

Supporting Information for

How Sodium Chloride Extends Lifetime of Bulk Nanobubbles in Water

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Contents

Lennard-Jones parameters used in the MD simulations (Table S1).....	3
Test on different time steps (Fig. S1).....	3
Comparison between the dynamic behaviors of a N ₂ bulk nanobubble and a O ₂ bulk nanobubble in pure water (Fig. S2).....	4
Linear fitting of Fig. 2(b) in the main text. (Fig. S3).....	4
Data used for calculation of the lifetime of the bulk nanobubble based on the Epstein-Plesset (EP) theory (Table S2).....	5
Test on an artificial negatively charged bulk nanobubble (Fig. S4).....	5
Cutoff values used for calculation of water coordination numbers of ions at various NaCl concentrations (Table S3).....	6
Time evolution of the number of water hydrogen bonds in the system with various NaCl concentrations and linear relationship between the number of water hydrogen bonds and NaCl concentration (Fig. S5).....	6
Linear relationship between the hydrogen bond lifetime and the diffusion coefficient of H ₂ O (Fig. S6).....	7
Calculation of surface tension.....	8
Calculation of diffusion coefficient.....	10
Calculation of differentiating the interface from the bulk.....	11
Calculation of hydrogen bond lifetime.....	12
References.....	13

Table S1. Lennard-Jones parameters used in the MD simulations. The SPC/E water model [1] is employed in the present study due to its satisfactory performance in predicting the dynamic, structural, and interfacial properties of water [2,3]. The parameters for molecular nitrogen and nitrogen-water are obtained from Ref. [4], which were specifically parameterized for air and air-water (SPC/E) interactions. The NaCl parameters compatible with the SPC/E water model were developed by Smith and Dang [5]. Any unspecified crossed parameters are determined by the Lorentz-Berthelot combining rule.

Atom (<i>i-j</i>)	ϵ_{ij} (kcal/mol)	σ_{ij} (nm)	q_i (<i>e</i>)
H-H	0.0000	0.0000	0.4238 (H)
O-O	0.1553	0.3166	-0.8476 (O)
O-N	0.1304	0.3243	N/A
N-N	0.0723	0.3320	0 (N)
Na-Na	0.1300	0.2350	1 (Na)
Cl-Cl	0.1000	0.4400	-1 (Cl)

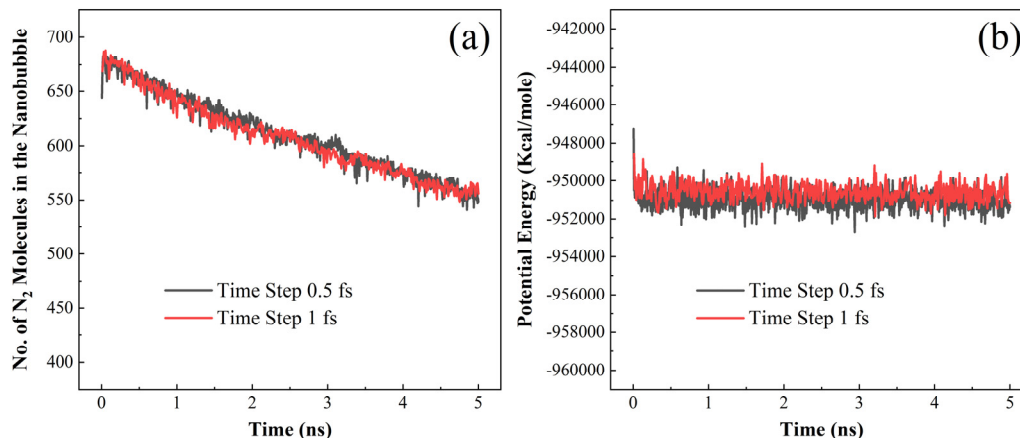


Figure S1. Time evolution of (a) the number of N₂ molecules in the nanobubble and (b) potential energy of the system during the 5 ns MD simulation of System 1 in Table 1 of the paper with a time step of 0.5 and 1 fs, respectively. The results of the simulation with a time step of 1 fs nearly overlap that with a time step of 0.5 fs, thereby demonstrating that the time step of 1 fs is sufficient to resolve the dynamics of the system (0.5 fs is a highly conservative value of time step used in classical MD simulations).

