EFFECT OF WALL ON THE LIFETIME OF NANOBUBBLES

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Summary We study the effect of wall on the lifetime of nanobubbles using binary (liquid, gas) or ternary (liquid, gas, solid) Lennard-Jones systems. Nanobubbles on the substrates have much longer lifetime than those in the bulk liquid which is owing to the inhomogeneity of systems. We also deal with not only the wall that consists of fixed particles but also thermal walls that behave as a heat bath. In the latter case, Knudsen gas behavior is not observed in nanobubbles.

INTRODUCTION

Nanobubbles are believed to be an important origin of the interesting behavior of fluids in microscopic systems, such as boundary slip of liquid in channels and long-range attractive force between hydrophobic surfaces. According to the classical diffusion model using Young-Laplace equation, the pressure in nanobubbles is much higher than in the bulk liquid and gas in the bubble dissolve into the bulk liquid immediately. The lifetime of the spherical bubble whose radius is 10-100nm, is estimated to be only 1-100μs [1] . In many experiments, however, remarkably stable surface nanobubbles are observed. Zhang et al. reported that air nanobubbles on hydrophobic walls survived for 4 days [2] , which is at least 8 orders of magnitude longer than predicted by the classical model.

The mechanism of the astonishing stability of nanobubbles is one of the outstanding question in fluid dynamics and has remained puzzling for decades. Many stabilizing mechanisms, for instance, ions or impurities on the gas liquid interface, have been provided and investigated performing extensive experiments and numerical simulations, but none of them have turned out to be a dominant cause.

Recently, Brenner et al. proposed the dynamic stabilizing mechanism for surface nanobubbles[3], that the influx of gas atoms near the contact line induced by hydrophobicity plays an important role to the nanobubble stability. Weijs et al. revealed the importance of substrate using molecular dynamics (MD) simulations of ternary system[4]. But MD simulations of surface nanobubbles are limited.

We investigate the effect of the substrate on the lifetime of nanobubbles using MD simulations of binary or ternary Lennard-Jones systems. Thermal wall is also employed to investigate the Knudsen behavior of gas atoms in nanobubbles provided by Seddon et al[5].

NUMERICAL METHOD

In MD simulations, liquid and gas particles are modeled on Ar and Ne respectively. Wall particles are also Lennard-Jones particles and are fixed or confined by harmonic potential on fcc lattice. We used GROMACS software for simulations.

Simulations consist of two steps: (A), creating stable nanobubbles; (B), simulations on shrinking nanobubbles. During the step (A), system temperature is controlled to be 85K and the system is in a stretched state. In the step (B), the system temperature is suddenly raised and controlled to be 104K. At this temperature, nucleation of bubbles does not occur and bubbles shrink in a short time.

Simulations are performed on 4 systems: (I), in a bulk liquid; (II), on a wall consisting of fixed particles; (III) and (IV), on a wall consisting of thermally vibrating particles. Berendsen thermostat is applied to liquid and gas atoms in the system (I) and the system (II). In the system (III) and the system (IV) on the other hand, the thermostat is applied only to wall particles,those should bahave as a heat bath. In the system (III), thermostat is also applied to liquid and gas atoms for 50ps between the step (A) and step (B) in order to raise the system temperature immediately, in contrast with the relatively slow increase of the liquid and gas temperature in system (IV). As shown in Fig.1A, the tempearture gap due to the thermal resistance at the solid liquid interface is observed in the system (III) and the system (IV). Note that we set $t = 0$ at the begining of the step (B) in all the figures.

RESULTS AND DISCUSSIONS

In the step (A), nanobubbles are stable due to the nagetive pressure of the system that accomplishes the balance between the surface tension and the pressure difference at the interface of bubbles. In the step (B), bubbles on the substreate have more than 20 times longer lifetime than that in the bulk liquid as described in Fig.2. In the system (I), the average pressure inside the bubble is higher than outside the bubble, which is consistent with Young-Laplace equation. However, the result is opposite in the systems (II)-(IV), from which the classical model predicts the shorter lifetime of bubbles.

One of the reasons of this puzzling high average pressure outside the bubbles is the inhomogeniety of liquid and gas atoms. The pressure around the bubble is lower than inside the bubble. This low pressure around the bubble is induced by the low density near the wall, which is consistent with preceding study[6], and have positive effect on the lifetime of the bubble.

