

## SUPPLEMENTAL INFORMATION

### **Simultaneous Ion and Neutral Evaporation in Aqueous Nanodrops: Experiment, Theory, and Molecular Dynamics Simulation**

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#### **INFORMATION AVAILABLE**

- Details on the parameters used in MD simulations
- Example radial distribution functions
- Neutral evaporation results for lower ion concentration nanodrops
- An example of experimentally inferred size distribution functions at discrete charge states
- A video of simultaneous neutral and ion evaporation in MD simulations (a separate .wmv file)

### MD Simulation Parameters

We used a combined Lennard-Jones-Coulomb potential function between atoms, described by the equation:

$$\phi(r_{ij}) = 4\epsilon_{ij} \left\{ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^6 \right\} + \frac{e^2}{4\pi\epsilon_0} \frac{q_i q_j}{r_{ij}} \quad (\text{S1})$$

where  $\phi(r_{ij})$  is the potential energy,  $\sigma_{ij}$  and  $\epsilon_{ij}$  are size and energy parameters, respectively,  $r_{ij}$  is the distance between atoms  $i$  and  $j$ ,  $e$  is the elemental charge,  $\epsilon_0$  is the permittivity in vacuum and  $q_i$  is the (partial) charge on each atom. The Coulomb interaction was accounted for with a periodic boundary using the Ewald method<sup>1</sup>. The coordinates of water molecules and ions were determined by solving Newton's equation of motion for each entity. The atoms within water molecules were held fixed with respect to one another, and water molecules were modeled with SPC/E rigid molecular model<sup>2</sup>, while the parameters of ions were taken from Dang et al<sup>3</sup>. All parameters used in simulations are summarized in Table S1. The Lorentz-Berthelot combining rules<sup>4</sup> were applied to determine the size and energy parameters between unlike atoms.

**Table S1.** Potential parameters used in MD simulations.  $r_{\text{OH}}$  [nm] denotes the oxygen-hydrogen bond distance in water molecules, while  $\angle \text{HOH}$  [°] denotes the water molecule bond angle.

	SPC/E		Dang
$\sigma_{\text{OO}}$ [nm]	0.3166	$\sigma_{\text{NaNa}}$ [nm]	0.2584
$\epsilon_{\text{OO}} \times 10^{-21}$ [J]	1.0797	$\epsilon_{\text{NaNa}} \times 10^{-21}$ [J]	0.6952
$q_{\text{O}}$	-0.8476	$z_{\text{Na}}$	1
$q_{\text{H}}$	0.4238	$\sigma_{\text{ClCl}}$ [nm]	0.4401
$r_{\text{OH}}$ [nm]	0.100	$\epsilon_{\text{ClCl}} \times 10^{-21}$ [J]	0.6952
$\angle \text{HOH}$ [°]	109.47	$z_{\text{Cl}}$	-1

