

Nonequilibrium molecular dynamics simulations of a bubble

Hisashi Okumura* and Nobuyasu Ito

Department of Applied Physics, School of Engineering, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

(Received 24 September 2002; published 11 April 2003)

Molecular dynamics simulations are performed to investigate the microscopic dynamics of a bubble when liquids are locally heated. We successfully observe that the heated atoms scatter the neighboring nonheated atoms and make a bubble, and then the bubble is cooled and compressed by the surrounding liquids. The bubble dynamics in this process agrees with the results of the Rayleigh-Plesset equation which describes the dynamics of a bubble in terms of macroscopic hydrodynamics. In this way, we clarify that the hydrodynamic description is reliable even for a microscopic bubble.

DOI: 10.1103/PhysRevE.67.045301

PACS number(s): 47.55.Dz, 64.70.Fx, 02.70.Ns

When liquids are locally heated to a temperature higher than their boiling points, a phase transition occurs from the liquid to gas, i.e., a bubble is created. After the heating is stopped, the surrounding liquids compress the bubble and annihilate it. In order to investigate such bubble dynamics, a hydrodynamic approach has been most frequently used [1–3]. The equation to describe the expansion and contraction of a bubble in terms of hydrodynamics is the Rayleigh-Plesset equation. Continuum hydrodynamics describes the behavior of fluids from a macroscopic point of view.

On the other hand, for the purpose of investigating the fluid behavior from a microscopic point of view, molecular dynamics (MD) simulations of liquids are also performed. There are some papers that discuss the relation between the MD simulations and the hydrodynamic analysis. However, these studies focused on phenomena such as the Rayleigh-Bénard convection [4–6] and the flow pattern behind an obstacle [7,8]. There is no study that compared the MD simulations and the hydrodynamics on the time evolution of a bubble.

This paper presents the discussion of these two methods used to study bubble dynamics. There are a few recent papers that describe making bubbles by MD simulations [9–12], however, a comparison of both methods was not done. We observed the atomic movement at the microscopic level during the entire process from the creation to the extinction of a bubble. We also detect all stages of the bubble dynamics.

An outline of this paper is as follows. First, we describe the MD simulation techniques for the bubble dynamics. Second, the MD simulation results are presented. We also provide a discussion in detail between our MD data and the hydrodynamic results using the Rayleigh-Plesset equation. Finally, our concluding remarks are presented.

In order to investigate the dynamics of a bubble, we performed MD simulations using the Lennard-Jones potential. In the following discussion, the length, the energy, and the mass are scaled in units of the Lennard-Jones diameter σ , the minimum value of the potential ϵ , and the atom mass m .

We used an asterisk (*) for the reduced quantities such as the reduced length $r^* = r/\sigma$, the reduced temperature $T^* = k_B T/\epsilon$, the reduced pressure $P^* = P\sigma^3/\epsilon$, the reduced mass density $\rho^* = \rho\sigma^3/m$, and the reduced time $t^* = t\sqrt{\epsilon/m\sigma^2}$.

Constant pressure MD simulations were performed by the Andersen method under the following conditions [13]. The number of particles N was 16 875 with periodic boundary conditions in the cubic unit cell. The equations of motion were integrated by the sixth-order Gear's predictor-corrector algorithm. The time step was $\delta t^* = 0.005$. The cutoff radius r_c^* was taken as 5.0. A cutoff correction was added for the pressure and potential energy.

The pressure was set at $P^* = 0.076$. The MD simulations were performed at a temperature $T^* = 1.0$ and a density $\rho^* = 0.71$. The boiling point at this pressure is $T_b^* = 1.2$ [14–16]. During the MD simulations, we selected 80 atoms near the center of the simulation cell and instantaneously heated them to $T^* = 11.0$ from $T^* = 1.0$ by velocity rescaling. As a result, the temperature in the area of the heated atoms was much higher than T_b^* . We then observed the atomic movement over 3000 steps.

Figure 1 shows snapshots of the bubble. These snapshots show the atoms that are in a 10% slab of the simulation cell in thickness. This figure shows that the heated atoms scatter the neighboring nonheated atoms and a bubble is created, and then the bubble is cooled and compressed by the surrounding liquid.

