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Cintia P. Lamas,^{1,2}  Carlos Vega,¹  Eva G. Noya,²  and Eduardo Sanz^{1,a)} 

AFFILIATIONS

¹Departamento de Química-Física I (Unidad de I+D+i Asociada al CSIC), Facultad de Ciencias Químicas, Universidad Complutense de Madrid, 28040 Madrid, Spain

²Instituto de Química Física Rocasolano, CSIC, C/ Serrano 119, 28006 Madrid, Spain

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^{a)}Author to whom correspondence should be addressed: esa01@ucm.es

ABSTRACT

The formation of vapor bubbles in a metastable liquid, cavitation, is an activated process due to the free energy cost of having both phases at contact. Such an energetic penalty enables the existence of the liquid beyond its thermodynamic borders. Establishing the stability limits of a liquid as ubiquitous as water has important practical implications and has thereby attracted a lot of attention. Different experimental strategies and theoretical analyses have been employed to measure and predict the cavitation line, or the pressure–temperature kinetic stability border of liquid water. Understanding the location of the cavitation line requires knowing the cavitation rate dependence on pressure and temperature. Such dependency is difficult to obtain in experiments, and we use molecular simulations with the TIP4P/2005 model to fill this gap. By deeply overstretching liquid water below the saturation pressure, we are able to observe and quantify spontaneous cavitation. To deal with a lower overstretching regime, we resort to the Seeding technique, which consists of analyzing simulations of a liquid containing a vapor bubble under the theoretical framework of Classical Nucleation Theory. Combining spontaneous cavitation with Seeding, we get a wide overview of the cavitation rate. We study two different temperatures (450 and 550 K) and complement our perspective with the results previously obtained at 296.4 K [Menzl *et al.*, *Proc. Natl. Acad. Sci.* **113**, 13582 (2016)] to establish a broad simulation-experiment comparison. We find a good agreement between simulations and both isobaric heating and isochoric cooling experiments using quartz inclusions. We are, however, unable to reconcile simulations with other experimental techniques. Our results predict a decrease in the solid–liquid interfacial free energy as the liquid becomes increasingly overstretched with a temperature independent Tolman length of 0.1 nm. Therefore, the capillarity approximation underestimates the nucleation rate. Nonetheless, it provides a fair indication of the location of the cavitation line given the steep rate vs pressure dependence. Overall, our work provides a comprehensive view of the water cavitation phenomenon and sets an efficient strategy to investigate it with molecular simulations.

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I. INTRODUCTION

Many microwave ovens display a sticker with a symbol recommending placing a spoon in the mug where water is heated. The spoon acts as a surface to aid the emergence of vapor bubbles. When bubbles are formed, a liquid–vapor equilibrium is established, and heat transferred by microwaves is employed in increasing the number of molecules in the vapor phase rather than in a further temperature raise. In the absence of a spoon, however, bubbles may not form, and the liquid may get superheated beyond the boiling temperature. In such cases, water can boil explosively when handled by

the user. Superheating is not the only manner to have metastable liquid water with respect to the vapor. Metastability can also be achieved by overstretching the liquid below the vapor saturation pressure. This route enables probing negative pressures, which is of great interest for the study of the thermodynamic behavior of liquid water and the understanding of its anomalies.^{1–4} The emergence of vapor cavities in the metastable liquid (cavitation) sets the limit for the superheating or the overstretching that the liquid can sustain. Cavitation plays an important role in many industrial, technological, and geological processes,^{5–11} which makes the understanding of the physics that governs it of paramount importance.

This interest has prompted numerous experimental studies of water cavitation where vapor bubbles arise upon isobaric heating,¹² application of acoustic waves,^{13,14} or isochoric cooling.^{1,15–18} In these experiments, the metastability limit of the liquid with respect to the vapor is determined. The boundary between the metastable liquid and the vapor is a cavitation line in the pressure–temperature plane below which bubbles readily nucleate.^{1,19,20} This cavitation line is analogous to the so-called homogeneous ice nucleation line,²¹ which sets the temperature boundary (along pressure) for the metastability of the liquid with respect to ice. In both metastability situations (liquid vs vapor and liquid vs solid), it is the unfavorable interfacial free energy between the emerging phase (vapor or ice) and the surrounding liquid that enables the survival of the latter beyond its thermodynamic stability limits.^{22,23}

Experimental investigations on cavitation have been complemented by theoretical work in the framework of Classical Nucleation Theory (CNT)^{2,24,25} or, more recently, Density Functional Theory,²⁰ with the aim of predicting and understanding the location of the cavitation line. The agreement between theoretical predictions and experiments is quite satisfactory^{1,19,20} if the interfacial free energy between the liquid and the vapor is allowed to decrease when moving away from coexistence.^{2,20}

An important drawback of both theory and experiments is that they do not have access to detailed information at the molecular scale. For instance, the critical bubble (that has a 50% chance of either growing or redissolving) cannot be visualized experimentally due to its small size and short lifetime. Computer simulations can bridge this gap, and they have been extensively used to study cavitation in model systems like the Lennard–Jones fluid.^{26–33} By contrast, simulation work for water cavitation is more scarce, due to the technical difficulty of studying a rare event like cavitation—which requires the use of special simulation methods—in a costly system from a computational point of view due to the presence of electrostatic interactions. Reference 3 pioneers in the simulation work on water cavitation. With the use of biased simulations that promoted the appearance of bubbles in the overstretched liquid, the authors of Ref. 3 were able to calculate the nucleation rate vs the liquid pressure for temperature $T = 296.4$ K. The nucleation rate—the number of critical bubbles that appear per unit of time and volume—is the central parameter in nucleation. By knowing the nucleation rate, one can estimate the pressure at which cavitation is going to take place in a certain experimental setup, which means that one can predict the location of the cavitation line. In fact, the authors of Ref. 3 report a cavitation pressure of -126 MPa at the studied temperature and for the selected water model (TIP4P/2005³⁴), which is in line with the measurements obtained in isochoric cooling in quartz inclusions,^{1,15} although at odds with acoustic cavitation experiments.^{14,35–38}

In this paper, we revisit the cavitation of overstretched water with simulations using the TIP4P/2005 water model.³⁴ We focus on two different temperatures as compared to Ref. 3, namely 450 and 550 K, enabling a more direct comparison with the regime where most experimental points of the homogeneous cavitation line are available. Moreover, we use an efficient computational approach based on directly simulating the liquid with a vapor bubble already formed at the beginning of the simulations.^{39–41} This strategy, called Seeding,^{29,42–46} combines average properties obtained in the simulations of the vapor bubbles with the theoretical formalism of CNT.^{47–49} We complement Seeding with unbiased

“brute force” molecular simulations in a high overstretching regime where bubbles appear spontaneously. Although such a regime is not attainable in experiments, we use brute force results to validate Seeding simulations that do overlap with experimentally relevant conditions.

