Collapse of a nanoscopic void triggered by a spherically symmetric traveling sound wave

Robert Holyst, † Marek Litniewski, † and Piotr Garstecki

Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland

(Received 10 August 2011; revised manuscript received 2 March 2012; published 14 May 2012)

Molecular-dynamics simulations of the Lennard-Jones fluid (up to $10^7$ atoms) are used to analyze the collapse of a nanoscopic bubble. The collapse is triggered by a traveling sound wave that forms a shock wave at the interface. The peak temperature $T_{\text{max}}$ in the focal point of the collapse is approximately $\Sigma R$, where $\Sigma$ is the surface density of energy injected at the boundary of a container of radius $R_0$ and $\sigma \approx 0.4-0.45$. For $\Sigma = 1.6 \text{ J/m}^2$ and $R_0 = 51 \text{ nm}$, the shock wave velocity, which is proportional to $\sqrt{\Sigma}$, reaches $3400 \text{ m/s}$ (4 times the speed of sound in the liquid); the pressure at the interface, which is proportional to $\Sigma$, reaches $10 \text{ GPa}$; and $T_{\text{max}}$ reaches $40000 \text{ K}$. The Rayleigh-Plesset equation together with the time of the collapse can be used to estimate the pressure at the front of the shock wave.

DOI: 10.1103/PhysRevE.85.056303 PACS number(s): 47.40.Nm, 47.11.Mn, 47.55.dd, 47.61.Jd

I. INTRODUCTION

Collapse of a bubble of vapor [1–5] may create high temperatures, ionization of gas, and emission of light (sonoluminescence) [2–4]. Here we examine the collapse triggered by a traveling sound wave. Our results allow us to postulate the scaling of the maximum temperature with (i) the energy put into the event, (ii) the size of the container, and (iii) the size of the bubble.

Classic experiments are those that study single-bubble sonoluminescence (SBSL) discovered by Gaitan and Crum [6] (see Ref. [2]). A standing wave of small amplitude (120–140 % of the ambient pressure) in a tank filled with degassed water makes a single bubble of micrometric diameter oscillate at the frequency of the wave (e.g., 20 kHz). The collapsing bubble emits pulses of light. The stability of the radial mode of oscillation allowed for measurements of important parameters, e.g., the width of the pulse $\sim 100 \text{ ps}$ [7] and the peak temperature $\sim 10^5 \text{ K}$ [8,9]. Unfortunately, the requirements for stability of SBSL narrow the ranges of parameters (temperature, pressure, frequency, and amplitude of the standing wave) available to change. Reaching higher temperatures (e.g., $\sim 10^6 \text{ K}$ needed for nuclear fusion [10]) necessitates the introduction of alternative experiments and different forcing schemes.

One such paradigm emerges from two different fields: microfluidics [11] and focusing of shock waves [12]. Microfluidics allows one to form bubbles at high rates [13–15], of small size [16], and on demand [17]. These techniques should allow one to replace a single bubble with one bubble at a time: Instead of using standing waves one could synchronize the appearance of bubbles with the accumulation of shock waves, which are known to produce emission of light in air [18]. Progress in this area calls for modeling to guide the design of experimental systems.

Shock waves can produce higher temperatures and increase the intensity of sonoluminescence even by three orders of magnitude in comparison to SBSL [6]. This has been exemplified in in vitro sonoluminescence [19], laser-induced shock wave formation [20], and transient cavitation in high-quality factor resonators at high static pressures [21]. Current modeling is based on the propagation of waves inside the vapor and/or coupling of the Navier-Stokes equations to the Rayleigh-Plesset (RP) equation for the motion of the interface or solutions of the full set of irreversible thermodynamics equations in the two-phase region [22–25]. None of these models is free from presumptions (e.g., about sealing of thermodynamic parameters at the interface) and none can predict how much of the initial energy injected into the system is focused and not dissipated during the collapse. Here we present molecular-dynamics simulations of bubble collapse (free from any a priori assumptions except for the intermolecular potential). This approach allows us to observe and monitor the appearance of the shock wave at the interface; to probe large velocities, pressures, and temperatures; and to analyze the energy dissipation in the system. We use this tool also to test the applicability of the RP equation that is commonly used in theoretical studies of sonoluminescence.

