## BUBBLE FORMATION IN THROTTLING A

SUPERSATURATED LIQUID
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Results are given from theoretical and experimental studies of the effects of hydrodynamic conditions on formation of bubble nuclei from supersaturated solutions of gases in liquids.

There are many papers [1-5] on the conditions for formation of a new phase; it has been established $[2,5,6]$ that the rate of mixing or turbulence tends to govern the nucleation rate, with reduction in the size of the nuclei as the motion increases, and consequently with increase in the number of nuclei. Various explanations are given for the effect; some consider that the nucleation rate is raised by accelerated diffusion of the solute to the nuclei-[7]. Another assumption is that excess energy is supplied to the supersaturated solution to the extent necessary to produce the surface of particles in the new phase [8]. These arguments cannot lead to quantitative results without discussion of a detailed model, although both these factors undoubtedly play a part in the nucleation, of which the first is a consequence of the second. Here we give an approximate theoretical analysis and also results from experiments on the formation of gas bubbles in throttling of a liquid containing a dissolved gas; this is a particular case of the general problem of nucleation that occurs in cavitation, pressure-head flotation, and throttling of superheated liquids.

Dean [9] has supposed that nucleation occurs at the centers of free vortices, which are induced in turbulent flows; an analogous assumption has been made as regards formation of bubbles by cavitation in a boundary layer of liquid [10], but this hypothesis did not receive quantitative evaluation.

One needs an approximate model in order to explain the effects of hydrodynamic conditions on the formulation of viable nuclei; as our basis we use Dean's hypothesis that viable nuclei are formed at the centers of free vortices, which is combined with results from the theory of turbulence.

We have as follows for the speed of a vortex in a viscous liquid:

$$
\begin{equation*}
u_{\mathrm{v}} R_{v}^{n}=u r^{n} \tag{1}
\end{equation*}
$$

where n is a coefficient less than $1 ; \mathrm{n} \simeq 1.0$ for liquids of low viscosity. From (1) and the equation for the conservation of energy in the form

$$
\begin{equation*}
P_{1}+\rho \frac{u_{v}^{2}}{2}=p+\rho \frac{u^{2}}{2}, \tag{2}
\end{equation*}
$$

TABLE 1. Size and Number of Bubbles in Relation to Supersaturation at $8.5 \mathrm{~m} / \mathrm{sec}$

| $\mathrm{N}_{2}, \mathrm{ml} /$ liter | \% supersatura- <br> tion | Expected mean <br> bubble size, $\mu \mathrm{m}$ | No. of bubbles per liter $\cdot 10^{-9}$ |  |
| :---: | :---: | :---: | :---: | :---: |
|  |  | found | calc. from [21] |  |
| 45 | 200 | 48 | 0,40 | 0,36 |
| 75 | 400 | 69 | 0,35 | 0,36 |
| 90 | 500 | 83 | 0,25 | 0,36 |
| 135 | 800 | 86 | 0,37 | 0,36 |

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Fig. 1. Scheme of installation for studying the amount and sizes of bubbles generating out of oversaturated liquids.
it is readily shown that $u \rightarrow \infty$ and $p \rightarrow-\infty$ for $r \rightarrow 0$. The pressure cannot physically be less than zero, so for some $r=r_{1}$ and $u=u_{1}$ we get a stable gas cavity, in which the pressure is less than the static pressure of the liquid; if we have then as follows for nucleation

$$
\begin{equation*}
r_{1} \geqslant r_{\mathrm{cr}}=\frac{2 \sigma}{P_{1}} \tag{3}
\end{equation*}
$$

the bubble nuclei will grow when the vortex breaks up, while if $r_{1}<r_{\mathrm{cr}}$, the nuclei will dissolve again in the liquid. Then the number of viable nuclei is related to $R_{V}$ and $u_{\mathrm{v}}$; approximate values for these may be determined from the theory of turbulence.