Our simulation results for the location of the homogeneous cavitation line compare satisfactorily with theoretical predictions^{20,25} and experimental measurements.^{1,15} Simulated bubbles have an interfacial thickness of about 1 nm for 450 K and 2 nm for 550 K. The equi-density²⁸ definition of the bubble radius gives a better consistency between Seeding and Brute Force simulations than the Gibbs equi-molar surface. We infer from our simulations that the interfacial free energy decreases as vapor bubbles become smaller (or as pressure decreases). We also find that the vapor bubble pressure obtained by equating its chemical potential to that of the surrounding liquid is consistent with that given by the density in the interior of the bubble. This result, although expected, is not verified in liquid-to-solid phase transitions.^{50–52} Overall, our work shows that water cavitation can be studied from a molecular perspective, giving experimentally relevant information in a rather efficient manner.

II. SIMULATION DETAILS

We use the TIP4P/2005 force field for water, which is a rigid model consisting of three fixed point charges and one Lennard–Jones (LJ) center.³⁴

Molecular dynamics simulations are performed with the GROMACS package 2018 (single precision).⁵³ When simulating in the NpT ensemble, we use the Parrinello–Rahman barostat,⁵⁴ with a relaxation time of 2 ps and a compressibility of 10^{-5} bar⁻¹. To control the temperature, we use the Nosé–Hoover thermostat⁵⁵ with a relaxation time of 2 ps. For the Verlet integration of the equations of motion, we use a time step of 2 fs. To deal with electrostatic interactions, we use particle mesh Ewald summations.⁵⁶ The cut-off radii for the neighbor list, the dispersive Lennard–Jones interactions, and the real part of the electrostatic interactions are 13 Å. Ewald summations have been previously used to deal with heterogeneous systems,⁵⁷ including water bubbles.^{3,58} We have checked for specific cases of bubble simulations that the energy barely changes by increasing the Ewald cutoff to 20 Å. Moreover, we find that even using a plain 20 Å cutoff for the electrostatic interactions does not almost change the average energy. These arguments give us confidence in the use of Ewald summations with the selected 13 Å real part cutoff. No tail corrections are added to the Lennard–Jones potential due to the presence of two phases with strongly different densities in our simulations. We use a switch radius of 12 Å, meaning that the LJ potential is not modified up to this radius, after which it is gradually switched off to reach zero at the cut-off radius. The LINCS algorithm is used to fix the geometry of the water molecules, with an order of six and four iterations.^{59,60}

III. RESULTS

Most results discussed below correspond to a temperature of 450 K. Only at the end, in Sec. III B 5, we add results corresponding to 550 K in order to establish a broader comparison with experiments.

A. Coexistence properties

The liquid–vapor equilibrium for this model has been characterized in Ref. 61. We recalculate here the coexistence pressure at $T = 450$ K to both test our simulation setup and to account for the use of a slightly different cutoff radius. We first equilibrate a liquid of 4096 water molecules in a cubic box in the NpT ensemble. After, we introduce some empty space next to the liquid, finishing with a box of $3.917\,24 \times 3.917\,24 \times 27.14$ nm³. We run this system (in the NVT ensemble) until equilibrium has been reached and obtain the pressure components of the system. The average pressure component normal to the vapor–liquid interface is the vapor (or coexistence) pressure, and it does not depend on the system size; in our case, $p_z = 4.49$ bar, in very good agreement with the values reported in Ref. 61 (4.46 bars) and Ref. 62 (4.5 bars). The average tangential components of the pressure depend on the system size and in our case are $p_x = -24.38$ bars and $p_y = -24.48$ bars. The interfacial free energy at coexistence, γ_c , is obtained using the mechanical route,⁶³

$$\gamma_c = \frac{L_z \left[\bar{p}_z - \frac{\bar{p}_x + \bar{p}_y}{2} \right]}{2}. \quad (1)$$

We obtain $\gamma_c = 40(1)$ mJ m⁻², which is similar to the value calculated in Ref. 62, $\gamma_c = 38.8$ mJ m⁻².

B. Cavitation rate

1. Cavitation rate by brute force molecular dynamics simulations

By lowering the pressure of the liquid below the coexistence value, one should observe the nucleation of vapor cavities (cavitation). Owing to the liquid–vapor interfacial free energy, this process is activated and can take a long time. At very low pressures, however, the thermodynamic drive for the emergence of the vapor phase is high, and the cavitation process is relatively quick. In fact, it is possible to observe it in brute force molecular dynamics simulations of the bulk liquid for negative pressures below -650 bar. This is shown in Fig. 1, where we plot the volume of the simulation box vs time for ten different trajectories starting from a bulk liquid consisting of 20 000 water molecules under periodic boundary conditions at 450 K and -700 bar. In all runs, the system abruptly increases its volume after some induction period (which varies stochastically from one trajectory to another) due to the sudden appearance and growth of a vapor bubble. The stochastic character of cavitation is a consequence of its activated nature. The fact that there is a long induction period indicates that a single bubble is formed in the system (an unlikely event does not happen twice or more at the same time). This enables us to estimate the bubble nucleation rate as

$$J = \frac{1}{\langle t \rangle \langle V \rangle}, \quad (2)$$

using 1 in the numerator because one only bubble forms in each run. $\langle t \rangle$ is the average time that it takes to observe the nucleation of a bubble, which is obtained as the arithmetic average between the times at which the volume sharply shoots up in our ten trajectories. $\langle V \rangle$ is the average volume of the liquid where bubble nucleation takes place. In Table I, we report the nucleation rates for different pressures alongside the variables required to compute them. Obviously, the lower

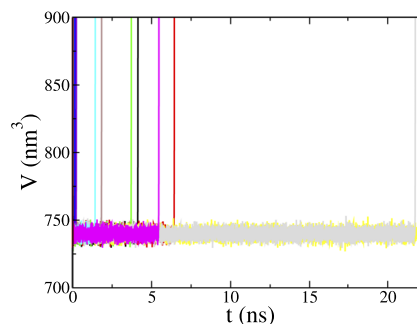


FIG. 1. Volume of the simulation box vs time starting from ten liquid configurations containing 20 000 molecules. The thermodynamic state point is 450 K and -700 bar.

the pressure, the higher the cavitation rate. With our brute force calculations, we span three orders of magnitude of the nucleation rate: from 10^{33} m⁻³ s⁻¹ at -750 bar to 10^{30} m⁻³ s⁻¹ at -650 bar. Probing lower nucleation rates with brute force calculation is too demanding computationally. It is important, however, to get estimates of lower nucleation rates given that in experiments one has access to rates of the order of Ref. 20 10^{15} m⁻³ s⁻¹. To do that, we resort to the Seeding technique, which is described in Sec. III B 2.

