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Equilibrium morphology of gas–liquid Janus droplets: A numerical analysis of buoyancy effect☆

Shaobin Zhang¹, Helen Yan², Yuhao Geng¹, Ke Wang³, Jianhong Xu^{1,*}

¹ The State Key Lab of Chemical Engineering, Department of Chemical Engineering, Tsinghua University, Beijing 100084, China

² College of Chemistry, University of California, Berkeley, CA 94728, USA

³ State Key Laboratory of Industrial Vent Gas Reuse, The Southwest Research & Design Institute of the Chemical Industry, Chengdu 610225, China



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ABSTRACT

In this article, a theoretical model for predicting the equilibrium morphology of gas–liquid Janus droplets was built. Based on this model, the effects of bubble radius and volume ratio on morphology change was systematically studied. The increase of bubble radius causes the two parts (bubble and oil drop) in Janus droplets tend to merge while the impact of volume ratio is complicated. When volume ratio increases, these two parts firstly tend to merge, then gradually separate. The accuracy of this model was verified by experimental results.

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1. Introduction

Emulsions are attracting extensive interests because of their potential applications in various fields [1–6]. Most of these researches are focused on microfluidic methods because microfluidics permits better control of the experimental conditions [7, 8] than other methods. Up to now, double emulsions are still the research focus within applications for emulsions, and a large number of investigations have been reported [9–13].

According to the value of spreading coefficients [14–17], there are three typical structures for double emulsions: core-shell, Janus, and totally separated. For different morphologies, there are different applications such as capsules for core-shell [16–19]. It is worth noting that Janus droplets are attracting more attention because of their unique anisotropic properties, which make them suitable for use in numerous applications [20–24]. For Janus droplets, the structure can be further adjusted as long as the spreading coefficients are in the exact range for Janus morphology [25]. Depending on the separation degree of two components, Janus droplets can be categorized into several types such as “perfect Janus emulsions”, “Dumbbell Janus emulsions”, etc. [26]. Also, Janus morphology could have an

important effect on their promising application. For example, the two parts in “perfect Janus droplet” are hemispherical, and they constitute a spherical Janus droplet, which has the potential to be used in display screen [27].

The equilibrium morphology of Janus droplets prepared by microfluidic methods is a result of force balance with three interfacial tensions. Some researchers have made a detailed analysis about equilibrium topology of Janus droplets. According to their models [28–30] for liquid–liquid Janus droplets, there are only two factors influencing the equilibrium morphology: interfacial tensions and two-phase volume ratio. Buoyancy and gravitational effects were neglected in these examinations. However, this theoretical model may be not suitable for gas–liquid Janus droplets because gas–liquid density difference is far greater than liquid–liquid density difference. Thus, it is necessary to make modifications to the previous model and build a new one that takes the effect of buoyancy into account.

In this article, we demonstrated that buoyancy need to be considered when the radius of microbubble is sufficiently large (>300 μm). Hence, we built a new model to predict the equilibrium morphology of gas–liquid Janus droplets by making modifications to the liquid–liquid model. Furthermore, the effects of volume ratio and microbubble radius on the morphology of gas–liquid Janus droplets were investigated. Finally, the theory model was verified by experimental results. The microfluidic device used is the same as the one (see supplementary material) we used in our previous work [31].

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* Corresponding author.

E-mail address: xujianhong@tsinghua.edu.cn (J. Xu).

