A Study on Encapsulated Liquid Drop Formation in Liquid-Liquid-Gas Systems*

(Fundamental Mechanism of Encapsulated Drop Formation)

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To investigate the critical condition of encapsulated drop formation in liquid-liquid-gas systems, the dynamic behavior of a rising gas bubble across the interface between two immiscible liquids was analyzed experimentally and theoretically. The experiment revealed that an encapsulated liquid drop was formed by a gas bubble passing through the liquid-liquid interface or rebounding from the interface without the rupture of the liquid film between the interface and the gas bubble. A theoretical analysis based on an effective and simple model was developed by considering interface tension and liquid viscosity. The numerical results agreed with the experimental results.

Key Words: Multiphase Flow, Numerical Analysis, Bubble, Encapsulated Liquid Drop, Compound Fluid, Dynamics of Interface.

1. Introduction

An encapsulated drop made of an outer liquid shell and an inner gas has recently become a subject of special interest. If an encapsulated drop can be simply and sequentially produced, it may improve a chemical reactor or a direct - contact heat and mass exchanger⁽¹⁾. Furthermore, the various solid shells, which are produced by controlling the encapsulated drop formation process at the liquid stage, can be applied to medicines, high-performance solid fuels and lightweight structural materials for spacecraft⁽²⁾. Shells filled with a molten salt or other phase change materials can be applied to energy storage systems⁽³⁾. In these applications, it is extremely important to stably and uniformly produce large quantities of encapsulated drops. However, the mechanism of encapsulated drop formation is not yet fully understood, and there are a number of unsolved problems regarding the production of encapsulated drops because of the

complicated drop formation process.

In this paper, the hydrodynamic mechanism of encapsulated drop formation in liquid-liquid-gas systems has been studied experimentally using a specially designed sequential encapsulated drop generator⁽⁴⁾. It is also important to clarify the phenomenon by the theoretical analysis because of the difficulty of correct measurement for the dynamic behavior of the encapsulated drop. There have been a few analytical⁽⁵⁾ and numerical⁽⁶⁾ reports on the body approaching the interface. However, these studies do not deal with the encapsulated drop and are based on static motion or on potential flow.

Since the present phenomenon is related closely to the dynamic instability of interface and the rupture of liquid film, an effective theory for the encapsulated drop formation was developed here by considering interface tension, liquid viscosity and the dynamic motion of a gas bubble below the interface. The numerical results based on this analysis agreed qualitatively with the experimental data. The results obtained here will provide useful suggestions for future research and the development of encapsulated drop production.

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2. Nomenclature

- d : inner diameter of gas injection nozzle
 P : pressure
 R : gas bubble radius
 Re : Reynolds number $= 2RV/\nu_1$
 S : liquid film thickness
 S_c : rupture thickness of liquid film
 t : time
 U : liquid flow-out velocity from liquid film
 V : rising velocity of gas bubble
 V_t : terminal velocity of gas bubble
 Z : gas bubble displacement
 α : dimensionless parameter $= \sigma_i/(R^2\rho_1g)$
 β : dimensionless parameter $= \sqrt{R^3g}/\nu_1$
 γ : dimensionless parameter $= \sqrt{R^3g} \cdot \rho_1/(\nu_2\rho_2)$
 ν : kinematic viscosity
 ρ : density
 σ : surface tension
- Subscripts and superscripts**
 0 : initial value
 1 : liquid 1 (lower liquid)
 2 : liquid 2 (upper liquid)
 f : liquid film
 g : gas
 i : liquid 1-liquid 2 interface
 * : dimensionless form by R or $\sqrt{R/g}$

3. Fundamental Mechanism of Encapsulated Drop Formation

A schematic view of a sequential encapsulated drop generator is shown in Fig.1. The generator comprises a transparent acrylic cylindrical container (400 mm long, 4 mm thick and 72 mm in inner diameter) containing two immiscible liquids and an injection

nozzle for gas (air) at the bottom. The gas jet from the nozzle breaks down into sequential gas bubbles which rise vertically in the liquid. Adjusting the gas flow rate and liquid properties, encapsulated drops are formed sequentially at the horizontal interface between the two immiscible liquids. In this generator, the encapsulated drop is very stable and does not break down as the drop rises to a distance of 300 mm above the interface⁽⁴⁾.

Kerosene was used as an upper liquid (liquid 2). Six kinds of lower liquids (liquid 1) and seven injection nozzles (inner diameter $d=0.1, 0.2, 0.25, 0.3, 0.4, 0.5, 1.0$ mm) were used. The gas flow rate Q through the nozzle was changed from 8.07×10^{-8} to 2.72×10^{-6} m³/s so that the number of gas bubbles reaching the interface was 10~60 for each second. The fluid temperature was kept at 6 to 10°C. The physical properties of the liquids used here are shown in Table 1.

