Supporting Information

Electrostrictive Cavitation in Water Induced by a SnO$_2$ Nanoparticle

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S1 Force Fields

SnO$_2$ Force Field

Table S1: Buckingham: $E_{ij} = B_{ij} \exp\left(-r_{ij}/\rho_{ij}\right) - C_{ij}/r_{ij}^6$ taken from$^1$

|        | $B_{ij}$ [kJ/mol] | $\rho_{ij}$ [Å] | $C_{ij}$ [kJ/mol Å$^6$] |
|--------|-------------------|------------------|------------------------|
| Sn-Sn  | 90547100          | 0.205            | 608                    |
| Sn-O   | 10364150          | 0.169            | 1544                   |
| O-O    | 465467            | 0.273            | 4699                   |
| O$_{\text{water}}$-O$_{\text{water}}$ | 279737          | 3.51485          | 3672.79                |

The force field developed by Bandura et. al was used to describe the SnO$_2$-SnO$_2$ interactions as well as the SnO$_2$-H$_2$O interactions in LAMMPS$^1$ (Tables S1, S2, S3). The SnO$_2$
Table S2: Lennard-Jones: $E_{ij} = A_{ij}/r_{ij}^{12} - C_{ij}/r_{ij}^6$ taken from\(^1\)

|          | $A_{ij}$ [kJ/mol A\(^{12}\)] | $C_{ij}$ [kJ/mol A\(^6\)] |
|----------|-------------------------------|-----------------------------|
| Sn-O\(_{\text{water}}\) | 600451                        | 1167                        |
| O\(_{\text{water}}\)      | 1978673                       | 3502                        |
| (H)O-O\(_{\text{water}}\) | 2561695                       | 3502                        |
| O\(_{\text{water}}\)-O\(_{\text{water}}\) | 2634130                       | 2617                        |

Table S3: Anisotropic Hydrogen-bonding term: $E_{ij}^{HB} = \epsilon_{HB} \left[ 5 \left( \frac{\sigma_{HB}}{r_{ij}} \right)^{12} - 6 \left( \frac{\sigma_{HB}}{r_{ij}} \right)^{10} \right] \cos^{4} \theta$

The angle $\theta$ in the hydrogen-bonding interaction is the angle between the oxygen atom accepting the hydrogen bond and the oxygen atom donating the hydrogen bond. Taken from\(^2\).

|          | $\epsilon_{HB}$ [kJ/mol] | $\sigma_{HB}$ [Å] |
|----------|--------------------------|------------------|
| H-H      | 1.346                    | 2.75             |

Table S4: Atom charges taken from\(^1\) and\(^2\) M and D refer to the dummy atom and Drud charge respectively.

| Atom      | $q$ (e) | $\sigma$ [Å] |
|-----------|---------|---------------|
| Sn        | 2.050   | -             |
| O         | -1.025  | -             |
| O\(_{\text{water}}\) | 2.0     | 0.7114        |
| H         | 0.597   | 0.4592        |
| M         | -1.194  | 0.5483        |
| D         | -2.0    | 0.7114        |

parameters were designed to work with a modified SPC/E water force field with harmonic angle bending instead of rigid molecules. The intra and inter forces between SnO\(_2\) and H\(_2\)O are described by a combination of electrostatic and short-range forces. The Buckingham potential describes the short range interactions for the SnO\(_2\) while the Lennard-Jones model is used for the SnO\(_2\)-H\(_2\)O interactions. The coefficients of both forces are given in Tables S1, S2, S3.

The atomic charge values (Table S4) were extracted from DFT calculations using the Vienna Ab initio Simulation Package (VASP). The coefficients for the SnO2 short range Buckingham interactions were calculated using the Generalized Utility Lattice Program (GULP) with the exception of the dispersion coefficient, $C_{ij}$ for the Sn-O interaction. The Sn-O dispersion coefficient was theoretically determined by using data from ref\(^3\) and the method
of Fowler et al.\textsuperscript{4}

**H2O Force Field**

The Hydrogen-Bonding Polarizable model of water was used to describe the H\textsubscript{2}O-H\textsubscript{2}O interactions. Specifically, the code provided in the supplemental material of\textsuperscript{2} was used to implement the force field in LAMMPS. The HBP model uses the rigid molecule structure of TIP4P with an O-H-O bond angle of 104.52° and an O-H bond length of 0.9572 Å. The dummy atom with the charge equal and opposite of the two hydrogen atoms was placed at the bisector of the HOH angle. To capture the polarizability of water, a single Drude oscillator is attached to the oxygen atom.

In lieu of point charges, the model uses Gaussian charges centered on the position of each atom to represent the electrostatic interactions. The charge density on atom \( i \) is given by:

\[
\rho_i = \frac{q_i}{(2\pi\sigma_i^2)^{3/2}} \exp\left(\frac{-|r - r_i|^2}{2\sigma_i^2}\right)
\]

The values of \( q_i \) and \( \sigma_i \) for the 4 different species in each water molecule are shown in Table S4. The anisotropic hydrogen-bonding term is used to account for the short-ranged effects caused by hydrogen bonding while the Van der Waals interactions between oxygen atoms are modeled through the Buckingham potential. The charge values for the oxygen and Drude oscillator were found to have little impact on the model when tested in.\textsuperscript{2} The only electrostatic interaction between the water molecules and the nanoparticle comes from the hydrogen and dummy atoms.

