

DYNAMICS OF BUBBLES IN CONDITIONS OF GAS HYDRATE FORMATION

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ABSTRACT

The objective of the present paper is to develop fundamentals of theory describing dynamics of gas bubbles in hydrate formation conditions. For this purpose our own experimental observations of methane bubble dynamics are analyzed and mechanisms of diffusion and heat transfer controlling bubble collapse are evaluated.

KEY WORDS: Gas hydrate, bubble dynamics, heat and mass transfer.

INTRODUCTION

Gas hydrates form at high pressures and low temperatures at some gas-liquid interfaces (Byk et al, 1980; Sloan, 1990; Makogon, 1997). Bubbles of hydrate forming gases at such pressures and temperatures can appear in deep-ocean environment (Maini and Bishnoi, 1981; Topham, 1984) and can be used in laboratory and industrial processes for efficient gas hydrate production. Properties of bubbles with gas hydrates can significantly differ from the properties of usual gas bubbles. The bubbles can be used for diagnostic and other applications. However, there exist few publications on bubble dynamics with gas hydrates. Existing experimental studies of bubble dynamics during hydrate formation reported qualitative behavior of the bubbles. In some experiments hydrates formed inside the bubbles (Saifeev and Lobkov, 1965), while in others hydrate formation was observed only on the bubble surface followed by shedding of hydrate particles, formation of rigid hydrate shells, and fast bubble collapse (Maini and Bishnoi, 1981). Different mathematical models for the dynamics of bubbles at conditions of hydrate formation were suggested by Topham (1984), Nigmatulin et al (1991), and Gumerov (1991). Generally, the rate of hydrate formation on the gas/liquid interface depends on kinetics of crystallization (Vysniauskas and Bisnoi, 1983; Makogon, 1985; Englezos et al, 1987), binary diffusion of hydrate forming agent and water in the gaseous, liquid, and solid hydrate phases (Gumerov, 1992), heat transfer (Gumerov, 1991, 1992), and the state of the hydrate layer such as 'mobile' (Topham, 1984), or 'snow-like' (Gumerov, 1991), and 'ice-like' (Nigmatulin et al, 1991). It was noticed that also stresses acting on the interface (Gumerov, 1991) and hydrodynamics of rising bubble (Topham, 1984) can drastically change the state of the hydrate layer coating the bubble

and define the regime and controlling mechanisms of hydrate formation.

In the present study we describe typical regimes of hydrate formation on methane bubbles observed in experiments and we make some theoretical estimations. The objective of the investigation is to build a base for mathematical theory of gas bubble behavior in hydrate formation conditions.

ORGANIZATION OF EXPERIMENTS

A photo of the high pressure cell used for visualization of the hydrate formation is shown in Fig. 1. The cell was fabricated from a thick-wall (5 cm) plexiglass cylinder of 21 cm height and 10 cm internal diameter that was tightly compressed between two stainless steel plates by steel bolts and sealed by neoprene o-rings. The bottom plate has an inlet and the top plate has an outlet. A steel needle of external diameter 1.65 mm and internal diameter 1.17 mm was used to inject compressed gas into the cell. The temperature and pressure in the cell were monitored by digital thermometer and pressure gauge. Commercial grade methane gas was supplied from a high pressure container through a pressure regulator to the cell nearly 95% filled by water obtained from molten ice. After bubbling, the gas can get out of the cell through a gas/liquid separator and a pressure valve. The cell was submerged into an ice/water mixture to operate at temperatures near the water freezing point.

In a typical experiment we started bubbling at the temperatures of the order of 4-5°C and maintained the pressures at 55-60 bars. Due to continuous cooling the temperature would slowly drop to 1.5-3°C. The size of the injected bubbles was 2-4 mm in diameter. Depending on the rate of bubbling, type of water, and degree of presaturation the time required to start forming hydrate in the systems varied from 25-30 minutes to several hours. Following this induction time required for saturation and creation of the first hydrate nuclei intensive hydrate formation was observed. First, on the free gas liquid interface growing spots of a thin non-transparent hydrate film appeared. After this bubbles rising under the influence of gravity did not disintegrate once they reached the free surface. Instead, they remained in an spherical shape 'glued' together without coalescing many hours and formed a large cell solid foam. Bubbles in the foam did not change their shape and sizes during the experiment and the foam disintegrated (melted like snow in warm water) only when the cell was depressurized.

