Molecular dynamics study of the lifetime of nanobubbles on the substrate

GCOE Symposium 2012 – Links of Hierarchies

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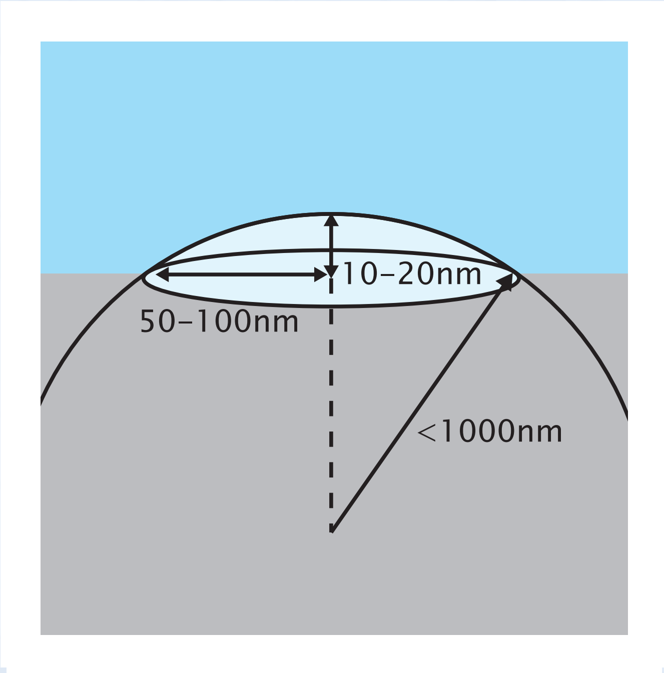
Outline

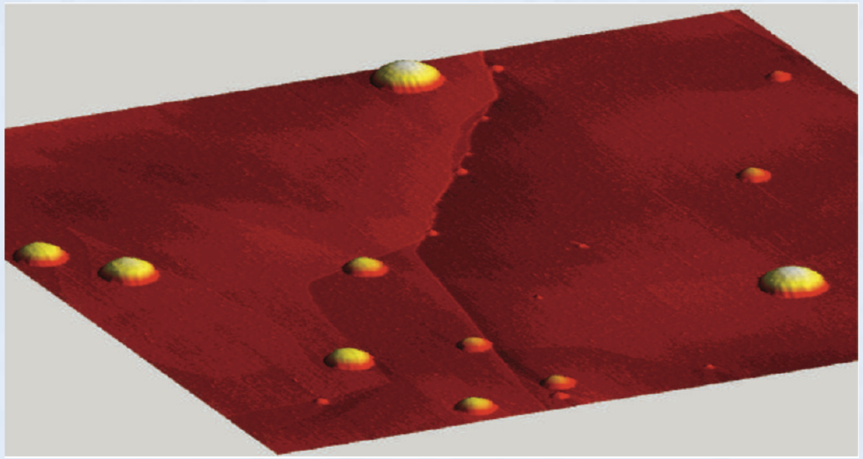
- Introduction
  - nanobubbles
  - stability of nanobubbles
  - preceding studies
  - purpose of this study
- Molecular dynamics simulations
- Numerical results
  - in the bulk liquid vs on the substrate
  - Knudsen gas ?
- Summary and remarks

Nanobubbles



Schematic illustration of typical nanobubble on a substrate

- radius ~< 1μm
- One cause of microscale behavior of fluids



Borkent et al.
Langmuir, **26**, 260 (2010)

- 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

$\boxed{\text{lifetime} < 100\mu s}$ (spherical bubble, diameter = 100nm)

cf. Ljunggren and Eriksson, Colloids Surf. A, **130**, 151 (1997)

- In experiment
  - Nanobubbles are stable

$\boxed{\text{lifetime} > \text{4days}}$

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.

Classical theory is applicable ?

