Heterogeneous nucleation of bubbles by molecular dynamics

Donguk Suh¹, Mitsuki Nakamura¹ and Kenji Yasuoka¹
¹Keio University, Department of Mechanical Engineering, Hiyoshi 3-14-1, Kohokuku, Yokohama 223-8522, Japan
E-mail: suh@mech.keio.ac.jp

Abstract. A homogeneous liquid system and a heterogeneous system with an impurity inserted inside it were used for investigation of bubble nucleation by molecular dynamics simulation. A constant particle number, volume, and temperature ensemble was used. The systems with the impurities showed an overall increase in bubble formation, which is consistent with previous studies. The shape of the impurities was changed to see if there was any direct influence on the bubble nucleation rate. With the limited number of systems investigated, the occurrence of a shape effect was inconclusive. As observed in previous heterogeneous nucleation studies with walls, the bubble initially forms remotely from the impurity and remains at some distance from the seed.

1. Introduction
Bubble nucleation is an important phenomenon in nature and industry, and studies have shown that the critical nucleus size can be as small as that of nano scale [1-3]. With the advent of lab-on-a-chips and nanomachinery, fluid flow and plugging of nanochannels due to bubbles is of great concern to the scientists that develop nano scale products [4]. Therefore, many studies have used molecular dynamics (MD) to understand the phenomenon for both homogeneous and heterogeneous systems [5-10]. The latter systems are known to produce higher nucleation rates (more bubbles) because these systems have a lower free energy barrier. However, most of the heterogeneous nucleation studies by MD on bubbles by MD are on two-dimensional surfaces [11,12]. The number of studies of bubble formation with a freely moving three-dimensional impurity in the system has been limited [13]. The scarcity in studies with regard to heterogeneous nucleation of impurities is unfortunate, since impurities with various shapes and sizes usually exist within a liquid. An understanding of the mechanism of how an impurity actually affects bubble formation is necessary.

In this study, an impurity or seed particle as in Fig. 1 is initially placed inside a subcooled liquid to examine by MD how the addition of the seed will influence bubble formation. The following section will explain the simulation setup and the results of the findings will ensue.

Figure 1. Representation of impurity that will be inserted into a liquid system (a) cube and (b) sphere.
2. Simulation Setup

For the heterogeneous system, a spherical and a cubic seed particle are each constructed by cutting out such volumetric regions from an aluminum block of a (100) face-centered cubic lattice. The aluminum atoms have Lennard-Jones parameters ($\sigma_{\text{Al}}=2.551\text{Å}$, $\epsilon_{\text{Al}}=0.65\times10^{-19}\text{ J}$) based on ref. [14] and are constrained by the RATTLE algorithm [15]. Further details of the process are in ref. [16,17]. Once the seed particle is made, it is immersed inside a cubic periodic system with liquid argon. Brownian motion of the impurity will take place inside the liquid. A homogeneous system is basically a heterogeneous system without the seed.

A constant number, volume, and temperature ensemble was used for the molecular dynamics simulation. The number of argon molecules in the system was 8788, and 108 or 110 aluminum atoms were added for creating a system with a cube or a sphere, respectively. The system volume was scaled with the addition of the seed molecules to keep the system isochoric. The initial system volume was set so the initial density of the system was at 1176 kg/m$^3$. The system was initially equilibrated to 144 K for 1.0 ns and the target temperature was decreased to 90.5 K, 95.0 K, and 99.9 K by velocity rescaling. Note that in an isochoric system, a temperature reduction is required for bubble nucleation to occur. The temperatures were set below the liquefaction temperature, where bubbles could be observed within the restricted time frame. The velocity rescaling method is a standard method that scales the molecular velocities to a target value depending on the temperature of the system based on statistical mechanics [15].

The Lennard-Jones 12-6 potential was applied for all interactions, and the Lorentz-Berthelot relations were used for argon and aluminum atom interactions. The time integration was performed by the velocity Verlet algorithm with a short $\Delta t$ of 1.0 fs.