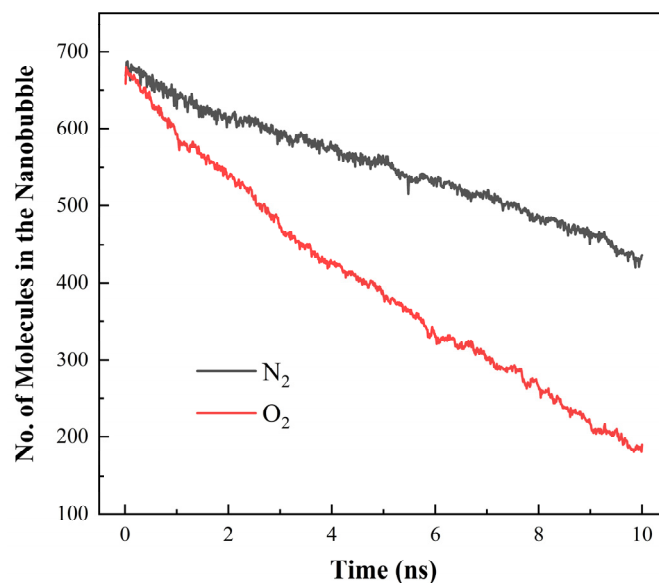


Figure S2. Time evolution of the number of gas molecules in the N₂ and O₂ bulk nanobubbles in pure water during the 10 ns MD simulation. The Lennard-Jones parameters for molecular oxygen and oxygen-water (as well as for molecular nitrogen and nitrogen-water mentioned in the main text) are obtained from Ref. [4], which were specifically parameterized for air and air-water (SPC/E) interactions.

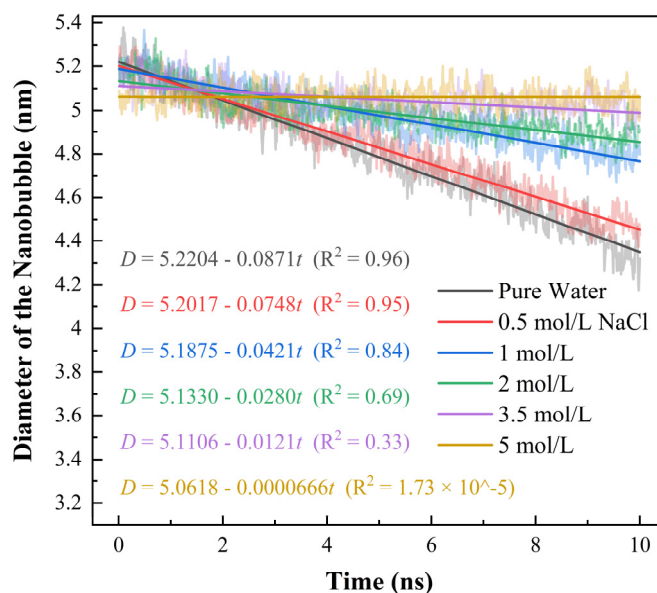


Figure S3. Linear fitting of Fig. 2(b) in the main text.

Table S2. Data used for calculation of the lifetime of the bulk nanobubble based on the Epstein-Plesset (EP) theory. Values of D , ρ , and γ are extracted from our MD simulation results.