Within the present experiment, it was consistently observed that the horizontal interface was deformed as the gas bubble approached. Then, a thin liquid 1 film between the gas bubble and the interface would be formed. Because the liquid in the film flows out accompanying the gas motion in the bubble and the change of film surface area as the gas bubble passes through the interface, the film thickness becomes very thin. If any point of the film thickness becomes thinner than a certain limited value (the so-called rupture thickness), the film ruptures and no encapsulated drop is formed. When the film thickness approaches the rupture thickness, a molecular force like the van der Waals force dominates rather than the conventional fluid dynamic forces. Finally, the film breaks down rapidly.

When the gas bubble rises with the terminal

Fig. 1 Schematic view of sequential encapsulated drop generator

Table 1 Physical properties of liquids

Liquids (Symbol)	σ (N/m)	ρ (kg/m ³)	ν (m ² /s)
			$\times 10^{-6}$
Distilled Water (W)	0.0730	999	1.08
55% Glycerin-Water (G1)	0.0605	1140	9.83
44% Glycerin-Water (G2)	0.0630	1100	3.73
23% Glycerin-Water (G3)	0.0650	1040	2.43
18% Ethanol-Water (E1)	0.0338	956	2.07
6% Ethanol-Water (E2)	0.0524	986	1.66
Kerosene (K)	0.0265	825	2.21

velocity through liquid 1, an encapsulated drop containing a few gas bubbles at the center is formed. Figure 2 shows the case. In this figure, liquid 1 is 44% glycerin-water colored for visualization. The interface curvature changes as the gas bubble rises vertically. It makes the film pressure high and works on the gas bubble as the downward force. If the downward force becomes larger than the upward buoyancy force, the gas bubble rebounds below the interface and then repeats up-and-down motion in liquid 1. The liquid viscosity tends to reduce the speed of the up-and-down motion. So, if the film due to the first rising gas bubble with the largest upward velocity (at this time, the film thickness may become thinnest) does not rupture, there is little possibility for rupture in the next upward motion. The next gas bubbles from the nozzle reach the interface sequentially as the first gas bubble repeats up-and-down motion below the interface, and the bubbles gather at one point below the interface and form a bubble cluster. Finally, the bubble cluster begins to rise because of the increase of buoyancy force. Because the rising velocity of the bubble cluster is relatively small and the outer border of the bubble cluster is rough, the liquid flow-out rate from the film is very small, and the film does not rupture. This supports the experimental finding that an encapsulated drop containing a few gas bubbles was consistently formed whenever the bubble cluster formed below the interface. Consequently, the encapsulated drop is formed when the rising gas bubble stops once below the interface before the film

ruptures.

When the gas-bubble rising velocity was very large or a large number of gas bubbles reached the interface, the compound vertical liquid 1 column containing the chained gas bubbles tended to appear at the interface, as shown in Fig. 3. In this case, the unstable interface wave appeared on the compound vertical column and the wave amplitude grew with time. Finally, the compound column broke down into an encapsulated drop at the top part of the column^{(4),(7)}. However, in order to grow the compound column, it is necessary to satisfy the following conditions: before the film ruptures, the bubble passes through the interface or stops once below the interface. These two conditions are the same as those described above.

4. Theoretical Approach

4.1 Theoretical model

As described in section 3, it is important for the estimation of encapsulated drop formation to analyze the dynamic behavior of the first gas bubble approaching the interface. Then, the theoretical analysis based on the model shown in Fig. 4 is developed. Z is the displacement of the gas bubble center from the standard point ($Z=0$) which is located at the distance of the gas bubble radius R from the stationary horizontal interface. The Z -direction is the opposite to that of gravity g . Time t starts from zero when the center of gas bubble reaches the standard point. P is pressure, u and v are the velocity of liquid 1 and liquid 2,

Fig. 2 Photograph of encapsulated drop formation

respectively, and subscripts r and θ denote the r - and θ -directions, respectively, where (r, θ) is the spherical polar coordinates with an axial symmetry, and S is the film thickness. The theoretical analysis is developed under the following assumptions with reference to the experimental results.

(1) The gas bubble is spherical. The gas bubble volume and the inner pressure do not change as the gas bubble approaches the interface.

(2) The fluids are incompressible and isothermal. The wall effect of the cylindrical container for the fluid motion is disregarded.