### Radial Distribution Functions

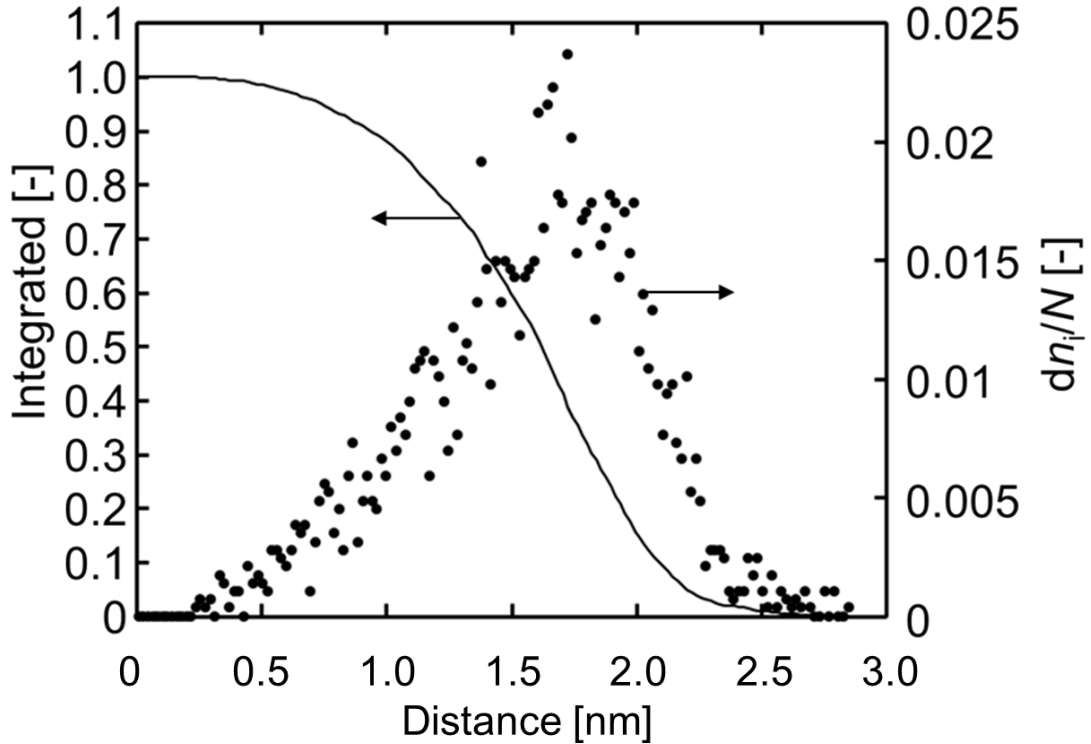
The coordinate of the center of mass ( $x_g, y_g, z_g$ ) in the simulation was monitored over time using the equations:

$$x_g = \frac{\sum_i M_i x_i}{\sum_i M_i}, y_g = \frac{\sum_i M_i y_i}{\sum_i M_i}, z_g = \frac{\sum_i M_i z_i}{\sum_i M_i} \quad (S2)$$

where  $x_i, y_i, z_i$  is coordinate of each entity and  $M_i$  is mass of each entity. The distance between center of mass and each point,  $r_{gi}$  was subsequently calculated with the equation:

$$r_{gi} = \sqrt{(x_g - x_i)^2 + (y_g - y_i)^2 + (z_g - z_i)^2} \quad (S3)$$

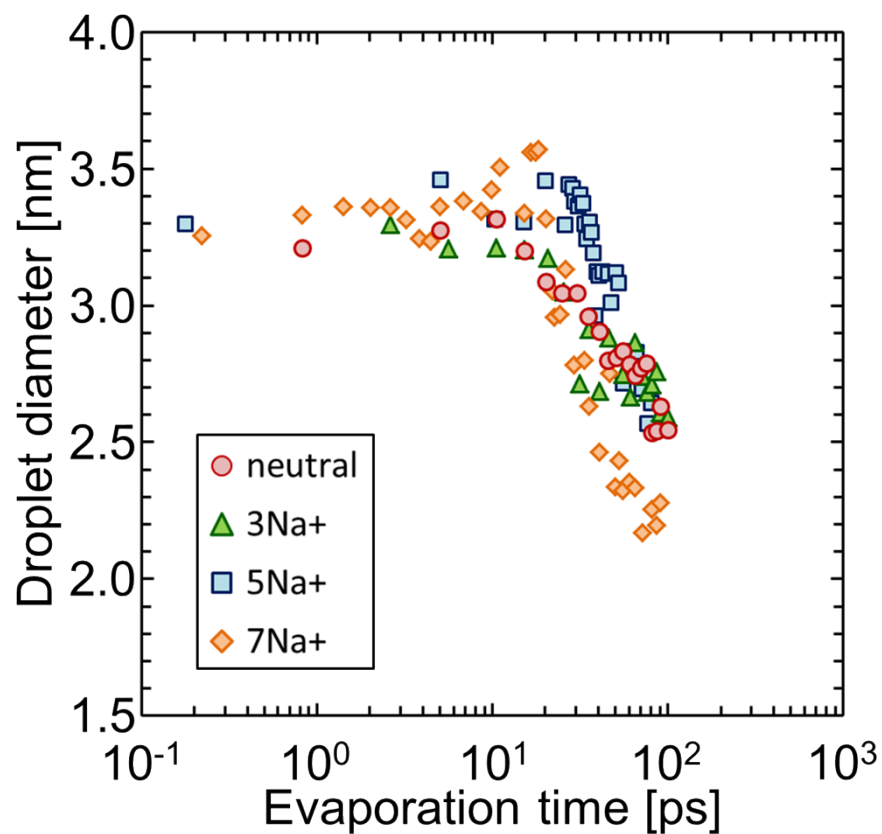
We obtained  $r_{gi}$  for all atoms and summed the number of atoms in given radial interval,  $dn_i$ .  $dn_i$  values were divided by total number of atoms (N), leading to normalized radial distribution functions. An example of a calculated radial distribution function (right vertical axis) is shown in figure S1. Also shown in the figure is the inverse of the normalized cumulative radial distribution function (left vertical axis, labeled “Integrated”).