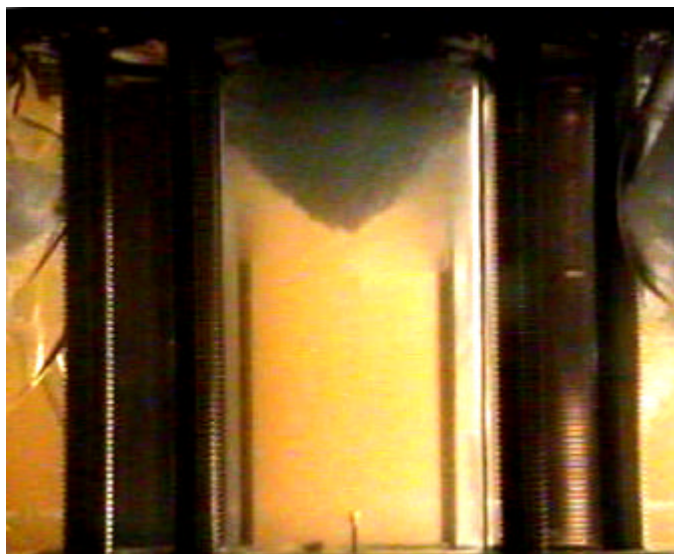


Fig. 1 The high pressure cell used for visualization of hydrate formation.

As soon as the foam started to form we substantially reduced the rate of bubbling using the pressure valve in order to observe the dynamics of single bubbles coming out of the injection needle. The process of growth, collapse, and detachment of the bubbles was video-recorded and photographed. To investigate the bubble collapse and obtain bubbles of various shapes and volumes, the gas flow was from time to time completely stopped, or the injection rate was changed using the valve. After the observations were completed the video records were processed using a graphical computer software to obtain quantitative data on the bubble dynamics and the hydrate formation rates.

OBSERVATION OF BUBBLES

In the experiments described above we observed several regimes of bubble behavior all at the same ambient pressure, temperature, and concentration conditions. Thus, these regimes depend on the rate of the gas influx to the growing bubbles, flow around the bubble, capillary effects, stresses acting on the hydrate layer, and on surrounding bubbles. We distinguish the following types of bubble behavior observed in our system.

Bubble Growth

Fast Growing Bubbles

Bubble growth on the needle due to gas injection strongly depends on the gas flow rate. At high rates bubbles visually were similar to usual gas bubbles without hydrates. The characteristic feature of such bubbles is a free gas/liquid quasi-spherical interface at the top (50-70% of the total surface) and a hydrate cap near the needle having a conical or shape (covers 30-50% of the bubble surface, see Fig. 2a). The hydrate layer was mobile and looked like an aluminum paint. The growth time for such bubble (from start to the moment of detachment) was from 0.1 s to several seconds.

Slow Growing Bubbles

At low gas flow rates the shape of the bubbles during the growth phase when their surface is almost completely covered with the

hydrate layer can be very unusual (elongated bottles and fingers, see Fig. 2b and 2c). The direction of the growth can be non-vertical (Fig. 2d). The characteristic feature of such bubbles is a small free gas/liquid interface near the top of the bubble. The time of growth for such bubbles is of order of 10-40 s. Note that the gas flow rate is the main variable between the different experiments, and that this influenced the bubble shape. Sometimes we observed bubbles attached to the needle for 30 s and more without any visible dynamics (finally all bubbles detached from the needle). Such bubbles were completely covered with hydrates. After bubble detachment we observed very strong shape deformation due to the liquid flow.

Bubble Collapse

Collapse of Partially Covered Bubbles

If we stop the gas supply to a bubble which was growing at a moderate rate the hydrate cap continued to increase with the upper edge of the hydrate layer propagating to the bubble top. At the same time the spherical cap of free gas/liquid interface at the top of the bubble shrinks, due to gas from the bubble being used to form hydrate. In some experiments the hydrate shell practically did not change, or changed very little, but the gas from the bubble top was sucked to the bottom (see Fig. 3). The time of collapse (from the maximum size to the moment of detachment) was 2-8 s.

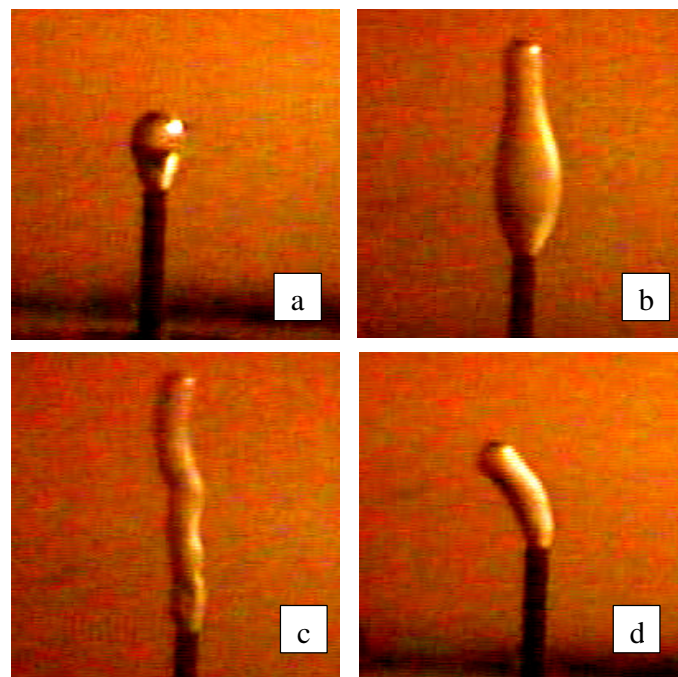


Fig. 2 Shapes of methane bubbles growing in water at $T = 275$ K and $p = 58$ bar.