Parameter	Value
Diffusion coefficient (D , 10^{-9} m ² /s)	Table 2
Density of gas (ρ , kg/m ³)	344
Gas saturation concentration (c_s , kg/m ³)	0.018 [6]
Surface tension (γ , mN/m)	Table S5
Atmospheric pressure (P_0 , Pa)	1.01×10^5
Gas oversaturation (ζ)	0 [7,8]

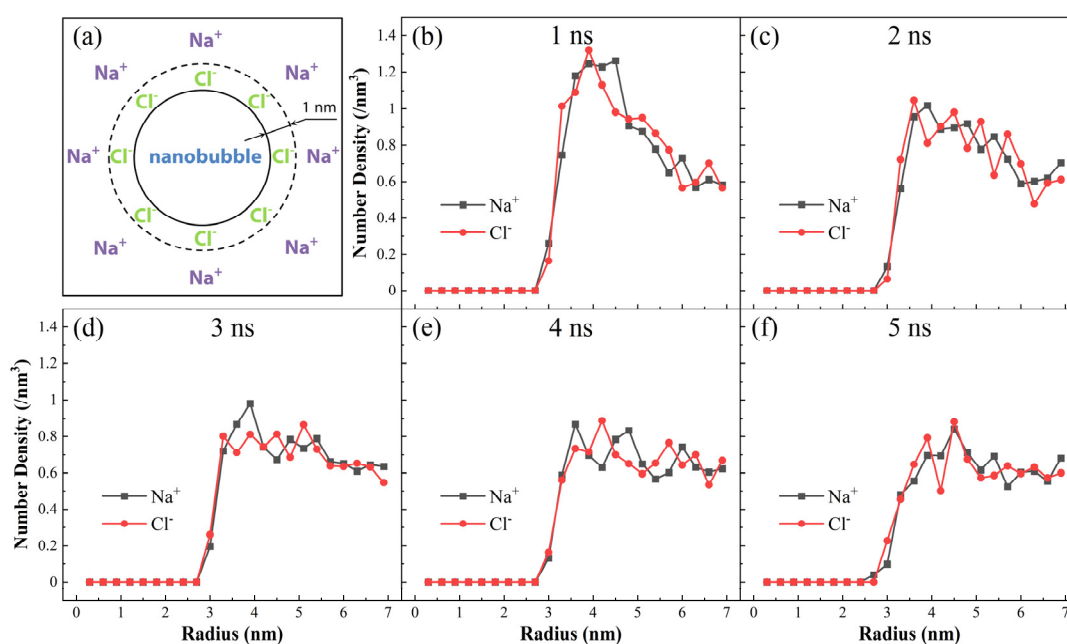


Figure S4. (a) Sketch of the 1 mol/L NaCl simulation system including an artificial negatively charged bulk nanobubble. Water molecules placed outside the nanobubble are not shown in the sketch. The nanobubble is surrounded by an 1 nm thick layer of Cl⁻ (all Cl⁻ in the system) and H₂O. The only difference between (a) and System 3 in Table 1 of the paper is the initial distribution of ions, where ions are randomly distributed in the solution region in System 3. (b)-(f) Radial number density profiles of Na⁺ and Cl⁻ at 1, 2, 3, 4, and 5 ns, respectively. The bin size in the radial direction used for calculation is 0.3 nm. Both Na⁺ and Cl⁻ ions are finally randomly distributed and the nanobubble still gradually dissolves in the solution during the 5 ns MD simulation.

Table S3. Cutoff values used for calculation of water coordination numbers of ions at various NaCl concentrations. $r_{\text{Na-O}}$ and $r_{\text{Cl-O}}$ are determined from the first minimum in the RDF shown in Fig. 5(a).

NaCl concentration (mol/L)	$r_{\text{Na-O}}$ (Å)	$r_{\text{Cl-O}}$ (Å)
0.5	3.18	3.83
1	3.18	3.88
2	3.18	3.93
3.5	3.18	3.98
5	3.18	3.98