II. SIMULATION METHOD

In a qualitative overview we conduct the simulations as follows. The initial thermodynamic state of the system is a bubble of vapor remaining in coexistence with the liquid, both enclosed in a nanoscopic container [Fig. 1(a)]. The system is large enough ($10^7$ atoms) for the occurrence of a spontaneous phase transition and for modeling the equilibrium coexistence of liquid and vapor. After the system reached equilibrium in a box with periodic boundary conditions, we cut a sphere of radius $R_0$ (equal to half the width of the original simulation box) and apply reflecting boundary conditions at the surface of the sphere [Fig. 1(b)]. Then we trigger a traveling pressure wave by transiently heating up a thin shell adjacent to the boundary (by scaling up all the instantaneous velocities of the Lennard-Jones (LJ) atoms that are within the shell within the short interval) [Fig. 1(c)]. Then we monitor the dynamics of the system.

Specifically, we use the molecular-dynamics constant energy and volume NVE method [26] with a truncated and shifted LJ potential $u(r_{ij}) = 4\epsilon[(\sigma/r_{ij})^{12} - (\sigma/r_{ij})^{6}] + (\sigma/r_{ij})^{12} - (\sigma/r_{ij})^{6}$ for $r_{ij} \leq r_c = 2.5\sigma$, and $u(r_{ij}) = 0$ otherwise, where $r_{ij}$ denotes the distance between atoms, $\epsilon = 140k_B \text{ K}$ is the unit
of energy, $k_B$ is the Boltzmann constant, and the LJ diameter $\sigma = 0.34$ nm sets the length scale. Units of temperature and time are given by $\varepsilon/k_B \approx 140$ K and $t_u = \sigma (m/\varepsilon)^{1/2} \approx 2.0$ ps ($m = 40$ amu is the LJ atom mass), respectively.

Each simulation consists of a series of 15–25 nonequilibrium simulation runs performed in a sphere of radius $R_0$ with reflecting boundary conditions on the surface. We test four system sizes $R_0 = 71.8–72.7$ (small), $R_0 = 78.8–100.8$ (medium), $R_0 = 121.5–124.0$ (large), and $R_0 = 151.5$ (very large) containing $N \approx 10^5, 2.7 \times 10^6, 5.1 \times 10^6$, and $9.3 \times 10^6$ atoms. Each simulation series is preceded by a simulation of a liquid system with the gas bubble of the radius $R$ all enclosed in a cube with width $2R_0$ with periodic boundary conditions. The equilibrium temperature $T_{eq}$ attained by the systems varies from 0.924 to 0.866, the liquid density $\rho_{liq} \in (0.6315, 0.6828)$, and the pressure $p_{liq} \in [(2 \times 10^{-3})–(6 \times 10^{-3})]$. We change the initial bubble radius $R_0$ from 11.8σ to 34.5σ. The initial values of particle positions and velocities for each nonequilibrium simulation run is taken from the equilibrium simulation data by cutting out a sphere of radius $R_0$ with the bubble of initial radius $R_0$ in the center and imposing the reflection condition at the sphere surface. Each run starts at $t = 0$. Within $t \in [0, 0.4]$, we inject energy $\Delta E_{in}$ at the surface of the sphere by scaling up the speeds of atoms within the shell $(R_0 - 5\sigma, R_0)$, creating a radial wave traveling towards the center.

The introduction of the reflecting surface at $R_0$ produces an artifact $\Delta E_{in}$ that is small in comparison to the deliberate injections (less than 15% of the lowest $\Delta E_{in}$). The total surface density of energy $\Sigma = (DE_{in} + DE_{add})/4\rho_0^2$ varies from 7.5 to 102.5. We solve Newton equations with the Verlet scheme [26,27] with a time step $\delta t \approx 10^{-2}\sigma(m/\varepsilon)^{1/2}$ in the initial stage and $\delta t \in [(4 \times 10^{-3})–(3.125 \times 10^{-3})]\sigma(m/\varepsilon)^{1/2}$ in the actual simulations adjusting $\delta t$ to the minimum value of $r_{ij}$ within $8\sigma$ of the center.

