Chapter 2

BUBBLES AS PHYSICAL OBJECTS

The bubble as a physical object has been observed and studied for centuries. Newton observed the formation of an air bubble while pressing liquid between two lenses, but he did not realize at the time from where the bubble originates (Trevena, 1987) . Euler, in 1754, was the first to predict that a liquid moving at high velocity could be subject to a tensile stress which might result in what is today termed cavitation. Berthelot in 1850 carried out an experiment for observing cavitation in a liquid known now as the "Berthelot tube method." Later Reynolds, in 1878, demonstrated experimentally cavitation by heating today referred to as boiling. Parallel to these physical experiments various engineering designs encountered the phenomenon of cavitation and the damage that it causes to propellers. The term "cavitation" describing the appearance of bubbles in liquids when the pressure falls to a sufficiently low value was coined by Froude, a naval architect, in 1895. Besides these milestone discoveries and experiments, many other investigations have built our contemporary knowledge of bubbles step by step.

Papers on bubble physics and dynamics are countless. It is difficult to cover

the topic completely in a single volume: most are oriented to one of the many aspects. Soo (1967) considers the fluid dynamics of multiphase systems with an accent on solid particles. Clift et al. (1978) give a good summary on bubbles', drops' and particles' motion in flows and the mass and heat transfers from and to particles. This text also provides a thorough discussion of bubble shape. Trevena (1987) emphasizes the experimental work on the creating tension in liquids, cavitation and erosion. Young (1989), who is a specialist in sonoluminescence, focuses on acoustic cavitation. Brennen (1995) provides the most complete coverage of bubble dynamics, with rigorous mathematical derivations of all dynamical equations. The basic theory of light scattering by small particles, including air bubbles, is given by Van de Hulst (1957), while Jerlov (1976) considers the same topic in the context of oceanography. Finally, the influence of surfactants on bubble characteristics can be better understood by considering not only the physics, but also the chemistry of the bubble interface and aqueous solution (Rosen, 1978; Adamson, 1982) . The following paragraphs follow these texts. Theory on bubbles is not widely used in this study, rather a more descriptive approach is chosen and only the basic relations are given.

2.1   Definition

Bubbles (= cavities, = voids) are *fluid particles* in the terms defined by Clift et al (1978) . Rigorously, a *particle* is a self-contained body with maximum dimension between 0.5 µm and 10 cm, separated from the surrounding medium by a recognizable interface. The material forming the particle is termed the *dispersed phase*, while the medium

surrounding the particle is the *continuous phase*. In these terms the vapor or/and gas filling the bubbles are the dispersed phase. Clouds of bubbles are formed when the concentration of bubbles homogeneously mixed within a continuous phase, water or any other liquid, exceeds some small value; such system is called a *multiphase system*.

2.2   Formation of Bubbles

2.2.1   Natural Mechanisms

As the appearance or collapse of a bubble within a liquid is actually a process of phase change from liquid to gas and vice versa, discussions on bubble formation usually start with the liquid state (Trevena, 1987; Brennen, 1985) .

Figure 2.1 gives the typical phase diagram for a substance. In the figure, point R is the *triple point* where solid, liquid and vapor states coexist. The line RC is the *saturated liquid/vapor line*; at pressure and temperature values along this line the liquid coexists in equilibrium with its vapor and the well-known process of evaporation across an interface is present. The creation of a cavity filled with the liquid's vapor within the liquid itself is another way in which vaporization can occur. Since appearance of a cavity involves the formation of a new interface, work has to be done. This can be realized in two ways. Referring to Figure 2.1, the first is to start from point A_1 in the liquid phase and gradually to reduce pressure isothermally to a value below the coexistence curve reaching point A. At this point, a substance would normally be a vapor, but by the way the coexistence line was passed

Figure 2.1   Typical phase diagram for a substance (from Trevena, 1987) .