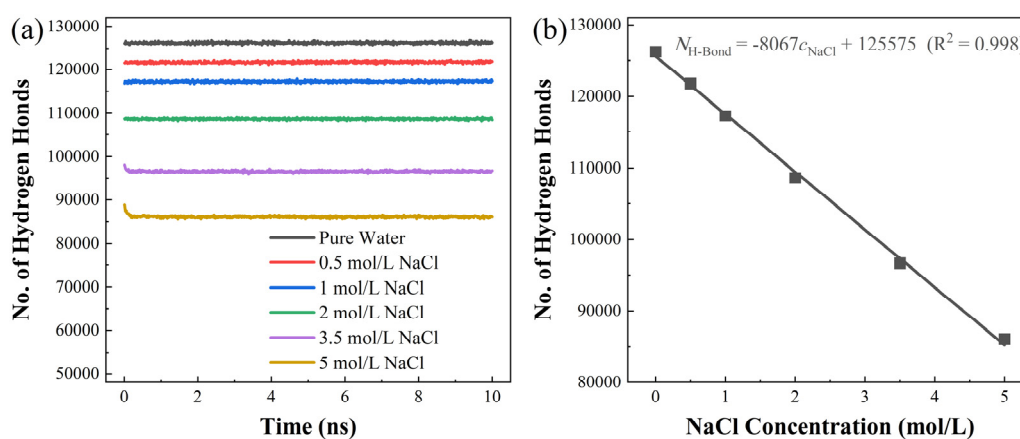


Figure S5. (a) Time evolution of the number of water hydrogen bonds in the system with various NaCl concentrations. (b) Linear relationship between the number of water hydrogen bonds and NaCl concentration.

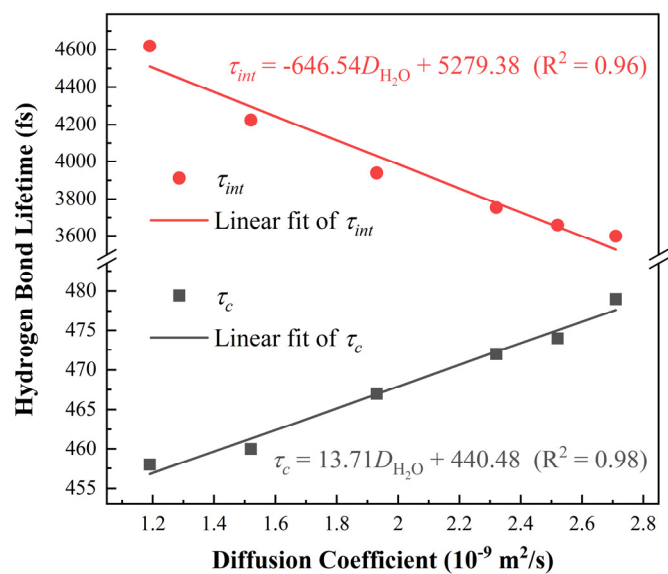


Figure S6. Linear relationship between the hydrogen bond lifetime and the diffusion coefficient of H₂O. Both τ_c and τ_{int} are linearly dependent on the $D_{\text{H}_2\text{O}}$.

Calculation of surface tension

We build comparable simulation systems with planar gas-liquid interface to calculate the surface tension of all studied systems in the main text. The detailed configuration of each simulation system is summarized in Table S4 and some representative initial simulation systems are shown in Fig. S7. A system (System 1) with no gas, which is close to an air-water system, is also included for comparison. The simulation details used are the same as described in Section 2, except that the NVT ensemble is employed instead of the NPT ensemble. To ensure that the new simulation systems are comparable with those studied in the main text, the number of different components in each system is determined based on the results of Fig. 3(a), and the sizes of the gas and liquid phases are accordingly adjusted. Each simulation system is run for 5 ns and the results are averaged over the last 1 ns (4-5 ns) of the simulation. The following equations are used to calculate the surface tension γ :

$$\gamma = \frac{1}{2} \int_0^{L_z} [P_N(z) - P_T(z)] dz \quad (\text{S1})$$

$$P_N(z) = P_{zz}(z) \quad (\text{S2})$$

$$P_T(z) = \frac{P_{xx}(z) + P_{yy}(z)}{2} \quad (\text{S3})$$

where P_N and P_T are the normal and tangential components of the pressure, respectively, L_z is the box length in the z direction (the direction normal to the interface), and P_{ii} is the ii element of the pressure tensor. The results are listed in Table S5.

Table S4. Configuration details of the simulation systems used for calculating the surface tension. The size of System 1 is $8 \times 8 \times 32 \text{ nm}^3$, as shown in Fig. S7(a). The size of other systems is accordingly adjusted based on the results of Fig. 3(a).

