



Molecular dynamics study on phase equilibrium around vapor bubbles in low-density liquid argon



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ABSTRACT

In this study, we investigate the vapor bubble stability in liquid argon using a molecular dynamics simulation. The Lennard–Jones (L–J) interparticle interaction potential is used to simulate the interaction forces between argon molecules. The discrimination method based on Stillinger's cluster criterion is employed to classify the vapor molecules evaporated from the bulk liquid. In this criterion, the vapor molecules are determined to have no neighboring molecules within a 1.23 to 1.32σ radius, where σ is the interaction radius in the L–J potential. It is found that the spherical bubble shape is maintained and the Young–Laplace equation applies mainly as a result of the large negative pressure of the liquid. The 10 – 90 thickness of the vapor–liquid interface was approximately 30 to 90% of the bubble radius in the present simulation. A certain frequency of condensation and evaporation was maintained in the smaller bubble case, which is not proportional to the decrease in bubble surface area.

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1. Introduction

In the recent years, many researchers conducted molecular dynamics (MD) simulations to discuss the balance between pressure and surface tension for the stability issue of ultrafine bubble in a liquid. For general droplets or bubbles in a liquid, the inner pressure P_V is associated with the surface tension γ and can be expressed with the help of the Young–Laplace (Y–L) equation,

$$P_V = P_L + \frac{2\gamma}{R}, \quad (1)$$

where P_L is the pressure of the bulk liquid and R the bubble radius of curvature. For very small bubbles, however, the Y–L equation is divergent since the value of R becomes very small. Therefore, the theory of Epstein & Plesset [1] predicts that nanobubbles may be crushed by surface tension over several microseconds.

On the other hand, Park et al. [2] evaluated the surface tension from the sum of the normal stress around the vapor bubble of the Lennard–Jones (L–J) molecules for the metastable state in which the density is lower than that of the saturated liquid state. Their calculation revealed that the surface tension closely approximated the bulk value and was independent of the bubble radius. This is in contrast to the Tolman equation [3], which predicted an increase in the surface tension with

decreasing bubble radius. Matsumoto et al. [4–7] suggested that the small bubble could only exist in the liquid under large negative pressure and there was a possibility that the Y–L equation would hold. However, the inner pressure of the vapor was estimated by the empirical equation of state because of the lack of identification of the vapor molecules, except in Ref. [5]. Tsuda et al. [8] reported the existence of small cavitation bubbles growing like Ostwald ripening [9] in the MD simulation. Similarly, the vapor pressure in the bubbles and the surface tension on the vapor–liquid interface were evaluated from the empirical values of liquid argon.

These literatures imply that the vapor nanobubbles in L–J fluids survive only in a large negative pressure or low-density metastable liquid, even if there is no non-condensable gas to support the surrounding pressure or no contaminations to reduce the surface tension. However, the calculation method of the inner pressure of the bubbles P_V is indistinct since the identification of the vapor molecules is obscure. The classification of the vapor and liquid phase in Refs. [2,4,6,7] was based on Maruyama's discrimination method [10], in which the “void” grid points in the calculation domain were regarded as a vapor region. The bubble consisted of the cluster of void grid points around which no molecules existed in a sphere of radius 1.6 to 0.6σ [11], where σ is the interaction radius in the L–J potential. Therefore, it was difficult to evaluate the inner pressure of the bubble since no vapor molecules could be identified in the vapor region.

In contrast to this method, Wang et al. [12] and Zhukhoviiskii [13] used another method to discriminate between vapor and liquid molecules using Stillinger's cluster criterion [14]. According to this method, two molecules are recognized to be neighbors; they are in the liquid

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phase if their distance is less than the threshold value $r_c \sim 1.6\sigma$. The value of r_c corresponds to the first minimum of the radial distribution function of the liquid under the same thermodynamic conditions. By using this method, the accuracy of estimation of the vapor and liquid pressure is improved owing to the identification of vapor molecules at each calculation step.

In the present work, we employ the method based on Stillinger's cluster criterion to detect the vapor molecules. The pressures of both the vapor and liquid phases are calculated by the virial equation to evaluate the establishment of the Y–L equation for the vapor bubble in the liquid argon. The characteristics of the phase equilibrium are addressed by evaluating the thickness of the vapor–liquid interface and by counting the number of molecules evaporating and condensing through the vapor–liquid interface.

