

Molecular Dynamics Simulation of nanobubbles in the bulk and on the substrate

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1 Introduction

Nanobubbles are considered to be one origin of characteristic behaviors of fluids in microscopic systems, such as boundary slip in channels and long-range attractive force acting between hydrophobic surfaces. In many recent experiments, nanobubbles on the hydrophobic substrates are observed with atomic force microscopy, infrared spectroscopy and other techniques. Observed nanobubbles are extraordinarily stable; for instance, Zhang et al. reported that air nanobubbles on hydrophobic walls survive for more than 4 days[1]. However, according to the classical diffusion model based on Young-Laplace equation, nanobubbles cannot be stable because the gas in the bubble diffuses rapidly into the surrounding liquid due to higher pressure in the bubble. The lifetime of the spherical bubble whose radius is 10-100nm, is estimated to be 1-100 μ s[2], which is at least 9 orders of magnitude shorter than the observed lifetimes.

Why nanobubbles are stable? This is one of the outstanding questions in fluid dynamics and has remained puzzling for decades. Mainly two types of stabilizing mechanisms are proposed in the preceding studies: (1) the effects of impurities on the liquid-gas interface, (2) non-equilibrium re-entrance of gas into the bubble. The former idea is that impurities on the liquid-gas interface reduce the surface tension and prevent diffusion of the gas into the surrounding liquid. The latter idea which is recently proposed by Brenner et al.[3] and supported by Weijs et al.[4] is that both the circulating flow of gas above the bubble created by a Knudsen gas behavior in the bubble[5], and an attraction of gas on the hydrophobic surfaces induce the influx of gas into the bubble near the contact line, which balances the diffusive outflux. There are some numerical results suggesting the existence of such the influx, but the mechanism of nonequilibrium is not clear. Note that nanobubbles in the bulk liquid are also observed to be stable[6]. To explain their astonishingly long lifetime, the former idea is partially applicable, but only the effects of impurities on the liquid-gas interface are not enough. There must be another stabilizing mechanism remaining unrevealed.

Molecular dynamics simulations are suitable to treat molecular interactions and observe gas behavior in the liquid. A lot of numerical simulations on nanobubbles have been reported so far, most of them treat not the collapse of bubbles and shrinking or sustained bubbles, but the nucleation of bubbles and growing or stable bubbles. Besides, only a few simulations have been performed in binary (liquid and gas) or ternary (liquid, gas and solid) systems.

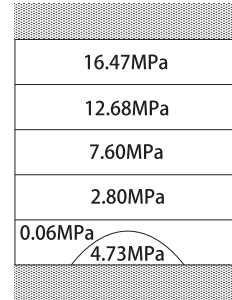


Fig. 1. Inhomogeneous pressure on the substrate.

2 Numerical Method

We perform molecular dynamics simulations of shrinking nanobubbles in binary or ternary Lennard-Jones systems using GROMACS software to investigate the dynamics of nanobubbles. Liquid and gas particles are Lennard-Jones particles modeled Ar and Ne respectively. Wall particles are also Lennard-Jones particles. In simulations, two types of wall are employed; the fixed wall consists of particles fixed to the FCC lattice positions and the thermal wall consists of thermally vibrating particles confined to the lattice positions by a harmonic potential. The simulations are performed under controlled temperature and divided into two steps: (I) creation of bubbles and (II) simulations of shrinking bubbles. In the step (I), the system is in a stretched state and nanobubbles are created and sustained stably. In the step (II), after the temperature is raised, nanobubbles start to shrink and collapse in a short time. Note that in all the figures, $t = 0$ is set to the time when the controlled temperature is raised.

3 Results and Discussion

3.1 shrinking nanobubbles in the bulk liquid or on the substrate

We performed MD simulations of shrinking nanobubbles in the bulk liquid (system (A)) or on the substrate (system (B)) and compared the lifetimes of nanobubbles. In the system (A), 50688 liquid atoms and 4608 gas atoms are in periodic cubic box 14.161nm on each side and gas atoms are initially placed at the center of the simulation box. In the system (B), the fixed wall of the thickness of 4.902nm is attached to the cubic box and gas atoms are initially placed near the wall.