1. Classical diffusion theory is not applicable ?
   - MD simulations of nucleation of stable nanobubbles

surface tensi

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

Nagayama et al. J. Heat. Mass. Trans., **49**, 4437 (2006)

- 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

Das et al. Phys. Rev. E, **82**, 056310 (2010)

more than x10^9 lifetime ? -> not enough

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

Dynamic Stabilizing Mechanism

influx near the contact line

balanced

need to be nonequilibrium

– th

Brenner and Lohse,

ow

the origin of the nonequilibrium

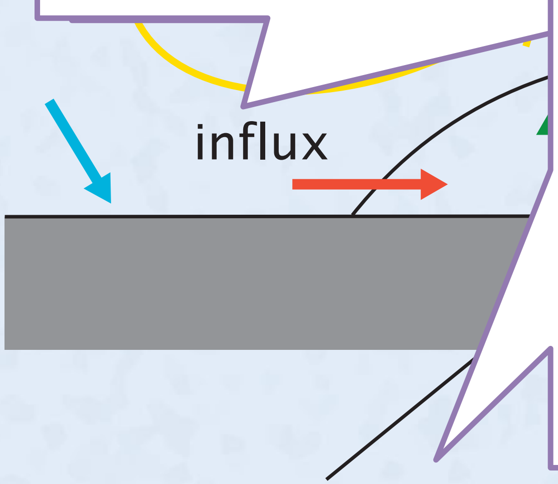
: wall = heat bath -> heat flux

How Nonequilibrium state sustained for a long time ?

circulating flow

– theoretical model and experiments

Seddon et al. Phys. Rev. Lett., **107**, 116101 (2011)



Knudsen gas behavior

- These models have not confirmed

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

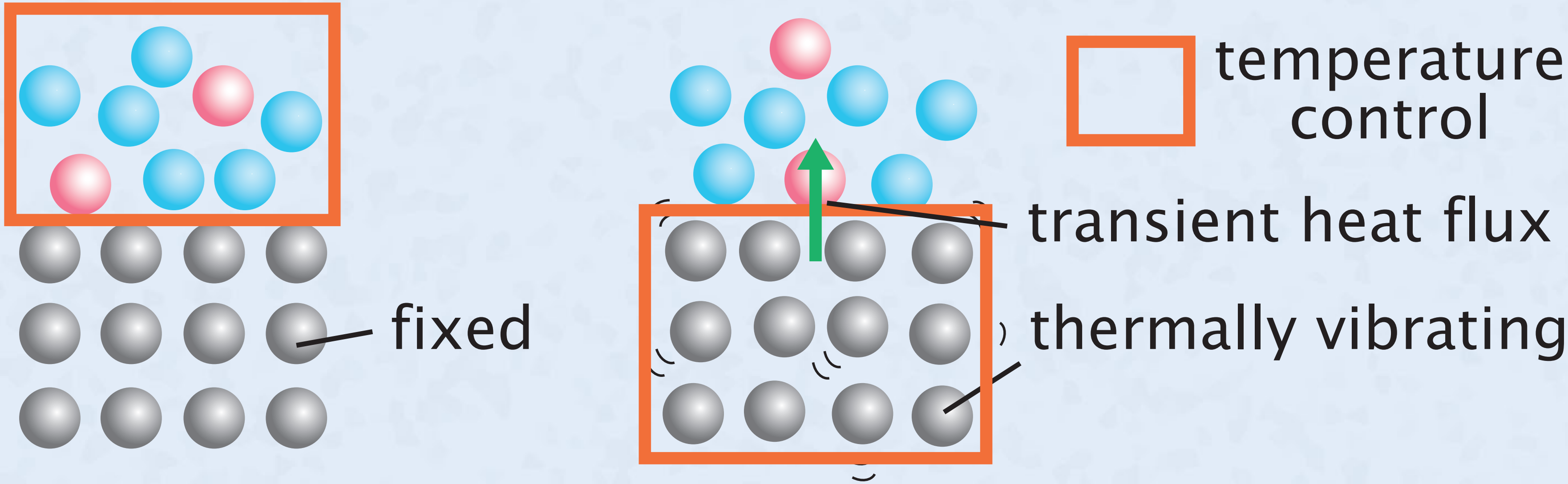
- Introduce nonequilibrium (transient heat flux)
  -> Thermal wall

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) = const.
- Liquid and gas – Ar and Ne respectively
- Fixed wall and thermal wall