Collapse of Completely Covered Bubbles

In some experiments bubbles covered with the mobile shell collapsed more in a quasi-cylindrical fashion (see the process in Fig. 4). The bubble looked like a balloon deflating from its central region while the two ends are maintained in place. This shell then pinches off and rises as a bubble but with a much slower velocity. Usually such bubbles had elongated shapes, which are cylindrical rather than spherical. The maximum observed collapse time was 10-15 s (this time depends on bubble size).

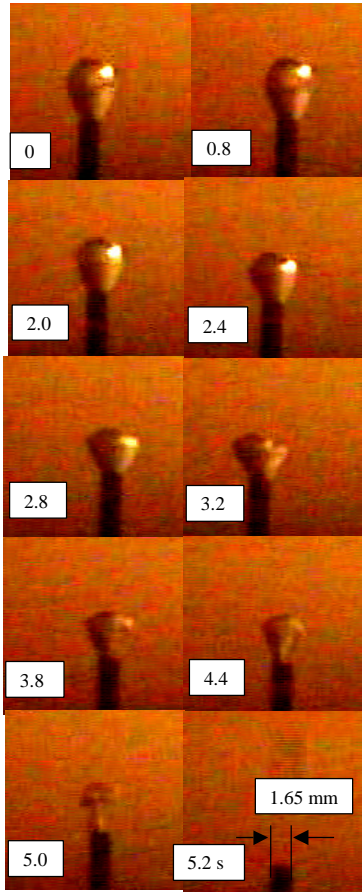


Fig. 3 Collapse of a methane bubble in water at $T = 275$ K and $p = 58$ bar. Labels show time in seconds.

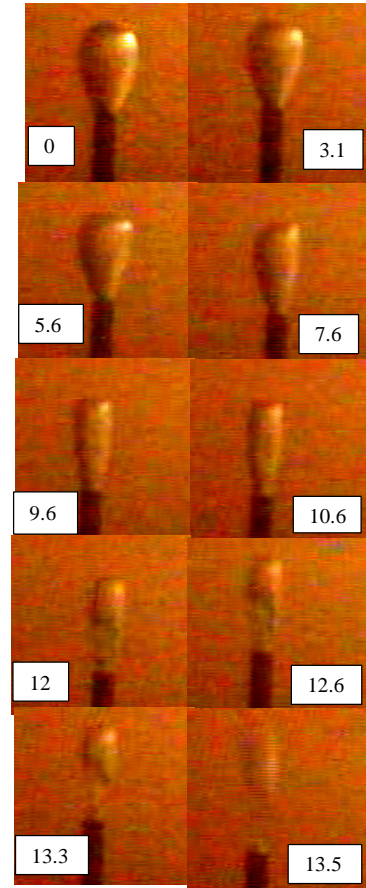


Fig. 4 Collapse of a methane bubble in water at $T = 275$ K and $p = 58$ bar. Labels show time in seconds.

Rising Bubbles

After detaching from the nozzle the bubbles completely change their shapes and rise. The process of rise under the influence of gravity and shape deformation is much faster than the processes of growth and collapse. In the present study we did not focus on the dynamics of such bubbles.

Rigid Bubbles

Such bubbles were observed in the foam formed at and below the initial free surface. The hydrate coated bubbles looked like ice, and seem to be semi-opaque (see Fig. 5). During the time of our observations of the foam (1-2 hours) no visible change of shape or volume was noticed.

THEORETICAL EVALUATIONS

Dynamics of Spherical Bubble Controlled by Diffusion

Diffusion in liquids and solids is much slower process than the heat transfer. Thus, in cases when phase transformations are limited by diffusion of participating agents to the phase transition interfaces thermal effects usually can be neglected. For hydrate formation this point is supported by theory and calculations given in (Gumerov, 1992).

Bubbles without Hydrates

This classical problem of heat and mass transfer at bubble interface without hydrate formation was considered by many investigators. We give some notations and formulas for further estimations and comparisons.