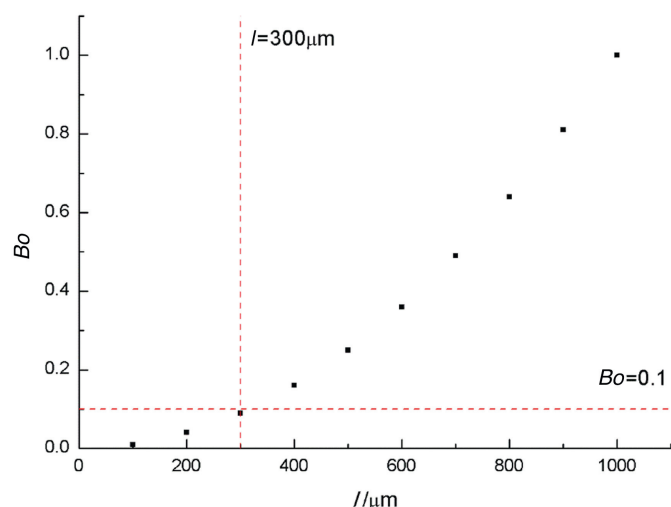


Fig. 1. The relationship between Bond number and characteristic length.

2. Fundamental Background

2.1. Preliminary calculation

Local Bond number [32] ($Bo = \Delta\rho g l^2 / \gamma$) can be used to assess the buoyancy effect, where $\Delta\rho$, g , and l represent density difference, gravitational constant, and the characteristic length of three phase contact line.

There are three phases in our experiments: air, oil, and water (A, O, and W represent air, oil, and water respectively). To simplify the calculation, we take the density of water (ρ_W) as the density difference between air and water (ρ_{AW}). The interfacial tension between oil and water (γ_{OW}) was used for calculation as it is the least of three interfacial tensions. Thus, $Bo = \rho_W g l^2 / \gamma_{OW}$. The value of (γ_{OW}) adopted is $10 \text{ mN} \cdot \text{m}^{-1}$, which is representative in experimental systems. As shown in Fig. 1, the buoyancy effect can't be neglected when the characteristic length l is larger than $300 \mu\text{m}$. At that time, Bond number is larger than 0.1, which means buoyancy is at the comparable magnitude order with interfacial tension. Thus, it is meaningful to investigate the buoyancy effect on the equilibrium morphology when microbubble grows to a certain size ($>300 \mu\text{m}$).

2.2. Theoretical model

Generally, the equilibrium morphology for gas–liquid Janus droplet is determined by two factors: the force equilibrium between interfacial tensions and buoyancy and the volume ratio of the two phases in the Janus droplet. However, buoyancy in this case is influenced by many parameters (see Eqs. (4)–(6)) such as the radius of the bubble in the Janus droplet, which makes the actual situation more complicated.

Fig. 2 demonstrates the force analysis and geometry analysis of a Janus droplet that is in equilibrium morphology (A, O, and W represent air, oil, and water respectively.) All the interfaces are assumed as sphere caps according to the references.

For force analysis:

$$\gamma_{AW} \cdot \sin\theta_1 + \gamma_{OW} \cdot \sin\theta_2 = \gamma_{AO} \cdot \sin\theta_3 \quad (1)$$

$$(\gamma_{AW} \cdot \cos\theta_1 - \gamma_{OW} \cdot \cos\theta_2 - \gamma_{AO} \cdot \cos\theta_3) \cdot L_c + F_B = 0 \quad (2)$$

Where γ_{AW} represents the interfacial tension between air and water, the same goes for γ_{OW} and γ_{AO} . F_B is the buoyancy, and L_c is the perimeter of contact line. θ_1 is the angle between γ_{AW} and vertical axis. θ_2 is the angle between γ_{OW} and vertical axis. θ_3 is the angle between γ_{AO} and vertical axis.

$$L_c = 2\pi \cdot r_{AW} \cdot \cos\theta_1 \quad (3)$$

Where r_{AW} represents bubble radius, the same goes for r_{OW} and r_{OA} .

$$F_B = V_O \cdot \rho_{OW} \cdot g + V_A \cdot \rho_W \cdot g \quad (4)$$

In Eq. (4), ρ_{OW} represents the density difference between oil and water. V_O and V_A represent the volume of oil part (oil drop, red) and gas part (bubble, green), and they can be obtained by combining the spherical canopy volume formula and the geometry relationship.

