Surface Tension and Stability of a Nanobubble in Water: Molecular Simulation*

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Abstract

Molecular dynamics simulations were carried out for a nanoscale spherical bubble in water at room temperature. The pressure difference between inside and outside of the bubble was investigated and the surface tension was evaluated with assumption of the Young-Laplace (Y-L) equation. The obtained surface tension shows little dependence on the bubble size and agrees with that of flat surface. Thus it is confirmed that the Y-L equation holds for nanobubbles in water. Based on the Y-L equation and the density-dependence of the liquid pressure, mechanical stability of a bubble in a finite system was discussed. The existence of mechanical instability leads to a mechanical definition of critical nucleus size in cavitation nucleation.

Key words : Microbubble, Nanobubble, Surface Tension, Young-Laplace Equation, Bubble Nucleation, Molecular Simulation

1. Introduction

Macroscopic force balance of a spherical microbubble of radius R is often described by the Young-Laplace (Y-L) equation

$$p_{vap} = p_{liq} + \frac{2\gamma}{R},\tag{1}$$

where p_{vap} is the pressure inside the bubble, p_{liq} is the pressure of surrounding liquid, and γ is the surface tension. The applicability of Eq. (1) has been questioned in the case of microbubbles and nanobubbles, because the pressure difference $\Delta p \equiv p_{vap} - p_{liq}$ diverges as the size decreases, $R \rightarrow 0$.

Using a simple model (Lennard-Jones liquid), we carried out molecular simulations of nano-scale vapor bubbles (i.e., bubbles containing no other gas than saturated vapor) to investigate Δp and evaluate γ .⁽¹⁾ We found that the Y-L equation holds even for nanobubbles, and that the surface tension and the saturated vapor pressure are almost independent of the bubble size. However, the molecular interaction we used is a short-ranged one; long-ranged interactions such as the Coulombic one may change the situation. In this paper, therefore, we investigate nanobubbles in water, where Coulombic interactions are supposed to play important roles.

2. Simulation Method

We performed canonical ensemble (N, T, V constant) molecular dynamics simulation of water molecules with TIP4P model interaction⁽²⁾ (combination of Lennard-Jones type interaction and Coulombic ones) confined in a cubic simulation cell. The cell size was fixed to be $V = 9.5 \times 9.5 \times 9.5 \text{ (nm)}^3$. Water molecules were treated as rigid rotors. Normal periodic boundary conditions were assumed for all three directions. The Coulombic interactions were calculated with the Ewald summation technique, and the interactions in real space were truncated at 1.6 nm; no long-range corrections were adopted.

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Table 1Simulation conditions: number of molecules N, initial radius of the cavity
 R_{init} , and radius of the bubble at equilibrium R (evaluated in §.3.2).

	Ν	R _{init} [nm]	<i>R</i> [nm]
System 1	26,811	1.1	1.70
System 2	26,695	1.3	1.91
System 3	26,580	1.5	2.03
System 4	25,942	2.0	2.38



Fig. 1 Cross-sectional view of a simulated nanobubble in water; System 1.



Fig. 2 Examples of cavity volume change during the simulation.

First, 27,000 water molecules were uniformly placed in the cell; the mass density of the initial configuration is 0.9413×10^3 kg/m³, which corresponds to a stretched, or "super-heated" state. We equilibrated the system at room temperature T = 300 K, and no cavitation was observed under this condition. After the equilibration, we removed molecules in a spherical region of radius R_{init} at the center of the cell to make a "bubble", and continued the simulation.

We successfully obtained four stable systems, each of which contains a single spherical "nanobubble" of different size. The system parameters are shown in Table 1. An example of snapshots is shown in Fig. 1 as a sectional view; as simulation goes on, the bubble slightly migrates from the original position.

3. Results and Discussion

3.1. Detection of Cavities

We divide the system into small cubic meshes of size 9.5/200 nm and count the vacant mesh points, or "cavities", to roughly estimate the position and the volume of the bubble. Examples of volume change are shown in Fig. 2. We found that the time evolution of cavity



Fig. 3 Density profile of the nanobubble in each system; *N* is the number of water molecules.

volume strongly depends on R_{init} ; for $R_{init} = 1.1$ nm (System 1) or larger, the bubble almost monotonically expands to reach some equilibrium, while the bubble with $R_{init} = 1.0$ nm rapidly shrinks and finally disappears. This instability will be discussed later in §3.5.

For the four systems shown in Table 1, we executed sufficiently long MD simulations (typically 200 ps) to accumulate molecular configurations for analyses of bubbles at equilibrium.

3.2. Density Profile

By use of the position vector $\vec{r_i}$ of cavity mesh points (i = 1, ..., N), we define the position of bubble center $\vec{r_0}$ as $\vec{r_0} \equiv \frac{1}{N} \sum_{i=1}^{N} \vec{r_i}$. Assuming the spherical symmetry around $\vec{r_0}$, we calculate the density profile $\rho(r)$ as a function of the radial distance r. The results are shown in Fig. 3.