2. Cavitation rate via NVT Seeding

We shall compute the nucleation rate for higher pressures (lower rates) using Seeding.^{42–46} In this method, instead of waiting for a bubble to spontaneously appear, the simulation is started from a configuration of a liquid containing a bubble. When equilibrated in the NVT ensemble, the bubble turns out to be the critical vapor nucleus at the simulation temperature and at the pressure acquired by the surrounding liquid.²⁹ With such pressure and the bubble radius, one can obtain an estimate of the nucleation rate using CNT.²⁹

To prepare the initial configuration, we first equilibrate liquid water in the NpT ensemble at 450 K and a selected pressure below saturation. Next, we remove the molecules inside a sphere in the center of the box. This system is then simulated in the NVT ensemble and allowed to equilibrate during 1 ns. We repeat this process with different pressures, box sizes, and cavity radii looking for trajectories having a stable vapor bubble (stabilizing spherical nuclei in the NVT ensemble is not always viable and depends on a subtle balance between the size of the box and that of the nucleus^{29,51}). In Table II, we summarize the system sizes employed in our Seeding simulations

TABLE I. Data leading to the calculation of J via brute force molecular dynamics simulations using a system of 20 000 TIP4P/2005 water molecules at 450 K.

p (bar)	$\langle t \rangle$ (ns)	$\langle V \rangle$ (nm ³)	J (s ⁻¹ m ⁻³)
-750	0.5(2)	747.8(1)	$3(1) \times 10^{33}$
-725	1.1(2)	743.73(6)	$1.2(2) \times 10^{33}$
-700	7(3)	739.81(3)	$2.0(8) \times 10^{32}$
-675	40(10)	736.15(1)	$3.1(8) \times 10^{31}$
-650	300(100)	732.798(7)	$4(2) \times 10^{30}$

TABLE II. Data corresponding to the different *NVT* Seeding simulations performed in this work. See the main text for the meaning of the different reported parameters.

<i>T</i> (K)	<i>N</i>	<i>L</i> (nm)	<i>p_l</i> (bar)	Δp (bar)	ρ_l (kg/m ³)	ρ_v (kg/m ³)	<i>R_{ed}</i> (nm)	<i>R_G</i> (nm)	$\log_{10}[J_{ed}/(\text{s}^{-1} \text{m}^{-3})]$	$\log_{10}[J_G/(\text{s}^{-1} \text{m}^{-3})]$
450	58 817	13.9305	-135.4	142.2	869.8	3.79	5.43	5.46	-293	-299
	64 085	13.9305	-150.4	156.9	868.6	3.65	4.88	4.92	-227	-233
	47 110	12.3315	-190.8	196.8	865.2	3.34	3.85	3.89	-124	-130
	49 774	12.3315	-225.5	231.2	862.2	3.13	3.24	3.29	-75	-80
	49 774	12.3315	-226.2	231.9	862.2	3.12	3.24	3.29	-75	-80
	51 785	12.3315	-295.4	300.6	856.0	2.79	2.45	2.50	-24	-29
	17 985	8.8216	-308.7	313.7	854.8	2.73	2.33	2.39	-17	-22
	18 548	8.8056	-391.0	395.6	847.0	2.44	1.80	1.88	7	2
	18 524	8.8023	-391.0	395.6	847.0	2.44	1.80	1.88	7	2
	8 950	6.9651	-435.5	439.8	842.6	2.31	1.58	1.69	15	9
550	50 691	13.1049	-73.2	110.9	710.2	20.92	2.93	3.05	7	2
	17 064	9.2936	-86.4	123.7	706.6	20.56	2.55	2.70	16	11
	17 737	9.2936	-116.4	152.8	697.8	19.78	1.99	2.18	26	21

alongside the radii of the stabilized bubbles averaged over 19 ns. We report two different radii for each bubble. One is *R_G*, the radius corresponding to the equi-molar Gibbs dividing surface, which is computed as follows:

$$R_G = \left(\frac{3(N - L^3 \rho_l)}{4\pi(\rho_v - \rho_l)} \right)^{1/3}, \quad (3)$$

where *N* is the total number of molecules, *L* is the length of the simulation box edge (since we work with a cubic system the volume of the box is *L*³), and ρ_l and ρ_v are the densities of the liquid and the vapor phases, respectively. The former is obtained via the average virial pressure, *p_l*, and the bulk liquid equation of state (see Table II). The latter is obtained by looking for the vapor that has the same chemical potential as the surrounding liquid:^{64,65} $\mu_l(T, p_l) = \mu_v(T, p_v)$. We search where this condition is satisfied by performing isothermal thermodynamic integration of both the bulk vapor and the bulk liquid molar volumes from the coexistence pressure, *p_{coex}*, as described

in Ref. 28. In Fig. 2, we show $\mu(p) - \mu(p_{coex})$ at 450 K for the liquid (black curve) and the vapor (red curve). The dotted vertical line at *p* = -295.4 bar corresponds to *p_l* for a bubble of 2.5 nm. The chemical potential of such liquid can be obtained from the intersection between the dotted line and the black curve. Then, we read from the intersection between the horizontal dashed line and the red curve, the pressure of the vapor that has the same chemical potential as the liquid, *p_v*. Δp , a key parameter in the CNT nucleation formalism, is the difference between *p_v* and *p_l*. The vapor pressures, *p_v*, and the corresponding densities, ρ_v , thus obtained for all simulated bubbles, are reported in Table II.

Alternatively, we compute the bubble radius by means of an average radial density profile starting from the bubble center, as shown in Fig. 3. Such a density profile is fitted to the following sigmoid function (dashed orange curve in Fig. 3):

$$\rho(r) = \frac{\rho_{v,dp} + \rho_{l,dp}}{2} + \left(\frac{\rho_{l,dp} - \rho_{v,dp}}{2} \right) \cdot \tanh[(r - R_{ed})/\alpha], \quad (4)$$

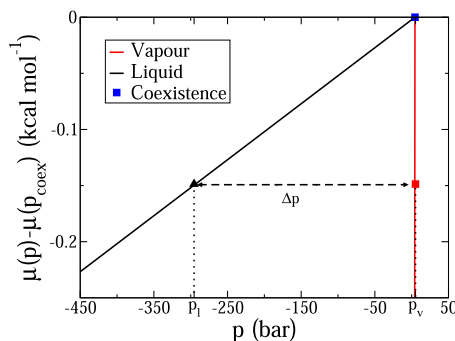


FIG. 2. Chemical potential difference with respect to the coexistence pressure at 450 K for the bulk liquid (black) and the bulk vapor (red) phases. Dashed and dotted horizontal and vertical lines guide the search for the condition of equal chemical potential in a bubble of radius ~2.5 nm (see main text for more details).