$$V_O = \frac{\pi \cdot r_{OW}^3 \cdot (2 \cdot (1 - \cos\mu) - \sin^2\mu \cdot \cos\mu)}{3} - \frac{\pi \cdot r_{OA}^3 \cdot (2 \cdot (1 - \cos\epsilon) - \sin^2\epsilon \cdot \cos\epsilon)}{3} \quad (5)$$

$$V_A = \frac{\pi \cdot r_{AW}^3 \cdot (2 \cdot (1 + \cos\eta) + \sin^2\eta \cdot \cos\eta)}{3} + \frac{\pi \cdot r_{OA}^3 \cdot (2 \cdot (1 - \cos\epsilon) - \sin^2\epsilon \cdot \cos\epsilon)}{3} \quad (6)$$

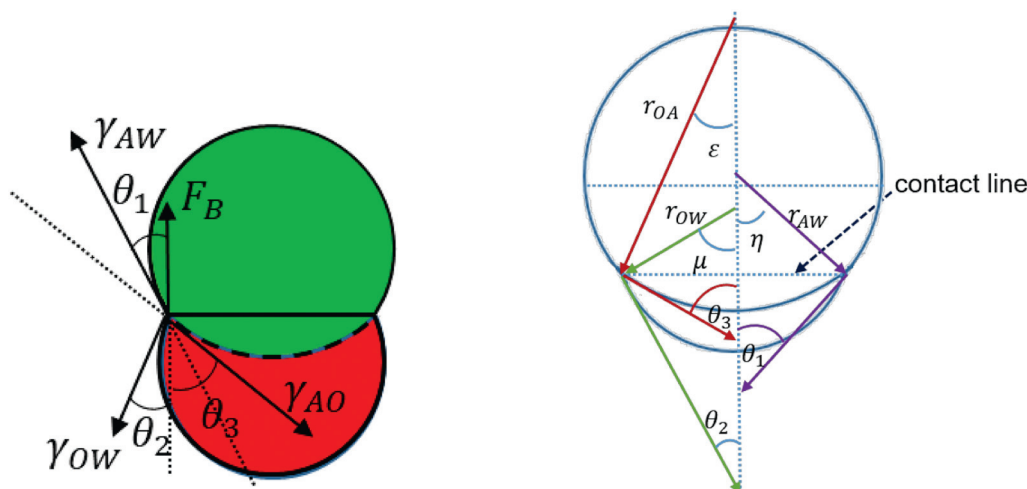


Fig. 2. Force analysis(left) and geometry analysis(right) for a Janus droplet. The upper part represents bubble while the lower part represents oil droplet.

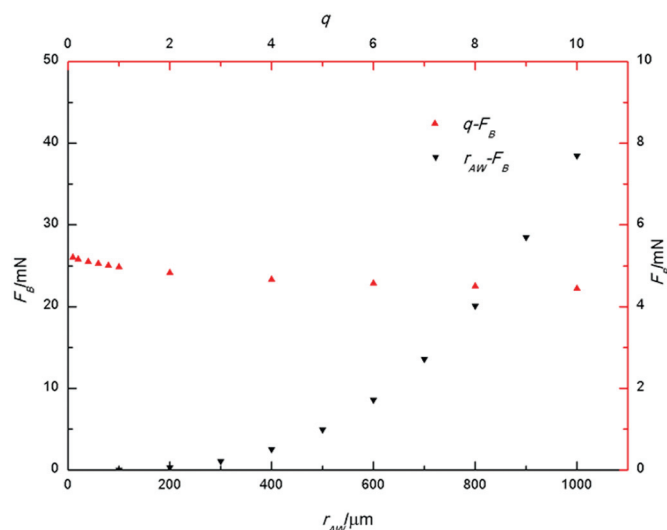


Fig. 3. The effects of volume ratio and bubble radius on buoyancy.

