenson, C. Temperature dependence of TIP3P, SPC, and TIP4P water from NPT Monte Carlo simulations: Seeking temperatures of maximum density. *J. Comput. Chem.* **1998**, *19*, 1179–1186.
- (28) Abascal, J. L. F.; Vega, C. A general purpose model for the condensed phases of water: TIP4P/2005. *J. Chem. Phys.* **2005**, *123*, 234505.
- (29) Noskov, S. Y.; Roux, B. Control of Ion Selectivity in LeuT: Two Na⁺ Binding Sites with Two Different Mechanisms. *J. Mol. Biol.* **2008**, *377*, 804 – 818.
- (30) Beglov, D.; Roux, B. Finite representation of an infinite bulk system: Solvent boundary potential for computer simulations. *J. Chem. Phys.* **1994**, *100*, 9050–9063.
- (31) Chandrasekhar, J.; Spellmeyer, D. C.; Jorgensen, W. L. Energy component analysis for dilute aqueous solutions of lithium(1+), sodium(1+), fluoride(1-), and chloride(1-) ions. *J. Am. Chem. Soc.* **1984**, *106*, 903–910.
- (32) McDonald, N. A.; Duffy, E. M.; Jorgensen, W. L. Monte Carlo investigations of selective anion complexation by a bis(phenylurea) p-tert-butylcalix[4]arene. *J. Am. Chem. Soc.* **1998**, *120*, 5104–5111.
- (33) Vega, C.; de Miguel, E. Surface tension of the most popular models of water by using the test-area simulation method. *J. Chem. Phys.* **2007**, *126*, 154707.
- (34) Varela, L. M.; Garcia, M.; Mosquera, V. Exact mean-field theory of ionic solutions: non-Debye screening. *Phys. Rep.* **2003**, *382*, 1–111.
- (35) Elton, D. C.; Fernández-Serra, M.-V. Polar nanoregions in water: A study of the dielectric properties of TIP4P/2005, TIP4P/2005f and TTM3F. *J. Chem. Phys.* **2014**, *140*, 124504.

- (36) Eigen, M. Proton transfer, acid-base catalysis, and enzymatic hydrolysis. Part I: elementary processes. *Angew. Chem. Int. Ed.* **1964**, *3*, 1–19.
- (37) Schuster, P.; Zundel, G.; Sandorfy, C. *Hydrogen bond; recent developments in theory and experiments*; North-Holland Publishing Company, 1976.
- (38) Asmis, K. R.; Pivonka, N. L.; Santambrogio, G.; Brümmer, M.; Kaposta, C.; Neumark, D. M.; Wöste, L. Gas-phase infrared spectrum of the protonated water dimer. *Science* **2003**, *299*, 1375–1377.
- (39) Vendrell, O.; Gatti, F.; Meyer, H.-D. Dynamics and infrared spectroscopy of the protonated water dimer. *Angew. Chem. Int. Ed.* **2007**, *46*, 6918–6921.
- (40) Valeev, E. F.; Schaefer III, H. F. The protonated water dimer: Brueckner methods remove the spurious C 1 symmetry minimum. *J. Chem. Phys.* **1998**, *108*, 7197–7201.
- (41) Vendrell, O.; Gatti, F.; Meyer, H.-D. Full dimensional (15-dimensional) quantum-dynamical simulation of the protonated water dimer. II. Infrared spectrum and vibrational dynamics. *J. Chem. Phys.* **2007**, *127*, 184303.
- (42) Pieniazek, P. A.; VandeVondele, J.; Jungwirth, P.; Krylov, A. I.; Bradforth, S. E. Electronic structure of the water dimer cation. *J. Phys. Chem. A* **2008**, *112*, 6159–6170.
- (43) Spura, T.; Elgabarty, H.; Kühne, T. D. “On-the-fly” coupled cluster path-integral molecular dynamics: impact of nuclear quantum effects on the protonated water dimer. *Phys. Chem. Chem. Phys.* **2015**, *17*, 14355–14359.
- (44) Auer, A. A.; Helgaker, T.; Klopper, W. Accurate molecular geometries of the protonated water dimer. *Phys. Chem. Chem. Phys.* **2000**, *2*, 2235–2238.
- (45) Wales, D. J. Rearrangements and tunneling splittings of protonated water dimer. *J. Chem. Phys.* **1999**, *110*, 10403–10409.
- (46) Chang, H.-C.; Wu, C.-C.; Kuo, J.-L. Recent advances in understanding the structures of medium-sized protonated water clusters. *Int. Rev. Phys. Chem.* **2005**, *24*, 553–578.
- (47) Tachikawa, M.; Shiga, M. Geometrical H/D isotope effect on hydrogen bonds in charged water clusters. *J. Am. Chem. Soc.* **2005**, *127*, 11908–11909.