We estimated the volume and the radius of the bubble as follows. First, all sides of the simulation cell were divided into 12 sections, therefore, the simulation-cell volume was divided into 12^3 small cubes. The side length ΔL^* of the small cube fluctuated between 2.39 and 2.41 during the constant pressure MD simulations. We calculated the density average for each small cube over 50 time steps. This number of time steps is much smaller than the time scale of the bubble dynamics (~ 1000 steps) and much larger than that of the atomic dynamics (~ 10 steps). We postulated that gas is the region in which the average density in the small cube is less than the critical density $\rho_c^* = 0.316$ and the liquid is the region in which the average density is greater than ρ_c^* [17]. We determined the bubble volume as the sum of the gas region. The bubble is not exactly a sphere, however, it ap-

*Present address: Department of Theoretical Studies, Institute for Molecular Science, Okazaki, Aichi 444-8585, Japan. Electronic address: hokumura@ims.ac.jp

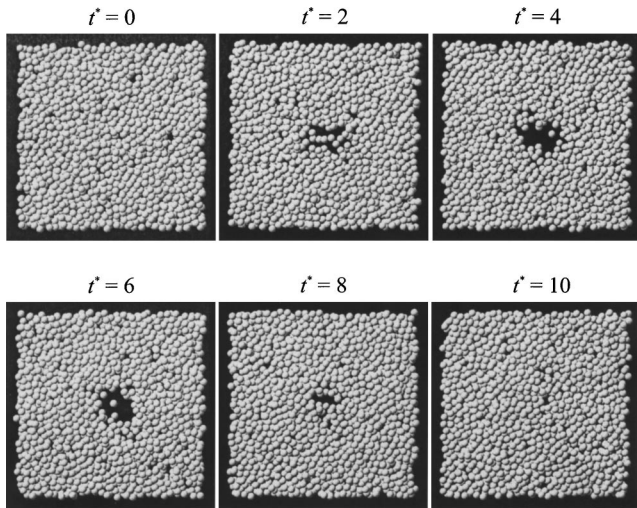


FIG. 1. Snapshots of the bubble. The heated atoms scatter the surrounding nonheated atoms and make a bubble, and then the bubble is compressed by the surrounding liquid.

proximates the spherical shape fairly well. We then calculated the bubble radius R^* from bubble volume V_{bub}^* as

$$R^* = \left(\frac{3}{4\pi} V_{\text{bub}}^* \right)^{1/3}. \quad (1)$$

For the purpose of estimating the statistical accuracies, we performed MD simulations from 15 different initial conditions. The error bar was calculated by the standard deviation of each value of R^* from these different initial conditions.

The time development of the calculated bubble radius is shown in Fig. 2. This figure shows that the bubble immediately grows after the heating. The bubble has the maximum size $R^* = 3.5$ at $t^* = 4.5$ and disappears at $t^* = 9$. The small value of R^* after $t^* = 9$ comes from the density fluctuations in the liquid. It does not imply the existence of small bubbles. The essentially important R^* value is only before $t^* = 9$.

The Rayleigh-Plesset equation in an incompressible and inviscid fluid, which is a hydrodynamic equation for describing the expansion and the contraction of a bubble, is written as

$$R^* \ddot{R}^* + \frac{3}{2} \dot{R}^{*2} = \frac{1}{\rho^*} \left\{ P^*(R^*) - P_\infty^* - \frac{2S^*}{R^*} \right\}, \quad (2)$$

