NONEQUILIBRIUM MOLECULAR DYNAMICS SIMULATION OF NANOBUBBLE GROWTH AND ANNIHILATION IN LIQUID WATER

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The objective of this article is to investigate nanosized bubble growth and annihilation processes in liquid water via nonequilibrium molecular dynamics (MD) simulation and compare the results with that obtained from the Rayleigh-Plesset equation. The TIP3P potential model is chosen to describe the structure of the water molecule. The SHAKE algorithm is used to hold two O-H bonds and H-O-H angle as rigid, and a harmonic bond style and a Charmm angle style are applied. The results show that the hydrodynamic model based on the Rayleigh-Plesset equation is not valid for predicting nanosized bubble growth and annihilation in liquid water.

KEY WORDS: water nanobubble, molecular dynamics, growth and annihilation

INTRODUCTION

Ranging from microdevices to macroscale hydraulic machinery developments, the increasing applications in industry require a deeper understanding of micro- or nanosized bubble behaviors; for example, bubble cavitation [1], nucleation [2], and stability [3]. Molecular dynamics (MD) simulation is a powerful method to study microscale bubble behavior in many different situations. With regard to cavitation and bubble nucleation, Park et al. numerically simulated the hysteretic process of bubble collapse [4]. Wu and Pan conducted MD simulation to study the bubble nucleation rate in homogeneous liquid argon [5]. Tsuda et al. focused on bubble nucleation in liquid oxygen with different impurities [6]. Zhai et al. investigated bubble nucleation in a supercritical carbon dioxide–hexadecane solution, which is widely used in the plastic production industry [7]. With regard to other aspects of bubble dynamics, Lugli and Zerbetto investigated nanobubble collapse in water and the effects of salts [8]. A stability study of helium bubbles during high energy displacement was carried out in order to investigate bubble damage in a fusion reactor [9]. Insepov and Hassanein calculated the density and diffusion coefficient in liquid lithium containing helium atoms during bubble formation by sampling data from MD simulation.
Nagayama et al. observed bubble formation in a nanochannel with an emphasis on the nucleation phenomenon in liquid argon [11]. Okumura and Ito investigated the processes of bubble formation and contraction simulation in liquid argon by MD simulation [12], and their results indicated that the Rayleigh-Plesset equation is valid for nanosized bubbles generated in liquid argon. Because most materials are composed of polyatomic molecules (like water), where a more complicated force field should be accounted for, bubble behavior in liquid water should be investigated.

The objective of this article is to investigate nanosized bubble growth and annihilation processes in liquid water and compare the results with those obtained from the Rayleigh-Plesset equation. Sampling of the atomic movement data at the microscopic level during the entire process from creation to extinction is discussed. The validities of the assumptions supporting the Rayleigh-Plesset equation are also analyzed.

In order to investigate the dynamics of a bubble, reduced MD simulations were performed by applying the Lennard-Jones potential. The characteristic length, energy, and mass were chosen as the Lennard-Jones diameter $\sigma$, the minimum value of the potential $\varepsilon$, and the atom mass $m$. An asterisk (*) represents the reduced quantities such as reduced length $r^* = r/\sigma$, and reduced temperature $T^* = T_kb/\varepsilon$, reduced pressure $P^* = P\sigma/\varepsilon$, reduced mass density $\rho^* = \rho\sigma^3/m$, reduced time $t^* = t(\varepsilon/m/\sigma^2)^{1/2}$, and reduced charge $q^* = q((4\pi\varepsilon_0\varepsilon\sigma)^{1/2})$. For the convenience of data analysis, the parameters of hydrogen atoms in water molecules were chosen as characteristic parameters during MD simulations. All dimensionless results were converted back to dimensional for discussion.

**PHYSICAL MODELS AND METHODS**

Nanobubble generation and dynamic behavior are mainly affected by the thermal conductivities and viscosities of the fluid. The TIP3P model did not show a significant difference in predicting either of these water properties [13, 14], although it is widely used for MD simulation. In addition, the TIP3P model is better than other three-site water molecules, such as SPC/E, for describing intermolecular potential and controlling system pressure [15]. TIP3P is also one of the most popular water models in the rigid TIP3P-CHARMM [16–18] model that specifies three interaction sites corresponding to three atoms in the water molecule. Thus, it was chosen to describe water’s molecular structure. For the bond and angle model, the SHAKE algorithm [18] is used to hold two O-H bonds and an H-O-H angle as rigid. Figure 1 shows the typical structure of a single water molecule with three-site.

