Coalescence Preference Depends on Size Inequality

Byung Mook Weon* and Jung Ho Je†

X-ray Imaging Center, Department of Materials Science and Engineering, Pohang University of Science and Technology, San 31, Hyoja-dong, Pohang 790-784, Korea

(Received 12 October 2011; published 29 May 2012)

During bubble or droplet coalescence, there is a puzzling tendency for the coalesced bubble or droplet to be preferentially placed closer to the larger of its two parents. We confirm that this preference is a function of parent size ratio by directly visualizing coalescing air bubbles on an oil-water interface and coalescing water droplets immersed in oil. We find that the final position of the coalesced sphere is controlled by surface energy release and is related to the parent size ratio by a power-law relationship.

DOI: 10.1103/PhysRevLett.108.224501 PACS numbers: 47.55.df, 47.55.D-, 47.57.Bc, 47.55.N−

Bubbles and droplets are important systems because of their fundamental properties and practical applications. Bubbles [1−8] and droplets [9−19] show interesting coalescence behaviors. The coalescence process—the tendency for two touching spheres to form a single larger sphere—occurs as a result of the surface energy minimization. The coalescence dynamics are important for a number of industrial processes involving foams and emulsions, from salad dressings to oil recovery, as well as in natural processes such as volcanic magmas [20] and raindrops [21]. In coalescence dynamics, the size inequality of the parent droplets plays a significant role in mass transport and topological change [2,14] due to the capillary pressure difference \( \Delta p = 2\gamma(r_S^{-1} - r_L^{-1}) \) between the droplets, where \( \gamma \) is the interfacial tension and \( r_S \) and \( r_L \) are the radii of two parents (\( r_S < r_L \) denotes the size inequality) [14]. The pressure difference drives capillary waves that carry momentum, whereas the fluid viscosity dissipates capillary waves and reduces the drainage rates from small to large parents [14]. A larger parent size ratio induces a larger pressure difference and helps overcome larger viscous stresses [14]. It is conceivable that the pressure difference created by the size inequality would cause a merged sphere to be preferentially oriented toward a larger parent sphere, as can be inferred from the drop coalescence [16−19]. However, detailed information about the physics that underlies the coalescence preference is lacking.

To gain insight into the coalescence preference, the detailed geometry of the process and the mechanical interactions between neighboring spheres must be observed. The conventional protocols for bubble experiments [1−4] use tiny nozzles to position parent bubbles. However, bubble pinning at the nozzles biases the coalescence process, meaning that a new experimental method is necessary if we wish to fully understand the coalescence dynamics. We have developed a feasible method to directly visualize coalescing air bubbles on a domed oil-water interface, based on x-ray imaging with the spatially coherent x-rays emitted by a synchrotron source [22]. This x-ray imaging technique delineates the boundaries of very small bubbles and makes it possible to measure coalescence geometry with high accuracy.

In this Letter, we report experimental confirmation of coalescence preference in both bubble and droplet systems. We demonstrate that this preference is a function of the parent size ratio through direct visualizations of (i) coalescing air bubbles on an oil-water interface and (ii) coalescing water droplets immersed in oil. Our main results show that the merged sphere position is critically dependent upon the parent size ratio \( r_L/r_S \); as the ratio increases, the merged sphere position becomes closer to the larger parent position. This dependence on parent size ratio is found to follow a power-law scaling for both bubbles and droplets. We find that the coalescence preference is enhanced by the size inequality and is attributable to the surface energy released during the coalescence process.

Experiments.—For bubbles, we used an oil-water interface in a plastic container [Fig. 1(a)] to largely suppress the influence of gravity [22]. After injection into water, microscopic air bubbles rise up to the oil-water interface; they then move along the interface towards its domed center due to their gravitation buoyancy \( f_b \). A simple force balance between \( f_b \) and the surface tension force \( f_S \) [23] for the three-phase system of air bubbles, oil, and water suggests that smaller bubbles have a higher sphericity [22]. At the raised center of the interface, rising bubbles coalesce together and the coalescence events were monitored with side-view x-ray imaging (from the PLS 7B2 beam line in Pohang, Korea) [22]. For comparison between bubbles and droplets, we worked on top-view optical imaging of coalescing water droplets immersed in oil (decalin) on the hydrophobic surface of a Petri dish with a water contact angle \( \sim 90^\circ \) [Fig. 1(b)]. The oil phase prevents water evaporation into the atmosphere.