the substance still remains a liquid. This *stretched* liquid in point A is in *metastable phase*. The second way to reach the state at point A is to start from a liquid at point A_2 and heat it slowly at constant pressure: again, the saturated liquid/vapor line is crossed and the liquid still does not vaporize. Such a liquid is *superheated* and is also in metastable phase. The first prerequisite to initiate the formation of a bubble is to have a substance in a metastable phase. If the liquid is over-stretched along the path $A_1 \rightarrow A$ it reaches the critical tension it can withstand, Δp_c, and vaporizes. So, the process of rupturing a liquid by tension Δp resulting from decrease of the liquid pressure p below the saturated vapor pressure p_V, ($\Delta p = p_V - p$), at roughly constant liquid temperature is called *cavitation*. In a similar way, a liquid taken along the path $A_2 \rightarrow A$ will eventually reach its superheating limit ΔT_c and also will vaporize. So, the process of rupturing a liquid by superheat ΔT resulting from increase of temperature T above the saturation temperature, T_s ($\Delta T = T - T_s$), at roughly constant pressure is called *boiling*. Cavitation and boiling are the major mechanisms of forming bubbles in a liquid.

Calculations have shown that liquids can withstand a tensile pressure of 3×10^5

atmospheres and larger values are necessary for the liquid to create a cavity. Typical values of the superheating limit are of order of $30 \rightarrow 300°K$ for different liquids and at further heating a cavity will be formed. Predicted superheating values are in accord with those actually observed. However, the large theoretical values of tensile strength are not in agreement with observations and rupture of the liquid is usually observed at 100 times lower tension. The discrepancy between the correctly predicted superheating values and unreachable tensile values necessary to provoke bubble formation, the *microbubble paradox* (Hammitt, 1980), has been ascribed to *nucleation*. That is, unlike heating to some critical temperature, the tensile strength limit is determined not only by its critical point but also by weaknesses (= nuclei, = inhomogeneities) within the liquid. As such weaknesses are ephemeral and difficult to quantify, the theoretical evaluation of the tensile strength necessary to initiate a cavity is greatly complicated. These nuclei can occur in several forms.

First, the thermal motion of the molecules within a pure liquid forms temporary microscopic voids that can constitute the nuclei necessary for a rupture and growth to macroscopic bubbles. This is *homogeneous nucleation*. Three basic relations constitute the homogeneous nucleation theory. These are: 1) between the critical radius r_c of the void and the critical tensile strength Δp_c that would lead to its growth to a visible bubble ($\Delta p_c = 2\gamma/r_c$, where γ is the surface tension); 2) the energy E_c ($= 4\pi r_c^2 \gamma/3$) necessary to be deposited in a pure liquid in order to create a nucleus of the critical size; 3) evaluation of the probability, namely Gibbs number (Gb), that the stochastic nature of the thermal motion of the molecules (typically related with their kinetic energy kT, where k is the Boltzmann's constant) would lead to a local energy perturbation of magnitude E_c (Gb $= E_c/kT$) .

Second, any microscopic voids pre-existing in the liquid would cause rupture when the pressure of the liquid is reduced below the critical value; this is *heterogeneous nucleation*. Usually theoretical considerations for heterogeneous nucleation deal with voids filled with liquid vapors. However, in all practical situations it is virtually impossible to eliminate the chance that some gas is dissolved in the liquid, especially in large volumes. Therefore, the equilibrium pressure in the liquid would be determined not only by the vapor pressure but also by the partial pressure of the gas within the nucleus: $p = p_v + p_g - 2\gamma/r$. Hence, the dissolved gas would decrease the value of the critical tension: $\Delta p_c = 2\gamma/r - p_g$. With increasing pressure of the dissolved gas p_g (i.e., going toward saturation of the liquid with gas) the tensile strength may become negative and bubbles would grow even at pressures greater than the vapor pressure (e.g., bubbles would be formed even at point A_1 in Figure 2.1). When the liquid is not saturated with gas the microscopic candidates for nuclei would dissolve quickly under surface tension or would rise to the surface and also disappear (i.e., degassing would leave no nucleus) . One must conclude then, that there is a mechanism stabilizing these microbubbles and making them persistent enough to become nuclei for macrobubbles at an appropriate moment.

There are two ways to explain how these small bubbles are stabilized. The first is the so-called *skin* model: a small bubble in a liquid starts to contract under the surface tension force and its internal pressure increases. According to Henry's law, the solubility of a gas is proportional to the gas pressure: the gas diffuses out through the bubble wall, so the bubble contracts further. But by this time the bubble also accumulated an organic film through adsorption onto its surface, forming a complete skin when the bubble becomes small

enough. This layer inhibits any further loss of gas and hence shrinkage of the bubble (i.e., the bubble is stabilized) . If, at a later stage, the liquid is subjected to tension, the skin will be torn apart, gas diffuses into the bubble and cavitation is initiated. This theory is completely valid for an air bubble in water, but for other liquids, such as alcohol, the theory does not always apply.