For volume ratio:

$$q = V_O/V_A \quad (7)$$

For the radius [28–30]:

$$r_{OW} \cdot \sin\mu = r_{AW} \cdot \sin\eta \quad (8)$$

$$r_{OW} \cdot \sin\mu = r_{OA} \cdot \sin\varepsilon \quad (9)$$

The relationship between θ_1 , θ_2 , θ_3 , and μ , η , ε are:

$$\cos\theta_1 = \sin\eta \quad (10)$$

$$\cos\theta_2 = \sin\mu \quad (11)$$

$$\cos\theta_3 = \sin\varepsilon \quad (12)$$

With the above equations, at a given microbubble radius (r_{AW}), it is sufficient to calculate the equilibrium morphology of gas–liquid Janus droplet. We used MATLAB to solve the above equations, and a numerical solution could be obtained. (The MATLAB code is provided in supplementary materials).

3. Results and Discussion

3.1. The parameters determining buoyancy

From Eqs. (4)–(6), we can see that buoyancy is determined by r_{AW} , r_{OA} , r_{OW} , μ , η , ε , ρ_{OW} , ρ_A . For a given system, γ_{AW} , γ_{OW} , γ_{AO} , ρ_{OW} , ρ_A are determined. Along with above equations, we can get the value of buoyancy as long as r_{AW} and q are known. Fig. 3 shows that buoyancy

increases with bubble radius. In comparison, buoyancy decreases when volume ratio increases, and the amplitude is limited.

3.2. The effect of bubble radius on equilibrium morphology

From above results, increasing bubble radius leads to the increase of buoyancy, which will cause a change in equilibrium morphology. To illustrate this effect, we chose an experimental system (air, water + 0.06 wt% fluoro-surfactant, and 1, 6-hexanediol diacrylate) with $\gamma_{AW} = 29.56 \text{ mN}\cdot\text{m}^{-1}$, $\gamma_{OW} = 10.01 \text{ mN}\cdot\text{m}^{-1}$, $\gamma_{AO} = 28.53 \text{ mN}\cdot\text{m}^{-1}$ as an example. The volume ratio is fixed to 1.

In Fig. 4, the morphologies obtained from the model considering buoyancy are compared with the morphology obtained from previous liquid–liquid model. There is visible difference between these two morphologies when bubble radius is larger than $300 \mu\text{m}$, which means that buoyancy effect cannot be neglected at this time. The result is consistent with that of preliminary calculation. The difference is more significant when bubble radius becomes larger. Furthermore, we can see that the coverage of bubble increases when bubble radius increases, which means the two parts in Janus droplets get closer with each other.

To make a quantitative analysis of this morphology change, we defined the angle between γ_{AW} and γ_{OW} as α , and α can be considered as an indicator of the separation degree of bubble and oil drop *i.e.* the morphology change (the bigger α , the smaller separation degree). The relationship between α and bubble radius was investigated, which is shown in Fig. 5(a). We can see that α increases with the increase of bubble radius, which means the separation degree decreases when bubble radius increases. And this phenomenon is in agreement with the increasing coverage. Fig. 5(b) demonstrates that both θ_1 and θ_2 decrease when radius increases, which can account for the increasing bubble α ($\alpha = 180 - \theta_1 - \theta_2$).

Through qualitative and quantitative analysis, we could draw the conclusion that the buoyancy effect on the equilibrium morphology of gas–liquid Janus droplets will become apparent when bubble radius increases to a certain extent. Bigger bubble radius makes the bubble and the oil drop in the gas–liquid Janus droplet become closer to each other.

3.3. The effect of volume ratio on equilibrium morphology

The same interfacial data was used, and bubble radius was fixed to $500 \mu\text{m}$ when volume ratio was changed. Fig. 6 shows that volume ratio has a big impact on the equilibrium morphology of gas–liquid Janus droplets, which is similar to that of the effect of volume ratio on morphology in liquid–liquid model.

