MOLECULAR DYNAMICS ANALYSIS FOR THE BROWNIAN MOTION OF NANO BUBBLE

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Key words: Molecular Dynamics, nano bubble, platinum particle, Brownian motion

Abstract. The smaller bubble whose diameter is below 1 micrometer is called nano-bubble or ultra-fine bubble. The size of nano bubble is so small and invisible that the diameter distribution is generally evaluated as a mean square distance(MSD) of brownian motion that is measured by Dynamic Light Scattering(DLS) method based on the Einstein-Stokes equation. The equation, however, is not clarified for the application to the bubble sizing. In our previous study, the different behavior between solid particle and bubble with the same diameter at sub-micro scale was confirmed. In this study, the Brownian motion of nano bubble as well as the solid Pt particle whose diameter are around a few nano meters were simulated with the Molecular Dynamics(MD) method. The simulation employed Lennard Jones(LJ) potential to estimate the MSD of the bubbles and particles by tracing the trajectories of the center of gravity of them and resulted that the displacement of solid particles in liquid argon was less than the predicted amount by the Einstein-Stokes equation. In order to confirm apparent viscosity caused by periodic boundary conditions, the drop velocity of the particle due to the gravity force is measured and apparent viscosity is obtained using Stokes' low with this velocity. Considering this apparent viscosity, the diameter of the solid particle is approximated using the Einstein-Stokes equation under its diameter of 4 nm. The bubble diameter obtained by the Brownian motion is lower than the Einstein-Stokes equation.

1 INTRODUCTION

Recently, nano bubble catches the great attention because it can stay in solvent for very long time and it has charge so that it has chance to be applied in various disciplines. For example, the existence of them can change the viscosity and thermophysical properties of the solvent. Since its diameter is smaller than wavelength of visible light, it can't be measured by the optical instruments dynamically. Thus, to evaluate the diameter distribution of nano bubble, Dynamic Light Scattering(DLS) method is generally used. That is the method of getting the diameter distribution based on the Einstein-Stokes equation from

a mean square distance(MSD) by sensing the scattered light caused irradiating a part of solvent where the particles are undergoing the Brownian motion with laser beam. The Einstein-Stokes equation, however, is just for solid particles, but is not clarified for the application to the bubble sizing. In our previous study[1], we experimentally investigated the difference of behavior between solid particle and the bubble with the same diameter sub-micro scale.

In this paper, we carried out Molecular Dynamics(MD) simulation of liquid argon to analysis the Brownian motion of the quite smaller bubble. It is suggested that the method of analysis for the Brownian motion of nano bubble enables to improve the accuracy of diameter distribution measurement by DLS method, that can help to develop more efficient and various application of nano bubble.

2 SIMULATION

We simulated the movement of the bubble and the solid particle in liquid argon applying the Lennard Jones(LJ) pair potential for the molecule interaction as follows:

$$\phi\left(r_{ij}\right) = 4\epsilon_{ij}\left\{\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right\} \tag{1}$$

r_{ij} is the distance of molecules and ϵ_{ij} and σ_{ij} are LJ potential parameters for each