III. EVOLUTION OF THE DENSITY, TEMPERATURE, AND PRESSURE PROFILES DURING THE COLLAPSE OF THE BUBBLE

Figure 2 compares the evolution of profiles of density, temperature, and pressure for a small bubble ($R_b = 11.8\sigma$) and a large bubble ($R_b = 28.7\sigma$). We calculate the pressure as the radial component of the Irving–Kirkwood tensor [28]. Upon collapse both the temperature and pressure increase sharply, reaching higher values for the smaller void. Figures 2(i) and 2(j) show the speed of the interface.

The collapses of small and large bubbles differ. Accumulation of energy, i.e., a maximum value of the temperature at the center (at time $t_u$), is over twice as high as for $R_b = 11.8\sigma$ than for $R_b = 28.7\sigma$. Notably, in the case of the small bubble the density at the interface rises above the liquid density and forms a shock wave propagating inward, which is absent in large bubbles. Similar effects are observed in solids where large voids partially fill with molecules from the boundary [as seen in Fig. 2(f)] while small voids collapse without partial filling [as in Fig. 2(a)]. This is because small bubbles collapse in time comparable to the time needed for sound to travel a distance $O(R_b)$, while large bubbles collapse slower.

From the simulation data we obtain the maximum temperature $T_\text{max}$ at the center of the collapsing bubble as a function of (i) the surface density $\Sigma$ of energy injected into the system, (ii) the size of the container $R_0$, and (iii) the size of the bubble $R_b$:

$$T_\text{max} \approx \Sigma f(R_b, \Sigma)R_0^2,$$

where $f$ is a slowly changing function of $\Sigma$, $\alpha \in [0.40, 0.45]$, and the relative error of Eq. (1) decreases with increasing $\Sigma$. In the simulation we define $T_\text{max}$ as the maximum value of temperature calculated from the total kinetic energy of particles in the sphere of the radius $3\sigma$ around the center (Fig. 3).

In Fig. 4 we use the relation (1) to graph the data obtained for a wide range of $R_b$, $R_0$, and $\Sigma$. From the plot of $T_\text{max}$ against $R_b$ we found that $\partial f/\partial R_b|_\Sigma$ is always negative (see Figs. 4 and 5). The relative decrease in $T_\text{max}$ is more pronounced for larger $R_b$, while $f^{-1}(\partial f/\partial R_b)|_\Sigma$ slowly converges to zero with increasing $\Sigma$ (Fig. 5).

The shock wave created at the boundary of the collapsing bubble bounces back after the collapse (Fig. 6). The shock wave moves at a speed that exceeds four times the speed of sound and carries, at its front, density and pressure that exceed the ambient values by orders of magnitude. The wave bounces...
COLLAPSE OF A NANOSCOPIC VOID TRIGGERED BY A . . .

PHYSICAL REVIEW E 85, 056303 (2012)