Each profile is well fitted to a hyperbolic function⁽³⁾ as

$$\rho(r) = \frac{\rho_{liq} + \rho_{vap}}{2} + \frac{\rho_{liq} - \rho_{vap}}{2} \tanh\left(\frac{r-R}{w}\right),\tag{2}$$

where the liquid density ρ_{liq} , the vapor density ρ_{vap} , the bubble radius *R*, and the interface width *w* are the fitting parameters. In our simulations of water at 300 K, however, the saturated vapor density is so low that the inside of the bubble is almost always empty; thus we set $\rho_{vap} = 0$ for all four systems. Also we found that the width *w* has little dependence on the bubble size; w = 0.199-0.210 nm for all systems. The obtained liquid density ρ_{liq} is discussed in §3.3.

The radius R of the largest bubble (System 4) is 2.38 nm; the cell size is 9.5 nm and we believe that the periodic boundary conditions have practically no interference with bubble properties.

3.3. Pressure and Density

We evaluate the liquid pressure p_{liq} via a usual virial expression in the bulk liquid region far from the bubble; here we use the region of r > R + 1 nm. The results are plotted against the bubble radius *R* in Fig. 4.

As similar to the systems of Lennard-Jones liquid⁽¹⁾, the obtained liquid pressure shows a large negative value, which suggests that the surrounding liquid is in a highly stretched state. This is confirmed from the liquid density ρ_{liq} obtained in Eq. (2), as plotted in Fig. 5. Here also shown is a result of planar surface system, which consists of a water membrane of area 4.43×4.43 (nm)² with 3,000 water molecules at T = 300 K.

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Fig. 4 Liquid pressure depending on the bubble radius. The error bars show the standard deviation obtained by dividing the total simulation into partial runs of 10 ps.



Fig. 5 Density of surrounding liquid depending on the bubble radius. The data at $R = \infty$ is the density of a planar surface system.



Fig. 6 Surface tension of a nanobubble estimated with the Young-Laplace equation. The errors are evaluated from the uncertainty of the liquid pressure.

3.4. Surface Tension

Now having data of the pressure difference $\Delta p = p_{vap} - p_{liq} \simeq -p_{liq}$ and the bubble size *R*, we can evaluate the surface tension γ by assuming the Y-L equation (1). The results are shown in Fig. 6. Similar to the Lennard-Jones case again,⁽¹⁾ γ has no discernible *R* dependence, and

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Fig. 7 Local ratio of hydrogen atoms: the bubble case (System 1, open square and solid curve) is compared with the case of planar surface (closed square and dotted curve). The horizontal axis is shifted so that the center position of the density profile agrees with each other.

agrees with the value of planar surface.

Note that, in this evaluation of γ , we have not distinguished the radius *R* in Eq. (2), or equimolar surface, and the surface of tension R_s .⁽³⁾ As the bubble size becomes smaller, the difference between *R* and R_s may have more importance, as in the case of droplets.⁽⁴⁾ From practical points of view, however, it will be more convenient if we can deduce the pressure difference Δp directly from the bubble radius *R* via Eq. (1); the above results just show that we can use the bulk value of γ in this approach. Detailed analyses at molecular levels may reveal some small difference between *R* and R_s dependence of γ .

It is well known that water molecules have some orientational order near the liquid surface⁽⁵⁾⁻⁽⁷⁾. There is a possibility that, in the case of nano-scale bubble surface, the orientational ordering is affected (probably weakened) by the large curvature. To roughly investigate the ordering, we plotted in Fig. 7 the local ratio of hydrogen atoms, $\frac{n_H/2}{n_O + n_H/2}$, where n_H and n_O are the local number density of hydrogen and oxygen, respectively. The ordering looks similar to the case of planar surface; in the vapor side exists a hydrogen-rich region, which means that water molecules on the surface protrude their hydrogen into the vapor phase. The details of molecular orientation are to be analyzed.

3.5. Bubble Stability

As mentioned in §3.1, we sometimes observed unstable bubbles, which shrink and vanish as the simulation proceeds. Here we discuss the bubble stability from a viewpoint of pressure balance.

Consider a spherical bubble of radius R in a simulation cell of finite volume V. Two liquid pressures should be considered. The Y-L equation, Eq. (1), gives

$$p_{liq} = p_{vap} - \frac{2\gamma}{R} \equiv p_{YL} \tag{3}$$

Another pressure, p_{sys} , is determined from the density of the liquid through an equation of state.

$$p_{sys} \equiv p(\rho_{liq}, T), \tag{4}$$

When the vapor density is low as in the case of here-considered water at room temperature, the density ρ_{liq} depends on the bubble radius as

$$\rho_{liq} \simeq \frac{mN}{V - \frac{4\pi}{3}R^3},\tag{5}$$

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Fig. 8 Pressure vs. density for liquid water in stretched states. The solid line is least square fitting to a linear function.