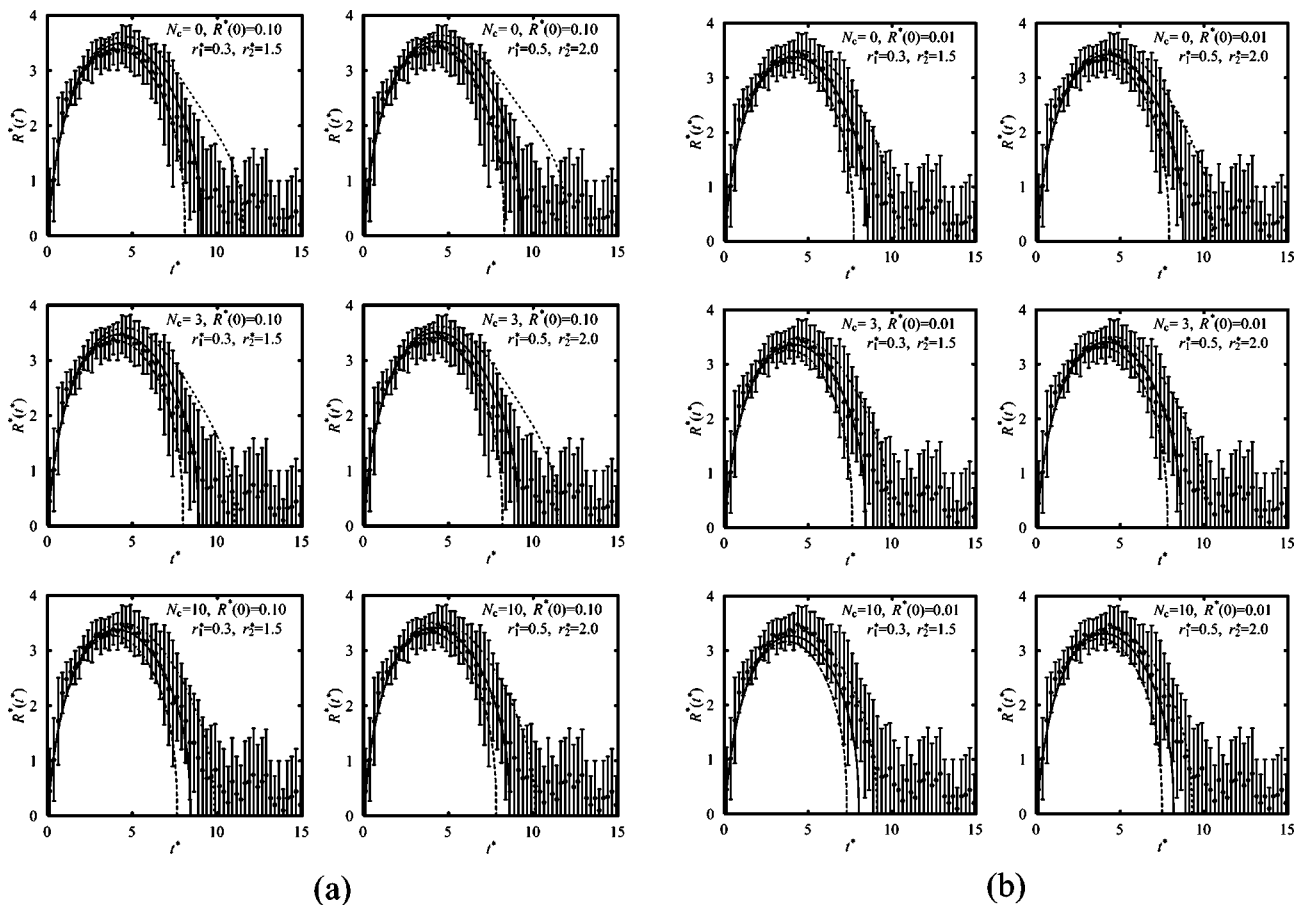


FIG. 2. The time development of the bubble radius $R^*(t^*)$. The filled circle was calculated by the MD simulations. The dotted, solid, and dashed lines were determined by the Rayleigh-Plesset equation for $S_\infty^* = 0.10, 0.15, 0.20$, respectively. The initial radii of the Rayleigh-Plesset equation are (a) $R^*(0) = 0.10$ and (b) $R^*(0) = 0.01$.

where $P^*(R^*)$ is the pressure at the bubble surface and P_∞^* is the pressure far from the bubble in the liquid and S^* is the surface tension of the bubble.

In such a small bubble, whose radius is a few times the atomic diameter, it is difficult to precisely determine $P^*(R^*)$. In this paper, we estimated the number of atoms constituting the bubble surface and calculated the pressure contribution from these atoms. We use this pressure as $P^*(R^*)$. We employed two methods to choose the atoms constituting the surface.

In the first method, we choose N_s atoms near the center of the MD simulation cell. We then computed the pressure from these N_s atoms as

$$P(R) = \frac{\rho}{3} \frac{1}{N_s} \sum_{i=1}^{N_s} [m\mathbf{r}_i^2 + \mathbf{r}_i \cdot \mathbf{F}_i], \quad (3)$$

where the suffix i is in order of the length between the center of the cell and the coordinate \mathbf{r}_i of the i th atom and \mathbf{F}_i indicates the force of the i th atom. We used 80 for N_s , since this is the number of atoms forming the surface whose radius is $R^* = 3$, because $4\pi/3(3^3 - 2^3) \approx 80$.

