Wave dynamics in a bubbly liquid during the synthesis of gas hydrate

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Abstract. In this work, on the basis of the equations of a bubbly liquid, a numerical simulation of the process of propagation of pressure waves of moderate amplitude, accompanied by the synthesis of gas hydrate in water with gas bubbles Freon-12, was carried out. The dynamics of plane-one-dimensional shock waves with a stepped profile, the volumetric gas content of the gas in the gas-liquid medium, and the average density of the gas hydrate are shown. The situation is considered when in the initial state of the bubble mixture hydrate formation does not occur, but when exposed to a shock wave, due to an increase in pressure in the bubbles and their fragmentation, favorable conditions for hydrate formation are created at the interface. Also, the use of gas hydrate synthesis technologies creates prerequisites for solving the problem of the greenhouse effect on the planet, and hence the climate. One of the solutions may be an increase in the interphase surface upon contact between water and hydrate-forming gas. Some theoretical calculations based on the model of gas hydration behind the pressure wave are presented.

1. Introduction

Recently, interest in gas hydrates has not decreased, but only increased. Hydrate can be considered as an unconventional source of energy, and at the same time, the production of such solid compounds can contribute to the development of technologies for the conservation of large volumes of gas, which may be more convenient and economical compared to others, especially for relatively small gas fields [1-3].

However, the formation of hydrate is a rather slow process and it is necessary to carry out various measures for its intensification [4-9]. Thus, when gas is bubbling through a layer of water, the effect of high pressure waves can enhance this process [10, 11]. In that works, the processes of dissolution and formation of hydrate behind the front of a shock wave in a bubbly liquid containing Freon-12 and carbon dioxide were experimentally investigated.

2. Basic equations and Description for bubble fragmentation

To simulate the process of gas hydrate synthesis by means of shock waves in a gas-liquid medium, we will take the following assumptions: the bubbles are equal in size and have the shape of a sphere, the effect of viscosity and thermal conductivity is considered only in interphase interaction, gas hydrate is formed in a layer near the bubble surface and does not resist the interaction of gas and water. Let us also assume that gas hydrate crystals do not influence the wave dynamics. Then, in the plane-one-
dimensional approximation, one can write equations for the conservation of masses and the number of bubbles:

\[
\frac{d\rho_i}{dt} + \rho_i \frac{\partial v}{\partial x} = -4\pi a^2 n_j, \quad \frac{dm_g}{dt} = -4\pi a^2 n_j g,
\]

\[
\frac{dm_h}{dt} = 4\pi a^2 n_j h, \quad \frac{dn}{dt} + n \frac{\partial v}{\partial x} = 0,
\]

\[
\rho_i = \rho_i^0 \alpha_i, \quad m_g = \frac{4}{3}\pi a^3 \rho_g^0, \quad m_h = \frac{4}{3}\pi ((a + \Delta a)^3 - a^3) \rho_h^0,
\]

\[
\alpha_g = \frac{4}{3}\pi a^3 n, \quad \alpha_h = \frac{4}{3}\pi ((a + \Delta a)^3 - a^3) n, \quad \alpha_i + \alpha_g + \alpha_h = 1,
\]

\[
j_h = j_g + j_t, \quad j_g = G j_h, \quad j_t = (1 - G) j_h.
\]

Indexes \(i = l, g \) and \(h \) refer to the parameters of liquid, gas and hydrate, \( \rho_i, \rho_i^0, \alpha_i, v, n, a, \Delta a_h \) are average and true phase densities, volumetric concentrations, velocity, number of bubbles per unit volume, bubble radius and thickness of the reduced hydration film. \( j_i \) is reduced intensity of mass transfer, \( G \) is mass content of gas in hydrate composition. During hydrate formation, we assume that the gas completely transforms into hydrate.

We write the momentum equation for a liquid as:

\[
\rho_i \frac{dv_i}{dt} + \frac{\partial p_i}{\partial x} = 0,
\]

where \( p_i \) is fluid pressure.

Taking into account the assumptions made, applying the equations for the change in the internal energy in the bubble and the law of conservation of gas mass, we can write the equation for the gas pressure in the bubble:

\[
\frac{\partial p_g}{\partial t} = - \frac{3\gamma p_a}{a} w - \frac{3(y-1)}{a} q_{(ga)} - \frac{3(y-1)}{a} c_{gy} T_a j_g,
\]

where \( c_{gy} \) is heat capacity of gas, \( \gamma \) is adiabatic exponent of Freon-12, \( j_g \) is the rate of hydrate formation per unit area of the bubble surface, \( q_{(ga)} \) is heat flux from the bubble to the interface.