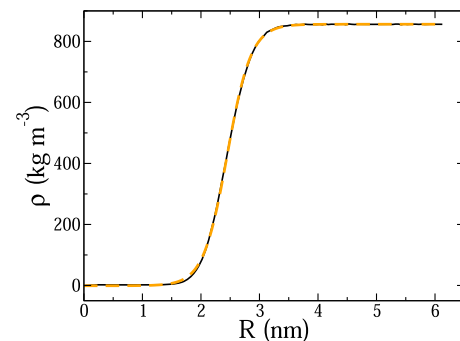


FIG. 3. Radial density profile starting from the bubble center averaged over 19 ns in the *NVT* ensemble (black line). The profile corresponds to a bubble surrounded by a liquid of pressure -295.4 bar. The dashed orange line is a fit to the simulation data given by Eq. (4).

where $\rho_{v,dp}$ and $\rho_{l,dp}$ are the densities of the vapor and the liquid phases obtained with the density profile (dp) fit, α is a parameter related to the width of the interfacial region, and R_{ed} is the critical bubble radius estimated as the distance at which the density is the average between both phases (“equi-density” criterion).²⁸ The equi-density radius, R_{ed} , reported in Table II is close to but systematically lower than R_G .

Both approaches obtain the radius [Eqs. (3) and (4)] assume a spherical bubble shape. In order to visually inspect the shape, we provide, in Fig. 4, a series of slabs cut through the bubble center at different times along a Seeding simulation containing a 2.5 nm bubble. The sequence of snapshots clearly shows that the bubble shape fluctuates around a sphere, which justifies our approach to obtain the bubble radius assuming an average spherical shape.

The fit parameter in Eq. (4) $\rho_{l,dp}$ is fully consistent with the density obtained by means of the overall virial pressure of the system and the bulk liquid equation of state. However, the vapor density provided by the fit given by Eq. (4), $\rho_{v,dp}$, is not accurate, given the small size of the bubbles (the sigmoid does not reach a true plateau in the interior of the bubble). Nevertheless, by estimating the vapor density as an average of the density profile in a region in the interior of the bubble, one does obtain consistent values with the vapor density resulting by imposing equal chemical potential between the bubble and the surrounding liquid. This consistency, although expected, should not be given for granted. For instance, for hard sphere crystallization, the density (and the mechanical pressure) of the crystal nucleus is lower than that obtained by imposing chemical potential homogeneity (in fact, the nucleus’s mechanical pressure is even lower than that of the surrounding liquid).^{50–52}

Knowing the bubble radius and Δp , we can use CNT to estimate the nucleation rate, J ,

$$J = A \exp\left(-\frac{\Delta G_c}{k_B T}\right), \quad (5)$$

where k_B is the Boltzmann constant, A is a kinetic pre-factor, and ΔG_c is the Gibbs free energy associated with the formation of the critical bubble, which is given by

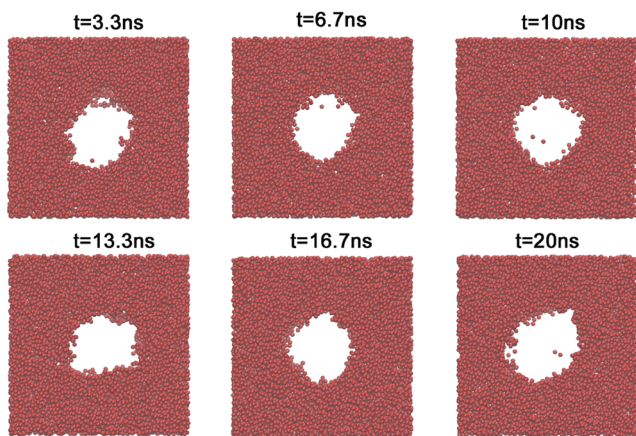


FIG. 4. Slab cuts of 20 Å thickness through the bubble center in a Seeding simulation at 450 K containing a ~2.5 nm radius sphere.

$$\Delta G_c = \frac{2\pi \times \Delta p \times R_c^3}{3}, \quad (6)$$

where R_c is the critical bubble radius that we identify either with R_G or with R_{ed} . The kinetic pre-factor is computed following Blander and Katz:²⁴

$$A = \sqrt{\frac{\Delta p \times R_c}{\pi m}} \rho_l, \quad (7)$$

where m is the mass of the molecule (18.02 u for water). This theoretical expression gives consistent results with other routes to estimate the kinetic pre-factor.⁶⁶ One can also obtain from the bubble properties an estimate of the interfacial free energy via the Laplace equation,

$$\gamma = \frac{\Delta p \times R_c}{2}. \quad (8)$$

In Table II, we provide the nucleation rates for all simulated bubbles alongside all parameters required for their computation. The kinetic pre-factor A can be obtained with the data reported in the table using Eq. (7) and is of the order of $10^{40} \text{ m}^{-3} \text{ s}^{-1}$ for all pressures and both choices of radius definition. The rates corresponding to R_G and R_{ed} are shown as filled black and red circles, respectively, in Fig. 5. Our data are consistent with those of Ref. 20, indicated with crosses in the figure, which were obtained with Density Functional Theory for two different temperatures, namely 423 and 523 K.

3. Surface free energy and the capillarity approximation

The surface free energy, γ , between the bubbles equilibrated in the NVT Seeding simulations and the surrounding liquid can be estimated from Eq. (8). We plot γ in Fig. 6 as a function of the liquid pressure for all bubbles. Again, black and red symbols correspond to the Gibbs and the equi-density definitions of the critical bubble radius, respectively. Both sets of data tend to the flat interface value (blue square) obtained from our liquid–vapor direct coexistence simulations via Eq. (1). This is a good consistency test passed by the Seeding approach. Given that γ is proportional to the bubble radius [see Eq. (8)] and that $R_{ed} < R_G$, γ coming from the equi-density radius definition is systematically lower. As one approaches coexistence (higher pressures/larger bubbles), both sets of data get closer to each other because the difference between both radii becomes a small fraction of the overall radius. The decrease of γ with pressure for the equi-density radius definition is about $1 \text{ mN m}^{-1}/100 \text{ bars}$ pressure drop, whereas it is approximately half that for the Gibbs radius. In either case, γ goes down by decreasing the pressure away from coexistence. This is consistent with the results obtained in Ref. 3 at another temperature (296.4 K).