The energy dissipation $\varepsilon$ per unit mass is largest for a scale $\lambda_{g}$ given by [11]

$$
\begin{equation*}
\lambda_{g}=\left(\frac{15 \mu}{\varepsilon}\right)^{0.5} u^{\prime} \tag{4}
\end{equation*}
$$

It is easily shown that this scale may be taken as 2 r in (1), since for $\mathrm{r}>\lambda_{\mathrm{g}}$ the turbulent pulsations produce rapid momentum exchange, and the pulsation velocity of eddies of scale $r>\lambda_{g}$ is unaltered, i.e., the n of $(1)=$ zero. On the other hand, there is rapid velocity damping [11], and so

$$
\begin{equation*}
u_{\mathrm{v}}=u^{\prime}\left(\frac{2 R_{\mathrm{v}}}{\lambda_{g}}\right)^{m} \tag{5}
\end{equation*}
$$

The flow is laminar for $2 R_{V}<\lambda_{g}$, so from (4) we have that $m=1.0$.
Then we can determine approximately the number of bubbles via the scale range $\left(2 R_{V}-\lambda_{g}\right)$ or $2 R_{V}$ $/ \lambda_{\mathrm{g}}$, which are the ones allowing formation of viable nuclei. Note that $\lambda_{\min }<2 \mathrm{R}_{\mathrm{v}}<\lambda_{\mathrm{g}}$.

We get from (2) subject to the condition that $\mathrm{P} \rightarrow 0$ at the center of a vortex that

$$
\begin{equation*}
P_{1}=\rho \frac{u_{\mathrm{v}}^{2}}{2}\left(\frac{u^{2}}{u_{\mathrm{v}}^{2}}-1\right) \tag{6}
\end{equation*}
$$

From (1) we have that $u / u_{v}=\left(R_{v} / r\right)^{n}$, while from (5) we then have

$$
\begin{equation*}
P_{\mathrm{I}}=\rho \frac{\left(u^{\prime}\right)^{2}}{2}\left(\frac{2 R_{\mathrm{v}}}{\lambda_{g}}\right)^{2}\left[\left(\frac{R_{\mathrm{v}}}{r}\right)^{2 n}-1\right] \tag{7}
\end{equation*}
$$

or, after transformation and substitution for r from (3), we get

$$
\begin{equation*}
1=\rho \frac{\left(u^{\prime}\right)^{2}}{2 P_{1}}\left(\frac{2 R_{v}}{\lambda_{g}}\right)^{2}\left[\left(\frac{2 R_{v}}{\lambda_{g}}\right)^{2 n}\left(\frac{\lambda_{g} P_{1}}{4 \sigma}\right)^{2 n}-1\right] \tag{8}
\end{equation*}
$$

As $\left(2 \mathrm{R}_{\mathrm{V}} / \lambda_{\mathrm{g}}\right)^{2}$ and $\left(\rho\left(\mathrm{u}^{\prime}\right)^{2} / 2 \mathrm{P}_{1}\right) \ll 1$, i.e., $\left(2 \mathrm{R}_{\mathrm{V}} / \lambda_{\mathrm{g}}\right)^{2 \mathrm{n}}\left(\lambda_{\mathrm{g}} \mathrm{P}_{1} / 4 \sigma\right)^{2 \mathrm{n}} \gg 1$, while we assume for simplicity that $\mathrm{n}=1.0$ (in eddy flows of a viscous liquid we find n as $0.8-1.0$ ), which gives

TABLE 2. Size and Number of Bubbles in Relation to Surface Tension of OP-10 Solution

| Surface tension at <br> interface with air, <br> $\cdot 10^{3} \mathrm{~J} / \mathrm{m}^{2}$ | Expected mean bubble <br> size, $\mu \mathrm{m}$ | No. of bubbles per liter $\cdot 10^{-9}$ |  |
| :---: | :---: | :---: | :---: |
|  | found | calc. from (21) |  |
| 72,5 | 28 |  |  |
| 61,2 | 25 | 6,5 | 5,2 |
| 51,3 | 23 | 9,7 | 6,4 |
| 42,0 | 22 | 10,7 | 8,8 |
|  |  |  | 10,2 |



Fig. 2


Fig. 3

Fig. 2. Curves of bubble distribution by sizes, $N$, number of bubbles of given diameter; $\mathrm{N}_{0}$, total number of bubbles; d , diameter of bubbles, $\mu \mathrm{m}$.
Fig. 3. Number of bubbles $N$ versus rate of solution throttling: 1) calculation; 2) experiment.

$$
\begin{equation*}
1 \approx \frac{\rho\left(u^{\prime}\right)^{2}}{2 P_{1}}\left(\frac{2 R_{\mathrm{V}}}{\lambda_{g}}\right)^{4}\left(\frac{\lambda_{g} P_{1}}{4 \sigma}\right)^{2} \tag{9}
\end{equation*}
$$