The second way of stabilizing bubbles is their "hiding" in tiny crevices in the container walls or in suspended solid particles. This idea emerged after an experiment in which a large pressure (1000 bar) was applied to a liquid in order to "eliminate" the cavitation nuclei. After removing this high pressure, the liquid could stand a greater tension and started to cavitate at higher tensile values than it would before. According to the crevice theory, a pocket of gas trapped in the crevices can exist in a stable equilibrium if a certain relation between the apex angle of the crevice and the contact angle at the liquid/vapor/solid intersection holds. As long as the condition of stabilization is fulfilled, the gas stays in the crevice. When this condition changes, gas in the pocket starts to grow and when it reaches the critical radius of nucleation a bubble can be formed.

Besides these mechanisms, a cosmic radiation may also create a nucleus in a pure liquid. This process is referred to as *particle cavitation*: a collision between a high energy particle and a molecule of the liquid can deposit sufficient energy to initiate nucleation in a system which otherwise have little chance to cavitate.

Now, the question is when, where and how are the conditions for bubble formation present? Perhaps the most common occurrence of cavitation is in flowing liquid

systems where hydrodynamic effects result in regions of the flow with pressure below the vapor pressure, called *hydrodynamic cavitation*. Any flow, whether cavitating or not, can be characterized with a dimensionless number called *cavitation number,* σ, which is the ratio between the static and dynamic pressure of the flow:

$$\sigma = (\text{ambient pressure} - \text{vapor pressure})/\text{flow velocity}.$$

When the cavitation number is large (i.e. the vapor pressure is less than the ambient pressure or the flow velocity is small) single-phase liquid flow occurs. However, if σ is reduced to some critical value, σ_i, the *incipient* cavitation number, either by overall pressure decrease or flow velocity increase, nucleation (called also *incipient cavitation*) will occur. With a further decrease of σ below σ_i, the number of bubble appearances will increase and their growth will take place. For an ideal steady flow, σ_i is a constant for a given flow geometry. However, when the effects of viscosity are included, it is expected that σ_i will depend on the Reynolds number. Other influences on σ_i are: 1) the existence of tension can cause a reduction of σ_i; 2) the existence of contaminant gas can cause an increase in σ_i; 3) turbulence effects can cause an increase in σ_i as the pressure in the vortex core may be much lower than the mean pressure of the liquid. All these effects make the prediction of σ_i for a given flow, hence cavitation in it, a difficult task in engineering investigations.

There are three types of cavitation depending on the motion of the bubbles formed by hydrodynamic cavitation: 1) *traveling cavitation*, in which a bubble forms in the liquid and then travels with the flow, expanding and subsequently collapsing; 2) *fixed cavitation*, which occurs when the formed bubble is attached to a rigid boundary of an

immersed body and remains fixed in position; 3) *vortex cavitation*, which occurs when a bubble is formed in the core of a vortex produced in a region of high shear.

There are two mechanisms for initiation of bubble formation in a non-flowing system. Cavitation can be provoked by changing the ambient pressure through sound waves, *acoustic cavitation*. If the amplitude of pressure variations caused by the sound is large enough to drop the pressure to or below the vapor pressure, any minute nucleus will grow to a bubble. Bubbles are set in motion, growing and contracting with the sound field. Finally, *optic cavitation* occurs when a high light intensity, say a laser pulse, focused in a liquid, provokes a rupture in it and bubbles form.

2.2.2 Artificial Means

The usual artificial means of producing bubbles for fluid dynamical investigation are capillary tubes, filters with fine pores, and submerged orifices. The theory of detachment of a bubble from a capillary is summarized by Soo (1967) .