High sphericity appears when gravitational effects are negligible with respect to surface tension effects. This is true if \( r \ll l = (\gamma/\Delta p g)^{1/2} \), where \( l \) is the capillary length, \( r \) is the sphere radius, \( \gamma \) is the interfacial tension (36 mN/m for bubbles and 51 mN/m for droplets), \( \Delta p \) is...
the sphere-medium density difference (800 kg/m$^3$ for bubbles and 100 kg/m$^3$ for droplets), and $g$ is the gravity acceleration (9.8 m/s$^2$). Thus high sphericity will occur when $r/l \sim 0.1$, so bubbles with $r < 0.2$ mm and droplets with $r < 1$ mm (as observed in our experiments) can be taken to be spherical. At the moment of coalescence, mass is conserved with $m_M = m_S + m_L$, where $m_S$ and $m_L$ refer to the smaller and larger spheres just before coalescence and $m_M$ to the final product. Using $m = 4\pi pr^3/3$, and assuming the typical relationship $(\rho - \rho_0) = k(p - \rho_0)$ [22], the mass conservation relationship is given as $(r_M^3 - r_S^3 - r_L^3) = -2\gamma k/\rho_0$ ($r_M^2 - r_S^2 - r_L^2$). The proportionality $k \sim 10^{-5}$ for air and $\sim 0.2$ kg/m$^3$/MPa for water at 300 K [24], so this expression can be simplified to $r_L^3 = r_S^3 + r_M^3$, as $2\gamma k/\rho_0$ is negligible. The mass conservation is valid for the parent size ratios of interest ($1 < r_L/r_S < 3$) when there is no satellite generation (that is, by enforcing the “no pinch-off” condition [2,7]). As a result, sphere coalescence events take place under conditions of high sphericity and mass conservation (see movies in [25]).

Coalescence geometry.—To describe the relative position of the merged sphere, $a_L/a_S$ is defined as the distance from the larger (smaller) parent center to the closest point on the line linking the parent centers to the position of the merged sphere center [Fig. 1(c)]. How is the relative position $a_L/a_S$ measured? Consider a triangle with its corners being the centers of the parent spheres and the merged sphere. The side lengths are then $a$, $b$, and $c$ [Fig. 1(c)]. Here, three important geometric constraints are given: (i) all spheres contact the ground interface, (ii) $r_S^3 + r_L^3 = r_M^3$, and (iii) $a = r_S + r_L = a_L + a_S$. The lengths $a_L = a - a_S$ and $a_S = c \cos \beta$ are determined by the side $c$ and the angle $\beta$ (between the sides $a$ and $c$). Because $\cos \beta = (a^2 + c^2 - b^2)/2ac$, the relative position $a_L/a_S$ can be measured through the side lengths:

$$\frac{a_L}{a_S} = \frac{a^2 + b^2 - c^2}{2ab}.$$

Here, the relative position $a_L/a_S$ is a function of the parent size ratio $r_L/r_S$ if and only if $a$, $b$, and $c$ are functions of $r_L/r_S$. $a_L/a_S$ can be precisely measured with side-view x-ray imaging (Fig. 2). Alternatively, the top-view visualization can be used to obtain the projected relative position on the ground interface $d_L/d_S$ [Fig. 1(c)], which provides a good approximation to $a_L/a_S$ (when $a_L/a_S > 10^{-2}$ by the small-angle approximation).

Bubble coalescence.—The relative position of the merged bubble $a_L/a_S$ is strongly dependent upon the parent bubble size ratio $r_L/r_S$ (Fig. 3 and Movie 2 [25]). This result confirms that the merged bubble becomes closer to the larger parent bubble ($a_L/a_S \downarrow$) as the parent size

---

**FIG. 1** (color online). (a) Coalescing bubbles. A domed oil-water interface in a plastic vessel traps air bubbles that then move along the interface toward the top, inducing bubble-bubble coalescence events. (b) Coalescing droplets. Water droplets immersed in oil on the hydrophobic surface of a Petri dish show droplet-droplet coalescence events. Coalescence events are directly visualized with x-ray and optical imaging methods. (c) Coalescence geometry. The relative position of the merged sphere $a_L/a_S$ is measured through the relations $a_S = a - a_L$ and $a_L = c \cos \beta$ and the side lengths $a$, $b$, and $c$ as a function of the parent radius ratio. The projected relative position on the ground interface $d_L/d_S$ is a good approximation to $a_L/a_S$.

---

**FIG. 2** (color online). (a) Schematic view of x-ray imaging. (b) Coalescence of two similar-sized bubbles (Movie 1 [25]). (c) Coalescence of many bubble systems (Movie 2 [25]). (d) The relative position of the merged bubble $a_L/a_S$ is measured with the parent bubble size ratio $r_L/r_S$ by subtracting the images before and after coalescence using IMAGE-PRO PLUS software (Media Cybernetics).
ideal case of two spheres (with radii $r_L$ and $r_S$) and surface energy $\gamma$). The power-law relationship between $a_L/a_S$ and $r_L/r_S$ with the exponent $p = 5.0849 \pm 0.4344$ (solid line; correlation coefficient; $R = -0.9494$) confirms that the merged bubble becomes closer to the larger parent bubble ($a_L/a_S \approx 1$) as the parent size ratio increases ($r_L/r_S \uparrow$). Here, $d_L/d_S$ can be seen to be a good approximation to $a_L/a_S (<10^{-2})$ (inset; solid line). Scale bar, 200 $\mu$m.

ratio increases ($r_L/r_S \uparrow$). Importantly, in the log-log scale of Fig. 3, the data seem to be well aligned, indicating the power-law relationship:

$$(a_L/a_S) \sim (r_L/r_S)^{-p}.$$ 

Here, the exponent $p = 5.0849 \pm 0.4344$ (fitted with a high correlation coefficient $R = -0.9494$) is found for the first time in this work. Notably, $d_L/d_S$ provides a good estimate for $a_L/a_S$ (especially for $a_L/a_S > 10^{-2}$) as seen in Fig. 3 (inset), where the solid line gives $d_L/d_S = a_L/a_S$.