System	No. of N ₂	No. of H ₂ O	No. of Na ⁺ /Cl ⁻	NaCl concentration (mol/L)
1	0	25618	0	0
2			0	0
3			230	0.5
4	9470	25618	460	1
5			920	2
6			1610	3.5
7			2300	5

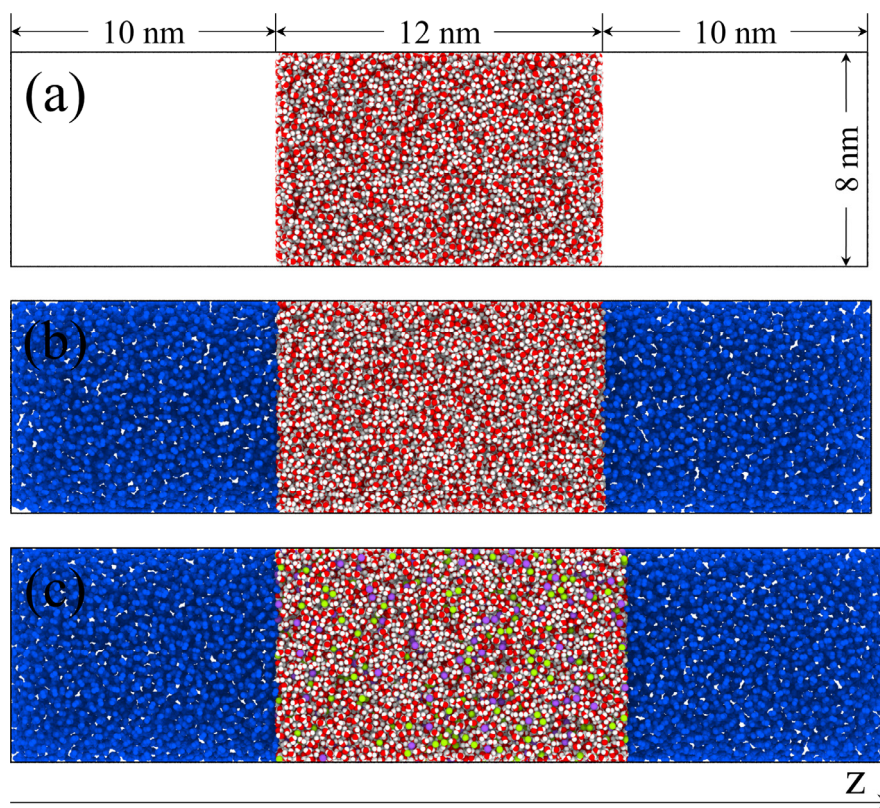


Figure S7. Demonstration of (a) System 1, (b) System 2, and (c) System 6 in Table S4.

Table S5. Calculated surface tension of all studied systems. γ_{long} is calculated by including the long-range LJ interactions.

System	Surface tension (γ , mN/m)	Surface tension (γ_{long} , mN/m)
1	57.36	63.15
2	49.82	51.53
3	50.14	N/A
4	52.42	N/A
5	55.10	N/A
6	58.82	N/A
7	62.53	N/A

Considering the simplified water model used in the present study, the difference between the γ_{long} of System 1 and the surface tension of water (about 72 mN/m) is acceptable, thereby demonstrating the effectiveness of the calculated surface tension in Table S5.

Calculation of diffusion coefficient

Since the bulk nanobubble keeps dissolving and does not reach equilibrium, we build new small but comparable systems to better estimate the diffusion coefficients (see detailed configuration of each system in Table S6). A previous study demonstrated that the system size does not have a significant effect on determining the diffusion coefficients [9]. The simulation details used are the same as described in Section 2 in the main text. Every simulation is run for 2 ns. Three independent runs are performed for each system, and the results are averaged for analysis. All diffusion coefficients are calculated by the mean square displacement (MSD) method using the following equation:

$$D = \frac{1}{6N} \lim_{t \rightarrow \infty} \frac{d}{dt} \sum_{i=1}^N [r_i(t) - r_i(0)]^2 \quad (\text{S4})$$

where N is the number of atoms in the molecule or ions, $r_i(t)$ is the position of atom i at

time t , and $r_i(0)$ is the initial position of atom i .