(3) The liquid film has the concentric spherical shape. The film thickness is uniform along the bubble surface and is extremely thin. The flow velocity along the film is the same as the gas velocity on the bubble surface, and the r -direction flow in the film is negligibly small.

(4) The flow around the gas bubble is expressed by the Hadamard-Rybczynski solution and the Levich solution according to Reynolds number as follows⁽⁸⁾.

$$\psi = -\frac{1}{2} \frac{dZ}{dt} (r^2 - rR) \sin^2 \theta \quad \text{for } Re \leq 1 \quad (1)$$

Fig. 3 Photograph of compound liquid column formation

Fig. 4 Theoretical model

$$\psi = -\frac{1}{2} \frac{dZ}{dt} \left(r^2 - \frac{R^3}{r} \right) \sin^2 \theta \quad \text{for } Re \geq 50 \quad (2)$$

Here, ψ is the stream function and Re is the Reynolds number. These equations are used in the ranges $r \geq R$ and $0 \leq \theta \leq \pi$. The fluid velocity or the drag coefficient of the gas bubble derived from Eqs. (1) and (2) is assumed to change linearly in proportion to Reynolds number in the range $1 < Re < 50$. That is, the coefficient f , for convenience, is expressed as follows [cf. Eq. (5) or (13)] .

$$f = \begin{cases} 1 & \text{for } Re \leq 1 \\ 1 + \frac{2(Re-1)}{49} & \text{for } 1 < Re < 50 \\ 3 & \text{for } Re \geq 50 \end{cases} \quad (3)$$

(5) The interface tension is uniform. Therefore, the continuity of normal stress across the liquid film-liquid 2 interface is expressed as follows⁽⁹⁾.

$$P_f - P_2 = \frac{2\sigma_i}{R+S} + 2\nu_1 \rho_1 \frac{\partial}{\partial r} \left(\frac{1}{r^2 \sin \theta} \frac{\partial \psi_f}{\partial \theta} \right) \Big|_{r=R+S} - 2\nu_2 \rho_2 \frac{\partial}{\partial r} \left(\frac{1}{r^2 \sin \theta} \frac{\partial \psi_2}{\partial \theta} \right) \Big|_{r=R+S} \quad (4)$$

4.2 Dynamic force on gas bubble

The second term in the right-hand side of Eq. (4) can be omitted here because of the negligibly small film thickness and the negligibly small r -direction velocity gradient. Since the pressure P_2 near the interface varies little during deforming of the interface due to the small gas bubble, P_2 equals P_1 approximately. From these simplifications and Eqs. (1)~(3), Eq. (4) can be rewritten as follows.

$$P_f - P_1 = \frac{2\sigma_i}{R+S} + \frac{dZ}{dt} \frac{2f\nu_2 \rho_2}{R+(f+1)S} \cos \theta \quad (5)$$

Here, the second order in S is neglected because $R \gg S$. The rebound force F_r on the gas bubble is obtained from Eq. (5) as follows.

$$F_r = \int_0^{\theta_c} (P_f - P_1) \cos \theta (2\pi R \sin \theta) R d\theta = 4\pi R^2 \left[\frac{\sigma_i}{2(R+S)} \sin^2 \theta_c + \frac{dZ}{dt} \frac{f\nu_2 \rho_2}{3\{R+(f+1)S\}} (1 - \cos^3 \theta_c) \right] \quad (6)$$

The buoyancy force F_b , the drag force F_d and the fluid added mass force F_f ⁽¹⁰⁾ due to the accelerated liquid motion are expressed as follows.

$$F_b = \frac{4}{3} \pi R^3 (\rho_1 - \rho_g) g \quad (7)$$

$$F_d = \frac{1}{2} C_d \pi R^2 \rho_1 \frac{dZ}{dt} \left| \frac{dZ}{dt} \right| \quad (8)$$

$$F_f = \frac{1}{2} \frac{4}{3} \pi R^3 \rho_1 \frac{d^2 Z}{dt^2} \quad (9)$$

In Eq. (8), the drag coefficient C_d of the gas bubble derived from Eqs. (1)~(3) is $16f/Re$. From Fig. 4,

the following equations are obtained.

$$\sin^2 \theta_c = \frac{(2R+S-Z)(S+Z)}{(R+S)^2}, \quad \cos \theta_c = \frac{R-Z}{R+S} \quad (10)$$

Neglecting the gas density ($\rho_1 \gg \rho_g$), the gas bubble motion below the interface is expressed as follows.