The lowering of γ by moving away from coexistence is a common feature with other systems like the Lennard–Jones fluid in the cavitation/condensation transition^{28–30,33} or ice nucleation in water.^{45,67} In our case, both the curvature of the interface and the pressure of the surrounding fluid change by moving away from coexistence. Both factors simultaneously contribute to the variation of γ , and their effects cannot be decoupled. Nevertheless, it seems intuitive that by lowering the pressure (or the density) of the liquid, the

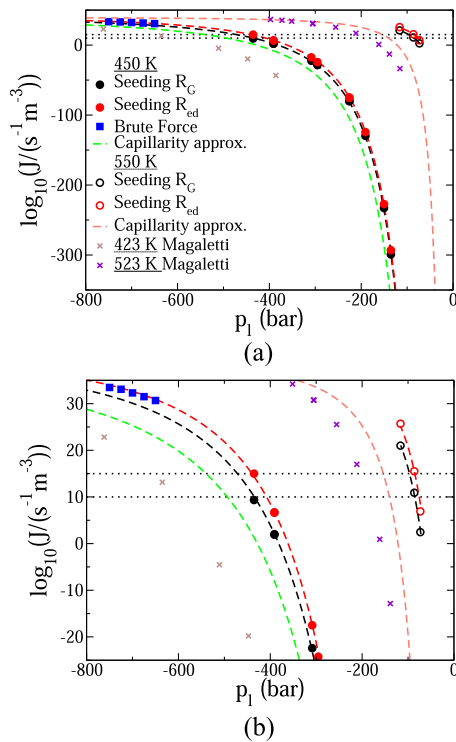


FIG. 5. (a) Decimal logarithm of the cavitation rate as a function of the liquid pressure. Blue squares are obtained by Brute Force simulations at 450 K. Circles are obtained with NVT Seeding (black circles using the Gibbs definition for the critical bubble radius [Eq. (3)] and red ones using the equi-density criterion [Eq. (4)]). Filled circles correspond to $T = 450$ K and empty ones to 550 K. The black and red dashed lines are fits to the NVT Seeding data using the CNT expressions given in the main text and the $\gamma(p)$ dependence shown in Fig. 6. The green (pink) dashed line represents the capillarity approximation for 450 K (550 K). The horizontal dotted lines indicate the expected rate range for cavitation in isobaric superheating¹² and quartz inclusions isochoric cooling experiments.^{1,15} Crosses correspond to Density Functional Theory for 423 K (brown) and 523 K (purple).²⁰ (b) Enlargement of the high nucleation rate regime.

similarity between the vapor and the liquid increases, which is in line with a γ decrease.

The decrease of γ with pressure looks rather linear [see Fig. 6(a)]. By fitting $\gamma(p)$ to a straight line (dashed in Fig. 6) and using Eqs. (5)–(8), we can fit the rate-pressure dependence²⁹ and obtain the dashed curves in Fig. 5, which we comment on in more detail in Sec. III B 4.

The variation of γ with curvature is often described by the following expression proposed by Tolman:⁶⁵

$$\gamma = \gamma_c \left(1 - \frac{2\delta}{R_c} \right), \quad (9)$$

where δ is the Tolman length, which can be obtained from the slope of a γ vs $1/R_c$ representation such as that shown in Fig. 6(c) (filled data correspond to 450 K). We use $R_c = R_{ed}$ to do such representation given that, as it will be shown later on, it turns out that R_{ed} better predicts the nucleation rate in the spontaneous cavitation regime. A positive δ is expected, given that γ diminishes as curvature increases.

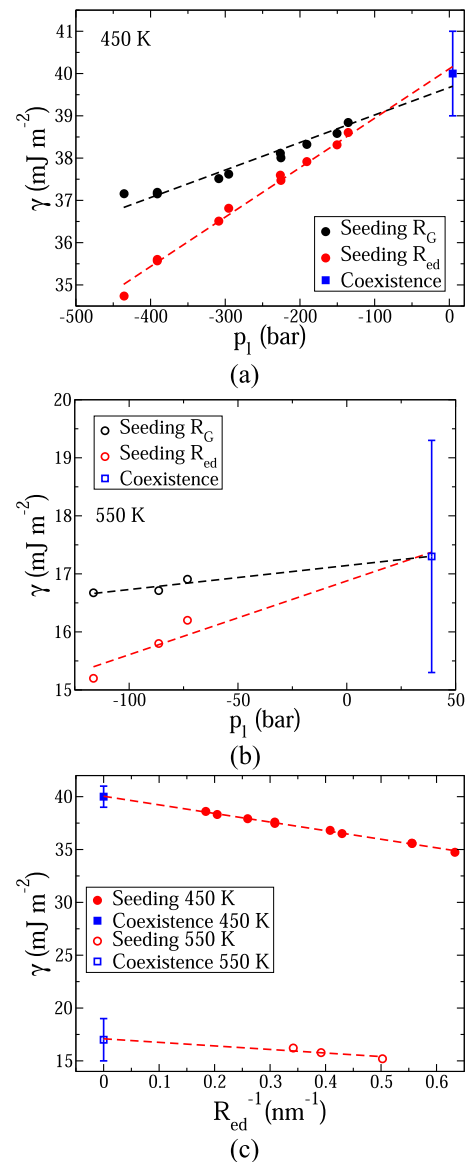


FIG. 6. (a) and (b) Interfacial free energy as a function of the liquid pressure. Black and red symbols correspond to estimates of γ from the NVT Seeding simulations using Eqs. (3) and (4) to obtain the bubble radius, respectively. The blue square corresponds to the coexistence value obtained with simulations of a flat vapor–liquid interface via Eq. (1). (a) and (b) correspond to 450 and 550 K, respectively. (c) Interfacial free energy vs the inverse equi-density radius for both temperatures as indicated in the legend.