We express the energy dissipation in (4) in the form

$$
\varepsilon=\frac{\rho\left(u^{\prime}\right)^{3}}{l_{\mathrm{c}}}
$$

we put

$$
\begin{equation*}
\lambda_{g}=\left(\frac{15 v l_{c}}{u^{\prime}}\right)^{0.5} \tag{10}
\end{equation*}
$$

We substitute (10) into (9) and use $\mathrm{P}_{1} \approx \rho\left(\mathrm{u}^{2} / 2\right)$ to get

$$
\begin{equation*}
1 \approx \frac{1}{4} \cdot \frac{u^{\prime}}{u}\left(\frac{2 R_{\mathrm{v}}}{\lambda_{g}}\right)^{4} \cdot \frac{\rho^{2} v l_{\mathrm{c}} u^{3}}{\sigma^{2}} . \tag{11}
\end{equation*}
$$

We put

$$
\begin{equation*}
A=\left(\frac{1}{4} \cdot \frac{u^{\prime}}{u}\right)^{0.25} \tag{12}
\end{equation*}
$$

Then

$$
\begin{equation*}
1 \approx A\left(\frac{2 R_{\mathrm{v}}}{\lambda_{\mathrm{g}}}\right)\left(\frac{\rho^{2} v l_{\mathrm{c}} u^{3}}{\sigma^{2}}\right)^{0,25} \tag{13}
\end{equation*}
$$

The range of scales leading to formation of viable nuclei tends to zero for ( $\lambda_{\mathrm{g}}-2 \mathrm{R}_{\mathrm{V}}$ ) $\rightarrow 0$ or $2 \mathrm{R}_{\mathrm{V}} / \lambda_{\mathrm{g}} \rightarrow 1$, so (13) shows that there is a critical velocity $u_{c r}$ below which bubbles are not formed. The condition for bubbles not to form is then put as

$$
\begin{equation*}
1 \approx A\left(\frac{\rho^{2} v l_{c} u_{\mathrm{cr}}^{3}}{\sigma^{2}}\right)^{0.25} \tag{14}
\end{equation*}
$$

One substitutes the $A$ of (12) into (14) to get an approximate value for $u_{c r}$; in a highly turbulent jet

$$
u^{\prime}=0.15-0.20 u
$$

Then the value is $u_{c r} \approx 6.9 \mathrm{~m} / \mathrm{sec}$; the observed result is $u_{\mathrm{cr}}=7.0 \mathrm{~m} / \mathrm{sec}$. Experimental values enable one to refine the value of constant $A$ and to use it in response to any variation in nozzle size and liquid properties. The analysis shows that one must take into account the width of the spectrum of vortex sizes that can produce viable nuclei as well as the scale of the vortices.


Fig. 4. Curves of bubble distribution by sizes at $u=8.5$ $\mathrm{m} / \mathrm{sec}$ and nitrogen concentration in water.

Then the number of viable nuclei produced in unit volume $V$ may be defined as

$$
\begin{equation*}
N=\frac{V}{\lambda_{\mathrm{av}}^{3}} W \tag{15}
\end{equation*}
$$

We determine $\lambda_{\text {av }}$ on the basis that for $u>u_{c r}$ we have $\lambda_{g} \gg 2 R_{v}$ and

$$
\begin{equation*}
\lambda_{\mathrm{av}}=\frac{\lambda_{\mathrm{g}}+2 R_{\mathrm{v}}}{2} \approx \frac{\lambda_{g}}{2} \tag{16}
\end{equation*}
$$

while $W$ is defined by

$$
\begin{equation*}
W=b \frac{\left(\lambda_{g}-2 R_{\mathrm{v}}\right)^{2}}{\left(\lambda_{g}-\lambda_{\min }\right)^{2}} \tag{17}
\end{equation*}
$$

As $\lambda_{\min } \ll \lambda_{g}$, we got

$$
\begin{equation*}
W=b\left(1-\frac{2 R_{v}}{\lambda_{g}}\right)^{2} \tag{18}
\end{equation*}
$$

As $W$ is reduced, we assume that $b=0.3$; we substitute into (15) from (10), (16), and (18) with allowance for the fact that $V=10^{-3} \mathrm{~m}^{3}$ to get

$$
\begin{equation*}
N=\frac{0.3 \cdot 10^{-3} \cdot 2^{3} \cdot\left(u^{\prime}\right)^{1.5}}{\left(15 v l_{\mathrm{c}}\right)^{1.5}}\left(1-\frac{2 R_{\mathrm{v}}}{\lambda_{g}}\right)^{2} \tag{19}
\end{equation*}
$$