Droplet coalescence.—For water droplets, we measured the relative position of the merged droplet $d_L/d_S (= a_L/a_S)$ from top-view optical imaging of coalescing water droplets suspended in oil (decalin) on the hydrophobic surface of a Petri dish (Fig. 4 and Movie 3 [25]). The power-law exponent $p = 4.3279 \pm 0.5414$ ($R = -0.9116$) supports the coalescence preference for droplets.

Theory.—The coalescence motions are, after initial neck growth [9,10,26–28], controlled by the slow release of surface energy $\gamma \Delta s$ ($s$ is the surface area) [27,28]. For an ideal case of two spheres (with radii $r_L$ and $r_S$) that form a new sphere (with radius $r_M$), the mass conservation dictates $r_M = (r_L^3 + r_S^3)^{1/3}$ [22,28]. The mass movement to the position of the merged sphere ($a_L$ or $a_S$) would be proportional to the kinetic energy ($k$) gained from the surface energy difference between the parent and the merged spheres. The relative kinetic energy corresponds to the fraction of the surface energy difference as $k_L \sim [(s_M - s_L)/s_L]$ for the large parent and $k_S \sim [(s_M - s_S)/s_S]$ for the small parent. The kinetic energy ratio $k_L/k_S$ is then given as

$$(k_L/k_S) = (s_M - s_L)/(s_M - s_S) = (r_L/r_S)^{-3/2}.$$ 

Here, $k_L$ or $k_S$ depends only on $r_L/r_S$ and their ratio $k_L/k_S$ equals $0.99(r_L/r_S)^{-5/3}$, as depicted by the solid line in Fig. 5. We find good agreement in $k_L/k_S = a_L/a_S$ (or $d_L/d_S$), suggesting that the coalescence preference is indeed controlled by the topological change by the energy release. Interestingly, our bubble systems are closer to the ideal case than are the droplet systems.

An obvious alternative is the center of mass (c.m.) theory. If the merged sphere is placed at the c.m. between the two parents, the relative position is given by the simple relationship $m_S u_S = m_L u_L (u = u_S + u_L)$, where $u_S$ is the separation between the small mass $m_S$ and the c.m. and $u_L$ is the separation between the large mass $m_L$ and the c.m. The simple relation leads to $u_S = m_L u_L/(m_S + m_L)$ and $u_L = m_S u_S/(m_S + m_L)$. Therefore, the predicted relative position is $u_L/u_S = (m_L/m_S)^{-1} = (r_L/r_S)^{-3}$ (where we have used $m = 4\pi \rho r^3/3$). The c.m. theory cannot explain our observations, as illustrated in Fig. 5 (dashed line).

The geometric preference of individual coalescence events is important in global assemblies of bubbles or droplets. The coalescence preference would be responsible for the continuous growth of a large bubble at the gradual expense of small bubbles (Fig. 3 and Movie 2 [25]), implying that “the rich get richer.” This quite possibly will have a significant effect on the global evolution of bubble and droplet systems.

Finally, we consider two limit cases in terms of $r_L/r_S$. A limit case is $r_L/r_S \to \infty$ (infinite parent size ratio). Our finding of $a_L/a_S \sim (r_L/r_S)^{-5}$ suggests that $a_L/a_S \to 0$ as $r_L/r_S \to \infty$, implying that the small parent is shifted into the infinite (flat) parent [2,7]. Another limit case is $r_L/r_S \to 1$ (equal-sized case), corresponding to
that the merged sphere position is a function of the parent size ratio through direct visualizations of coalescing systems. We measured this preference as a function of the fluid viscosity [26].

Energy release holds regardless of the existence of a ground interface. The universal nature of the coalescence preference requires further studies in terms of fluid wettability [17] or fluid viscosity [26].

In conclusion, we have experimentally confirmed the coalescence preference that a merged sphere is placed closer to a larger parent sphere in both bubble and droplet systems. We measured this preference as a function of the parent size ratio through direct visualizations of coalescing air bubbles on an oil-water interface and of coalescing water droplets immersed in oil. Our main results show that the merged sphere position is a function of the parent size ratio $r_L/r_S$ ($r_S < r_L$). The preferential positioning of the merged sphere is described by a power-law relationship $a_L/a_S \sim (r_L/r_S)^{-3}$ with the relative lengths $a_S$ and $a_L$ from the smaller and the larger parent positions. This power-law scaling is in good agreement with the surface energy release model, described as the kinetic energy ratio $k_L/k_S \sim (r_L/r_S)^{-5.3}$. The coalescence preference should be universally important in understanding the stability and the statistics of coalescing bubbles and droplets.

This research was supported by the Creative Research Initiatives (Functional X-ray Imaging) of MEST/NRF.

*bmweon@hotmail.com

†hje@postech.ac.kr