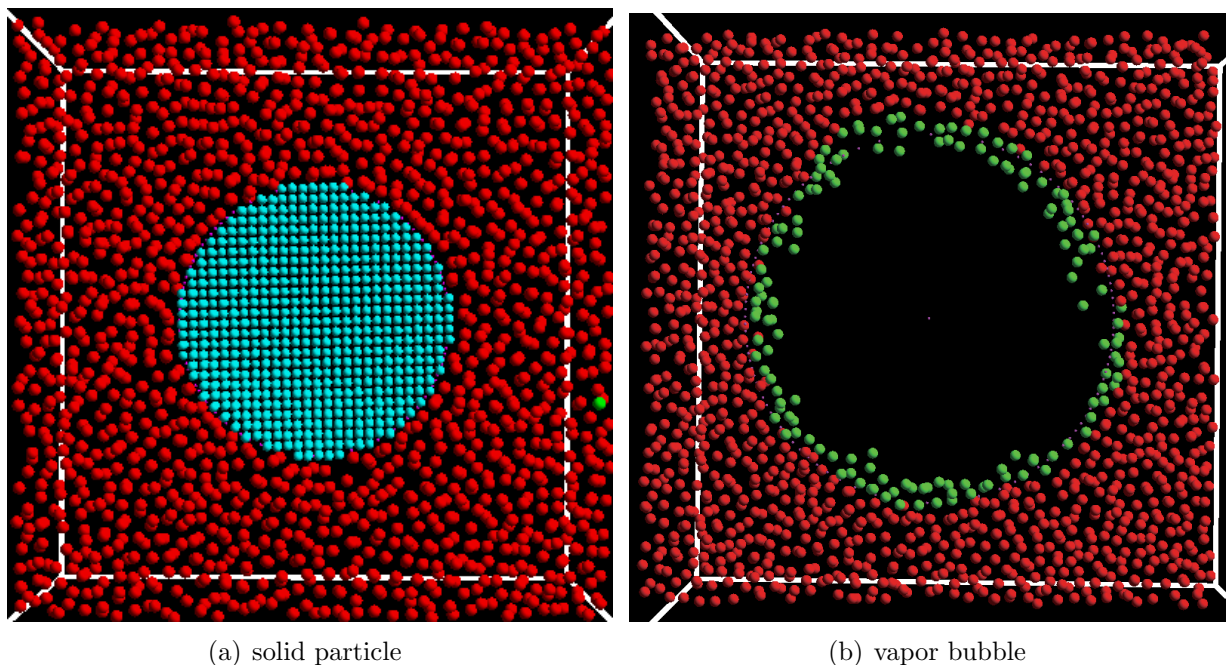(a) solid particle   (b) vapor bubble

Figure 1: The cross section view of simulation box. In both pictures, the red molecules are liquid Ar, light blue molecules are solid Pt and green molecules are interface argon molecules.

Table 1: The simulation conditions

Conditions	N	N_{Pt}	Particle radius [nm]	Cell size [nm]
Pt 1	32000	100	1.39	11.48
Pt 2	32000	500	2.44	11.46
Pt 3	32000	1000	3.03	11.42
Pt 4	32000	5000	5.13	11.08
Bu 1	10976	–	5.46	8.60
Bu 2	16384	–	6.46	9.82
Bu 3	32000	–	8.00	12.28

interactions. The corresponding potential parameters of argon-argon interactions are $\epsilon_{Ar} = 119.8$ K and $\sigma_{Ar} = 3.405$ Å, platinum-platinum interactions are $\epsilon_{Pt} = 6047.88$ K and $\sigma_{Ar} = 2.475$ Å, and argon-platinum interactions are $\epsilon_{Ar-Pt} = \alpha \left(\epsilon_{Ar} \times \epsilon_{Pt} \right)^{1/2}$ and $\sigma_{Ar-Pt} = \left(\sigma_{Ar} + \sigma_{Pt} \right) /2$, where α is the potential energy factor indicating the strength of hydrophilic interaction[3, 4]; $\alpha = 0.1$ in this study. The equations of motion are integrated by the leapfrog Verlet algorithm[2]. To reduce the time, the cut-off radius of $3\sigma_{Ar}$ is selected and we apply the book keeping method with the radius of $3.2\sigma_{Ar}$ every 10 steps, and cell dividing method with cell size of lager than the $3.2\sigma_{Ar}$ every 100 steps. All simulations are performed with a time step of 10 fs. Periodic boundary conditions are applied in all three directions and temperature is set at 90K.

In order to simulate the Brownian motion of the solid particle, we consider 32000 argon and platinum atoms in the simulation cell whose size is adjusted to be saturated density of solvent 1.398 kg/m^3, as shown in Figure 1. We arranged various particle diameter by varying the number of Pt molecules as shown in Table 1. Initially, we equilibrate the system in the (N, V, T) ensemble for 10^5 steps with the velocity scaling method. After the equilibration, we terminate, stop the velocity scaling and a (E, V, T) ensemble simulation undergo for 10^6 steps to obtain the data of MSD of the solid particle. In this study, the molecules are sorted to vapor, liquid, solid and each interface to define the interface of bubble and solid particle by number density in a distance of 2.5 times diameter. The number density of the molecule in liquid phase nearly equals to saturated density, in solid phase equals to solid bulk density of its element and in air phase is about zero. A number density of interface is between the value of two phases. We obtain the diameter and the coordinate of the center of the particle by calculating least square sphere of this interface molecules. Moreover, to test the effect of the particles in the neighbor replica cells that are caused periodic boundary conditions on the mobility of the particle, we investigate the mobility of the particle in solvent evaluating its viscosity by sedimentation method. The gravity force 9.8×10^{10} kg $\cdot$ m/s^2 is applied to only the solid particle at the same configuration as described above.

Also to simulate the Brownian motion of the vapor bubble, we consider 10976, 16384

and 32000 argon atoms in the each simulation cell whose size is adjusted to be the liquid density of 0.82 times lower than saturated density as shown in Figure 1. First, a (N, V, T) ensemble simulation undergo for 10^5 steps with the velocity scaling method to equilibrate and to make formation of the argon vapor bubble. Next, a (E, V, T) ensemble simulation undergo for 10^6 steps to obtain the data of MSD of the bubble or so. We obtain the diameter and the coordinate of the center of the bubble by calculating least square sphere of interface molecules that are determined sorting to gas, interface and liquid molecule by number density. Table 1 shows the conditions of simulations undergone in this study.