Consider a spherical gas bubble of radius R placed in a liquid having at infinity pressure p_∞ , a temperature T_∞ , and a mass concentration of the dissolved gas c_∞ . At the characteristic bubble sizes, pressures and temperatures of our experiments, the characteristic times for equalizing pressure and temperature inside and outside the bubble are much smaller than the time of the mass diffusion in the liquid. Capillary pressure and vapor pressure are negligible. The mass conservation for the bubble can be written in the form

$$\begin{aligned} \mathbf{r}_{g\infty} \dot{V} &= -Sj, \\ j &= \frac{\mathbf{r}_l D_l Sh \Delta c_l}{2R}, \quad Sh = - \left. \frac{2R}{\Delta c_l} \frac{\partial c_l}{\partial r} \right|_{r=R}, \\ \Delta c_l &= c_{le}(p_\infty, T_\infty) - c_\infty, \\ \mathbf{r}_{g\infty} &= \mathbf{r}_g(p_\infty, T_\infty), \end{aligned} \quad (1)$$

where V and S are the bubble volume and surface area, $\mathbf{r}_{g\infty}$ the gas density at the ambient pressure and temperature, Δc_l the concentration drop in the liquid, \mathbf{r}_l and D_l the liquid density and mass diffusivity, j

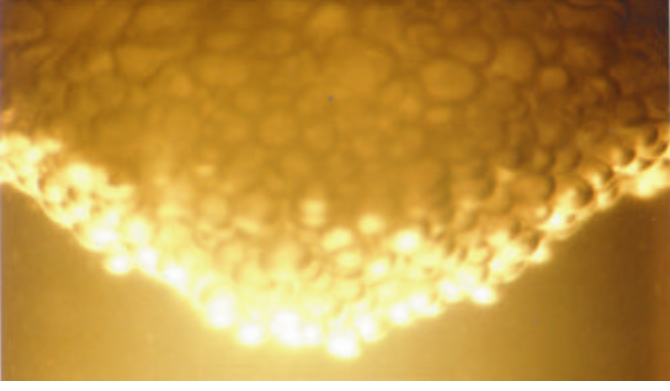


Fig. 5 Hydrate foam formed near the top of the high pressure cell. Water-methane system at $T = 275$ K and $p = 58$ bar.

the mass flux of gas to the liquid through a unit area of the interface, c_{le} the equilibrium concentration in the liquid, Sh the Sherwood number, and $\partial c_l / \partial r|_{r=R}$ the value of the gradient of concentration at the interface. These formulas can be also rewritten in the following dimensionless form

$$2\mathbf{b} \frac{d\mathbf{b}}{d\mathbf{t}} = -Ja^{(D)} Sh, \quad (2)$$

$$\mathbf{b} = \frac{R}{R_0}, \quad \mathbf{t} = \frac{D_l t}{R_0}, \quad Ja^{(D)} = \frac{r_l \Delta c_l}{r_{g\infty}}.$$

Here \mathbf{b} and \mathbf{t} are the dimensionless bubble radius and time, R_0 the initial bubble radius, and $Ja^{(D)}$ the diffusional Jacob number. In conditions of experiment $r_l \sim 10^3$ kg/m³, $r_{g\infty} \sim 50$ kg/m³, and $\Delta c_l \leq c_{le} \sim 2 \cdot 10^{-3}$, we can determine that the characteristic diffusional Jacob number is small, $Ja^{(D)} \leq 0.04$.

Asymptotic analysis of the bubble collapse at small Jacob numbers was performed by Gumerov (1989) and the following expression for the collapse time, t_c , was obtained

$$t_c = \frac{R_0^2}{2D_l Ja^{(D)}} \left[1 - \left(\frac{2Ja^{(D)}}{p} \right)^{1/2} - \frac{Ja^{(D)}}{2p} \ln \frac{2p}{Ja^{(D)}} + O(Ja^{(D)}) \right]. \quad (3)$$

Thus, in the absence of hydrates the time required for bubble collapse of a characteristic radius $R_0 \sim 10^{-3}$ m due to diffusion in liquid ($D_l \sim 10^{-9}$ m²/s) should be $t_c \geq 10^4$ s ≈ 3 hours.

The collapse times for bubbles attached to the needle in our experiments were in order of several seconds (say, 10 seconds), that is much less than the obtained estimation. This means that the decrease of the bubble volume in our case is not controlled by the mass flux from the bubble to the bulk of the liquid. Consequently, the free gas goes from the inside of the bubble mostly to the hydrate, and very little goes into the liquid.