**Figure S1.** An example radial distribution of atoms included in a simulated droplet at 0 ps. The solid line in the graph is the integrated distribution function (from the outside to the center of mass). We defined the nanodrop diameter as the 50% point of the integrated distribution.

### *Neutral evaporation of lower ion concentration nanodrops*

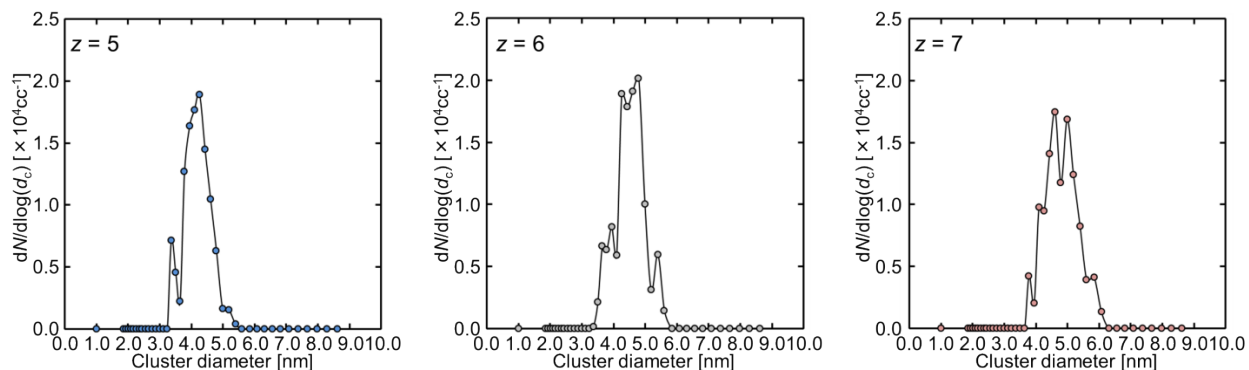
We have conducted simulations for water nanodrops containing several  $\text{Na}^+$  (0, 3, 5 and 7) ions, without excess cation-anion pairs. The droplet diameter versus time curves for these systems are plotted in Figure S2. The evaporation rates observed are slightly higher than the system containing excess sodium chloride. Unfortunately, in the later stage of evaporation, droplet structures were highly non-spherical, making difficult estimates of diameter



**Figure S2.** Plots of the nanodrop diameter as a function of time for nanodrops contain 0, 3, 5, and 7 excess  $\text{Na}^+$  ions, and no additional sodium chloride.

### Size Distribution Functions

Example size distribution functions for sodium chloride clusters of specific charge states (rounded to the nearest integer value) are shown in figure (S3). “Local maximum” peaks are evident in each of these distributions, and for each, the smallest diameter peak with a  $dn/d\log(d_c)$  value exceeding  $5000 \text{ cm}^{-3}$  was identified as  $d_{min}$  for clusters, and used in determination of  $\alpha_E$  (which weakly influences ion evaporation kinetics).



**Figure S3.** Examples of charge state specific size distribution functions for sodium chloride clusters.

## References

1. P. P. Ewald, *Annalen der Physik*, 1921, **369**, 253-287.
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3. L. X. Dang, J. E. Rice, J. Caldwell and P. A. Kollman, *Journal of the American Chemical Society*, 1991, **113**, 2481-2486.
4. M. P. Allen and D. J. Tildesley, *Computer Simulation of Liquids*, Oxford Science Publications 1987.