Two Steps of Simulations

Step1 : Creation of nanobubbles
T = 85K

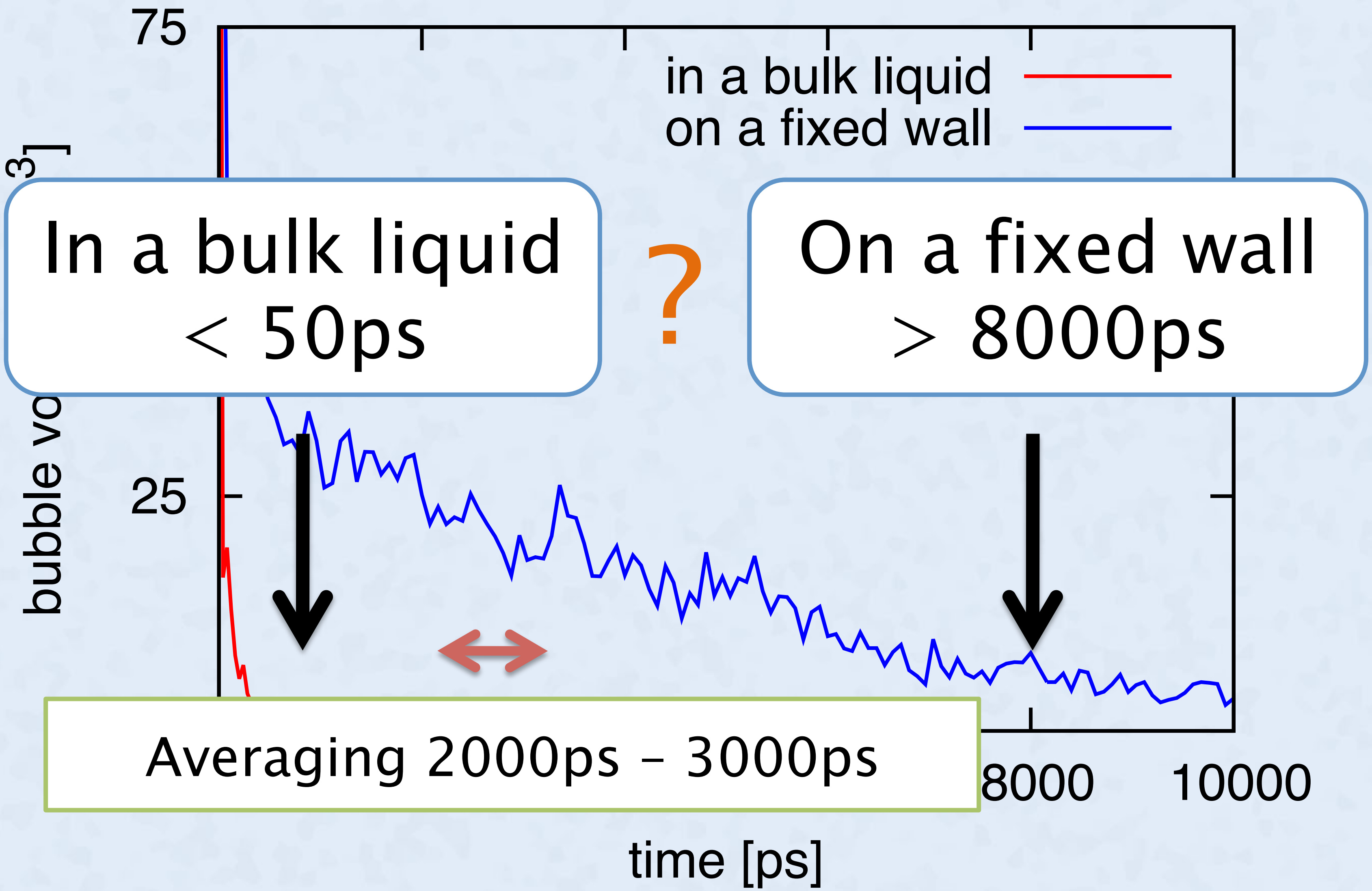
- Nanobubbles are stable
- Bubble nucleation occurs spontaneously
- Negative system pressure (stretched state)

Step2 -> Step1 : Quenching (bubble nucleation)