FIG. 2. Profiles of density, temperature, and pressure for initial radius (a)–(c) $R_b = 11.8$ and (f)–(h) $R_b = 28.7$ at different instants after injection of energy into the system: $t_2 = 8.76$ (solid line), $t_1 = 11.48$ (short-dashed line), $t_2 = 12.60$ (dash-dotted line), $t_3 = 13.72$ (long-dashed line), and $t_4 = 14.04$ (dotted line) for $R_b = 11.8$ and $t_0 = 4.76$, $t_1 = 7.96$, $t_2 = 14.36$, $t_3 = 17.56$, and $t_4 = 18.52$ for $R_b = 28.7$. At $t = t_4$ the temperature attains its maximum value. (d), (e), (i), and (j) After reaching the interface the sound wave travels with the interface. The location of (d) and (i) the interface $R(t)$ and (e) and (j) its velocity $dR(t)/dt$ in the same simulations was measured by tracing three points of densities $\rho_{\text{liq}}/2 - 0.1$, $\rho_{\text{liq}}/2$, and $\rho_{\text{liq}}/2 + 0.1$ at the front of the wave and taking the average in order to reduce errors. (d) and (e) For the small bubble $dR(t)/dt$ finally exceeds even the speed of sound in liquid $c (\cong 5$ in these units) or $[29] 813\text{ m/s at } T \cong 87\text{ K}$, whereas the speed of sound in the vapor is 1.2). The pressure at the front exceeds the ambient pressure by more than three orders of magnitude. The parameters are $R_b = 72.7$, $\Sigma = 7.5$, starting from $\rho_{\text{liq}} = 0.6315$, $T_{\text{eq}} = 0.9235$, and $\rho_{\text{liq}} = 0.005$ for $R_b = 11.8$ and $R_b = 71.8$, $\Sigma = 7.5$, $\rho_{\text{liq}} = 0.6763$, $T_{\text{eq}} = 0.8734$, and $\rho_{\text{liq}} = 0.004$ for $R_b = 28.7$. The velocity of the interface scales as a square root of the energy injection per unit area $\Sigma$ and pressure scales linearly with $\Sigma$.

At later times the wave bounces back and after few oscillations a final state of the system with uniform density, pressure, and temperature is reached.

FIG. 3. Maximum value of the kinetic temperature at the center of the collapsing bubble $T_{\text{max}}$ (calculated from the sphere of the radius $3\sigma$ around the system center) scaled by $\Sigma R_0^2$ as a function of the surface density $\Sigma$ of injected energy. The scaling exponent $\alpha = 0.42$. The bubble radius (a) $R_b = 15.2$ and (b) $R_b = 19.8$. The data are represented as follows: open squares, small systems ($R_b \approx 72.3$); up-pointing open triangles, medium systems ($R_b \approx 100.4$); down-pointing open triangles, large systems ($R_b \approx 123.5$); and solid circles, very large systems ($R_b = 151.5$).

back and forth several times until the system equilibrates to uniform density, pressure, and temperature.

IV. COMPARISON OF THE COMPUTER SIMULATIONS WITH THE SOLUTION OF THE RAYLEIGH-PLESSET AND KELLER EQUATIONS

It is well known that RP equation does not correctly describe the motion of the interface moving at speeds exceeding the speed of sound in the liquid. Nonetheless, this equation is frequently used to model the evolution of the radius $R(t)$ of a bubble during collapse [30,31]. Here we compare the evolution of the terms in the RP equation with the analogous terms recorded in our simulations. We use the RP equation in a simplified form

$$R \frac{d^2 R}{dt^2} + \frac{3}{2} \left( \frac{dR}{dt} \right)^2 = -\frac{p(t)}{\rho_{\text{liq}}}, \quad (2)$$

which assumes that the dominant term on the right-hand side comes from the liquid pressure $p(t)$. The simplification is fully justified since the terms containing the surface tension, the liquid shear viscosity, and the gas pressure are of low importance for LJ liquids even for the freely collapsing voids [30].

We solve Eq. (2) numerically taking $p(t)$ as the maximum value of pressure at the front of the wave [Figs. 2(c) and 2(g)]. This pressure is three to five orders of magnitude larger than the equilibrium pressure in the liquid $\rho_{\text{liq}}$, usually used in Eq. (2).
FIG. 4. Maximum value of the temperature at the center of the bubble $T_{\text{max}}$ scaled by $R_0^{0.42}$ (as in Fig. 3) as a function of $R$ for $\Sigma = 7.5, 13.6, 19.7, 24.6,$ and $31.7$. The data are represented as follows: open squares, small systems; open triangles, medium systems; and solid triangles, large systems. The value of $T_{\text{max}} R_0^{0.42}$ is approximately proportional to $\Sigma$ (see Fig. 2).