We believe that the first method gives a reasonable estimate of the pressure at the surface, since there are only a few atoms in the bubble as shown in Fig. 1. However, we employed the second method to verify our result. In order to eliminate the effects of the atoms in the gas, we excluded the contribution of N_c atoms which were closest to the center of the simulation cell from the sum in Eq. (3) as

$$P(R) = \frac{\rho}{3} \frac{1}{N_s - N_c} \sum_{i=N_c+1}^{N_s} [m\mathbf{r}_i^2 + \mathbf{r}_i \cdot \mathbf{F}_i]. \quad (4)$$

We calculated this equation for $N_c = 3$ and 10. Equation (3) is equivalent to Eq. (4) in the limit of $N_c = 0$.

The time evolution of $P^*(R^*)$ is shown in Fig. 3. The difference in $P^*(R^*)$ among these values of N_c is very small. It is only 6% at its maximum. The pressure $P^*(R^*)$ increases until $t^* = 0.04$. This is because some accelerated atoms approach one another and the virial term becomes large. The pressure $P^*(R^*)$ then relaxes to the equilibrium value.

The pressure far from the bubble P_∞^* is 0.076, which is the pressure set in the constant pressure MD simulations.

The surface tension is treated as a fitting parameter in this paper. It varies with the bubble radius. The shorter the radius R^* , the weaker the surface tension S^* [18]. In fact, it smoothly varies, however, for simplicity, we approximated the R^* dependence of S^* using the following form:

$$S^* = \begin{cases} 0 & (0 < R^* \leq r_1^*) \\ S_\infty^*/(r_2^* - r_1^*) & (r_1^* < R^* \leq r_2^*) \\ S_\infty^* & (r_2^* < R^*), \end{cases} \quad (5)$$

where r_1^* and r_2^* are the typical distances at which S^* varies, and S_∞^* is the surface tension of the flat plane. According to Ref. [18], r_1^* and r_2^* are on the order of 0.3–0.5 and 1.5–2.0,

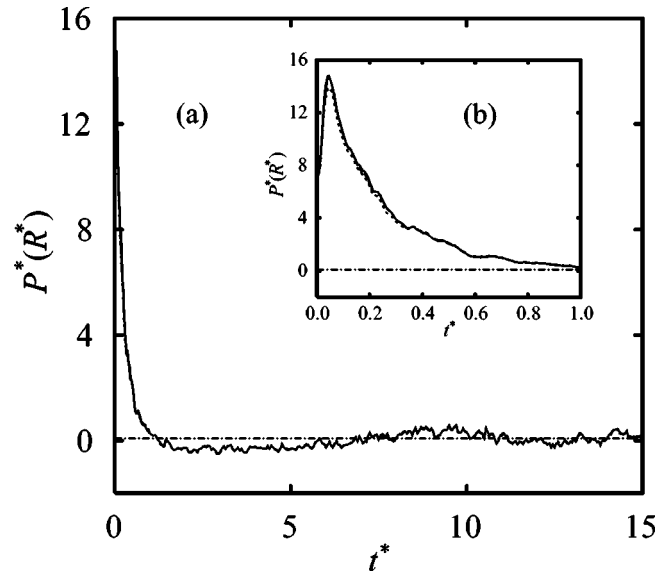


FIG. 3. Time development of $P^*(R^*)$. Solid line: $P^*(R^*)$ for $N_c = 0$. Dashed line: $P^*(R^*)$ for $N_c = 3$. Dotted line: $P^*(R^*)$ for $N_c = 10$. Chain line: the pressure far from the bubble, $P_\infty^* = 0.076$. (a) The pressure $P^*(R^*)$ in the long time scale of $t^* = 0-15$, (b) the pressure $P^*(R^*)$ in the short time scale of $t^* = 0.0-1.0$.

respectively. The surface tension is on the order of $S_\infty^* = 0.1-1.0$ at the $R^* \rightarrow \infty$ limit. We investigated whether the Rayleigh-Plesset equation agrees with the MD simulations using the reasonable values of these surface tensions. We use the three values of $S_\infty^* = 0.10, 0.15, 0.20$ and two pairs of $(r_1^*, r_2^*) = (0.3, 1.5), (0.5, 2.0)$.