The interaction between two water molecules in TIP3P is represented as:

$$E_{ab} = \sum_{i}^{on.a} \sum_{j}^{on.b} kC q_{ai} q_{bj} r_{ai,bj}^{-1} + \sum_{i}^{on.a} \sum_{j}^{on.b} 4\varepsilon_{ai,bj} \left[ \left( \frac{\sigma_{ai,bj}}{r_{ai,bj}} \right)^{12} - \left( \frac{\sigma_{ai,bj}}{r_{ai,bj}} \right)^{6} \right],$$  \hspace{1cm} (1)$$

where $kC$ is the electrostatic constant and has a value of 332.06 Å·kcal/mol; $q_i$ are the partial charges relative to the charge of the electron; $r_{ij}$ is the distance between charged sites; and $\sigma_{ai}$ and $\sigma_{bj}$ are the Lennard-Jones parameters. The values of the dimensionless parameters are provided in Table 1. An arithmetic average was used to calculate the Lennard-Jones potential between oxygen and hydrogen atoms.

The particle–particle, particle–mesh method (PPPM) [19, 20] is an accurate and computationally efficient method for calculating interactions in MD simulation, and its
complexity is only $N \log(N)$ [19]. Therefore, the long-range Coulomb solver, PPPM, was used to calculate the long-range force between the water molecules. During the computation, the PPPM solver maps the water molecule’s hydrogen and oxygen atoms charge in a 3D mesh and then uses 3D fast Fourier transforms to solve the Poisson equation on each mesh. Finally, it interpolates from the grids to calculate the electric field and corresponding long-range Coulomb force on each charged atom. A careful choice of mesh size is required before applying the PPPM approach in order to achieve comparable precision of the Ewald summation [21]. Here, 60 was selected as the mesh size in the $x$-, $y$-, and $z$-directions, based on a pair of test cases for thermal conductivity (278.15 K) calculation carried out by employing reverse nonequilibrium molecular dynamics (RNEMD [22]). In one case, the long-range electrostatic force contribution was computed with PPPM and the other case was based on Ewald summation. It was found that when the size was set at 60, the value from PPPM was $0.967 \pm 0.012$ W/mK, and the value for the Ewald-based case was $0.954 \pm 0.013$ W/mK. Therefore, a size of 60 is a reasonable choice. In addition, because the latter results were based on statistical average, the error introduced by the PPPM method was negligible.

Constant-pressure MD simulations were carried out [23] by performing time integration on Nose-Hoover style non-Hamiltonian equations of motion. All positions and velocities of the atoms were generated from and NPH (isenthalpic-isobaric ensemble) ensemble using the Verlet algorithm with the following conditions. The cubic simulation box (6 nm $\times$ 6 nm $\times$ 6 nm) with periodic boundary conditions contained 7,200 water molecules. For a short-range pair force, the widely used atom-atom interaction model of CHARMM potential with long-range coulomb effect [24] was chosen to compute the potential energy and corresponding force (contributed by the interaction of van der Waals and Coulombic forces) by employing an additional switching function $S(r)$ that ramps both the energy and force smoothly to zero between an inner and outer cutoff:

$$E(r) = \begin{cases} 
LJ(r) + C(r), & r < r_{in} \\
S(r)LJ(r) + S(r)C(r), & r_{in} < r < r_{out}, \\
S(r)LJ(r) + S(r)C(r), & r > r_{out}
\end{cases}$$

(2)

where $r_{in}$ and $r_{out}$ were set to be $20\sigma$ and $25\sigma$, respectively. Other functions in Eq. (2) are

<table>
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<th>Table 1 TIP3P water model parameters</th>
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<td>Items</td>
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<td>$R_{OH}^0$</td>
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*Characteristic dimensions.*
where $\sigma$ and $\varepsilon$ are determined by atom type, and $f_{\text{damp}}(r)$ in Eq. (4) is determined not only by the distance between atoms but is also related to the $G$-Ewald parameter, which is adjusted through mesh size based on desired precision.