The resulting δ is 0.1 nm. Later on, in Sec. III B 5, we extend our study to a temperature of 550 K in order to compare our simulations with experiments. Here, we anticipate the results for this temperature regarding the Tolman length. From the representation in Fig. 6(c) (empty symbols), we get the same δ as for 450 K, 0.1 nm, suggesting that δ is temperature independent. A very recent simulation estimate of δ at $T = 296.4$ K (0.091 ± 0.008 nm) using the same

model as in this work confirms the non-dependence of the Tolman length with temperature.⁵⁸

Taking into account, the decrease of γ when lowering the liquid pressure is crucial to get accurate estimates of the nucleation rate. To illustrate this, we compute the rate that would be obtained by considering γ constant and equal to its value at coexistence (capillarity approximation). To obtain such a rate, we express Eqs. (7) and (6) as a function of γ via Eq. (8). Thus, one gets

$$\Delta G_c = \frac{16\pi\gamma^3}{3\Delta p^2}, \quad (10)$$

and

$$A = \rho_l \sqrt{\frac{2\gamma}{\pi m}}. \quad (11)$$

Inserting Eqs. (11) and (10) into Eq. (5) and using the coexistence γ for every pressure gives rise to the green dashed curve in Fig. 5, which lies at lower rates as compared to Seeding or Brute Force data. The capillarity approximation actually underestimates J by 6 orders of magnitude when compared to Brute Force. The conclusion is that a theoretical or a simulation treatment (Seeding and Brute Force in the present case) that takes into consideration the variation of γ with pressure/curvature is indeed needed to obtain accurate cavitation rates in overstretched water (it is not enough the use of the capillarity approximation). It was also concluded that the capillarity approximation fails to provide accurate nucleation rates for water cavitation, in previous simulation and theoretical studies.^{2,3,20}

4. Cavitation rate: Brute force vs Seeding

In Fig. 5 we plot the rate vs the liquid pressure as obtained from Brute Force simulations (blue squares) and Seeding (black and red circles using R_G and R_{ed} as definitions for the critical radius, respectively). More than 300 orders of magnitude of the nucleation rate are spanned by our data. Brute Force data cover the highly negative pressure regime, where cavitation is spontaneous in the simulation time, whereas Seeding is used to obtain rate estimates in a higher pressure regime, where the rate is much lower and nucleation does not spontaneously occur. As discussed later on, the Seeding regime is more relevant to experiments.

The Gibbs radius systematically gives smaller rates than the equi-density one (by about 4–5 orders of magnitude), given that the nucleation barrier is proportional to the cubed bubble radius [Eq. (6)] and $R_G > R_{ed}$. An extrapolation to low pressures of the fits to Seeding data [done by linearly extrapolating the $\gamma(p)$ fits shown in Fig. 6(a)] suggests that by using R_{ed} as radius definition, a better consistency with Brute Force is achieved [see the enlargement shown in Fig. 5(b)]. We stress that the Brute Force rate is exempt from theoretical approximations. In this respect, R_{ed} seems to be a better definition than R_G of the critical bubble radius, R_c , in the CNT expressions given by Eqs. (6)–(8).

In Fig. 7, we plot the Gibbs free energy barrier, ΔG_c , computed according to Eq. (6), from our Seeding simulations (dots) fitted via the linear $\gamma(p)$ dependence found in Fig. 6. The predicted free energy barrier height in the spontaneous cavitation pressure range (–750 to –650 bars) goes from 15 to 20 $k_B T$ according to the R_{ed} radius definition. These barrier heights are typical of spontaneous nucleation events in simulations.^{50,68} This consistency further

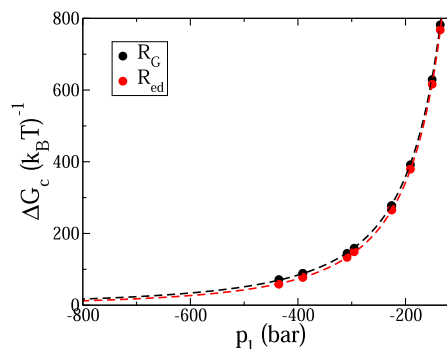


FIG. 7. Gibbs free energy as a function of the liquid pressure from Seeding simulations considering the equi-density radius definition. 450 K. Black (red) circles are data obtained using the Gibbs (equi-density) radius definition. Dashed curves are fits based on the linear $\gamma(p)$ dependence shown in Fig. 6.

demonstrates the match between Brute Force and Seeding extrapolated via the $\gamma(p)$ linear dependence of the data obtained with the equi-density radius definition.

5. Comparison with experiments

Experimental studies of cavitation, rather than having direct access to the nucleation rate, detect the thermodynamic state point at which a liquid water sample undergoes cavitation. In Fig. 8, the cavitation pressure is plotted against temperature. Empty and solid symbols correspond to experimental measurements and simulations, respectively. Lines correspond to theoretical predictions.

We compare first our data against experiments of isobaric superheating¹² and isochoric cooling, the latter performed with quartz inclusions.^{1,15} The cavitation rate probed in these experiments, J_{exp} , is determined by the (inverse) product of the employed volumes and observation times and ranges from 10^{10} to 10^{15} ($\text{m}^{-3} \text{s}^{-1}$).^{1,15,19,69} Therefore, in order to compare our simulations against experiments, we have to find the pressure range that gives the aforementioned rates (indicated with dotted horizontal lines in Fig. 5). By using this strategy of identifying iso-rate lines we were able to satisfactorily predict with simulations the location of the so-called homogeneous ice nucleation line in studies of ice nucleation.⁷⁰

Using the $J(p)$ curves in Fig. 5, we can estimate by interpolation that cavitation in the experiments mentioned in the previous paragraph will occur between $p(J = 10^{10} \text{ m}^{-3} \text{ s}^{-1}) = -41$ MPa and $p(J = 10^{15} \text{ m}^{-3} \text{ s}^{-1}) = -44$ MPa at 450 K (we used the R_{ed} radius definition for this estimate, but the values obtained using R_G are very similar). This pressure range is quite narrow due to the large slope of the $J(p)$ curve. Such pressure range is our simulation estimate for the occurrence of cavitation in experiments of isobaric superheating or isochoric cooling (in quartz inclusions) at 450 K and is indicated with a red dot for R_{ed} and with a black dot for R_G in Fig. 8 [the size of the dot includes the values of $p(J = 10^{10} - 10^{15} \text{ m}^{-3} \text{ s}^{-1})$]. It is worth pointing out that at the pressures where we predict cavitation to occur in experiments (–41 to –44 MPa), we obtain a ΔG_c of 60–70 $k_B T$ from the fit to the R_{ed} data shown in Fig. 7. These barrier heights are typical of nucleation experiments.