The radial velocity of the bubble walls according to [12] is written in the form:

\[
w = w_R + w_A,
\]

where \( w_R \) is determined by the Rayleigh-Lamb equation and \( w_A \) we find from the solution of the problem of spherical unloading on a sphere of radius \( a \) in a fluid:

\[
\frac{a}{2} \frac{d w_R}{dt} + \frac{3}{2} w_R^2 = \frac{p_g - p_l}{\rho_l^2}, \quad w_A = \frac{p_g - p_l}{\rho_l^2 c_A a^2}.
\]

Here \( v_l \) is fluid viscosity and \( C_l \) is speed of sound in liquid (\( C_l = 1500 \) m/s).

To close the reduced system, we write down the heat balance equation at the interface:

\[
-q_{(ga)} + q_{(al)} = j_h l_h,
\]

where \( q_{(al)} \) is heat flux from the bubble surface to the liquid and \( l_h \) is specific mass heat of formation of hydrate.

We write the intensity of the heat flux from the gas phase and from the interface into the liquid like [12]:

\[
q_{(ga)} = \text{Nu} \lambda_g \frac{T_g - T_a}{2a}, \quad q_{(al)} = -\lambda_l \left( \frac{\partial T_l}{\partial r} \right)_{a} = -\lambda_l \left( \frac{a}{a_0} \right)^2 \left( \frac{\partial T_l}{\partial r_0} \right)_{a_0}.
\]
where $T'_l$ is temperature distribution in the liquid around the bubbles, $r$ and $r_o$ are Euler and Lagrangian radial microcoordinates, $T_g$ and $T_a$ are gas temperatures in bubbles and at the interface, $\lambda_l$ and $\lambda_g$ are thermal conductivity of phases, $Nu$ is Nusselt number.

Let us solve the heat conduction equation in Lagrangian variables to describe the heat fluxes around the bubbles:

$$\rho_l c_l \frac{\partial T'_l}{\partial t} = \frac{1}{r_o^2} \frac{\partial}{\partial r_o} \left( r_o^2 \lambda_l \frac{\partial T'_l}{\partial r_o} \right) \quad (a_0 < r_0 < \infty)$$

(8)

with boundary conditions:

$$T'_l = T_a \text{ when } r_0 = a_0 \text{ and } T'_l = T_0 \text{ when } r_0 \rightarrow \infty.$$  

The formation of hydrate is accompanied by diffusion processes and nonequilibrium effects of phase transitions, therefore, using an analogy with the theory of nonequilibrium phase transitions in vapor-liquid systems, one can describe the intensity of the formation of gas hydrate [12]:

$$J_g = \frac{\beta(p_g-p_s(T_a))}{\sqrt{2\pi K T_a^4}} \quad p_s(T_a) = p_s0 \exp \left( \frac{T_a-T_0}{T_s} \right), \quad p_{s0} = p_s(T_0),$$

(9)

where $\beta$ is a single empirical parameter (describes the formation and growth of gas hydrate crystals) and $p_s(T_a)$ is equilibrium pressure of formation of gas hydrate (corresponds to temperature $T_a$).

Bubble fragmentation strongly depends on the pressure wave amplitude.

We will assume that the main mechanism leading to fragmentation is the Kelvin – Helmholtz instability [13], which takes into account the relative bubble velocity $v_g$ and which reaches its maximum value at the time of the first compression. Then, according to [12], we can write:

$$We = \frac{2\alpha_0 r_0^2 v_g^2}{\sigma} < We_c = 2\pi \chi.$$  

(10)

Here $We$ is Weber number, $\sigma$ is surface tension coefficient, $\chi$ is empirical parameter ($\chi = 2$). Taking into account the main forces acting on the bubble, according to [12], we have $v_g t \approx 2v_l t$.

Then for the Weber number we can write:

$$We = \frac{8\alpha_0 r_0^2 v_l^2}{\sigma}.$$  

(11)

This number will take its greatest value at the moment of the first maximum compression of the bubble to the radius $a^{(m)}$. If the Weber number is less than the critical one, then splitting does not occur ($We_c(m) \leq We_c$), otherwise the bubble is divided into fragments with a radius $a^{(m)}_*$ which can be determined from the equation:

$$\frac{2a_*(m) \rho g v_l(m)^2}{\sigma} = We_c(m) = 2\pi \chi,$$

(12)

The number of fragments into which the bubble is split is found from the condition of equality of volumes before and after splitting:

$$N = \left( \frac{a^{(m)} / a^{(m)}_*}{3} \right)^3.$$  

(13)

The calculation will be carried out taking into account the increase in the specific interface area. For this, we introduce a correction factor $N^{1/3}$ for parameters $J_g$ and $q_a$.