A harmonic bond model [24] was used to compute the bond force between oxygen and hydrogen atoms and the potential energy contribution was calculated:

$$E = K(r - r_0)^2$$

The CHARMM angle style [24], which considers the potential energy contribution from the alteration of bond angle from balanced $\theta_0$ with an additional Urey-Bradley term, was chosen as the angle model; that is,

$$E = K(\theta - \theta_0)^2 + K_{UB}(r - r_{UB})^2,$$

where $K$, $\theta_0$, $K_{UB}$, and $r_{UB}$ are coefficients defined for each angle type.

The system pressure, after 20,000 time steps (each time step was $0.005t^*$ or 0.46 fs) equilibrated through a Langevin thermostat, was well controlled to be 0 (1 bar; for $P = 1$ bar, $\sigma = 0.4$ Å, $\varepsilon = 0.0460$ Kcal/mol, the reduced pressure was $P^* = P\sigma/\varepsilon = 2 \times 10^{-10}$, which is extremely close to 0), and initial temperature is equilibrated to 12.0 (278.15 K). Eighty molecules near the center of the simulation box were selected and instantaneously heated to 132 (3059.65 K) by velocity rescaling. The temperature in the domain including the heated atoms was much higher than the boiling point, which is 16.11 (373.5 K) at 1 atm. During the latter 11,000 time steps, the atomic movement of the system was recorded until bubble extinction.

The volume and radius of the bubble were estimated using the following method. First, all sides of the simulation cell were divided into 10 sections so the simulation box was divided into 1,000 small cubes. The side length $\Delta L^*$ of the small cube fluctuated between 14.87 (5.95 Å) and 14.95 (5.98 Å) during the MD simulations. The average density was calculated for each small cube over 100 time steps, which is much smaller than the timescale of the bubble dynamics (11,000 steps) and much larger than that of the atomic dynamics ($\sim 20$ steps). The vapor region was recognized as the one in which the average density in the small cube was less than the critical density $\rho_c^* = 6.83 \times 10^{-4}$ (320 kg/m$^3$) [25], and the liquid region was the one in which the average density was greater than $\rho_c^*$. The bubble volume was calculated as the sum of the volumes of the vapor regions. Because the bubble was fairly spherical in shape, the effective bubble radius $R^*$ was estimated from the bubble volume $V_{\text{bab}}^*$ using the following equation:

$$R^* = \left( \frac{3}{4\pi} V_{\text{bab}}^* \right)^{1/3}.$$
For MD simulations, the statistical results based on multiple cases were more meaningful than the single cases. In order to improve the statistical accuracy, 15 MD simulations with randomly chosen initial molecule configurations (initial atom positions and velocities) were performed. The final results were based on averaging over 15 cases and the error bar was calculated by the standard deviation of $R^*$ from the 15 cases.

On a macroscopic scale, a hydrodynamic equation, namely, the Rayleigh-Plesset equation, which is applicable for an incompressible and inviscid fluid, can be used to describe expansion and contraction of a bubble:

$$R^* \dddot{R}^* + \frac{3}{2} \ddot{R}^* \dot{R}^* = \frac{1}{p_l^*} \left[ P^* (R^*) - P^*_\infty - \frac{2 S^*}{R^*} \right],$$

where $P^*(R^*)$ is the pressure at the bubble surface, $P^*_\infty$ is the pressure far from the bubble in the liquid region, and $S^*$ is the reduced surface tension of the bubble. The initial condition for Eq. (9) is. It is difficult to precisely determine $P^*(R^*)$ because the radius of the generated bubble is only a few times the molecular diameter.

In this work, the molecules constituting the bubble surface were used to estimate the surface pressure of the water bubble:

$$P^*(R^*) = \frac{\rho^*_c}{3 N_s - N_c} \left\{ \sum_{i=1}^{N_s} m_i^* r_i^2 + \left[ \sum_{n=1}^{N_s} (r_i \cdot f_i) \right]_{b,a,s,k} \right\},$$

where $N_s$ is the molecule number within $R_{outer}$ of the MD simulation cell (see Figure 2) and can be simply calculated by

$$N_s = V^* \rho^*_l,$$

where the density at the edge of the effective bubble is assumed to be liquid density, and $V^*$ is the volume of the spherical shell, which can be estimated by

$$V^* = 4\pi \left[ R_{outer}^* \frac{3}{3} - (R_{outer}^* - d_m^*) \right] / 3.$$