Bubbles with Rigid Hydrate Shell

Theoretical analysis of rigid hydrate coated bubbles and mechanism of the hydrate bubble destruction ('eggy-effect') was performed by Nigmatulin et al (1991) and Gumerov (1990). It was shown that such bubbles are stable only in saturated or supersaturated solutions. Otherwise the hydrate shell inevitably cracks due to stresses in the shell exceeding the strength limit of the hydrate. The mechanism

of the 'eggy-effect' is the following. The rigid hydrate shell prevents the pressure to even between the inside and outside of the bubble. The gas pressure drops due to the gas consumption for hydrate formation. On the other hand the thickness of the shell first increases due to hydrate formation and then decreases due to the dissolution of the hydrates in surrounding solution (if it is subsaturated). So at some moment of time stresses in the shell reach the strength limit of hydrate and shell disintegrate. An asymptotic analysis performed for a single spherical bubble by Gumerov (1990) shows that the time required for the rigid bubble destruction can be estimated as

$$t_c \sim \frac{R_0^2}{3D_l Ja^{(D)}} \left(1 - \frac{\mathbf{s}_0}{\mathbf{s}_*} \right) \left(1 - \frac{p_e(T_\infty)}{p_\infty} \right) \quad (4)$$

$$\mathbf{s}_0 \sim \frac{3r_h c_h p_\infty}{2r_{g\infty}}, \quad (5)$$

where p_e is the equilibrium pressure of the hydrate formation (three-phase line), \mathbf{s}_0 is the initial stress developed in the hydrate layer of zero thickness, \mathbf{s}_* the hydrate strength limit, and c_h and r_h are the mass concentration of gas in the hydrate and hydrate density.

When $\mathbf{s}_0 \ll \mathbf{s}_*$, t_c in the conditions of our experiments ($R_0 \sim 10^{-3}$ m, $p_e(T_\infty)/p_\infty \sim 0.5$, $Ja^{(D)} \sim 0.04$) can be estimated as $t_c \sim 1.5$ hours. If we consider stability of bubbles in hydrate foam the actual time required for the described instability can be several orders larger, since the liquid in the foam is close to saturation ($\Delta c_l \ll c_{le}$). Another estimation showing again very large times for developing of the 'eggy-effect' instability for the bubble cluster can be obtained, if instead of the radius of the single bubble R_0 we substitute in Eq. (4) the characteristic size of the bubble cluster.

Thus, in our case the rigid bubbles found in foam can be considered as stable. This is consistent with our observations the experiment. On the other hand, hydrate covered bubbles placed on the needle show some dynamics after the gas supply is stopped. That shows that this model is not acceptable for such bubbles.

Bubbles with Mobile Hydrate Shell

Let us assume that the hydrate shell of the bubble can move due to its very small thickness. We also assume that despite the presence of a hydrate shell that separates the gas and liquid the pressure between inside and outside the bubble equalizes.

The characteristic thickness of the unsteady diffusional boundary layer in the liquid and gas are, respectively,

$$\mathbf{d}_l^{(D)} \sim \sqrt{D_l t}, \quad \mathbf{d}_g^{(D)} \sim \sqrt{D_g t}. \quad (6)$$

For characteristic times of bubble collapse observed in our experiments, $t \sim 10$ s, and $D_l \sim 10^{-9}$ m²/s, $D_g \sim 2 \cdot 10^{-5}$ m²/s we have $\mathbf{d}_l^{(D)} \sim 10^{-4}$ m and $\mathbf{d}_g^{(D)} \sim 10^{-2}$ m. The characteristic bubble radius is $R \sim 10^{-3}$ m. This means that a planar one-dimensional approximation can be accepted, where the gas can be considered as saturated. In this case we can estimate the rate of hydrate formation using an analytical solution (Gumerov, 1992) for the self-similar growth of the hydrate layer of thickness $d_h(t)$ controlled by diffusion in the hydrate and liquid:

$$d_h = \frac{r_l \mathbf{g}}{r_h} \left(\frac{D_l t}{p} \right)^{1/2}, \quad (7)$$

$$\mathbf{g} = \left[(\Delta c_l)^2 + \frac{2pr_h^2 D_h}{r_l^2 D_l} \frac{\Delta c_h}{c_h(1-c_h)} \right]^{1/2} - \Delta c_l,$$

$$\Delta c_h = c_{hg}(p_\infty, T_\infty) - c_{hl}(p_\infty, T_\infty),$$

where D_h is the mass diffusivity of the hydrate, c_{hg} and c_{hl} the equilibrium mass concentrations of the gas in the hydrate at the hydrate/gas and hydrate/liquid interfaces respectively, Δc_h the concentration drop in the hydrate, and \mathbf{g} the coefficient depending on diffusion in the liquid and hydrate.

Thus, the rates of hydrate formation, j_h , and gas consumption, j , per unit area of the bubble interface can be evaluated as

$$j_h = \mathbf{r}_h \dot{d}_h, \quad j = c_h j_h. \quad (8)$$

Substituting this value to the first Eq. (1) and integrating we obtain

$$R(t) = R_0 - \frac{c_h \mathbf{r}_h}{\mathbf{r}_{g\infty}} d_h(t). \quad (9)$$

From here we can find that the characteristic time of the bubble collapse ($R(t_c) = 0$) is

$$t_c = \frac{pR_0^2}{D_l} \left(\frac{\mathbf{r}_{g\infty}}{c_h \mathbf{r}_l \mathbf{g}} \right)^2. \quad (10)$$

The experimental data on the coefficient of diffusion for the hydrate of methane reported by Makogon (1985) vary between $D_h \sim 5 \cdot 10^{-10}$ m²/s and $5 \cdot 10^{-12}$ m²/s. Eq. (10) shows that to evaluate the minimum of possible t_c we should use maximum of possible $D_h \sim 5 \cdot 10^{-10}$ m²/s. Using $\Delta c_h \sim 10^{-3}$, $c_h \sim 0.1$, $\mathbf{r}_h \sim 10^3$ kg/m³, and parameters of our experiments we find that $t_c \geq 5.5$ hours. This time also appear to be huge in comparison with times observed in experiments.