$$\begin{aligned} \frac{d^2 Z^*}{dt^{*2}} = & 2 - 3\alpha \frac{(2+S^*-Z^*)(S^*+Z^*)}{(1+S^*)^3} \\ & - \frac{2}{\gamma} \frac{dZ^*}{dt^*} \frac{f}{1+(f+1)S^*} \\ & \times \left\{ 1 - \left(\frac{1-Z^*}{1+S^*} \right)^3 \right\} - \frac{6f}{\beta} \frac{dZ^*}{dt^*} \end{aligned} \quad (11)$$

Here, superscript * shows the dimensionless form by the representative length R and the time $\sqrt{R/g}$. Equation (11) is used in the range $0 \leq Z \leq 2R$. Dimensionless parameters α , β and γ are expressed as follows.

$$\alpha = \frac{\sigma_i}{R^2 \rho_1 g}, \quad \beta = \frac{\sqrt{R^3 g}}{\nu_1}, \quad \gamma = \frac{\sqrt{R^3 g}}{\nu_2} \frac{\rho_1}{\rho_2} \quad (12)$$

4.3 Flow of liquid film

From Eqs.(1)~(3), the flow-out velocity U from the film is expressed as follows.

$$\begin{aligned} U = & -\frac{1}{r \sin \theta} \frac{\partial \psi}{\partial r} \Big|_{r=R, \theta=\theta_c} \\ = & \frac{f}{2} \frac{dZ}{dt} \sin \theta_c \end{aligned} \quad (13)$$

From Fig. 4, the film surface area δ is expressed as follows.

$$\delta = \int_0^{\theta_c} (2\pi R \sin \theta) R d\theta = 2\pi R^2 \frac{S+Z}{R+S} \quad (14)$$

Because the variety of film surface areas is very large in this phenomenon, the equation of continuity of film flow for the constant film surface area in a small time period^{(5),(11)} is not effective. The more detailed equation of continuity is expressed as follows.

$$S\delta - U(2\pi R \sin \theta_c) S dt = (S+dS)(\delta+d\delta) \quad (15)$$

Here, dS , dZ and $d\delta$ are the small varieties of S , Z and δ corresponding to the small time dt . Rearranging by substituting Eqs.(13) and (14) into Eq.(15), considering $R \gg S$ and neglecting the second order in dS and dZ , the dimensionless equation of continuity is obtained as follows.

$$\begin{aligned} \frac{dS^*}{dt^*} = & \left\{ -\frac{f}{2} \frac{dZ^*}{dt^*} (2-Z^*)(S^*+Z^*) \right. \\ & \left. \times S^* - S^* \frac{dZ^*}{dt^*} \right\} / (2S^*+Z^*) \end{aligned} \quad (16)$$

Finally, the displacement of the gas bubble and the film thickness can be obtained as a function of the time by solving Eqs.(11) and (16) simultaneously under the specific initial conditions.

5. Numerical Results and Discussion

5.1 Initial condition

The initial displacement of the gas bubble is zero and the initial velocity of the gas bubble is V_0^* . The

initial film thickness S_0^* is selected to be 1×10^{-1} on referring to the experimental data showing that a falling liquid drop approached the liquid-liquid interface⁽¹²⁾.

5.2 Rupture thickness of liquid film

The rupture thickness of liquid film seems to be less than 1×10^{-5} m^{(11),(12)}. In this study, considering that the gas bubble radius R is smaller than 1×10^{-2} m, S_c^* is assumed to be 1×10^{-3} .

5.3 Displacement of gas bubble and thickness of liquid film

The relation of Z^* to t^* at $\beta=100$, $\gamma=100$ and $V_0^*=1$ for various α is shown in Fig. 5. This figure shows the bubble behavior for no rupture. It is seen from Fig. 5 that Z^* increases monotonously in the small range of α (for example, $\alpha=0.1$ or 0.5), and that Z^* has the maximum value in the large range of α ($\alpha=1, 2$ or 5). If $\beta, \gamma \rightarrow \infty$, and $V_0, S_0 \rightarrow 0$, the analytical solution of Eq.(11) can be introduced as follows.

$$Z^* = A \left\{ \text{SN} \left(\sqrt{\frac{aB}{2}} \cdot t^* \right) \right\}^2 \quad (17)$$

Here, $A = 3/2 - \sqrt{9-8/a}/2$, $B = 3/2 + \sqrt{9-8/a}/2$, and SN is Jacobi elliptic function. The modulus x of the complete elliptic integral of the first kind is $\sqrt{A/B}$. Equation (17) is periodic for time and is applicable to the region $\alpha \geq 8/9$. This suggests the relation of Z^* to α shown in Fig. 5.