A polarizable model of water was selected in part due to the ability to reproduce the dielectric constant of liquid water. The HBP model has a dielectric constant of 76 ±4 compared to an experimental value of 78 at 298.15 K at 1 bar\textsuperscript{2} which is a significant improvement over TIP4P water which predicts a dielectric value of 58.

The HBP O-O parital correlatoin function over estimates the first peak and under esti-
mates the first minimum implying that the model predicts a more structured form of water than found in experiment.\textsuperscript{2}

The ab initio work done by Bandura et al. shows that water has a tendency to dissociatively adsorb on the surface of SnO\textsubscript{2}; however, our simulations with HBP did not allow bond breaking or formation. To verify the validity of the HBP water with the Bandura SnO\textsubscript{2} field, water adsorption simulations were performed. Water droplets of radii 7 and 10 Angstrom were placed on the (001) surface of a 46.004x47.86x47.86 Angstrom block of SnO\textsubscript{2} at room temperature (297.3 K). In each simulation the water droplet was allowed to expand over the surface over 300 ps; however, the water stabilized on the surface within 150 ps in both cases. The Ab Initio results of Bandura et al. say that the associative adsorption is unlikely on the 001 surface; however mixed adsorption has an energy of -117.8 eV. The HBP force field produced energies of -163 kJ/mol and -173 kJ/mol for first and second layer water molecules respectively. The HBP force field produces adsorption energies of correct order of magnitude with respect to the ab initio results. We would not expect full fidelity as the HBP model uses different atomic charges than the SPC/E water model and it does not allow for dissociation as mentioned above.

\textbf{S2 Water without Nanoparticle}

Cavitation was observed in every electric field simulation with applied electric fields, $E_{\text{app}}$, ranging from 0.042 V/Å to 0.25 V/Å. Water only simulations were also performed for high electric field values $E_{\text{app}} = 0.25, 0.125$; however, no cavitation was observed within 200 ps. Before the electric field has been applied, when the system is still in equilibrium, small cavities arise and collapse do to thermal fluctuations. These transient cavities are on the order of 100 Å\textsuperscript{3} and occur both in the presence and absence of a nanoparticle (Figure S1). Once the electric field is applied the water atoms rapidly polarize with a relaxation time dependent on the strength of the electric field. At some time, $t_{\text{onset}}$, cavities begin to congeal.
Figure S1: Tin dioxide nanoparticle in water (a) and pure water (b) with no applied electric field. Transient cavities on the order of 100 Å$^3$ and smaller form within one nanoparticle radius ($r_{np} = 1.5$ nm) of the nanoparticle. The cavity begins to grow either through the absorption of the thermally induced cavities or the pressure differential caused by the electric field in the void and in the water.

S3 Simulation Details

Creation of the tin dioxide nanoparticle began by first simulating bulk SnO2 crystal in a 84x95x95 Å$^3$ box with 62400 atoms. The bulk structure was heated to 1000 K over 25 ps with a Berendsen thermostat in the NVE ensemble. The Berendsen thermostat was disabled and the system continued to run for another 150 ps. From this simulation, a spherical nanoparticle with a 15 angstrom radius (1110 atoms) was extracted. Charge neutrality and stoichiometry were ensured by removing the appropriate number of Sn and O atoms based on their radial distance from the center of the nanoparticle. The nanoparticle was then heated to 1400 K over 25s with a Langevin thermostat to adequately sample phase space before being cooled and then cooled to 300 K.

Separately, a 139.8 x 93.5 x 93.5 Å$^3$ waterbox of HBP water was prepared to 300 K, 1 atm and a density of 0.997 g/cm$^3$. A 16.5 Å radius sphere of water was removed from the center of the box and replaced with the SnO$_2$ nanoparticle. The combined SnO$_2$-H$_2$O system was
run for 100 ps while the atoms (H, O, Sn, M) were attached to a Langevin thermostat at 300 K and the Drude oscillators were simultaneously connected to a 200 K Langevin thermostat. The total system was comprised of 199970 atoms.

The combined water and nanoparticle system was used as the starting point for the simulations below. Simulations ran from 100 ps to 1.2 ns. Uniform electric fields ranging from 0.042 to 0.25 V/Å were applied along the x direction on the simulation timescale using the "fix efield" command in LAMMPS. This adds an effective electric field by directly adding a force $f = qE$ to each atom.