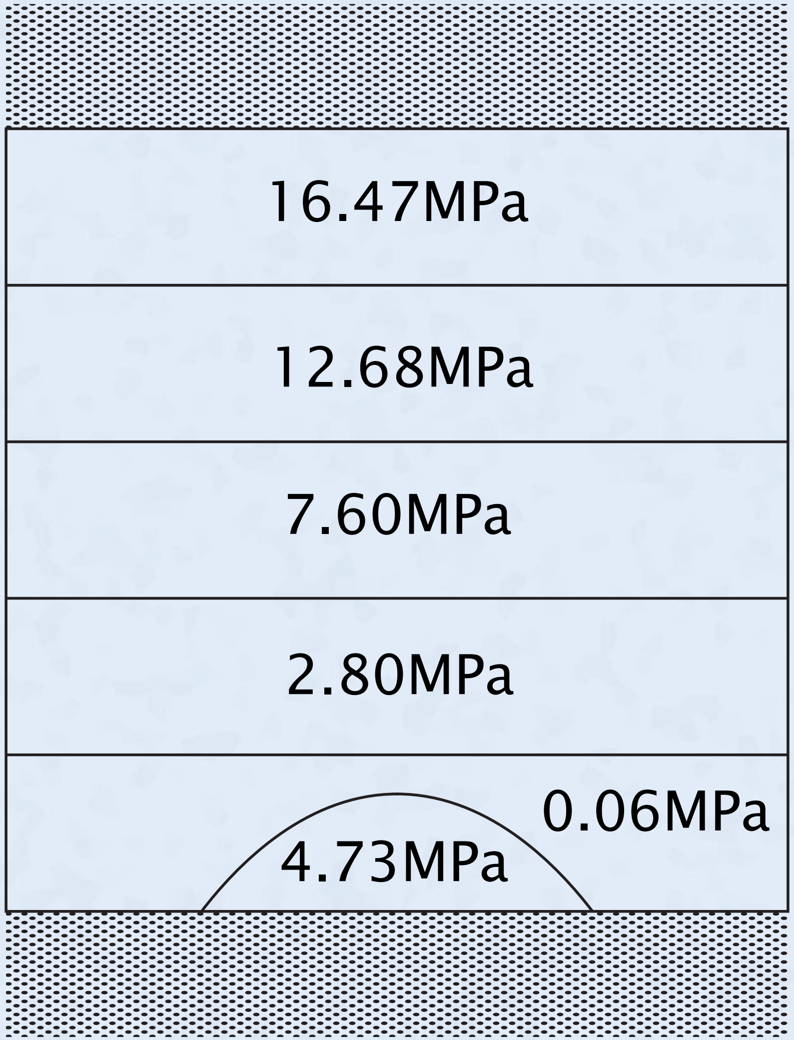
Step2 : Simulations of shrinking nanobubbles
T = 104K

- Nanobubbles are unstable
- Bubble nucleation does not occur
- Positive system pressure

Lifetime of Nanobubbles



Inhomogeneity of the System



Averaged pressure

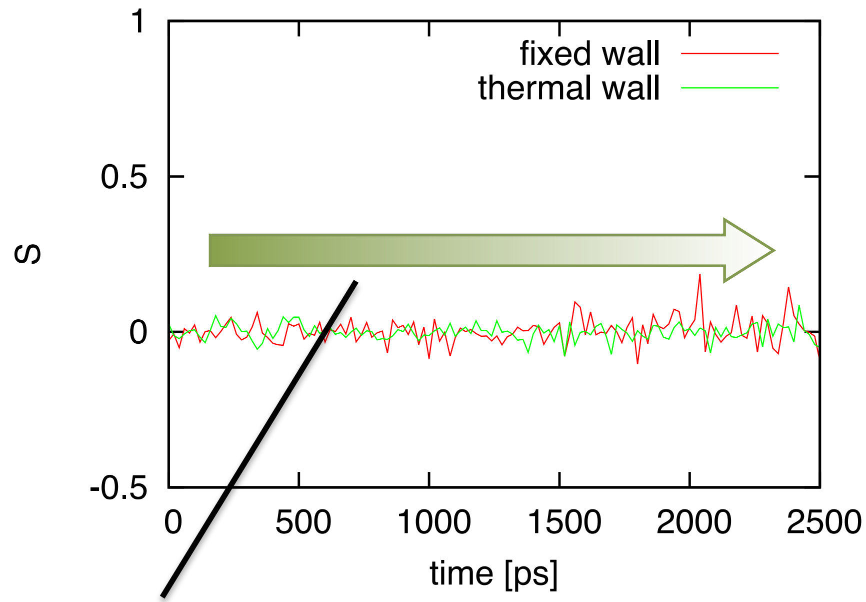
- 2000ps – 3000ps
- 5 regions parallel to the wall