$N_c$ in Eq. (10) is the molecule number within the inner spherical region, as shown in Figure 2, and its contribution to pressure will not be accounted for. The subscripts $b, a, s, k$, in Eq. (10) represent bond and angle interactions, the internal constraint force applied

![Figure 1](image_url) Water molecule illustration (color figure available online).
RESULTS AND DISCUSSION

All MD simulations in this article were performed using LAMMPS, which is an open source software developed by Sandia National Laboratories. Figure 3 shows snapshots of the bubble formation and annihilation using Visual Molecular Dynamics [26] software. These snapshots show that the molecules within 10% thickness of the simulation box in the depth direction. It can be seen that the heated molecules scattered the neighboring nonheated molecules until a bubble was created, and then the bubble was cooled and compressed by the surrounding subcooled liquid later. Physically, the molecules in the center (shown in white) were rescaled to the desired temperature at time 0, and heat was transferred to the surrounding molecules along the temperature gradient by collision between the hot molecules and the cold ones. As a result, a bubble was generated as shown during the period from time 0.368 to 2.162 ps. A 0.368-ps time lag existed before a clear bubble emerged. After time 2.162 ps, the bubble was compressed by the surrounding cold liquid molecules, causing it to become smaller and smaller until it finally disappeared.

The density profile within the 10% slab of the simulation box in the depth direction was computed by uniformly partitioning the box into 1,000 small cubes whose density was obtained by averaging the 15 cases (see Figure 4). At time 0 ps, the density was not uniformly distributed but fluctuated around 1,000 kg/m³, which is the density of liquid water at a pressure of 1 bar. It can be observed that bubble expanded from 0 to 2.162 ps annihilation began during the latter period. The density increased to 1,000 kg/m³ again at 5.06 ps. To demonstrate the heat spreading around the bubble, the temperature distribution
was also computed and is shown in Figure 5. At the beginning, it can be seen that the region around the heated zone had almost the same temperature. Within a very short period (0.368 ps), a clear temperature difference around the hot bubble was observed due to the rapidity of the heat spreading to the surrounding cold liquid.

Figure 6 shows the calculated pressure at the surface of the generated bubble. The results from $N_c = 0, 3, 5$ were not significantly different, which means that the pressure estimated from $N_s = 20$ is reliable. It can be seen that the pressure value reached 1,450 Mpa in 0.025 ps and then decreased relatively slowly to atmospheric pressure during the following period from 0.025 to 0.375 ps. The fluctuation period from 0.375 to 5 ps indicates that the pressure is decreased to the system pressure of 1 atm again. Interestingly, the pressure dramatically increased from 0.1 to 1,450 Mpa within a very short time, 0.025 ps, after the system was heated. Indeed, a comparison of time evolution between Figure 6 and the bubble behavior history shown in Figure 4 (or Figure 5) indicated that the bubble was still expanding even though the pressure was reduced to atmosphere pressure. Later, this pressure history was used to predict the evolution of the bubble radius using Eq. (9).
Figure 7 shows the time history of the calculated bubble radius. The hydrodynamics line was obtained by using the hydrodynamic model (Rayleigh-Plesset equation). It was observed that if a nonzero surface tension was used, the span of the bubble radius evolution curve could not fit the one obtained from MD simulation. Indeed, even if a decent piecewise function of surface tension ($S(R)$) was used in the hydrodynamic model, the radius of bubble decreased to zero within a much shorter time than that obtained from MD. Therefore, in order to cover the whole period of bubble behavior, the surface tension was set to 0. The error bar line (MD) represents the statistical result obtained from the 15 MD cases; the curve fitting line was fitted based on MD simulation results, which will be discussed later. It can be seen that the bubble immediately grew after heating and reached a maximum radius during the 4.6-ps-long period. In other words, the bubble achieved a maximum radius of 0.6 nm at $t = 1.69$ ps and disappeared at $t = 4.6$ ps. It is worth mentioning that the lower fluctuation in the radius after $t = 4.6$ ps was due to the density fluctuations in the liquid, which means that the bubble size was zero during the period after 4.6 ps. Thus, the important $R$ values were those shown before $t = 4.6$ ps. The radius predicted by the Rayleigh-Plesset equation was obviously larger than that from MD simulation throughout the entire process.
Various possible surface tension functions were tested in order to match the variation in radius obtained from MD simulation. However, as reported above, a possible surface tension function could not be found.