The value $p(t)$ has a physical meaning only for $t < \tau$, where $\tau$ is the collapse time.

Since Eq. (2) overestimates the collapse time, we need to extrapolate $p(t)$ for $t > \tau$. We take $p(t > \tau) = p(\tau)$, i.e., the maximum value of $p(t)$ during the collapse. Table I shows the results: The RP equation overestimates the time of collapse by 30–50%. The analysis of the left-hand side of Eq. (2) shows (Fig. 7) the main reason for the overestimation of the collapse time by the RP equation. The wave strongly accelerates at the gas-liquid interface. As a consequence, there is a sharp minimum at large negative values in $R(d^2 R/dt^2) + (3/2)(dR/dt)^2$, in disagreement with the right-hand side of Eq. (2). This acceleration results in a significant decrease of $\tau$ in comparison to the solution of the RP equation.

We try also to estimate $\tau$ by solving numerically the Keller equation [32,33]

$$\left(1 + \frac{1}{c} \frac{dR}{dt}\right) R \frac{d^2 R}{dt^2} + \frac{3}{2} \left(1 - \frac{1}{3c} \frac{dR}{dt}\right) \left(\frac{dR}{dt}\right)^2 = -1/\rho_{\text{liq}} \left(1 - \frac{1}{c} \frac{dR}{dt} + \frac{R}{c} \frac{dR}{dt}\right) p(t),$$

where $c$ is the speed of sound in the liquid and, as in Eq. (2), $p(t)$ gives the dominant term. Unfortunately, Eq. (3) gives nonphysical results. Its right-hand side is valid to $O(1/c^2)$ and the approximation fails since $(dR/dt)/c$ is no longer a small correction that happens at times larger than about $\tau/2$ (see Table I). The description by the Keller equation also does not lead to any improvement in comparison to the RP equation. At the

TABLE I. Total time of collapse from simulations $\tau$ for $\Sigma = 7.5$ and from the RP equation $\tau_{\text{RP}}$ for different initial radius $R_0$ of the bubble. In order to obtain the time of the collapse correctly we had to replace the ambient pressure usually used in Eq. (2) for a free collapse of the bubble [30] by the three orders of magnitude larger pressure at the front of the collapsing wave. In fact, Eq. (2) can be used to estimate the actual pressure from the knowledge of the collapse time.

<table>
<thead>
<tr>
<th>System size</th>
<th>$R_0$</th>
<th>$\tau_{\text{RP}}$</th>
<th>$\tau$</th>
</tr>
</thead>
<tbody>
<tr>
<td>small</td>
<td>11.8</td>
<td>4.0</td>
<td>3.1</td>
</tr>
<tr>
<td>small</td>
<td>20.4</td>
<td>8.8</td>
<td>6.3</td>
</tr>
<tr>
<td>small</td>
<td>28.7</td>
<td>16.9</td>
<td>11.3</td>
</tr>
<tr>
<td>large</td>
<td>34.5</td>
<td>17.5</td>
<td>12.7</td>
</tr>
</tbody>
</table>
possible. We hope that the results of the collapse of nanoscopic bubbles triggered by traveling sound waves initiated at the boundary of the container by laser heating [20] in miniaturized microfluidic devices will allow for significant progress in reaching the maximum temperatures orders of magnitude larger than the presently attainable $10^4$ K.

**ACKNOWLEDGMENTS**

This work was supported by the Ministry of Science and Higher Education/European Science Foundation - Physical and Engineering Sciences program “Exploring Physics of Small Devices” and by the Project operated within the Foundation for Polish Science Team Programmes cofinanced by the EU European Regional Development Fund Contract No. TEAM/2008-1/1.

[34] V. Babin and R. Holyst, http://pepe.ichf.edu.pl/diffuse-interface/condensation.html. The movie on this web page shows the solutions of the irreversible thermodynamics in the two-phase region without any a priori assumptions concerning the interface. It shows the evolution of the density and temperature of the traveling sound wave for high vapor pressure inside the bubble.