Low pressure near the bubble

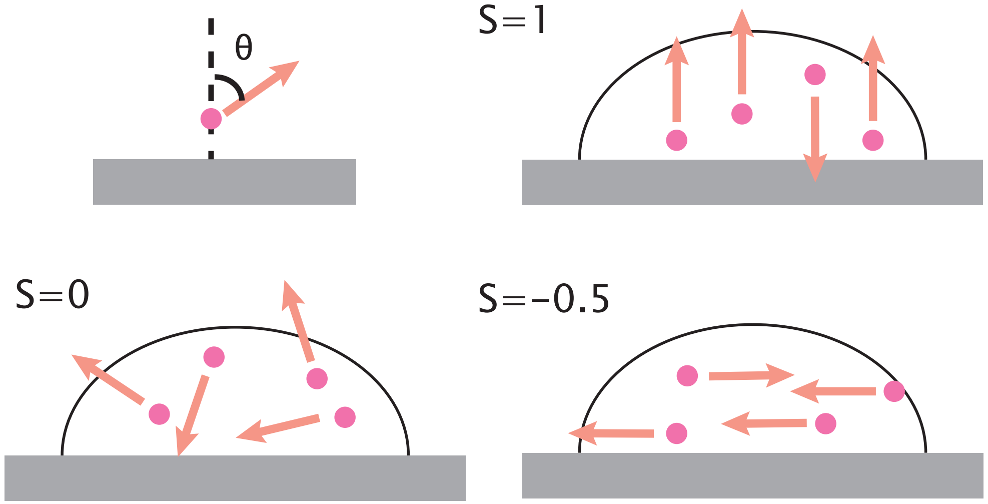
↓

Increases lifetime of the bubble

Knudsen Gas Behavior ?



transient heat flux exists :
wall -> liquid & gas
(thermal wall)



$$S = \left(3\langle \cos^2\theta\rangle - 1\right)/2$$

- No anisotropic motion of gas atoms observed

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 nanobbubbles are smaller than real nanobubbles.

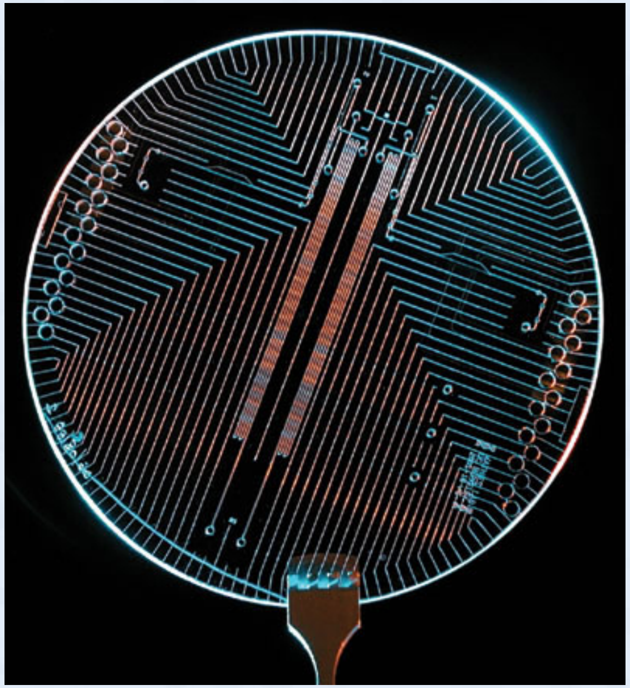
-> Larger calculations

- More detailed analysis is needed to investigate flux of atoms.