2. Simulation method

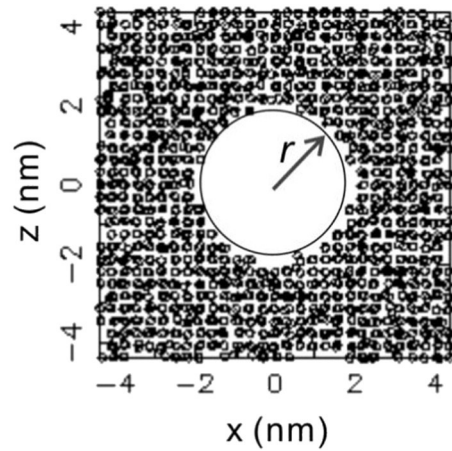
We used a 12–6 L–J potential for the calculation of intermolecular force:

$$\phi(r_{ij}) = 4\epsilon \left\{ \left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right\}, \quad (2)$$

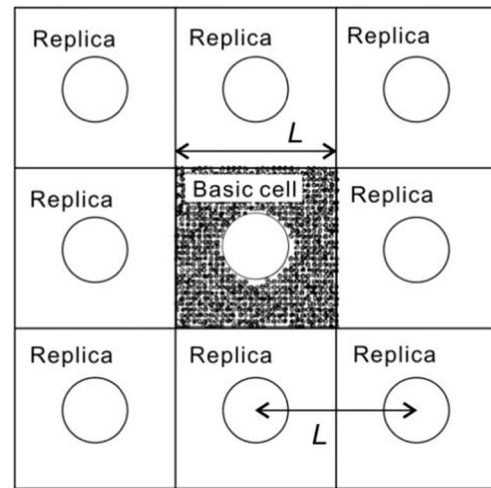
where r_{ij} is the distance between molecular- i and molecular- j . It is known that the L–J potential can describe the van der Waals forces of noble gases, such as argon, well. In some cases, the calculated results for L–J fluids are described by non-dimensional parameters. However, in the present case, the parameters $\epsilon/k_B = 120$ K and $\sigma = 0.34$ nm of argon were used for comparison with literature [2,5,6,8,10,12]. The normalization of temperature are given by $T^* = k_B T / \epsilon$ and length r/σ , respectively, where k_B is the Boltzmann constant. We employed a Verlet algorithm to calculate the momentum equation. The time step and the cut off radius of the intermolecular force calculation were 0.2 fs and 3.2σ , respectively. The argon molecules were arranged in a face-centered cubic lattice in a cubic calculation domain at the initial stage of calculation. The periodic boundary condition was applied to each surface of the calculation domain.

First, we provided a spherical vacuum void of radius 4.0 to 10σ in the center of the calculation domain to induce the bubble nucleus, as shown in Fig. 1. Thereafter, we performed an energy relaxation calculation with velocity scaling in NVT-constant ensembles to cause the vapor evaporation to progress from the liquid phase around the initial void sphere. The appropriateness of the relaxation time was confirmed by the stability of the Hamiltonian, which is the sum of the kinematic and potential energy of the molecules, in the preliminary calculation. Then, after 4 ps, we converted the NVT-constant ensembles to NVE-constant ensembles to evaluate the time evolution of the vapor bubble.

Fig. 2 shows the dependence of the non-dimensional initial liquid number density on the initial bubble diameter before subtracting the vacuum region. The solid symbol indicates the present conditions and the open symbol indicates the conditions employed by Matsumoto [4]. He reported that the Y–L equation held for $T^* = 0.7$ and 1.0 in Fig. 2. These conditions have a constant density close to the saturation curve of L–J fluids (e.g. Fig. 31 in Ref. [15]) for $T^* = 0.8$ and 1.0, and have various initial void radii along the transverse axis. Here, the temperature $T^* = 0.67$ is the triple point temperature and $T^* = 1.25$ is the vapor–liquid critical temperature of argon [5]. Then, we set the temperature conditions $T^* = 0.8$ and 1.0, closely approximating the values in the literature [4]. The specific conditions of the number of particles, cell size, etc. are listed in Table 1. The numeral in Fig. 2 corresponds to the case number in Table 1. The size of the calculation domain was changed from 7.37 to 10.6 nm so that the initial liquid number density was adjusted to be on the fit curve of Matsumoto's condition for a given spherical void size.



(a) Initial state in basic cell ($t = 0.2$ ps)



(b) Periodic boundary condition

Fig. 1. Calculation domain.

The threshold value r_c range to identify the vapor molecules was determined to be $r_c = 1.23$ to 1.32σ by the preliminary calculation so that the vapor molecules appeared not only in the region of the bubble surface, but also inside the bulk liquid phase. Our threshold value closely approximated the cavity cluster criteria (1.2σ) chosen by Maruyama [10] and Tsuda [8], and it was slightly lower than that of Whang [12] and Zhukhoviiskii [13] (1.6σ).

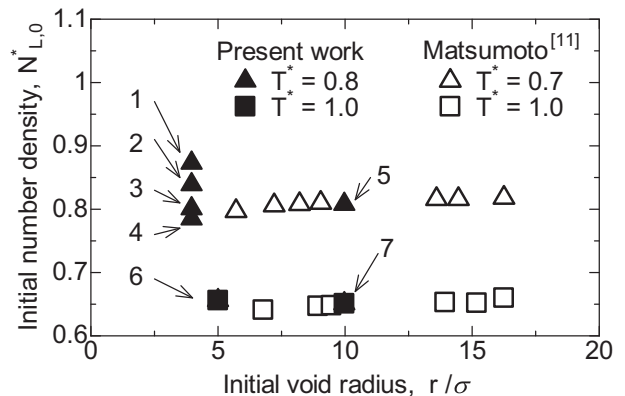


Fig. 2. Liquid number density in comparison with literature.

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