Table S6. Configuration details of the new small simulation systems used for estimating the diffusion coefficients. The initial size of all the simulation systems is $8 \times 8 \times 8 \text{ nm}^3$. The N_2 molecules are randomly distributed in the simulation box with no nanobubble in the system.

System	No. of N_2	No. of H_2O	No. of Na^+/Cl^-	NaCl concentration (mol/L)
1			0	0
2			154	0.5
3	50	17100	308	1
4			616	2
5			1078	3.5
6			1540	5

Calculation of differentiating the interface from the bulk

The procedure below is followed to differentiate the interface from the bulk in the system. The time-averaged vapor-liquid density profile can be fitted to the hyperbolic tangent function in Eq. (S5) [10]:

$$\rho(z) = \frac{\rho_l + \rho_v}{2} - \frac{\rho_l - \rho_v}{2} \tanh\left(\frac{z - z_0}{d}\right) \quad (\text{S5})$$

where ρ_l and ρ_v are the bulk densities of the liquid and vapor phases, respectively, z is the radial distance, z_0 is the position of the Gibbs dividing surface ($\rho(z_0) = (\rho_l + \rho_v)/2$), and d is a parameter for thickness of the interface. The thickness of the interface, t , based on the “10-90 thickness” rule [11], is related to d by $t = 2.1972d$. By fitting Eq. (S5) using the results of Fig. 3(a) in the main text, we obtain $d = 0.3 (\pm 0.01) \text{ nm}$ for all studied systems, which suggests that there is no significant difference in the interfacial thickness of the system with different NaCl concentrations. The interfacial thickness t is then estimated as 0.66 nm . To study the different properties between the interface and the bulk, we use the “full 100 thickness” of the interface, $t' = 0.82 \text{ nm}$, to distinguish the interface from the bulk

in the system.

Calculation of hydrogen bond lifetime

The hydrogen bond lifetime is calculated as follows [12]. Equation (S6) gives the time autocorrelation function, $C_x(t)$, used to measure the hydrogen bonds:

$$C_x(t) = \left\langle \frac{\sum h_{ij}(t_0)h_{ij}(t_0 + t)}{\sum h_{ij}(t_0)^2} \right\rangle \quad (\text{S6})$$

where h_{ij} is a binary measurement that if there is a hydrogen bond formed between a molecular pair ij (1 for yes, 0 for no). The summation is performed over all possible pairs. The angular brackets represent an average of the results starting from different initial observation time points, t_0 , in the trajectory. The subscript x refers to the two different definitions (continuous or intermittent) for measuring h_{ij} at future time points, where the continuous definition measures the time that a hydrogen bond remains continuously intact, whereas the intermittent definition allows the hydrogen bond considered broken to be subsequently reformed and counted again at a future time point. The results of $C_x(t)$ are fitted to an exponential function series, as shown in Eq. (S7):

$$C_x(t) = \sum_{i=1}^n A_i \exp(-t / \tau_i) \quad (\text{S7})$$

with $n = 2$ for the continuous lifetime and $n = 3$ for the intermittent lifetime. The final pre-exponential factor A_n meets the condition in Eq. (S8):

$$A_n = 1 - \sum_{i=1}^{n-1} A_i \quad (\text{S8})$$

For both definitions, the relevant hydrogen bond lifetime, τ_x , can then be obtained from Eq. (S9):

$$\tau_x = \int_0^{\infty} C_x(t) dt \quad (\text{S9})$$

We employ the same system configuration and simulation procedure described in “Calculation of diffusion coefficient” but increase the output frequency of the trajectory to 0.1 ps to obtain more accurate results of the hydrogen bond lifetime. Each simulation system is run for 3 ns and the trajectory from 2-3 ns is extracted for analysis. 20 different starting points (t_0) in the trajectory are used to average the results.

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