Fig. 7 illustrates that volume ratio has a complicated impact on α . With the increase of volume ratio, α firstly increases to the maximum value, and then gradually decreases. This is because the changes for θ_1 and θ_2 are complex. In general, θ_1 decreases with the increase of volume ratio while θ_2 rises with increasing volume ratio. However, the rates of change for these two angles vary when volume ratio is changed. At the beginning, the reduction rate of θ_1 is bigger than the increase rate of θ_2 , thus α increases when volume ratio becomes larger. When volume ratio increases to a certain extent, the reduction rate for θ_1 is smaller than the increase rate for θ_2 , which leads to a smaller α .

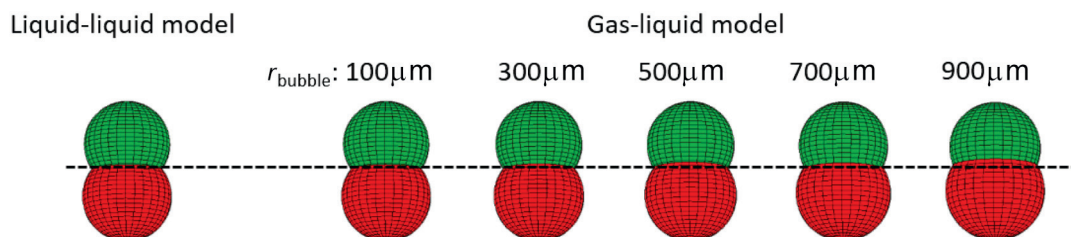


Fig. 4. Morphological comparison between two models.

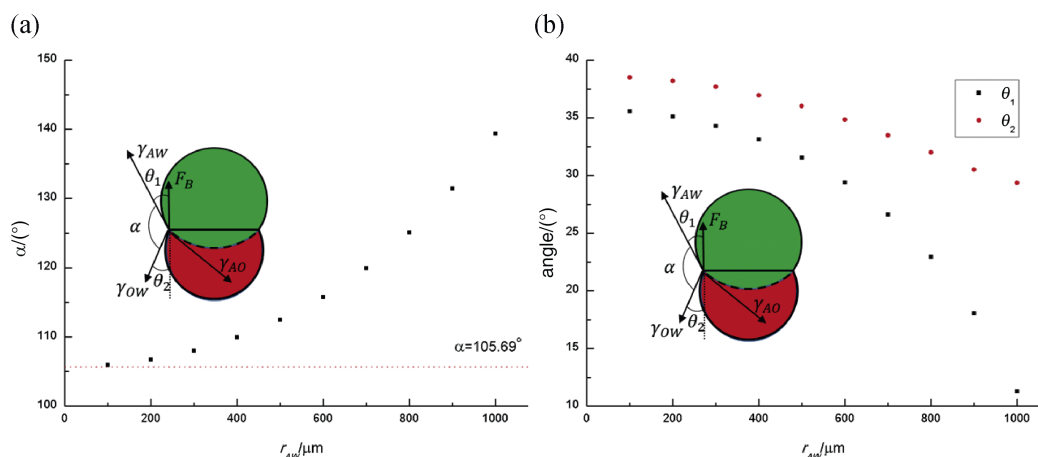


Fig. 5. (a) The effect of bubble radius on α . The dash line represents the value of α for liquid–liquid model, which is constant at given interfacial data. (b) The effect of bubble radius on θ_1 and θ_2 .

Interestingly, for previous model, α will not change with the change of volume ratio. In liquid–liquid model, α is only determined by three interfacial tension relationship, thus α is a constant for a known system. When buoyancy is considered, volume ratio is also needed to get the value of α . So volume ratio plays a role in determining α as well.