In the steps (I), sustaining nanobubbles are created at the temperature of 85K. In the steps (II), after the controlling temperature is suddenly raised to 104K, although

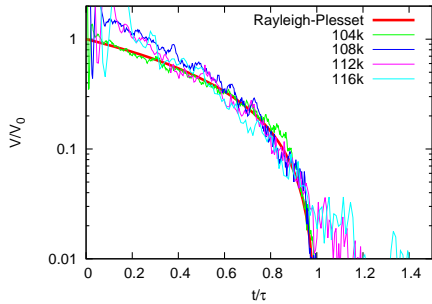


Fig. 2. Time evolution of the bubble volume. Bold line is calculated by Rayleigh-Plesset equation.

both nanobubbles in the bulk liquid and on the substrate begin to shrink rapidly, the lifetime of the nanobubble on the substrate is more than 20 times longer than that in the bulk liquid.

In the system (B), the inhomogeneity of the particle density perpendicular to the wall was observed as schematically illustrated in Fig1. The low pressure near the bubble extends the lifetime of the bubble and this is one cause of relatively long lifetime of the nanobubble on the substrate.

3.2 collapse of nanobubbles in the bulk liquid

We have investigated the details of collapse of nanobubbles in the bulk liquid using molecular dynamics simulation of binary systems. We place 405504 liquid atoms and 36864 gas atoms in the simulation box 28.322nm on each side. In the step (I), the temperature of the system is controlled to be 85K and raised to various temperatures at the beginning of the step (II).

Using the Rayleigh-Plesset equation, the volume of the rapidly shrinking nanobubble at time t is

$$V(t) = V_0(1 - t/\tau)^{6/5}, \quad (1)$$

where V_0 is the initial volume and τ is the lifetime of the bubble. As illustrated in fig2, the time evolution of bubble volume is well described by the equation(1), except the beginning of the shrinking process which is influenced by a sudden increase of the temperature. This is qualitatively consistent with the preceding simulations performed in single component systems[7].

3.3 Knudsen gas behavior

Shrinking nanobubbles on a fixed wall and on a thermal wall are compared in order to investigate the Knudsen gas behavior of gas atoms in the bubble on the substrate. In the fixed wall case, thermostat is applied to the liquid and gas atoms directly. In the thermal wall case, on the other hand, thermostat is applied only to the wall atoms and the temperature of the liquid and gas atoms is controlled indirectly. In the thermal wall case, transient heat flux from the wall to the liquid and gas particles exists for more than 2ns, which may induce Knudsen gas behavior in the bubble.

The calculated anisotropy $S = (3\langle \cos^2 \theta \rangle - 1)/2$ is described in fig3, where θ is the angle between the direction in which the gas atom moves and the upward direction perpendicular to the wall. $S = 1$, $S = -1/2$ and $S = 0$

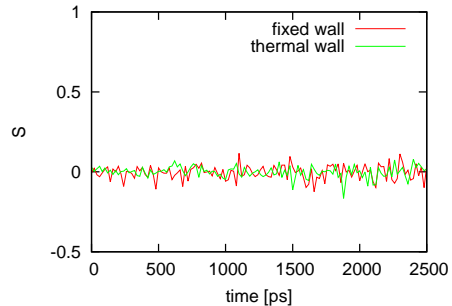


Fig. 3. Calculated anisotropy of motion of gas atoms in nanobubbles.

mean that all the gas atoms are moving in directions perpendicular to the wall, parallel to the wall and in random directions respectively. As shown in fig3, no anisotropic motion of the gas particles indicating the Knudsen gas behavior is observed in the thermal wall case, same as in the fixed wall case.

4 Concluding remarks

In the simulations described in sec3.1 and sec3.2, thermostat is applied directly to liquid and gas atoms, which can affect the dynamics of the gas in the liquid. To remove the effect of thermostat, indirect temperature control is needed.

In the simulations described in sec3.3, the thermal flux is not sustained but transient. We have to introduce some mechanisms that drive the sustaining thermal flux. We also have to reduce the density in the bubble, because the gas density in the simulated nanobubble was a little higher than the condition proposed by Lohse et al.

Acknowledgements

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