3. Results

During the calculations, the following parameter values were taken: $p_0 = 10^5 \text{ Pa}$, $T_0 = 274 K$, $\alpha_e = 0.104$, $\lambda_g = 8.76 \cdot 10^{-3} \text{ (W/m \cdot K)}$, $\gamma = 1.14$, $c_g = 590 \text{ (J/kg \cdot K)}$, $\beta = 10^{-4}$, $G = 0.3$. The
amplitude of the step-profile shock wave is $\Delta p_0 = 1.3 \cdot 10^5 Pa$. In numerical calculations, the cases of the absence of bubble fragmentation are considered, as well as their fragmentation into 10 and 1000 fragments. The calculation results are shown in figure 1.

![Figure 1](image)

**Figure 1.** Profiles of pressure waves, volumetric gas content and average density of hydrate in the absence of division of bubbles (a), their fragmentation into 10 fragments (b) and 1000 (c).

The propagation of pressure waves through a bubbly liquid containing Freon-12 gas is modeled for a shock tube 1.5 m long. As it moves, the wave approaches the impenetrable pipe wall and is reflected from it. The reflected wave is shown in the figure at 39ms. The results show that as the pressure waves propagate, their amplitude decreases with time due to the formation of hydrate. By the decrease in the volumetric content of the hydrate-forming gas in the bubbly medium and the increase in the average density of the hydrate, one can judge the degree of intensity of hydrate synthesis, and if there is no bubble fragmentation (figure 1a), then this value is relatively small. The increase in the intensity of the synthesis of gas hydrate, as can be seen from the results, occurs when the bubble breaks up. So when the bubble is divided into 10 pieces (figure 1b), the formation of hydrate becomes more intense, as a result of which the amplitude of the reflected wave decreases more strongly. If the number of fragments increases to 1000 (figure 1c), then practically all the gas under these conditions passes into the hydrate state.

4. Conclusions
The calculations performed illustrate the dynamics of pressure waves in a liquid with a hydrate-forming gas at a different number of fragments of a shattered bubble, and also make it possible to estimate the characteristic times of a partial or complete transition of a gas to a hydration condition.
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References
[1] Sloan E D and Koh C A 2008 Clathrate hydrates of natural gases (Abingdon: CRC Press)
[2] Kuhs W F, Genov G, Staykova D K and Hansen T 2004 Ice perfection and onset of anomalous preservation of gas hydrates J. Phys. Chem. 6 4917-20
[3] Stern L A, Circone S, Kirby S H and Durham W B 2001 Anomalous Preservation of Pure Methane Hydrate at 1 atm J. Phys. Chem. (B) 105 1756-62
[4] Karamoddin M, Varaminian F and Daraei M 2013 Experimental Measurement and Kinetic Modeling of Ethane Gas Hydrate in the Presence of Sodium Dodecyl Sulfate Surfactant Gas Processing Journal 1(2) 1-12
[5] Khanlarkhani M, Pahlavanzadeh H and Mohammadi A H 2015 Clathrate hydrates and nano particles Advances in Nanotechnology 14 149-62
[6] Pang W X, Chen G J, Dandekar A, Sun C Y and Zhang C L 2007 Experimental study on the scale-up effect of gas storage in the form of hydrate in a quiescent reactor Chemical Engineering Science 62 2198-208
[7] Pooladi-Darvish M, Zatsepina O and Hong H 2008 Behaviour of Gas Production from Type III Hydrate Reservoirs Proc. of the 6th Int. Conf.on Gas Hydrates 1-11 available at https://ihsmarkit.com/pdf/behavior-gas-production-type-iii-paper_227059110913049832.pdf
[8] Rossi F, Filipponi M and Castellani B 2012 Investigation on a novel Reactor for Gas Hydrate production Applied Energy 99 167-72
[9] Zhang P, Wu Q and Yang Y 2013 Characteristics of Methane Hydrate Formation in Artificial and Natural Media Energies 6(3) 1233-49
[10] Doncov V E, Nakoryakov V E and Chernov A A 2007 Shock waves in water with Freon-12 bubbles with the formation of gas hydrate Applied mechanics and technical physics 48(3) 58-75
[11] Doncov V E, Chernov A A and Doncov E V 2007 Shock waves and the formation of carbon dioxide hydrate at an increased initial pressure in a gas-liquid medium Thermophysics and Aeromechanics 14(1) 23-9
[12] Nigmatulin R I 1987 Dynamics of multiphase media (Moscow: Nauka press)
[13] Shagapov V Sh, Lepikhin S A and Chiglintsev I A 2010 Propagation of compression waves in bubbly liquid with hydrate formation Thermophysics and Aeromechanics 17(2) 1-13