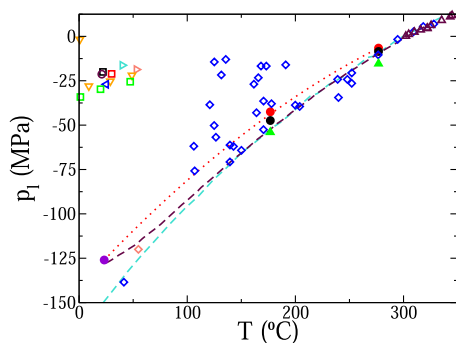


FIG. 8. Cavitation pressure as a function of temperature obtained with experiments (empty symbols), simulations (filled symbols), and theory (dashed lines). Black and red filled dots correspond to our Seeding simulation predictions using R_G and R_{ed} as the radius definition, respectively, whereas the purple dot corresponds to transition sampling simulations.³ The dotted line is a spline fit to simulation data to help visualize the trend predicted by TIP4P/2005. Filled green up triangles are predictions combining simulation equations of state with the capillarity approximation (see main text). The pale blue dashed line is a CNT-like prediction from Refs. 1 and 25 and the maroon one is a density functional approach.²⁰ Blue¹ and pink¹⁵ empty diamonds correspond to isochoric cooling experiments using inclusions. Empty maroon up triangles are data from isobaric superheating experiments.¹² Right triangles correspond to Berthelot isochoric cooling experiments, in pale blue¹⁶ and in pink.¹⁷ Centrifuge experiments are represented with orange down triangles,⁷² shock wave experiments with blue left triangles,⁷³ and acoustic experiments with squares, in black from Ref. 14, in red from Ref. 37, and in green from Ref. 38. The maroon circle is obtained using artificial trees.¹⁸

The dot in Fig. 8 obtained from our simulations at 450 K lies in the low pressure limit of the rather scattered experimental data cloud (blue empty diamonds) found around 450 K. This is consistent with the hypothesis that, around this temperature, there might be heterogeneous cavitation in the experiments,¹ which is a pathway that leads to bubble nucleation at higher pressures than its homogeneous counterpart. Our simulation point, obviously, corresponds to homogeneous nucleation, which is why it stands close to the lowest attainable experimental pressures.

At high temperatures, the experimental data are not scattered anymore, and they all nicely fall into a neat line. In order to compare our simulations with experiments in such a temperature regime, we performed extra *NVT* Seeding simulations at 550 K. The simulation details are identical to those described for 450 K except that we used a lower integration time step, namely 1 fs. At 550 K, we find a coexistence pressure of 39(1) bars and an interfacial free energy of 17(2) mJ m⁻², both consistent with Ref. 61 (38.01 bars) and Ref. 62 (38.3 bars and 17.4 mJ m⁻²).

We run first a bubble of radius about 3 nm. We observe that the interfacial width at 550 K doubles that of 450 K (2 vs 1 nm). In equilibrium at 550 K, the bubble is surrounded by a liquid of $p = -73.2$ bars. Since its corresponding rate, $J = 10^7$ m⁻³ s⁻¹ (with the R_{ed} radius criterion), turned out to lie below the J range relevant to experiments, 10^{10} – 10^{15} m⁻³ s⁻¹, we decided to equilibrate a couple of smaller bubbles in order to enable the interpolation. The rates calculated from the three Seeding runs are reported in Table II and are represented as empty circles in Fig. 5 [the kinetic pre-factor, which can be obtained with the data of the table using Eq. (7), is of the same order of magnitude as that found at 450 K: 10^{40} m⁻³ s⁻¹]. The $\gamma(p)$

dependence shown in Fig. 6(b) is used to fit the $J(p)$ data at 550 K (dashed lines through empty circles in Fig. 5). By interpolation, we estimate that cavitation at 550 K will take place between -7.6 and -8.5 MPa (using the R_{ed} radius definition). This pressure interval is included as a red dot in Fig. 8 and is quite close to the experimental line, which highlights the ability of the TIP4P/2005 model, in combination with the Seeding technique, to predict and justify the experimental cavitation behavior. In Fig. 8, we also include two low temperature data coming from inclusion experiments (pink empty diamond¹⁵) and simulations (purple solid circle³). Again, simulations and inclusion experiments seem to be fully consistent with each other.

To summarize, our simulations seem to be in good agreement with superheating¹² and with quartz inclusion experiments¹ at high temperatures, and those of Ref. 3 are consistent with more recent quartz inclusions experiments performed at lower temperatures.¹⁵ We include in Fig. 8 a spline fit (red dotted line) to the three available simulation data (450 and 550 K from this work and 296.4 K from Ref. 3) to give a visual idea of the cavitation line predicted by the TIP4P/2005 model. A direct comparison between the model and the experiment is enabled by the fact that TIP4P/2005 predicts quite well the critical temperature and the surface tension.⁶¹ The model seems to mildly overestimate the cavitation pressure, which indicates that TIP4P/2005 overestimates the nucleation rate. Such overestimation could be due to the model having a smaller γ than real water.⁶² Also, it should be taken into account that γ is very sensitive to the employed cutoff and that using larger cutoff distances could improve the agreement between simulation and experiment.^{62,71} In any case, the model predictions shown in Fig. 8 are already very satisfactory.

However, the scenario is not fully clear yet: measurements of the cavitation pressure with other strategies, such as the Berthelot, centrifuge, acoustic cavitation, and artificial tree techniques, indicated with empty symbols of different colors forming a cloud located at around -25 MPa and between 0 and 25 °C, do not agree with the trend set by our simulations and those of Ref. 3. All these experiments find cavitation pressures well above those predicted by the simulations. In acoustic cavitation experiments, according to Ref. 35, the accessible rate is of the order of 10^{20} m⁻³ s⁻¹. This is 5 orders of magnitude higher than the highest value we have used in this paper (and in Ref. 3) to compare with inclusion experiments. However, if we had used the 10^{20} m⁻³ s⁻¹ rate, we would have found an even larger discrepancy because we would have predicted a lower cavitation pressure (pressure goes down as the rate goes up). Hence, we are unable to explain the discrepancy with acoustic cavitation experiments. What about Berthelot's experiments? In such experiments, isochoric cooling is performed as in quartz inclusions but in much larger volumes (about 5 orders of magnitude larger, 10^{-10} vs 10^{-15} m³).¹⁶ Also, the observation time is longer in Berthelot experiments (10^4 vs 10 s). With these time and volume scales, rates as low as 10^5 m⁻³ s⁻¹ could be probed in Berthelot experiments. Inferring the cavitation pressure from $J = 10^5$ m⁻³ s⁻¹, which is 5 orders of magnitude below the lower rate bound here considered, would go in the right direction, although it is not enough: both in our work at 450 K and in that of Ref. 3 at 296.4 K, one can see that, in the experimentally relevant region (that given by the dotted lines in Fig. 5), the pressure barely changes 3 MPa every 5 orders of magnitude change of the rate. This is clearly insufficient to explain the ~ 100 MPa

difference between simulations and Berthelot experiments shown in Fig. 8. Possibly, the explanation for such a large discrepancy between simulations and Berthelot or other sorts of experiments is that cavitation occurs at large pressures via heterogeneous nucleation in these experiments.