Hydrate Formation Controlled by Vapor Diffusion

The above schemes show that the diffusion in the liquid and through the hydrate layer are very slow processes to explain the experimental data. Since the diffusivity of the gas is 4 orders of magnitude higher than the diffusivity of liquid and the hydrate it is reasonable to consider the following scheme of the hydrate formation controlled by diffusion of water vapor in the gas.

Consider a bubble having both a free liquid/gas interface and a hydrate layer (such as shown in Fig. 3). At the same pressure and temperature the vapor concentration at the gas/liquid interface is higher than at the gas/hydrate interface, and this difference, Δc_v , at conditions of experiment can be estimated as $\Delta c_v \sim c_{ve} \sim 10^{-4}$, where c_{ve} is the equilibrium vapor concentration. The drop of concentrations drives a diffusion flux of vapor, j_v :

$$j_v \sim \mathbf{r}_{g\infty} D_g \frac{\Delta c_v}{\mathbf{d}_g^{(D)}}. \quad (11)$$

The characteristic thickness of the unsteady diffusional boundary layer at characteristic collapse times is much greater than the bubble size (6). So we can consider that we have quasi-steady diffusion and can use for evaluations

$$\mathbf{d}_g^{(D)} \sim R. \quad (12)$$

The rates of hydrate formation and gas consumption can be found using j_v :

$$j_h = \frac{j_v}{1-c_h}, \quad j = \frac{c_h j_v}{1-c_h}. \quad (13)$$

Taking into account (11) and (12), and the fact that only \mathbf{a} fraction of the interface is covered by hydrates we can substitute j to the modified equation (1) and find:

$$R\dot{R} = - \frac{\mathbf{a} c_h D_g \Delta c_v}{1-c_h}. \quad (14)$$

Since $\mathbf{a} < 1$ the collapse time can be estimated as

$$t_c \geq \frac{R_0^2 (1-c_h)}{D_g c_h \Delta c_v}, \quad (15)$$

that for $R_0 \sim 10^{-3}$ m is $t_c \geq 1.5$ hours, which is of the order of collapse times in the case of bubble dynamics controlled by diffusion in the liquid and in the hydrate shell.

Thus, the above estimations show that bubble collapse observed in our experiments is not controlled by diffusion. However, we should notice that diffusion can control the dynamics of the hydrate coated bubbles of other sizes and in other conditions, than the conditions of our experiments.

Dynamics of Bubbles Controlled by Heat Transfer

The collapse of spherical gas bubble with the mobile shell in the thermal regime of hydrate formation was considered by Gumerov (1991). Here we consider a simplified case to provide estimations.

The rates of hydrate formation can be much higher if we assume that the hydrate forms at immediate contact between the gas and the liquid, so there is no diffusion limitations to supply material for hydrate formation to the point of reaction. In this case we should assume that the gas or water can penetrate through the hydrate shell much faster then it is allowed by diffusion in solid hydrate. This can occur, for instance, if the shell is porous. Porous or 'cracked' shells can form when the strength limit of hydrate is lower than the stresses in the shell developing due to pressure fluctuations and flow around the bubble.

The reaction of hydrate formation is exothermic so the temperature at the point of reaction is higher than T_∞ . On the other hand it cannot exceed the equilibrium temperature T_e of the coexistence of liquid, gas, and hydrate (three-phase line). The pressure in the system can be assumed uniform, p_∞ . Thus, if the process is not limited by chemical kinetics of reaction, it will be controlled by the ability of the participants of the reaction to transfer the heat from the place of the reaction having temperature $T_e(p_\infty) > T_\infty$.

The thickness of the unsteady thermal boundary layer in the liquid, gas, and hydrate having thermal diffusivities \mathbf{k}_l , \mathbf{k}_g , and \mathbf{k}_h , can be evaluated as

$$\mathbf{d}_l^{(T)} \sim \sqrt{\mathbf{k}_l t}, \quad \mathbf{d}_g^{(T)} \sim \sqrt{\mathbf{k}_g t}, \quad \mathbf{d}_h^{(T)} \sim \sqrt{\mathbf{k}_h t}. \quad (16)$$

At pressures and temperatures of our experiment we have $\mathbf{k}_l = 1.5 \cdot 10^{-7}$ m²/s, $\mathbf{k}_g = 2 \cdot 10^{-7}$ m²/s, $\mathbf{k}_h = 7 \cdot 10^{-7}$ m²/s. Thus, $\mathbf{d}_l^{(T)} \sim \mathbf{d}_g^{(T)} \sim \mathbf{d}_h^{(T)} \sim 10^{-3}$ m, that is comparable with the bubble size.