3. Results

Both homogeneous and heterogeneous systems were examined under the same thermodynamic conditions. The rate of nucleation is evaluated by the nucleation time, which is defined as the first instant, at which the bubble reaches its maximum volume within the system. The maximum volume is the largest volume to which the bubble grows within the observed time frame. This definition is necessary since the bubble size fluctuates continuously. A summary of the nucleation time for all target temperatures in the homogeneous and heterogeneous systems is presented in table 1. At 99.9K nucleation was not observed in any of the systems within the observed time frame of 1.5 ns.

| Target Temperature | HON  | Cube | Sphere |
|--------------------|------|------|--------|
| 90.5 K             | 220 ps | 70 ps | 100 ps |
| 95.0 K             | 590 ps | 700 ps | 450 ps |
| 99.9 K             | -     | -    | -      |

3.1. Homogeneous nucleation (HON)

Figure 2 shows sliced snapshots of bubble nucleation for a homogeneous system. The slice thickness is 2.0 $\sigma_{\text{Al}}$. At the onset of quenching in Fig. 2(a) argon is randomly dispersed within the system, whereas once the bubble is formed, a clear void in the volume of argon molecules can be observed. Note that argon vapor molecules are seen within the void, as documented in previous studies.
3.2. Heterogeneous nucleation

Impurities are added to the homogeneous system as in Fig. 3. Only a selection of plots are shown since the overall tendencies of the phenomenon did not drastically vary with the seed shape or thermodynamic condition. Figure 3 shows an example of nucleation with a cube. Fig. 3(a) is at the onset of quenching after equilibration of the system, which in Fig. 3(b) led to two voids that were created separately and subsequently in Fig. 3(c) merged into one large bubble. The voids form at a distance from the impurity, and once a bubble forms, there is no evidence that the impurity and the bubble directly interact.

The nucleation times are shown in table 1. Insertion of the impurity clearly produces faster nucleation at the strongest quenching (90.5 K). At moderate cooling (95.0 K) the results are mixed, the cube being slower than the homogeneous system. The irregularities in the results can be attributed to the lack of repetitions at this stage of the study. Nucleation is a highly stochastic phenomenon, so more samples need to be taken in order to obtain a clearer general tendency.

As previously stated, no clear shape effect has been observed at present due to the lack of statistics. Furthermore, a longer simulation time will most likely provide nucleation times for the 99.9 K systems.
Acknowledgements
This work was supported in part by grant-in-aid Mizuho Foundation for the Promotion of Sciences.

References
[1] Schmelzer J W P, Boltachev G S and Abyzov A S 2013 *Journal of Chemical Physics* **139**
[2] Xiao C, Heyes D M and Powles J G 2005 *Physica Status Solidi (B) Basic Research* **242** 749-61
[3] Lubetkin S D 2003 *Langmuir* **19** 2575-87
[4] Parthiban P and Khan S A 2012 *LChip* **12** 582-8
[5] Kinjo T, Ohguchi K, Yasuoka K and Matsumoto M 1999 *Computational Materials Science* **14** 138-41
[6] Novak B R, Maginn E J and McCready M J 2007 *Physical Review B* **75**
[7] Sekine M, Yasuoka K, Kinjo T and Matsumoto M 2008 *Fluid Dynamics Research* **40** 597-605
[8] Bazhirov T T, Norman G E and Stegailov V V 2008 *Journal of Physics-Condensed Matter* **20**
[9] Tsuda S, Takagi S and Matsumoto Y 2008 *Fluid Dynamics Research* **40** 606-15
[10] Wang Z J, Valeriani C and Frenkel D 2009 *Journal of Physical Chemistry B* **113** 3776-84
[11] Maruyama S and Kimura T 2000 *Heat and Technology* **18** 69-73
[12] Chen M, Yang J, Gao Y, Chen Y and Li D 2014 *Journal of Heat Transfer-Transactions of the Asme* **136**
[13] Hoyt J J and Potter A A 2012 *Metallurgical and Materials Transactions a-Physical Metallurgy and Materials Science* **43A** 3972-7
[14] Agrawal P M, Rice B M and Thompson D L 2002 *Surface Science* **515** 21-35
[15] Allen M P and Tildesley D J 1989 *Computer Simulation of Liquids* (New York: Oxford University Press, USA)
[16] Suh D and Yasuoka K 2011 *Journal of Physical Chemistry B* **115** 10631-45
[17] Suh D and Yasuoka K 2012 *Journal of Physical Chemistry B* **116** 14637-49