3.4. The effect of interfacial tensions on equilibrium morphology

For different systems, γ_{AW} , γ_{OW} , r_{AO} are different. This variation not only influences the values of interfacial tensions in force balance, but also influences other parameters in those equations. To investigate

this effect, two realistic systems (one has already been shown above, the other consists of air, water + 0.04 wt% fluoro-surfactant + 0.06 wt% SDS, and tetradecane with $\gamma_{AW} = 28.62 \text{ mN}\cdot\text{m}^{-1}$, $\gamma_{OW} = 6.94 \text{ mN}\cdot\text{m}^{-1}$, $\gamma_{AO} = 26.98 \text{ mN}\cdot\text{m}^{-1}$) were used. Bubble radius and volume ratio was fixed to $500 \mu\text{m}$ and 1 respectively.

We changed the value of γ_{AO} in first system to 28.53, while the value of γ_{OW} in second system was adjusted to 6.94 (still in the range for Janus morphology). Then we could use these four sets of data (shown in Table 1) to research how interfacial tensions influence the equilibrium morphology. By comparing system 1 and system 2, we could see that separation degree increases when γ_{AO} increases. Similar analyses

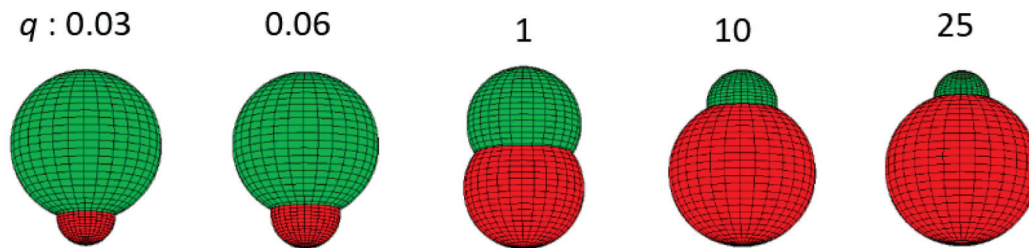


Fig. 6. Equilibrium morphology at different volume ratio.

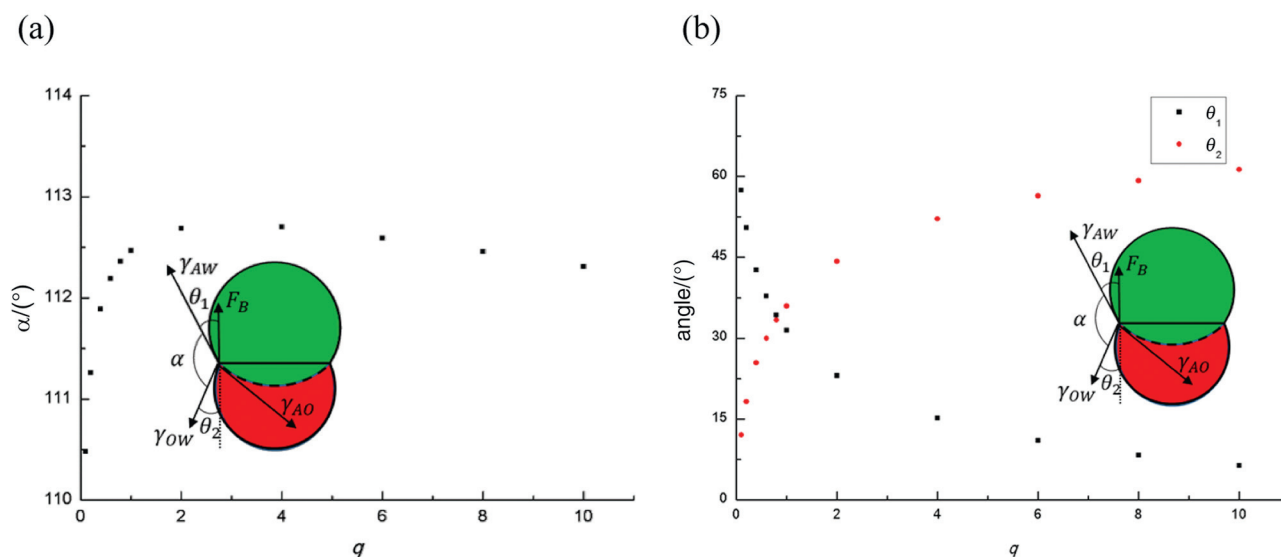


Fig. 7. (a) The effect of volume ratio on α . (b) The effect of volume ratio on θ_1 and θ_2 .