Let the ends of a capillary of radius R, be connected to a liquid reservoir of pressure p_L and a gas reservoir of pressure p_g. A meniscus dividing the liquid and the gas is formed in the capillary. If the pressure difference is less than the surface tension force, $p_g - p_L < 2\gamma/R$, the meniscus retreats inside the capillary. If the pressure difference is greater than the surface tension force, $p_g - p_L > 2\gamma/R$, the meniscus passes up the capillary. When it has just begun to protrude into the liquid, the pressure in the incipient bubble, p_b, is given by

$$p_b = p_L + 2\gamma/R.$$

When the bubble begins to expand at the end of the capillary, its radius, $r = d/2$, will become

greater than R, and the pressure inside the bubble falls to

$$p_b = p_L + 2\gamma/r$$

making it more buoyant. It is assumed that the buoyancy force ($= 4/3\ \pi r^3\ \Delta\rho g$) is the only

one that contributes to the release of bubble from the capillary orifice and it interacts with

the surface tension force ($= 2\pi R\gamma\cos\theta f[R/r_{in}]$) for the initial bubble radius, r_{in}. The

surface tension force simplifies to $2\pi R\gamma$ with the assumptions for a perfect wetting angle

($\theta = 0$), and for producing of a spherical bubble which gives a shape factor $f(R/r_{in}) = 1$.

Since the two forces equalize for a given bubble size ($4/3\ \pi r^3\Delta\rho g = 2\pi R\gamma$) a bubble with

radius r is blown slowly from the capillary orifice:

$$r = (\frac{3}{2}\ \frac{R\gamma}{\Delta\rho g})^{1/3}$$

For a system involving air and water at 20°C, this equation reduces to $R = 9.05r^3$. The

volume, V_b (in cm^3), of the bubble formed is thus related to the diameter of the orifice, 2R,

the surface tension of the liquid, γ (in dyn cm^{-1}), and density difference, $\Delta\rho$ (in g cm^{-3}), of the

liquid and the gas in the bubble:

$$V_b = 2\pi R\gamma/g\Delta\rho$$

If bubbles are produced by a capillary in a sample of sea water, this relationship suggests the

following influences. The volume, hence the bubble size, is inversely proportional to the liquid density. Since sea water is denser, the bubble size tends to decrease. The bubble volume is proportional to surface tension and the bubble size should increase with increasing surface tension. As sea water has low surface tension, the bubbles tend to be smaller. Both liquid density and surface tension are dependent on temperature but in opposite manners. While the liquid density decreases with increasing temperature, causing an increase in its volume, the reduction in surface tension with rising temperature compensates for this trend. Thus, the volume of a bubble stays constant. The influence of orifice diameter operates in two ways. On the one hand, the direct proportionality implies that the smaller the orifice, the smaller the bubble formed. On the other hand, at a given orifice diameter the bubble size varies considerably as the flow rate to the orifice is varied (Figure 2.2) . At low gas velocities the bubble volume is independent of flow rate and remains constant up to some critical value.

Figure 2.2   Variations of the bubble size with the flow rate (from Soo, 1967) .

In such a way separated bubbles are formed. At high flow rate, however, bubble volume varies as the bubbles are not of uniform size, and coalescence may take a place in a stream of rising bubbles. Formation of bubbles in series is referred to as chain bubbling. In this case, bubble diameters are independent of orifice diameter and increase with increasing flow rate, since coalescence of successive bubbles is observed.

2.2.3   Bubble Shape

While natural solid particles can occur in any imaginable form, bubbles, as fluid particles, take only a few shapes (Clift et al., 1978) . A static bubble on a liquid surface is called a floating bubble and is shaped like a cap. Bubbles moving in infinite media under the influence of gravity, as are bubbles in the ocean, occur in three regimes: spherical, ellipsoidal, and spherical or ellipsoidal cap. The bubbles are spherical when surface tension and/or viscous forces are more important than inertial forces. It is known that the relation of viscous force to the inertial force is presented by Reynolds number, $Re = ud/\nu$, where u and d are the bubble velocity and diameter respectively and ν is the kinematic viscosity. The ratio of surface tension force to inertial force gives the Weber number: $We = 2d\rho u^2/\gamma$, where γ is the surface tension and ρ is the dispersed phase density (i.e., the density of the gas within the bubble) . With increasing Reynolds number, reflecting a relative decrease of the viscous forces' importance, a spherical bubble adopts an oblate spheroidal shape. However, a bubble can remain nearly spherical even at high Reynolds number (up to 400), provided that the Weber number remains small (i.e., the surface tension value stays high) . At higher Reynolds

numbers, the bubbles become flattened, passing from ellipsoidal to spherical cap shape. Bubbles formed at an orifice and rising in a column of liquid follow closely this range of shapes and can be associated with specific orifice sizes:

1) For a circular orifice up to 0.4 mm in diameter, the bubbles are substantially spherical and after an initial acceleration on release, travel upward at a uniform velocity following a linear path.

