Molecular dynamics study of the lifetime of nanobubbles on the substrate

GCOE Symposium 2012 – Links of Hierarchies

KOHNO Shunsuke

Division of Physics and Astronomy, Graduate School of Science, Kyoto University
Outline

• Introduction
  – nanobubbles
  – stability of nanobubbles
  – preceding studies
  – purpose of this study

• Molecular dynamics simulations

• Numerical results
  – in the bulk liquid vs on the substrate
  – Knudsen gas?

• Summary and remarks
Nanobubbles

- radius \(<\ 1\ \mu m\)
- One cause of microscale behavior of fluids

Schematic illustration of typical nanobubble on a substrate

- Observed in experiments using AFM or IR spectroscopy

Nanobubbles are stable?

- Theoretical prediction
  - Nanobubbles are unstable

  Young–Laplace equation
  - High pressure in nanobubbles

  \[ \Delta p = \gamma \left( \frac{1}{R_1} + \frac{1}{R_2} \right) \]

  --> Gas in nanobubbles dissolve immediately

  **lifetime < 100\mu s** (spherical bubble, diameter = 100nm)


- In experiment
  - Nanobubbles are stable

  **lifetime > 4days**
Suggestions for stability

1. Young–Laplace equation is NOT applicable to nanobubbles.

2. Young–Laplace equation IS applicable to nanobubbles. But surface tension is reduced and bubbles shrink slowly.

3. Gas atoms in the bubble do dissolve, but outflux is balanced by the influx in nonequilibrium state.
1. Classical diffusion theory is not applicable?
   - MD simulations of nucleation of stable nanobubbles

   Young-Laplace equation is applicable to nanobubbles.
   (confirmed in many MD simulations of nucleation evaluating surface tension)


   - single component
   <-> real nanobubbles are filled with gas
Why nanobubbles are stable?

2. Reduction of surface tension
   - Theoretical model and experiments
     • Impurities on gas–liquid interface
       - Reduce surface tension
       - Prevent dissolution of gas
   -> Nanobubbles shrink slowly


more than $x10^9$ lifetime? -> not enough

3. Nonequilibrium stabilizing mechanism
   : Outflux is balanced by an equivalent influx
Dynamic Stabilizing Mechanism

- Knudsen gas behavior
- Circulating flow
- The origin of the nonequilibrium state: wall = heat bath -> heat flux

How Nonequilibrium state sustained for a long time?
- Theoretical model and experiments

These models have not confirmed

- Influx near the contact line balanced
- Influx near the contact line balanced
- Need to be nonequilibrium

14 Feb. 2012
GCOE Symposium 2012
Purpose of this study

- Investigate dynamics of nanobubbles
  -> Molecular dynamics simulations

- Only a few MD simulations of nanobubbles in ternary systems (liquid + gas + wall) have performed.
  -> Create stable nanobubbles and survey shrinking nanobubbles

- Introduce nonequilibrium (transient heat flux)
  -> Thermal wall
Molecular Dynamics Simulations

- Interaction – Lennard-Jones 6–12 potential

\[ U(r) = 4\varepsilon_{ij} \left\{ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right\} \]

- \( N,V,(T) = \text{const.} \)
- Liquid and gas – Ar and Ne respectively
- Fixed wall and thermal wall

**Diagram**
- Fixed wall and thermally vibrating wall
- Temperature control
- Transient heat flux

**Image**
- Fixed wall and thermally vibrating wall
Two Steps of Simulations

Step 1: Creation of nanobubbles
T = 85K
- Nanobubbles are stable
- Bubble nucleation occurs spontaneously
- Negative system pressure (stretched state)

Step 2: Simulations of shrinking nanobubbles
T = 104K
- Nanobubbles are unstable
- Bubble nucleation does not occur
- Positive system pressure

Step 2 → Step 1: Quenching (bubble nucleation)
Lifetime of Nanobubbles

In a bulk liquid: < 50 ps
On a fixed wall: > 8000 ps
Averaging 2000 ps – 3000 ps
Inhomogeneity of the System

Averaged pressure
- 2000ps – 3000ps
- 5 regions parallel to the wall

Low pressure near the bubble

Increases lifetime of the bubble
Knudsen Gas Behavior?

- No anisotropic motion of gas atoms observed

\[ S = \frac{3\langle \cos^2 \theta \rangle - 1}{2} \]
Summary

- Lifetime of nanobubbles on a substrate is more than 100 times longer than in a bulk liquid.
- Inhomogeneity of the system increases the lifetime of nanobubbles
- Lifetime of simulated nanobubbles was shorter than 1µs. (No stabilizing mechanism is implemented in simulations.)
- Thermal wall is also employed to realize transient nonequilibrium state.
- Knudsen gas behavior is not observed.
Remarks

· Knudsen number in simulated nanobubble Kn~2 is slightly higher than proposed condition.
  --> Create lower density nanobubbles

· Simulated nanobubbles are smaller than real nanobubbles.
  --> Larger calculations

· More detailed analysis is needed to investigate flux of atoms.
Microfluidics*

Microscale behavior of fluids
- Apparent slip on walls
- Attractive force between walls

= differ from macroscale

Surface tension
Hydrophobicity of the wall

Technological application
- Flow or mixing control in microfluidic devices
  ...and more

Lab on a chip for DNA sequencing
diameter of the wafer = 100mm
Molecular Dynamics Simulations

- Solve equation of motion for each particle
- Interaction – Lennard–Jones 6–12 potential

\[ U(r) = 4\varepsilon_{ij} \left\{ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right\} \]

Interaction between different species
- Berthelot–Lorentz law

\[ \sigma_{\alpha\beta} = \frac{\sigma_{\alpha} + \sigma_{\beta}}{2} \]
\[ \varepsilon_{\alpha\beta} = \sqrt{\varepsilon_{\alpha} \varepsilon_{\beta}} \]

Cut off length = 2.24nm (6.58 \varepsilon_{\text{LiqLiq}})

- NVT = const.

Motion of the center of mass is removed in order to avoid “flying ice cube”
Particle Settings

- Liquid and gas – Ar and Ne respectively
  \[
  \sigma_{\text{LiqLiq}} = 0.3405\text{nm} \quad \sigma_{\text{GasGas}} = 0.2750\text{nm} \\
  k_B\epsilon_{\text{LiqLiq}} = 119.8\text{K} \quad k_B\epsilon_{\text{GasGas}} = 35.05\text{K}
  \]

- Fixed wall – fixed to FCC lattice
  (Thermostat is applied to liquid and gas)

- Thermal wall
  – confined to FCC lattice by harmonic potential
  – behaves as a heat bath
  (Thermostat is applied only to wall particles)
Simulations

• Initial Conditions

Liq: 50688
Gas: 4608
Wall: 24336

• System configurations

(I) In a bulk liquid
(II) On a fixed wall
(III) On a thermal wall
(IV) On a thermal wall

(Temperature raised immediately)

(Temperature raised slowly)
Visualized Shrinking Nanobubbles

After temperature suddenly raised