Finally, in Fig. 8, we also include the capillarity approximation prediction for the cavitation pressure in isobaric superheating or quartz inclusion experiments (green upward triangles). These triangles lie at lower pressures than circles corresponding to Seeding predictions. This is justified as follows: We have already discussed in Fig. 5 that the rate obtained from the capillarity approximation is lower than that coming from Seeding due to the decrease of γ as the bubble radius diminishes (see Fig. 6). Since the capillarity rate is lower, the pressure at which capillarity predicts a certain rate is lower too. However, it is perhaps surprising that the capillarity approximation prediction for the cavitation pressure is quite close to that obtained by Seeding despite the fact that capillarity rates lie 5–10 orders of magnitude below Seeding (see Fig. 5). Again, this is explained by the steep $J(p)$ curve in the experimentally relevant region (large rate changes correspond to rather small pressure variations). This justifies the proximity between Seeding and capillarity predictions of the cavitation pressure and between different theoretical approaches shown in Fig. 8, disregarding^{1,25} or taking into account²⁰ the variation of the interfacial free energy with pressure.

IV. SUMMARY AND CONCLUSIONS

We investigate water cavitation with molecular dynamics simulations using the TIP4P/2005 model. Our first goal is to establish the cavitation rate vs pressure curve at 450 K. For that purpose, we first evaluate the coexistence properties by simulating the liquid in contact with the vapor phase in direct coexistence. We find that the coexistence pressure is 4.49 bars and that the interfacial free energy is $40(1) \text{ mJ m}^{-2}$. We then simulate the liquid at large negative pressures until we find a regime where vapor bubbles spontaneously form in the course of an unbiased simulation. Due to the small size of the simulation volumes as compared to experimental ones, this regime is found at very low pressures: below -650 bar. In such simulations, we can estimate the nucleation rate by computing the average time required for a bubble to appear in the simulated liquid volume. We find nucleation rates in the range of 10^{30} – $10^{33} \text{ m}^{-3} \text{ s}^{-1}$ when lowering the pressure from -650 to -750 bar. We cannot simulate lower pressures because there is no longer an induction period before the appearance of a bubble. To compute the nucleation rate at larger pressures, which are more relevant to experiments, we resort to the Seeding method, which consists in simulating a bubble surrounded by the liquid in the *NVT* ensemble, in our case at 450 K. In such simulations, we compute the average pressure of the surrounding liquid with the virial expression and the bubble radius by means of radial density profiles (equi-density criterion). Alternatively, the radius is estimated using the definition of the equi-molar Gibbs dividing surface, which only requires knowing the volume of the simulation box, the total number of molecules, the liquid density, and the vapor density. To obtain the latter, we use thermodynamic integration of the equation of state of both phases, previously obtained with bulk phase simulations, and impose the condition of homogeneous chemical potential throughout the system. The vapor density thus

obtained is consistent with that inferred from the density profile. This is expected in vapor–liquid transitions but is not generally true in solid–liquid equilibrium.^{51,52} We combine the aforementioned simulation information (pressure of both phases, and bubble radius) with CNT to obtain estimates of the nucleation rate and the interfacial free energy. We get a huge variation of the nucleation rate (from 10^{-300} to $10^{10} \text{ m}^{-3} \text{ s}^{-1}$) in the pressure range going from -130 to -430 bar. The interfacial free energy goes down from its coexistence value as pressure goes down. The Gibbs radius definition predicts an interfacial free energy drop of $\sim 0.5 \text{ mN/m}$ /100 bars decrease whereas the equi-density definition predicts approximately double that. Both criteria to identify the bubble radius give a similar rate trend although the Gibbs criterion gives lower values because it predicts higher interfacial free energies. By fitting the variation of the interfacial free energy with pressure to a straight line, we can fit the rate data obtained with Seeding. We find that the fit to the Seeding data obtained with the equi-density radius definition extrapolates better to the regime where we computed the nucleation rate with unbiased simulations. Thus, the equi-density radius seems to be more appropriate to describe water cavitation with CNT. The γ variation with curvature obtained with the equi-density radius is fitted by a 0.1 nm Tolman length. We also compare the Seeding rate curves with those obtained using the capillarity approximation, i.e., by assuming that the interfacial free energy does not vary with pressure. Obviously, the capillarity curve predicts lower rates because it does not take into consideration the lowering of the interfacial free energy when moving away from coexistence. Finally, we compare our results with experiments. The experimental data available at 450 K are rather scattered so we decided to run a few extra Seeding simulations at 550 K where there are cleaner data. To compare with experiments, we need to predict the pressure at which the system undergoes cavitation at a given temperature. We do this prediction by interpolating, in our rate vs pressure curves, the rate at which it is expected that cavitation takes place in the experiments. With this strategy, we get a successful comparison with both isobaric heating and isochoric cooling experiments with small volumes (quartz inclusions). However, we find irreconcilable discrepancies with the cavitation pressures obtained with other experimental techniques like Berthelot or acoustic cavitation. We hypothesize that there could be heterogeneous bubble nucleation in such experiments, given that cavitation occurs at much higher pressures than predicted by our simulations and those of Ref. 3, performed at 296.4 K. Overall, our work shows an efficient manner to investigate and understand the factors that control and affect water cavitation using molecular simulations.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Cintia P. Lamas: Conceptualization (equal); Data curation (equal); Formal analysis (equal); Investigation (equal); Methodology (equal); Writing – original draft (supporting); Writing – review & editing (equal). **Carlos Vega:** Conceptualization (equal); Funding acquisition (equal); Project administration (equal); Supervision (equal); Writing – review & editing (equal). **Eva G. Noya:** Conceptualization (equal); Data curation (equal); Project administration (equal); Resources (equal); Supervision (equal); Validation (equal); Writing – review & editing (equal). **Eduardo Sanz:** Conceptualization (equal); Data curation (equal); Funding acquisition (equal); Methodology (equal); Project administration (equal); Supervision (equal); Writing – original draft (equal); Writing – review & editing (equal).

DATA AVAILABILITY

The data that support the findings of this study are available within the article.

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