Microfluidics*

Microscale behavior of fluids

- Apparent slip on walls
- Attractive force between walls



Lab on a chip for DNA sequencing
diameter of the wafer = 100mm
Nature **444**, 985 (2006)

= differ from macroscale

Surface tension
Hydrophobicity of the wall

Technological application

- Flow or mixing control in microfluidic devices

…and more

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 low

$$\sigma_{\alpha\beta} = \frac{\sigma_\alpha + \sigma_\beta}{2}$$

$$\varepsilon_{\alpha\beta} = \sqrt{\varepsilon_\alpha \varepsilon_\beta}$$

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

- 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

$$\sigma_{\mathrm{LiqLiq}} = 0.3405\mathrm{nm} \qquad \sigma_{\mathrm{GasGas}} = 0.2750\mathrm{nm}$$
$$k_B\varepsilon_{\mathrm{LiqLiq}} = 119.8\mathrm{K} \qquad k_B\varepsilon_{\mathrm{GasGas}} = 35.05\mathrm{K}$$

Baidakov and Protsenko, J. Chem. Phys., **26**, 1701 (2008)

- Fixed wall – fixed to FCC lattice

(Thermostat is applied to liquid and gas)

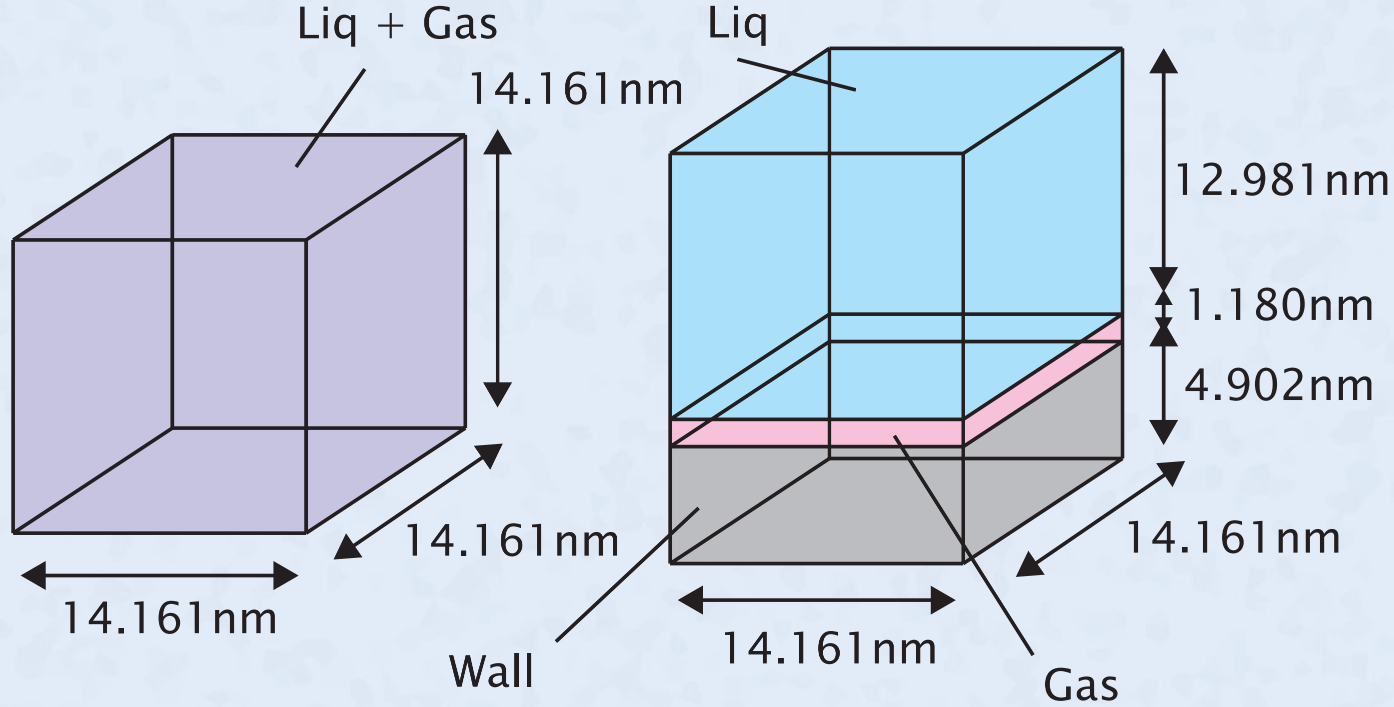
- Thermal wall
  - confined to FCC lattice by harmonic potential
  - behaves as a heat bath

(Thermostat is applied only to wall particles)