The MSD of Brownian motion of the particles in solvent is related to the particle diameter, temperature and viscosity of solvent as the Einstein-Stokes equation as shown in equation (2)[5], where d is the particle diameter, t is measuring time, λ^2 is the MSD of the particle, k_{B} is Boltzmann's constant, T is temperature and η is viscosity of solvent. Using this equation, we can obtain the particle diameter by measuring the MSD of the particle.

$$d = 2\frac{t}{\lambda^2}\frac{k_{\mathrm{B}}T}{\pi\eta} \tag{2}$$

The equation of motion of the particle in solvent in this study is denoted as follows:

$$\frac{\pi}{6}d^3\rho_s g - C_d\pi\left(\frac{d}{2}\right)^2 \rho_w v^2/2 = 0 \tag{3}$$

where ρ_s is the density of the particle, g is gravity acceleration for the particle, C_d is the drag coefficient, ρ_w is the density of solvent and v is the velocity of the particle. In the field of view, there is no buoyancy since gravity force apply for only the solid particle. If particle Reynolds number Re^* is small enough, the drag coefficient can be approximated as follows[6]:

$$C_d = \frac{24}{Re^*} = \frac{24\eta}{vd\rho_w} \tag{4}$$

The particle Reynolds number is less than 0.03 at a maximum in this study so this approximation can be applied. From equation (3) and (4), the following relation is obtained:

$$\eta = \frac{\rho_s g d^2}{18v} \tag{5}$$

Using equation (5), the viscosity of the particle is obtained by measuring the sedimentation velocity of the particle.

3 RESULT and DISCUSSION

The temporal change of MSD of the particle λ^2/t with various particle diameter are obtained by simulation and shown in Figure 2. All values of MSD by simulation are much lower than theory regardless of diameter. The result depicts that solvent gets to be hard and interferes with particle movement for some reason in MD simulation. Focusing on the rate of the decreasing, the rate drops drastically with increasing the particle diameter. It suggests that the lower mobility of the particle is due to the periodic boundary conditions. With applying periodic boundary conditions, there are particles at interval of cell size in neighbor replica cells around the particle that we trace. It is suppposed that the existence of those particles blocks the particle to move. The effect of this grows as increasing the particle size to be the bigger ratio to cell size.

To evaluate this effect, we measure the apparent viscosity by sedimentation as the indication of lower mobility of the particle. The result is shown in Figure 3. The apparent viscosity is more than the value of bulk liquid argon. In addition, the larger particle cause to get solvent viscosity greater predictably. The solid curve in Figure 3 is the least square fitting to $y = ax/(L - x) + \eta_b$, L is the simulation cell size and η_b is viscosity of bulk liquid argon. The reason of using this function is that when the diameter is zero, this effect is negligible and when the diameter equals to the cell size, the particle can't move. The apparent viscosity is determined from this curve.

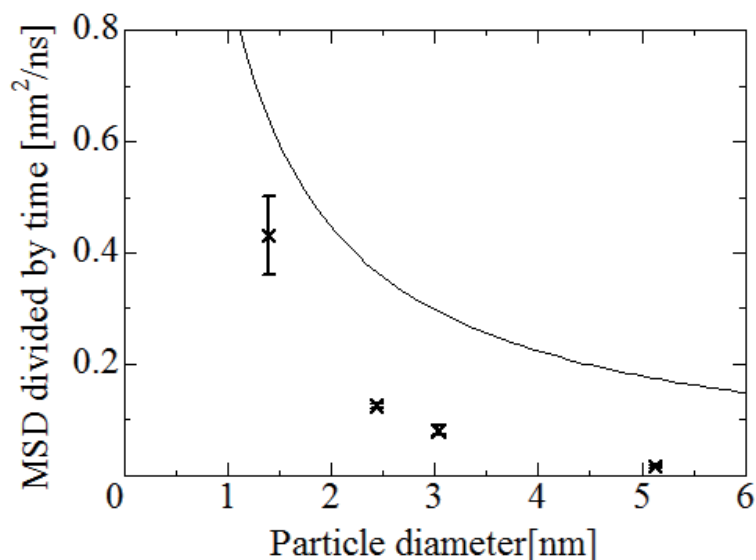Involving this apparent viscosity, the diameter of the solid particle and the bubble