Fig. 9 Stability of a spherical bubble; the pressure P_{YL} (solid curve) derived from the Young-Laplace equation is compared with P_{sys} (dotted) defined in Eq. (6) with the parameters of System 1. In general, there exist two crosspoints, a stable radius (open circle) and an unstable one (closed circle).

where N is the number of molecules and m is the molecular mass. Note that we approximated in Eq. (5) that the vapor density is negligibly small; taking account of finite vapor density instead of the vacuum approximation is straightforward, but it would lead to a too cumbersome equation.

Now that the pressure is well approximated to be a linear function of ρ_{liq} in the range of stretched states here considered, as shown in Fig. 8, the liquid pressure is expressed as

$$p_{sys} = A \frac{mN}{V - \frac{4\pi}{2}R^3} + B,\tag{6}$$

where the constants A and B are determined by least square fitting. The radius R of a bubble with pressure balance should therefore satisfy the equation

$$p_{vap} - \frac{2\gamma}{R} = A \frac{mN}{V - \frac{4\pi}{3}R^3} + B \tag{7}$$

Now plotted in Fig. 9 are p_{YL} and p_{sys} as functions of the radius *R*, with parameters N = 26,811 (System 1) and $V = 9.5 \times 9.5 \times 9.5 (\text{nm})^3$ as an example. There exist two solutions for $p_{YL} = p_{sys}$ when the system parameters (*N* and *V*) are appropriately chosen. The bubble should shrink in the case of $p_{YL} < p_{sys}$, and will expand when $p_{YL} > p_{sys}$. Thus, the solution of larger *R* corresponds to the stable bubble. The solution of smaller *R* is unstable, which means that a bubble smaller than this should vanish. For the case of System 1 as shown

in Fig. 9, a bubble with initial radius $R_{init} < 1$ nm will shrink and vanish, which agrees with our observation (Fig. 2). This suggests that the threshold of unstable *R* gives a mechanical description of the critical nucleus in bubble nucleation (cavitation) process; comparison with thermodynamic description of nucleation models will be made elsewhere.

When we use smaller N or larger V, the curve of p_{sys} shifts to more negative pressure; the radius of the unstable bubble decreases and the stable bubble becomes larger. In contrast, there may not be solutions with larger N or smaller V, which of course means that vapor bubbles cannot exist in such dense (or high pressure) liquid.

These results are for finite systems with N molecules in volume V. When we consider an α -times larger system (i.e., with αN molecules in αV), Eq. (7) becomes

$$p_{vap} - \frac{2\gamma}{R} = A \frac{m\alpha N}{\alpha V - \frac{4\pi}{3}R^3} + B = A \frac{mN}{V - \frac{4\pi}{3}\frac{R^3}{\alpha}} + B$$
(8)

The curve of p_{vap} in Fig. 9 tells that, under conditions similar to the one considered here, the stable radius increases about $\alpha^{1/3}$ times while the unstable one is almost the same. Thus, in the infinite system ($\alpha \rightarrow \infty$), there will be no stable bubbles; once the size of a bubble exceeds the instability threshold, it increases infinitely. A similar discussion of stability/instability about gas bubbles was given by Ward et al.⁽⁸⁾ for gas bubbles.

4. Summary

Our molecular simulation of nano-scale spherical vapor bubbles (radius 1.7–2.4 nm) at equilibrium in water at room temperature reveals that

(1) The liquid surrounding the bubble is in a highly stretched state and has large negative pressure.

(2) The surface tension evaluated by assuming the macroscopic Young-Laplace equation is little dependent on the bubble size and agrees with the bulk value (surface tension of planar surface).

These conclusions are the same as our previous study with the Lennard-Jones liquid⁽¹⁾; in short, the Young-Laplace equation is applicable even to nanobubbles.

As for a bubble in a system of finite volume, we have shown, based on the Y-L equation and the equation of state of stretched liquid, that the pressure balance equation has stable and unstable solutions; the latter has little dependence on the system size and corresponds to the critical nucleus in bubble nucleation process.

We have so far considered "ideal" bubbles, which have no adsorption on their surface. In practical cases of water and aqueous solutions, however, various adsorbents (especially ionic ones) can drastically change the situations. For example, microbubbles have often been shown to have negative charge,^{(9),(10)} mainly due to adsorption of hydroxide (OH⁻) ions. The reported ζ potential (-50 ~ -80 mV) suggests that the surface concentration is not very high (typically $3-5 \times 10^{-5}e$ per 1 (nm)², where *e* is the elementary charge), but they can still affect surface properties and mechanical stability of bubbles. Further investigation of ion adsorption from molecular viewpoints is required.

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