From (13) and (14) we find that

$$
\begin{equation*}
\frac{2 R_{\mathrm{V}}}{\lambda_{g}}=\left(\frac{u_{\mathrm{cr}}}{u}\right)^{0.75} \tag{20}
\end{equation*}
$$

Then (20) gives the number of viable nuclei as

$$
\begin{equation*}
N=\frac{4 \cdot 10^{-5}\left(u^{\prime}\right)^{1.5}}{v^{1.5} l_{\mathrm{c}}^{1.5}}\left[1-\left(\frac{u_{\mathrm{cr}}}{u}\right)^{0.75}\right]^{2} \tag{21}
\end{equation*}
$$

It is clear from (21) that the number of viable nuclei is proportional to the pulsation speed, inversely proportional to the viscosity and nozzle size, and dependent inexplicitly on the surface tension (via ucr). The term in brackets characterizes the range of scales of the pulsations that can produce viable nuclei, and this term has been observed experimentally [10]. It has been shown for cavitation on flow over a surface that bubbles are not formed near the wall, where the scale of pulsations is small.

Figure 1 shows the apparatus used to test this relationship; the tests were done with distilled water containing nitrogen. The water was poured into vessel 1 under pressure, and the vessel was fitted with a filter sprayer for nitrogen 2, a pressure gage 3 , and a safety valve 4 . The solution from the vessel was passed at a set pressure through the nozzle 5 and entered cell 6 at atmospheric pressure, the front and rear walls of this cell having glass windows and the cell in front of the microscope 7, which had the photographic fitting 8. The resulting very small bubbles were recorded photographically and were measured as to diameter on the film. As the sizes were small $(<100 \mu \mathrm{~m})$, the bubbles were taken as spherical. The results were used in histograms for the size distribution, and then the number of bubbles per liter of water was calculated. In the first series of runs, the water was saturated with nitrogen at pressures of $2,3,4$, 5 , and 8 atm , and at these pressures it passed to the cell; the diameter of the nozzle $d_{c}$ was 1.0 mm , and the corresponding flow speeds were $8.5,10.4,12.0,13.4$, and $17.0 \mathrm{~m} / \mathrm{sec}$. First we determined $u_{c r}$, which was found as $7.0 \mathrm{~m} / \mathrm{sec}$. Figure 2 shows the size distributions, while Fig. 3 shows the calculated number of bubbles as a function of $u$. This figure also shows the curve calculated from (21) on the basis that $l_{\mathrm{c}}=1 / 3 \mathrm{~d}_{\mathrm{c}} \approx 0.3 \cdot 10^{-3} \mathrm{~m}$.

The subsequent experiments were done with a constant speed of $8.5 \mathrm{~m} / \mathrm{sec}$ and various nitrogen concentrations corresponding to saturation at 4,5 , and 8 atm : Fig. 4 shows the distribution curves, while Table 1 gives N as a function of gas concentration. The latter shows that N varies very little with the nitrogen concentration in the water, which confirms the hydrodynamic theory of bubble formation.

Table 2 gives results for the number of bubbles for various values of the surface tension; the tests were done with distilled water saturated at 5 atm with nitrogen, the nozzle speed being $13.4 \mathrm{~m} / \mathrm{sec}$. The surface tension was adjusted by adding OP-10 surfactant.

The calculated number of bubbles was determined as follows. From (12) we calculated A, and then we determined $u_{c r}$ from (14), and then from (21) we calculated $N$ : as the equations are approximate, we consider the agreement between the values of Table 2 from experiment and calculation to be in satisfactory agreement.

## NOTATION

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u liquid velocity;
u' root mean square value of the component of turbulent velocity fluctuations;
u}\mp@subsup{v}{v}{}\quadvelocity at the boundary of vortex of radius R R ; 
R
r radius of vortex, with velocity u at the boundary;
r
rcr radius of "critical" bubble;
P
P static pressure at distance of radius-vector r
\rho density of liquid;
\sigma surface tension of liquid at liquid-gas boundary;
V liquid volume;
l}\mp@subsup{l}{\textrm{C}}{}\mathrm{ nozzle size;
\mu dynamic viscosity of liquid;
\nu \quad ~ k i n e m a t i c ~ v i s c o s i t y ~ o f ~ l i q u i d ;
\lambdaav mean size of vortices forming bubbles;
W spectral probability of presence of given scale vortices;
b coefficient equal to 0.25-0.30;
\lambdamin}\mathrm{ internal turbulent scale.
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