The relation of film thickness S/S_0 to t^* is shown in Fig. 6. Z_p indicates the bubble passing out ($Z=2R$) and Z_s indicates the bubble stopping once ($dZ/dt=0$); these are obtained from Fig. 5. The dash-dotted line at $S_c/S_0=1 \times 10^{-2}$ corresponds to rupture thickness. For example, at $\alpha=0.1, 0.5$ or 1 , the film ruptures before the gas bubble reaches the point Z_p or Z_s . On the other hand, at $\alpha=2$ or 5 , the film does not rupture before the rising gas bubble stops once. This would be expected to form an encapsulated drop containing a few gas bubbles.

Using the same method as described above, the effects of β, γ and V_0^* on the encapsulated drop formation were estimated numerically. Consequently, it

Fig. 5 Relation of gas bubble displacement to time

was found that the encapsulated drop was not formed easily if β , γ and V_0^* were large.

5.4 Region of encapsulated drop formation

Figure 7 shows the region where the encapsulated drop is formed for various V_0^* . The arrow sign on the solid border line indicates the drop formation region. The calculation time was limited within $t^* < 10$. This corresponds to $t < 0.1$ in $R = 1 \times 10^{-3}$ m. It is seen from Fig. 7 that the drop formation region becomes small as V_0^* becomes large. If V_0^* is small and β is large, the drop formation region approaches the region $\alpha \geq 8/9$ where Eq. (17) has the periodic solution.

The drop formation region at $V_0^* = V_t^*$ for various γ is shown in Fig. 8, where V_t^* is the terminal velocity of the gas bubble and is equal to $\beta/(3f)$, considering $F_b = F_d$. The arrow sign on the solid border line in Fig. 8 indicates the drop formation

Fig. 6 Relation of liquid film thickness to time

Fig. 7 Region of encapsulated drop formation at $\gamma=100$

region. The closed circle shows a representative experimental sample when the gas bubble ($R = 1 \times 10^{-3}$ m, $V_0^* = V_t^*$) reaches the interface between 44% glycerin-water and kerosene, namely, $\alpha = 3.39$, $\beta = 26.5$, $\gamma = 59.7$ and $V_t^* = 2.94$. These values were determined from Table 1 and the interface tension was determined by Antonow's law ($\sigma_i = |\sigma_1 - \sigma_2|$). It is seen from Fig. 8 that the experimental result agrees with the numerical result and that γ does not have much effect on the drop formation when $\gamma \geq 10$. In $V_0^* = V_t^*$, $\alpha \leq 10$ and $\gamma \geq 10$, the encapsulated drop can never be formed in the range $\beta > 60$. This corresponds to the region $Re_t > 800$, where Re_t is the Reynolds number; $Re_t = 2RV_t/\nu_1 = 2\beta^2/(3f)$.

6. Comparison of Theory with Experiment

The detailed dynamic behavior of the gas bubble below the interface was observed using a high-speed camera. The gas bubble radius R was within 0.648×10^{-3} to 1.78×10^{-3} m. The effect of γ could be neglected because the experimental value of γ was in the range $27.1 \leq \gamma \leq 129$. The comparison of theory with the experiment in a single gas bubble is shown in Fig. 9. All plots are experimental data. The closed circle indicates that the probability of the gas bubble stopping once below the interface for at least 20 events was more than 90%, the open circle indicates that the probability was less than 10% and the half-closed circle indicates the intermediate state between the above two cases. The arrow denotes the drop formation region; the solid border lines correspond to the numerical results at $\gamma=10$ and $\gamma=100$. It is seen from Fig. 9 that the numerical results qualitatively agree with the experimental data. Furthermore, our previous experiment⁽⁴⁾ ($\alpha < 10$, $\gamma > 10$) with the apparatus

Fig. 8 Region of encapsulated drop formation at $V_0^* = V_t^*$

Fig. 9 Comparison of theoretical and experimental results

shown in Fig.1 revealed that the encapsulated drop was never formed in the region $Re_t > 700$. The numerical result described in section 5 suggests that the estimated region is $Re_t > 800$. The difference between the experimental and theoretical results is small. The agreements supported the assumption that the encapsulated drop formation could be predicted approximately using this simple theoretical model.

7. Conclusions

The main features of this study were as follows.

(1) The dynamic behavior of the gas bubble below the interface was observed and the hydrodynamic mechanism of encapsulated drop formation was clarified.

(2) The strong dependence of gas bubble motion and the film flow on the encapsulated drop formation was recognized experimentally.

(3) A theoretical analysis based on the effective model has been developed by considering interface

tension and liquid viscosity. The critical condition of encapsulated drop formation was obtained quantitatively.

(4) Comparing the numerical results with the experimental results, the validity of the theoretical model was confirmed.

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