To simplify the model, let us assume that the hydrate layer covers the entire bubble surface and that its temperature is $T_e(p_\infty)$ because of

an ongoing reaction. The heat fluxes to the gas and to the liquid can be estimated as

$$q_g \sim \frac{I_g \Delta T_g}{d_g^{(T)}}, \quad q_l \sim \frac{I_l \Delta T_l}{d_l^{(T)}}, \quad (17)$$

$$\Delta T_l = T_e(p_\infty) - T_\infty,$$

where I_g and I_l are the thermal conductivities of the gas and the liquid, and ΔT_g and ΔT_l are characteristic temperature drops. Since the initial temperature of the gas is about T_∞ we have $\Delta T_g \sim \Delta T_l$. We also have $d_l^{(T)} \sim d_g^{(T)}$. However, $q_g \ll q_l$ because $I_g \ll I_l$ (in the conditions of experiment $I_g/I_l = 0.05$) and the total heat flux, $q = q_g + q_l$ is close to q_l . This estimation shows that the heat transfer in the liquid plays a dominant role, while the heat transfer in the gas can be neglected.

The amount of heat released in the reaction is proportional to the mass of the produced hydrate, $q_l = l j_h$, where l is the latent heat of hydrate formation. Since the rate of the gas consumption is $j = c_h j_h$ we can rewrite the first Eq. (1) in the following dimensional and dimensionless forms

$$\mathbf{r}_{g\infty} l \dot{R} = -c_h q_l, \quad (18)$$

$$2\mathbf{b} \frac{d\mathbf{b}}{dt} = -Ja^{(T)} Nu,$$

where the dimensionless variables are introduced by

$$\mathbf{b} = \frac{R}{R_0}, \quad \mathbf{t} = \frac{\mathbf{k}_l t}{R_0^2}, \quad (19)$$

$$Nu = -\frac{2Rq_l}{I_l \Delta T_l}, \quad Ja^{(T)} = \frac{c_h \mathbf{r}_l C_l \Delta T_l}{\mathbf{r}_{g\infty} l}.$$

Here Nu and $Ja^{(T)}$ are the Nusselt number and the thermal Jacob number and C_l is the heat capacity of the liquid.

In the conditions of our experiment we have $C_l \sim 4 \cdot 10^3$ J/(kg·K), $l \sim 4 \cdot 10^5$ J/kg, and $\Delta T_l \sim 5$ K, that give $Ja^{(T)} \sim 0.1$. Due to the fact that this number is small and by analogy between heat and mass transfer and equations (18) and (2) we can use the asymptotic result (3), where we need to change D_l with \mathbf{k}_l and $Ja^{(D)}$ with $Ja^{(T)}$. This gives us the collapse time for $R_0 \sim 10^{-3}$ m bubble, $t_c = 23$ s.

The obtained value is of the same order of magnitude as the observed collapse times. This time is sensitive to the bubble size (3). The geometry of the bubble also influences this time and the character of the function $\mathbf{b}(\mathbf{t})$. The actual collapse time can be smaller than the estimated value, because in (18) and (3) we assumed that the interface covered with hydrates decreases (as $4\mathbf{p}R^2$), but frequently it does not decrease (we observed 'wrinkles' and irregularities on the bubble surface and decreasing rather the gas/liquid interface than liquid/hydrate interface).

We also should mention that the bubble volume never reaches zero, but tends to V_{end} because the hydrate occupies some volume inside the bubble. V_{end} can be estimated if we consider that all the gas in the bubble, occupying initially the volume V_0 , finally transits to the hydrate phase:

$$\frac{V_{end}}{V_0} = v_e = \frac{\mathbf{r}_{g\infty}}{\mathbf{r}_h c_h}. \quad (20)$$

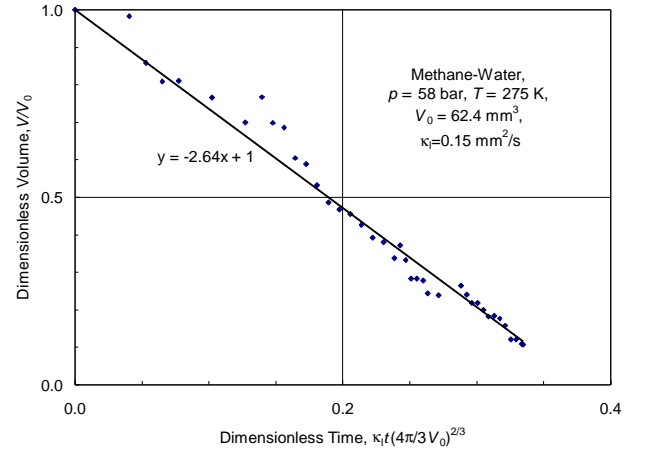


Fig. 6 Dynamics of the bubble volume collapsing in water. Experimental data correspond to the bubble shown in Fig. 4. Best fit line is also shown in the graph. Dimensionless time is based on the characteristic time of heat transfer in water.