Simulations

- Initial Conditions

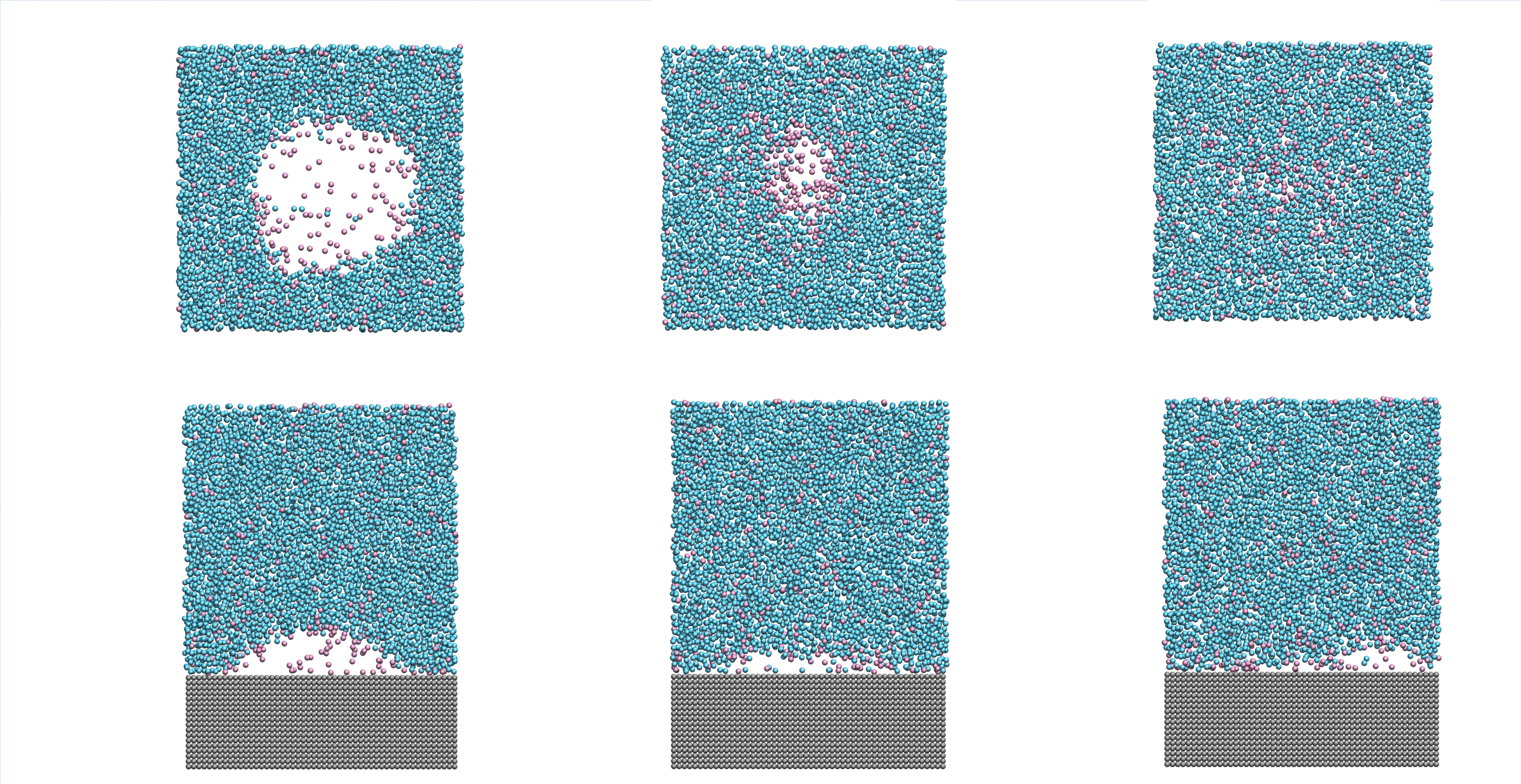
Liq : 50688
Gas : 4608
Wall : 24336



- System configurations

(I) In a bulk liquid
(II) On a fixed wall
(III) On a thermal wall
(Temperature raised immediately)
(IV) On a thermal wall
(Temperature raised slowly)

Visualized Shrinking Nanobubbles



After temperature suddenly raised