Table 1
Interfacial tensions for different systems

System	$\gamma_{AW}/\text{mN}\cdot\text{m}^{-1}$	$\gamma_{OW}/\text{mN}\cdot\text{m}^{-1}$	$\gamma_{AO}/\text{mN}\cdot\text{m}^{-1}$	$\alpha/(^{\circ})$
1	28.62 ^①	6.94	26.98	122.28
2	28.62	6.94	28.53	108.71
3	29.56	6.94	28.53	116.71
4	29.56	10.01	28.53	112.47

^① The value is an average of 10 measurements.

show that γ_{AW} has negative effect on separation degree while γ_{OW} has positive effect on separation degree.

3.5. Verification by experimental results

To verify the accuracy of gas–liquid Janus model used in this article, a series of experiments were performed. We chose system 4 in Table 1 for experiments. At different flow rates, gas–oil Janus droplets were obtained using a coaxial microfluidic device through one-step approach. Then these Janus droplets were transferred to an observation cell and observed by a microscope. Side view of gas–liquid Janus droplets can be obtained, thus we could measure the realistic angle between γ_{AW} and γ_{OW} (termed as α'). By comparing α' with α , we can assess the accuracy of model.

Fig. 8 shows the side view of Janus droplets. When bubble radius is 250 μm , the value of α' is well consistent with that of α (103.10° vs 107.29°). Meanwhile, the value of α' is also well consistent with the calculation result of previous model (103.10° vs 105.69°). For our model, the good consistency can still be seen (112.46° vs 114.00° and 126.25° vs 120.10°) when bubble radius becomes larger (549 μm and 704 μm). However, there is noticeable difference between the value of α' and the figure obtained from previous model (112.46° vs 105.69° and 126.25° vs 105.69°), and this difference will become larger when bubble radius increases. This phenomenon shows that buoyancy cannot be neglected when bubble radius grows to a certain extent.

A bigger difference ($\sim 6^{\circ}$) was observed when bubble radius is 704 μm . The reason for this is that bubble has been deformed (as seen in Fig. 8), and the deformation can cause an impact on the equilibrium morphology, which made the value of α' larger than it should be. However, the relative error between α and α' is approximately 5%, which is still accurate enough, so this model can be used to predict the

equilibrium morphology of gas–liquid Janus droplet. We will make a thorough study about the deformation in our future work.

4. Conclusions

In summary, we built a theoretical model used to calculate the equilibrium morphology of gas–liquid Janus droplets by taking buoyancy effect into account. Then we investigated how bubble radius, volume ratio and interfacial tensions influence the equilibrium morphology. The results show that bigger bubble radius leads to a smaller separation degree in gas–liquid Janus droplet while volume ratio and interfacial tensions have complicated influence on that of Janus droplet. Finally, we verified this theory model with experiments, which shows that calculation results are in agreement with experiment results. Thus, this model can be used to predict the equilibrium morphology of gas–liquid Janus droplets.