In the Rayleigh-Plesset equation, the initial radius $R^*(0)$ must not be zero, since a bubble at zero initial radius cannot grow. To estimate the initial size of the bubble we refer to the size of the gap among the atoms in the equilibrium state. It is evaluated by subtracting the atomic diameter, 1, from the average interatomic distance, $1/\sqrt[3]{\rho^*}$, that is, $(1/\sqrt[3]{\rho^*} - 1) = 0.1$ in the reduced units. For the purpose of investigating the $R^*(0)$ dependence of $R^*(t^*)$, we also employed $R^*(0) = 0.01$ as well as $R^*(0) = 0.1$. The time derivative of the initial radius $\dot{R}^*(0)$ is set to zero. This is because the radius does not change in the equilibrium state.

Figure 2 also shows $R^*(t^*)$ calculated by the Rayleigh-Plesset equation using the parameters described above. This figure indicates that the Rayleigh-Plesset equation agrees with the MD simulations within the error bars in these parameter variations. The parameters that do not change $R^*(t^*)$ very much are N_c , $R^*(0)$, and (r_1^*, r_2^*) . On the other hand, $R^*(t^*)$ is sensitive to the surface tension S_∞^* at $R^* \rightarrow \infty$. With increasing S_∞^* , the bubble radius $R^*(t^*)$ decreases. In the case of $S_\infty^* = 0.15$, the agreement between the MD simulations and the hydrodynamic Rayleigh-Plesset equation is the best. Therefore, even for a microscopic bubble, whose radius is a few atomic diameters, it does not exhibit a singular behavior that cannot be described by the macroscopic hydrodynamics.

In conclusion, microscopic MD simulations were performed to investigate the dynamics of a bubble. We success-

fully observed that heated atoms scattered the neighboring nonheated atoms and made a bubble, and then the bubble was compressed. We compared this bubble dynamics to the Rayleigh-Plesset equation which describes the expansion and contraction of a bubble in terms of macroscopic hydrodynamics. Good agreement was obtained by choosing the appropriate parameters. In this way, we clarified that the hydro-

dynamic description is reliable even for a microscopic bubble.

We thank Professor F. Yonezawa and Professor Y. Okamoto for the valuable discussions. H.O. was supported by the Japan Society for the Promotion of Science for Young Scientists.

-
- [1] M.S. Plesset, *J. Appl. Mech.* **16**, 277 (1949).
[2] N. Xu, L. Wang, and X. Hu, *Phys. Rev. E* **57**, 1615 (1998).
[3] M. Versluis, B. Schmitz, A. van der Heydt, and D. Lohse, *Science* **289**, 2114 (2000).
[4] D.C. Rapaport, *Phys. Rev. Lett.* **60**, 2480 (1988).
[5] M. Mareschal, M. Malek Mansour, A. Puhl, and E. Kestemont, *Phys. Rev. Lett.* **61**, 2550 (1988).
[6] A. Puhl, M.M. Mansour, and M. Mareschal, *Phys. Rev. A* **40**, 1999 (1989).
[7] D.C. Rapaport, *Phys. Rev. A* **36**, 3288 (1987).
[8] S.T. Cui and D.J. Evans, *Mol. Simul.* **9**, 179 (1992).
[9] Y. Kinjo and M. Matsumoto, *Fluid Phase Equilibria* **144**, 343 (1998).
[10] Y. Kinjo, K. Ohguchi, K. Yasuoka, and M. Matsumoto, *Comput. Mater. Sci.* **14**, 138 (1999).
[11] S.H. Park, J.G. Wang, and C.L. Tien, *Int. J. Heat Mass Transf.* **44**, 1849 (2001).
[12] C. Xiao, D.M. Heyes, and J.G. Powles, *Mol. Phys.* **100**, 3451 (2002).
[13] H.C. Andersen, *J. Chem. Phys.* **72**, 2384 (1980).
[14] H. Okumura and F. Yonezawa, *J. Chem. Phys.* **113**, 9162 (2000).
[15] H. Okumura and F. Yonezawa, *Physica B* **296**, 180 (2001).
[16] H. Okumura and F. Yonezawa, *J. Phys. Soc. Jpn.* **70**, 1006 (2001).
[17] H. Okumura and F. Yonezawa, *J. Phys. Soc. Jpn.* **70**, 1990 (2001).
[18] M.P. Moody and P. Attard, *J. Chem. Phys.* **115**, 8967 (2001).