To prevent Joule heating, a Langevin thermostat was applied and kept at 300 K for the atoms and 200 K for the Drude oscillator particles. Unfortunately, modern experiments able to apply sufficient electric fields are unable to simulataneously deal with the resultant heating making the application of the thermostats somewhat unrealistic. Solving the equations of motion for the Drude particles in the self-consistent field (SCF) regime requires minimizing the energy of the Drude particles at each timestep which is computationally expensive. In keeping with standard practice, the Drude particle was assigned a small mass to allow for faster relaxation and thermalized to a lower temperature than the bulk system. Lamoureux et al showed that in keeping the Drude temperature low, the thermodynamic and dynamic properties of the system closely approximated those given by SCF. The lower Drude particle temperature serves to minimize the kinetic energy of the Drude particles while still allowing them the ability to respond to changes in the electric field or movement of their corresponding oxygen atoms.

The system’s pressure was calculated in LAMMPS. The force due to the external electric field was taken account in the LAMMPS calculated virial. Pressure distributions were observed using the compute/stress/atom feature and binning the atoms into rectangular slices along the x direction. In the longer simulations (those on the order of a nanosecond), the total system pressure show large fluctuations on the order of MPa. At the simulation onset however, the total system pressure values were within an order of magnitude of the predicted
negative pressure by Equation (2) in the main text. For example, using $\alpha = 1.4$, $\epsilon = 79$ the predicted negative pressure for an applied field was $0.125 \, \text{V/Å}$ is -700 MPa while the observed system pressure oscillated around -150 MPa for the first 50 ps.

**S4 Void volume measurement**

Figure S2: Cavity volume analysis. (a) Raw void volume versus time. (b) Cavity volume versus time. Calculated using voxel chains of 15 or larger. (c) Spherical and cylindrical growth rates as a function of applied electric field. Some of the simulations runs were not run for sufficient lengths of time to see cylindrical growth. Comparing, for example, the 0.042 curve from part (b), the red star corresponds to the first linear region from 600 ps to 750ps while the green star corresponds to the slope in the region between 760 ps and 850 ps.
The cavity volume was calculated using a home made python script. The simulation box is divided into a grid of cubic voxels. Atoms are assigned to a voxel based on their position coordinates. The void volume is calculated by summing the number of empty voxels. In order to more accurately measure the rate of growth of the main cavity, only voxel chains above a certain threshold, $n_{\text{thresh}}$ value were considered. The chains of contiguous empty voxels were identified through depth first search. To analyze the data from the simulations, a voxel length of 3Å was used. The raw voxel void data is shown in Figure S2 a ($n_{\text{thresh}} = 1$) while the filtered data is shown ($n_{\text{thresh}} = 15$) in Figure S2 b.

From the filtered data, the two regions of growth, spherical and cylindrical, can be more easily identified; however, due to the short simulation lengths for some of the applied electric field runs, there are missing data points. Generally, the rate of growth in both the phases tended to increase as electric field was increased (S2 c). The volume growth may scale linearly with electric field strength; however, currently the data is too noisy to determine this definitively.

**S5 $\beta$ Discussion**

When subtracting out the initial time, a value of $\beta = 1/3$ arises from our data see (S3). Analysis of many sets of dielectric data produced a value for $\beta$ equal to 1/3 for low frequency electric fields. In a strong electric field, the excitations (alignments of the polar molecules) do not find sinks but instead relax locally to the applied external field. In a parallel plate capacitor, there is only one effective dimension, that between the two plates which yields a value for $f$ of 1/3. Plugging into Eq 7 from the main paper in turns gives $\beta = 1/3$ as reported which is in agreement with our alternatively calculated $\beta$ value.

Identifying the long timescale value of $\beta$ will provide evidence for the mechanism behind cavitation. If, the value is $\beta = 3/7$ then the most likely mechanism, is that the exitations, i.e the thermally activated cavities, diffuse into the main cavity by the nanoparticle. The
Figure S3: (a) $\bar{E}$ vs T: Blue markers are the data used to calculate the exponential relaxation coefficient $\beta$. The temporal data spans an order of magnitude (60 to 635 ps). The green (blue) line is plotted stretched exponential with $\beta = 0.324 (\beta = 0.424)$ and $\tau = 90.16$ ps ($\tau = 134.6$ ps). The blue line is plotted stretched exponential (b) $\log(-\log(\bar{E}))$ vs $\log(T_{\text{onset}})$. (c)$\log(-\log(\bar{E}))$ vs $\log(T_{\text{onset}} - \min(T_{\text{onset}}))$

next step would be then identifying the mechanism in which the thermal cavities interact. If instead, the long term value ends up being $1/3$, then the mechanism will likely be tied directly to long term relaxation of the water dipoles in the electric field. Given the stability of the electric field after the initial pulse, the author find this unlikely; however this needs to be looked into further. In order to verify the value for $\beta$, longer simulations will need to be run. Typically, $\beta$ is calculated by looking at data corresponding to $100\tau$. The calculated $\tau$ from our simulations is on the order of 100 ps. This would require simulations lasting 10 ns;
however, cavitation may not occur over such lengthy timescales.\textsuperscript{9}

S6 Video

The attached video is the tin dioxide simulation (red and yellow) with an applied electric field of 0.629 V/Å from 100 to 300 ps. Initially, one can see the formation of local density fluctuations. These eventually congeal into the cavity. The void (teal) appears over the course of 100s of picoseconds.

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