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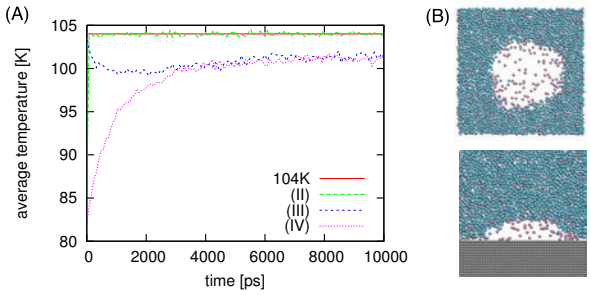

Figure 1. (A) Average temperature of liquid and gas in the systems (II)-(IV). In the system (III) and the system (IV), temperature is a few degrees Kelvin lower than 104K due to the thermal resistence at the wall surface. (B) Examples of visualized nanobubbles.

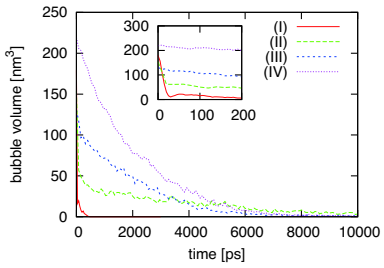

Figure 2. Volume of nanobubbles in the systems (II)-(IV). The bubble in the bulk liquid shrinks in a few hundred ps as illustrated in the inset. Surface nanobubbles have the lifetime of a few thousand ps.

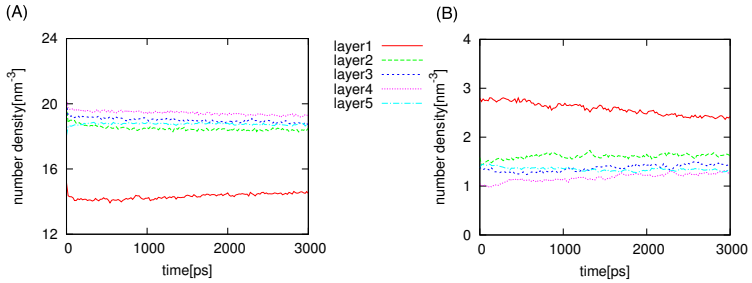

Figure 3. Number density of liquid (A) and gas (B) atoms averaged in layers divided in the direction parallel to the wall in the system (II). The bubble is in layer1.

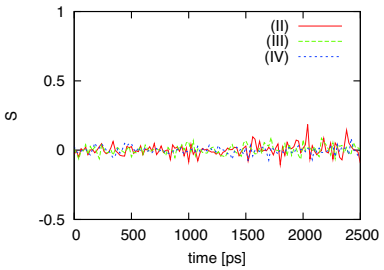

Figure 4. S values of the systems (II)-(IV). Gas velocity in surface nanobubbles is isotropic.

In the system (II) we also performed double sized calculations. The bubbles obtained are not similar to those in the smaller box because the volume of a bubble is determined not by the system size but by the balance between the surface tension and pressure difference between inside and outside the bubble. However, no qualitative differences are observed.
To investigate the velocity anisotropy of gas atoms in nanobubbles, the value $S = (3\langle\cos\theta^2\rangle - 1)/2$, θ is the angle between velocity of each atom and axis perpendicular to the wall,is calculated, which is plotted in Fig.4. $S = -1/2$ means that all the atoms are moving in directions parallel to the wall, $S = 1$ in directions perpendicular to the wall and $S = 0$ in random directions. As illustrated in Fig.4, no velocity anisotropy is observed in the system (II) and the system (III). Although there exists apparent heat flux from the wall to the liquid and gas for a few ns in the system (IV), no anisotropic motion of gas atoms in the bubble is observed. This result is not consistent with the mechanism proposed by Seddon et al., but the Knudsen number in nanobubbles in this study $\mathrm{Kn} \sim 0.5$ is slightly lower than the proposed condition $\mathrm{Kn} > 1$. So the gas density in nanobubbles should be lowered a little more and further study is required.

CONCLUDING REMARKS

We have performed MD simulations on nanobubbles in the bulk liquid or on the substrate for binary or ternary systems and shown that the wall plays an important role in determing the lifetime of nanobubbles. However, there may be another nanobubble stabilizing mechanism for realistic nanobubbles. Furthermore, thermal walls behaving as a heat bath can not realize Knudsen gas behavior in our systems. This may be due to an inappropriate conditions in our systems.

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