2) For orifices between 0.4 and 4 mm in diameter, the bubbles are spherical at the orifice, but on release rapidly assume an ellipsoidal shape with the longer axis horizontal. In this form they travel upward, following a zig-zag (helical) path.

3) With orifice diameter exceeding 4 mm, the bubbles become unstable. They assume a spherical or ellipsoidal cap shape.

As bubbles rise through the liquid, they expand with the diminution of hydrostatic pressure and in consequence a bubble having a stable spherical or ellipsoidal form near the orifice may expand into the range of instability.

2.3   Bubble Dynamics

2.3.1   Single Bubble Dynamics

Once cavitation is initiated in a liquid, a bubble grows from the nucleus and later collapses under the influence of the steady liquid pressure at infinity. Bubble dynamics concerns the bubble wall motion and the primary result of the mathematical analysis is the

variation of bubble radius with time. First, Rayleigh gave a model for the bubble collapse

(Trevena, 1987) . The assumptions for the derivation are: a vapor-filled spherical bubble of

radius r is in an infinite domain of liquid with constant temperature and known pressure far

from the bubble, T_∞ and p_∞ respectively. If the bubble starts to collapse at t = 0, the motion

of the bubble wall at time t is given by:

$$\frac{p_b(t) - p_\infty(t)}{\rho_L} = r\frac{d^2r}{dt^2} + \frac{3}{2}\left(\frac{dr}{dt}\right)^2$$

where ρ_L is liquid density, μ_L is dynamic viscosity, and T_b and p_b are the temperature and

pressure inside the bubble, respectively. By integration, Rayleigh obtained the time for total

collapse of a bubble from some initial radius r_0 to zero to be:

$$t = 0.915r_0\left(\frac{\rho_L}{p_\infty - p_b}\right)^{1/2}$$

Though the initial problem in deriving this equation was bubble collapse, it applies equally to

growth. In Rayleigh's equation the bubble wall motion is driven only by inertial forces, so

both terms on the right-hand side are called inertial terms. If the viscous and surface tension

terms are included, the generalized Rayleigh-Plesset equation for bubble dynamics is obtained:

$$\frac{p_b(t) - p_\infty(t)}{\rho_L} = r\frac{d^2r}{dt^2} + \frac{3}{2}\left(\frac{dr}{dt}\right)^2 + \frac{4\nu_L}{r}\frac{dr}{dt} + \frac{2\gamma}{\rho_L r}$$

Although viscosity can be eliminated from the equation of motion, the boundary condition for the liquid pressure at the bubble wall involves it in the consideration. The effect of viscosity is to reduce the rates of growth or collapse compared to those attained in an inviscid liquid.

The consideration of the bubble contents further generalizes this equation. If the bubble contains some gas whose partial pressure is p_g at some reference bubble size r' and temperature T_∞ and the mass transfer of gas to or from the liquid is negligible, the pressure inside the bubble will be the sum of the vapor, p_V, and gas, p_g, pressures:

$$p_b(t) = p_V(T_b) + p_g(\frac{T_b}{T_\infty}) (\frac{r'}{r})^3$$

Using this expression for the bubble pressure, the Rayleigh-Plesset equation becomes:

$$\frac{p_V(T_\infty) - p_\infty(t)}{\rho_L} + \frac{p_V(T_b) - p_V(T_\infty)}{\rho_L} + \frac{p_g}{\rho_L} (\frac{T_b}{T_\infty}) (\frac{r'}{r})^3 =$$

$$= r\frac{d^2r}{dt^2} + \frac{3}{2} (\frac{dr}{dt})^2 + \frac{4\nu_L}{r} \frac{dr}{dt} + \frac{2\gamma}{\rho_L r}$$

The three terms on the left-hand side of this equation correspond to the instantaneous tension (driving term), the thermal effect (thermal term), and to the bubble contents (gaseous term). Those on the right are the inertial (actually 2 terms), viscous and surface tension terms. As

time proceeds from the moment of incipient cavitation, the relative importance of the various terms changes. Up to the so called first critical time, the most important term is the driving term. If the bubble contents include not only vapor but also some gas, the gaseous term is also of importance. After the first critical time is exceeded, the thermal term becomes larger than the inertial, and if tension remains constant, the bubble becomes thermally controlled. With further increase of time the inertial, viscous, gaseous and surface tension terms rapidly decline in importance and the growth of bubble decreases substantially.