The existence of such a surface tension function was further studied by assuming that the Rayleigh-Plesset equation is still valid in liquid water. The bubble radius time history function $R(t)$ was obtained based on the radii from MD simulations by curve fitting, and then the following polynomial equation with $R^2 = 99.97\%$ was obtained:

$$R(t) = 1.053 \times 10^{-7}t^5 - 1.289 \times 10^{-5}t^4 + 1.272 \times 10^{-3}t^3 - 8.778 \times 10^{-2}t^2 + 2.258t - 3.415$$  \hfil (13)

By substituting the fitted equation of $R(t)$ into the Rayleigh-Plesset equation, both $S(t)$ and $S(R)$ were obtained and are plotted in Figure 8. Figure 8a shows the variation in surface tension with time. Figure 8b shows that the surface tension varied with corresponding...
radius. Both figures show that a nonphysical surface tension function (nonpositive surface tension) should be applied to reproduce results from MD simulation. A closer look at Figure 8a indicates that, during the time period from 0 to \(\sim 0.1\) ps, a surface tension of 0 should be applied and then a positive surface tension is used from \(\sim 0.1\) to \(\sim 0.3\) ps.
Finally a long nonpositive value is used to drag the expanding bubble down. It can be seen from Figure 8b that there exists a pair of $\sigma$ corresponding to one radius due to expanding and compressing. The surface tension $\sigma$ corresponding to one radius does not exactly overlap but has similar trends, which makes this method acceptable for finding possible $S(R)$. Figure 8 indicates that a reasonable surface tension function $S(R)$, which can reproduce the results of MD simulation, does not exist.

From a physics aspect, the surface tension in a water bubble is contributed to by a more complicated force field than monatomic argon liquid. In fact, the atomic structure of a water molecule consists of two positively charged hydrogen atoms joined to one negatively charged oxygen atom with a bond angle of 104.52°. This unique composition causes one side of the molecule to have a positive charge and the area in the opposite direction to have a negative charge [27]. Therefore, water molecules are attracted to each other and form strong molecular bonds as a result of the polarity of charge in a single molecule. Comparing argon liquid and water liquid, the main difference is that a water molecule includes electrostatic force, bond, and angle interactions. In other words, it has a more complicated force field. Considering the fact that there are many other possible water models existing in the literature (three-site, four-site, five-site, rigid, flexible, etc.), the surface tension contributed by this complicated force field should be further investigated for liquid water at a microscale in order to further verify the hydrodynamic equation. Thus, based on the current results for the TIP3P model, it can only be concluded that predicting water bubble dynamics using the Rayleigh-Plesset equation does not match predictions from MD simulation, which are different from that for growth and annihilation of a nanosized bubble in the monatomic liquid argon.

CONCLUSIONS

Nanobubble formation and annihilation processes were simulated in polyatomic molecule liquid (water) through nonequilibrium MD simulation. After equilibration for 20,000 time steps, 80 molecules near the center of the simulation box were selected and instantaneously heated to 3059.65 K by velocity rescaling. During the later 11,000 time steps, the atomic movement of the system was observed until bubble extinction. In order to improve the statistical accuracies, 15 MD simulations with different initial molecule
configurations were performed. The pressure at the surface of the nanosized bubble immediately increased to 1,450 Mpa from 0.1 Mpa within 0.025 ps and later decayed to 1 bar within 0.4 ps. The bubble fully expanded to \( R = 0.6 \) nm at 1.69 ps and disappeared at 4.6 ps. A time lag of about 0.368 ps was observed before a clear bubble emerged after heating the molecules. The density profile within the heated simulation box was recorded to show the evolution of density distribution and a clear bubble capture. The results, based on the TIP3P model, showed that the hydrodynamic model based on the Rayleigh-Plesset equation is not valid in predicting nanosized bubble growth and annihilation in liquid water. Because different force fields can lead to different surface tensions on the bubble, and considering the existence of many possible water models, further investigation on the validity of the Rayleigh-Plesset equation should be carried out.

REFERENCES