In the conditions of our experiments we have $v_e = 0.43$. We did not observe such values in the experiments. This could be related to the fact that some hydrates formed inside the injection needle.

The injection needle was made from metal that has much higher thermal conductivity than water and provided better conditions to transfer heat of hydrate formation. Also the surface area of the needle was larger than the bubble surface and it did not change with time. This explains an almost linear decreasing of the gas volume (1) observed in the experiments (see Fig. 6). In the future we plan to make the needle from material with low thermal conductivity to provide more accurate measurements of bubble dynamics and to control better the interruption of the gas injection into the bubble.

Notice on Kinetics of Hydrate Formation

The process of hydrate formation which can be thought of both as a chemical reaction or a phase transition of the water/gas mixture generally can be controlled by three main mechanisms: kinetics, mass diffusion and heat transfer. The last two mechanisms were evaluated above. The kinetics mechanism of hydrate formation includes formation of hydrate nuclei (homogeneous nucleation), surface growth of the hydrate layer (propagation of the layer along the surface), and non-equilibrium phase transitions at gas/hydrate and liquid/hydrate interfaces (or kinetics of chemical reaction).

It was noticed in many studies on hydrate formation (e.g. Byk et al, 1980; Vysniauskas & Bishnoi, 1983; Makogon, 1985; Sloan, 1990) that the process of homogeneous nucleation can be quite long. This was also observed in our experiments (the induction time at low degree of subcooling and low gas flow rate was sometimes several hours). However once hydrates formed we did not observe any problems with nucleation and bubble dynamics occurred in conditions of heterogeneous nucleation. Without any exception (even for very fast growing bubbles) substantial part of the bubble surface was covered with hydrates. Thus, the nucleation in our case occurred already in the injection needle or at its edge.

The velocity of propagation of the methane hydrate layer in the conditions of experiment can be estimated of the order of 0.1 mm/s. This is in a good agreement with data reported by Makogon (1985) on the radial velocity of growth of hydrate layer treated as kinetic data. We should notice, however, that the crystal growth on the gas/liquid interface can be controlled not only by traditional kinetics (Volmer,

1939), but also by heat and mass transfer. In the case of fast kinetics the contact line hydrate/liquid/gas will be in local quasi-equilibrium conditions and have the temperature $T_c(p_\infty)$. The temperature of the hydrate/liquid and hydrate/gas interfaces can be lower depending on the intensity of hydrate formation that can be limited by diffusion. The quasi-equilibrium concentrations at the liquid/gas, hydrate/gas, and hydrate/liquid interfaces are also different. Thus, the temperature and diffusion gradients appear near the layer and the propagation velocity can depend on the solution of the heat and mass diffusion problems in the bulk of the gas, liquid, and hydrate. This also can involve solution of capillary problems near contact lines depending on hydro- and thermodynamics.

The kinetics of non-equilibrium phase transitions at gas/solid and liquid/solid interfaces can reduce, but not increase the rate of hydrate formation determined within the quasi-equilibrium scheme of phase transformations. Thus, consideration of diffusion and heat transfer controlled hydrate formation gives maximum possible rates. Even those rates were found too low or close to experimentally observed data. This means that more efforts should be done towards the theory of bubble dynamics controlled by diffusion and heat transfer.

CONCLUSIONS

The results of our experiments and theoretical evaluations allow us to make the following conclusions.

1. There can be several regimes of bubble dynamics in conditions of hydrate formation depending on the way of bubble generation, hydrodynamics, and conditions for heat and mass transfer.

2. Bubbles of various shapes unusual in normal conditions were observed. Such shapes depend on the rates of gas supply to the bubble and appear due to developing hydrate layer and elimination of effects of surface tension on the part of the boundary covered with such layer.

3. Bubble clusters stable for many hours are observed. The stability of such clusters can be explained by the presence of rigid dense hydrate layer that prevents direct gas/liquid contact.

4. Collapse of bubbles partially and completely covered by hydrates in the temporal scale of several seconds was observed. Such times are of the same order of magnitude as times of heat conduction in the liquid and the bubble collapse can be controlled by the heat transfer in liquid, but not by diffusion in gas, hydrate, or liquid.

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