Nomenclature

Bo	the local Bond number
F_B	the buoyancy, N
g	the gravitational constant, $\text{m}\cdot\text{s}^{-2}$
L_c	the perimeter of contact line, m
l	the characteristic length of three phase contact line, m
O	oil
q	the volume ratio
r_{AW}	the radius of oil drop, m
r_{OA}	the radius of virtual water drop, m
r_{OW}	the bubble radius, m
V_A	the volume of bubble, m^3
V_O	the volume of oil drop, m^3
W	water
α	the angle between γ_{AW} and γ_{OW} , ($^{\circ}$)
α'	the realistic angle between γ_{AW} and γ_{OW} , ($^{\circ}$)
γ	the interfacial tension, $\text{N}\cdot\text{m}^{-1}$
γ_{AO}	the interfacial tension between air and oil, $\text{N}\cdot\text{m}^{-1}$
γ_{AW}	the interfacial tension between air and water, $\text{N}\cdot\text{m}^{-1}$
γ_{OW}	the interfacial tension between oil and water, $\text{N}\cdot\text{m}^{-1}$
ε	the angle between r_{OA} and the central axis, ($^{\circ}$)
η	the angle between r_{AW} and the central axis, ($^{\circ}$)
θ_1	the angle between γ_{AW} and vertical axis, ($^{\circ}$)
θ_2	the angle between γ_{OW} and vertical axis, ($^{\circ}$)
θ_3	the angle between γ_{AO} and vertical axis, ($^{\circ}$)

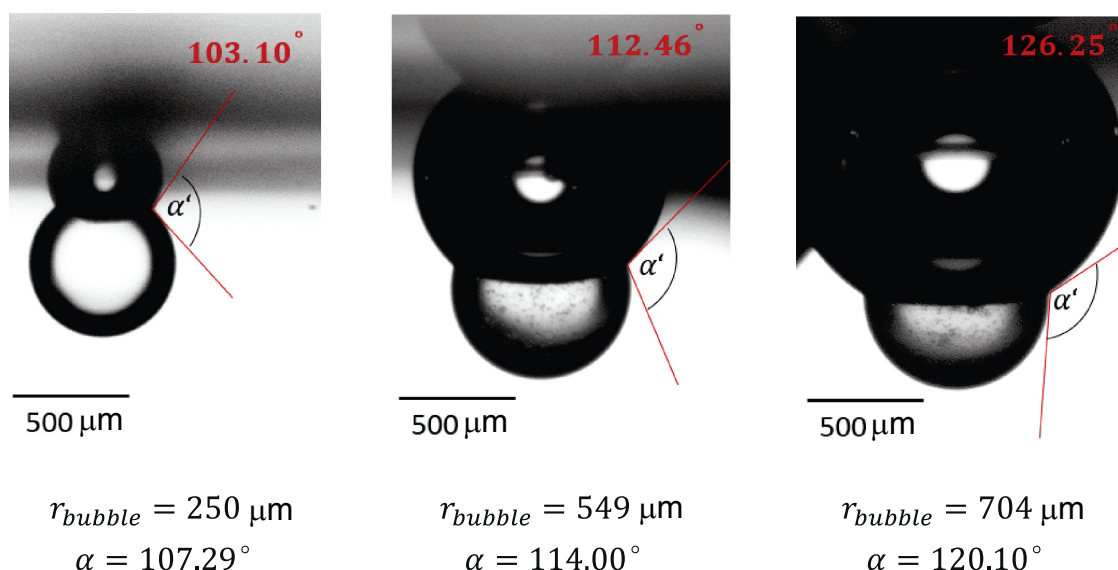


Fig. 8. Janus droplets with different equilibrium morphology.

μ	the angle between r_{OW} and the central axis, ($^{\circ}$)
ρ_A	the density of air, $\text{kg}\cdot\text{m}^{-3}$
ρ_{AW}	the density difference between water and air, $\text{kg}\cdot\text{m}^{-3}$
ρ_O	the density of oil, $\text{kg}\cdot\text{m}^{-3}$
ρ_{OW}	the density difference between water and oil, $\text{kg}\cdot\text{m}^{-3}$
ρ_W	the density of water, $\text{kg}\cdot\text{m}^{-3}$
$\Delta\rho$	the density difference, $\text{kg}\cdot\text{m}^{-3}$

Supplementary Material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cjche.2018.06.007>.

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