Figure 2: MSD divided by time, λ^2/t with respect to the particle diameter. The solid line is the value from equation (2) assuming that solvent viscosity is same as bulk at 1 atm.
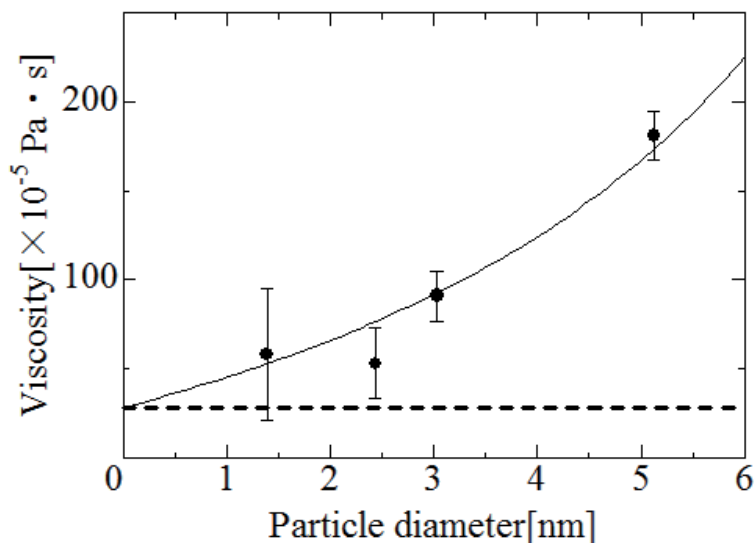
Figure 3: The apparent viscosity by sedimentation with relate to the particle diameter.The solid line is least square fitting to $y = ax/(L-x) + \eta_b$ and The dash line shows the value of bulk solvent.

from those MSD by equation (2) are calculated. We compare the diameter of this one and another that calculated by least square sphere of interface particles in simulation. The result is shown in Figure 4. The both diameters of the solid particles have a good agreement below 4 nm. It is possible to analyze the small particle movement by evaluating evaluating the apparent viscosity by sedimentation. However the particle its diameter of about 5 nm has lower mobility even considering the effect of replica cells. The bubble diameter by Brownian motion is less than ractual diameter. This result means that the bubble moves more actively than solid particle in MD simulation, which disagrees with our previous experimental result of microbubble in water. This is because that bubble intends to shrink and causes pressure down of liquid surrounding the bubble.

4 CONCLUSION

In this study, we investigate the movement of nano vapor bubble and solid platinum particle at equilibrium in liquid argon at 90K. The particle in molecular dynamics simulation with periodic boundary conditions has lower mobility than bulk. This is due to the particle interaction between neighboring particles in the connecting replica cells. The effect get stronger as the greater volume occupied by the particle in simulation cell. Considering apparent viscosity measured with sedimentation, we can obtain approximate diameter of the particle below 4 nm. The diameter of bubble calculated from the Einstein-Stokes equation with its MSD is lower than the value from the Einstein-Stokes equation
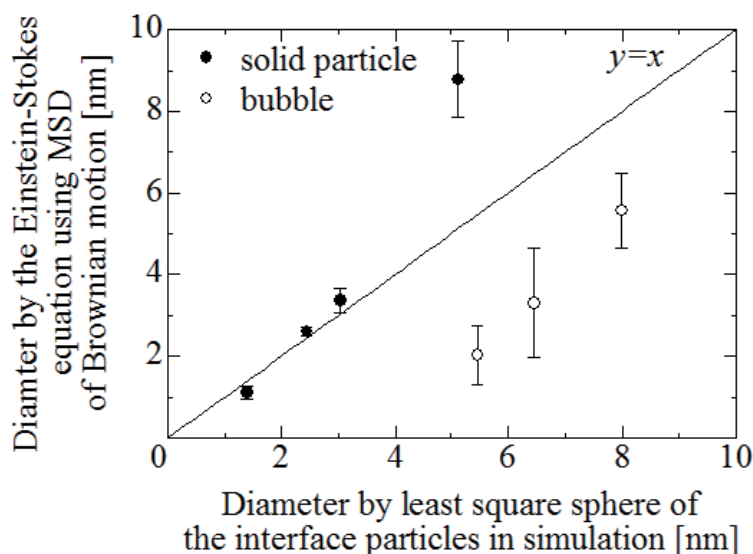
Figure 4: The comparison the diameter of by least square sphere of the interface particle in simulation and by the Einstein-Stokes equation using the value of MSD of Brownian motion.

theoretically. It can be said that the bubble makes pressure down of liquid surrounding the bubble because it intends to shrink. The particle size is sufficiently small with respect to the cell size, we can analysis quite small particle by considering apparent viscosity caused by periodic boundary conditions measured by sedimentation.

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