- (48) Park, M.; Shin, I.; Singh, N. J.; Kim, K. S. Eigen and Zundel forms of small protonated water clusters: structures and infrared spectra. *J. Phys. Chem. A* **2007**, *111*, 10692–10702.
- (49) Wang, H.; Agmon, N. Reinvestigation of the infrared spectrum of the gas-phase protonated water tetramer. *J. Phys. Chem. A* **2017**, *121*, 3056–3070.
- (50) Mouhat, F.; Sorella, S.; Vuilleumier, R.; Saitta, A. M.; Casula, M. Fully quantum description of the Zundel ion: combining variational quantum Monte Carlo with path integral Langevin dynamics. *J. Chem. Theory Comput.* **2017**, *13*, 2400–2417.
- (51) Xantheas, S. S.; Dunning Jr, T. H. Ab initio studies of cyclic water clusters (H₂O)_n, n= 1–6. I. Optimal structures and vibrational spectra. *J. Chem. Phys.* **1993**, *99*, 8774–8792.
- (52) Yu, Q.; Bowman, J. M. High-level quantum calculations of the IR spectra of the Eigen, Zundel, and ring isomers of H⁺(H₂O)₄ find a single match to experiment. *J. Am. Chem. Soc.* **2017**, *139*, 10984–10987.
- (53) Yu, Q.; Bowman, J. M. Classical, Thermostatted Ring Polymer, and Quantum VSCF/VCI Calculations of IR Spectra of

- H7O3+ and H9O4+ (Eigen) and Comparison With Experiment. *J. Phys. Chem. A* **2019**,
- (54) Burnham, C. J.; Petersen, M. K.; Day, T. J.; Iyengar, S. S.; Voth, G. A. The properties of ion-water clusters. II. Solvation structures of Na⁺, Cl⁻, and H⁺ clusters as a function of temperature. *J. Chem. Phys.* **2006**, *124*, 024327.
- (55) Petersen, M. K.; Iyengar, S. S.; Day, T. J.; Voth, G. A. The hydrated proton at the water liquid/vapor interface. *J. Phys. Chem. B* **2004**, *108*, 14804–14806.
- (56) Hvelplund, P.; Kurten, T.; Støchkel, K.; Ryding, M. J.; Nielsen, S. B.; Uggerud, E. Stability and structure of protonated clusters of ammonia and water, H⁺(NH₃)_m(H₂O)_n. *J. Phys. Chem. A* **2010**, *114*, 7301–7310.
- (57) Silverstein, T. P. The Aqueous Proton Is Hydrated by More Than One Water Molecule: Is the Hydronium Ion a Useful Conceit? *J. Chem. Educ.* **2014**, *91*, 608–610.
- (58) Chuev, G. N.; Fedorov, M. V.; Chiodo, S.; Russo, N.; Sicilia, E. Hydration of ionic species studied by the reference interaction site model with a repulsive bridge correction. *J. Comp. Chem.* **2008**, *29*, 2406–2415.
- (59) Ufimtsev, I. S.; Martinez, T. J. Quantum chemistry on graphical processing units. 3. Analytical energy gradients, geometry optimization, and first principles molecular dynamics. *J. Chem. Theory Comput.* **2009**, *5*, 2619–2628.
- (60) Ahadi, E.; Konermann, L. Surface charge of electrosprayed water nanodroplets: A molecular dynamics study. *J. Am. Chem. Soc.* **2010**, *132*, 11270–11277.
- (61) Kwan, V.; Malevanets, A.; Consta, S. Where do the ions reside in a highly charged droplet? *J. Phys. Chem. A* **2019**, *123*, 9298–9310, PMID: 31589448.
- (62) Zakharov, V. V.; Brodskaya, E. N.; Laaksonen, A. Surface tension of water droplets: A molecular dynamics study of model and size dependencies. *J. Chem. Phys.* **1997**, *107*, 10675–10683.
- (63) Zakharov, V. V.; Brodskaya, E. N.; Laaksonen, A. Surface properties of water clusters: a molecular dynamics study. *Mol. Phys.* **1998**, *95*, 203–209.
- (64) Jackson, J. D. *Classical Electrodynamics*, third ed. ed.; John Wiley & Sons: New York, NY, 1998.
- (65) Savelyev, A.; Papoian, G. A. Molecular renormalization group coarse-graining of electrolyte solutions: Application to aqueous NaCl and KCl. *J. Phys. Chem. B* **2009**, *113*, 7785–7793, PMID: 19425537.
- (66) Beck, T. L. The influence of water interfacial potentials on ion hydration in bulk water and near interfaces. *Chem. Phys. Lett.* **2013**, *561*, 1–13.
- (67) Sharawy, M.; Consta, S. Effect of counterions on the charging mechanisms of a macromolecule in aqueous nanodrops. *J. Chem. Phys.* **2014**, *141*, 104321.