Under conditions when the difference between the unknown T_b and the known T_∞ temperatures is negligible, the thermal term is zero as the vapor pressures at both temperatures will be equal. Then the equation, denoting an absence of thermal effects, can be written as

$$\frac{p_V(T_\infty) - p_\infty(t)}{\rho_L} + \frac{p_g}{\rho_L} \left(\frac{r'}{r}\right)^3 = r\ddot{r} + \frac{3}{2}(\dot{r})^2 + \frac{4\nu_L\dot{r}}{r} + \frac{2\gamma}{\rho_L r} \, ,$$

where the overdot denotes d/dt.

This equation can be solved numerically to find r(t), given the input $p_\infty(t)$, T_∞ and the other constants. Initial conditions are also required and for cavitating flow it is appropriate to assume that the microbubble (nucleus) of radius r_0 is in equilibrium at t = 0 in the fluid at a pressure $p_\infty(0)$ so that $p_g = p_\infty(0) - p_V(T_\infty) + 2\gamma/r_0$ and dr/dt$|_{t=0}$ = 0. A typical solution for Rayleigh-Plesset equation is shown in Figure 2.3: after the nucleus passes through low-pressure region, $p < p_\infty(0)$, at a dimensionless time of 0 the cavitation is initiated

Figure 2.3   Typical solution of the Rayleigh-Plesset equiation for spherical bubble
                (from Brennen, 1995) .

and a bubble starts to grow fairly smooth and reaches some maximum size, $r/r_0 \approx 90$, around

dimensionless time 400, then it collapses catastrophically to the original pressure at a

dimensionless time of 500; successive rebounds and collapses follow. In the absence of

dissipation mechanisms such as viscosity these rebounds would continue indefinitely without

attenuation.

        Though governed by one and the same equation, the growth and collapse of

a bubble are considered separately due to the dramatic consequences that bubble collapse has.

Calculations show that at the moment of collapse pressure about 10^{10} bar and temperature

4×10^4 times higher than the ambient temperature may be generated. A hint for these

consequences comes first from the Rayleigh analysis for the ideal case: the neglecting of the

liquid compressibility leads to an infinite bubble-wall collapse velocity as the radius approaches zero. Many factors such as the diffusion of gas from the liquid into the bubble and the effect of liquid compressibility, limit the estimated values. For example, the effect of including the liquid compressibility in theoretical considerations results in a strong reduction of the collapse velocity for radius less than 10^{-2} of the initial one. Nevertheless, the potential for generation of pressure pulse (shock waves) and noise, and material damage remains considerable.

A dominant feature in the collapse of many vapor-filled bubbles is the development of a reentrant jet due to an asymmetry such as the presence of a nearby solid boundary. Such an asymmetry causes one side of the bubble to accelerate inward more rapidly than the opposite side and this results in a high-speed jet that penetrates the bubble. The bubble then emerges from the collapse as a cloud of smaller bubbles, rather than as a single bubble, which continue to grow and collapse collectively. In addition, the solid boundary causes the jet to be oriented toward it thus creating highly localized and transient surface stresses. The repetition of this effect causes local surface fatigue of the solid boundary and the subsequent detachment of pieces of material. This is the reason for the damage to the blades of flow pumps or propellers. Another asymmetry that can cause the formation of a reentrant jet is the proximity of other neighboring bubbles in a cloud of bubbles. The bubbles in the outer edge of a such cloud tend to develop jets directed toward the center of the cloud. The bursting of the bubbles near a free surface is another example of a reentrant jet directed away from the free surface. Of course, the distance of the bubbles to the boundary plays a role and the jet develops differently. The violent collapse of bubbles

results in the production of noise as well as the material damage near a solid surfaces. The noise is a consequence of the momentary large pressures that are generated when the contents of the bubble are highly compressed.

2.3.2 Dynamics of a Bubble in a Flow

The next important step in bubble dynamics considerations is the motion of individual bubbles (or drops or solid particles) through a fluid. In this case the dynamics of relative motion rather than the dynamics of growth and collapse is in focus. In the analysis of a flow around a particle the usual approach to construct the equations for the translational velocity of the particle $u_i(t)$ at given velocity of the fluid $U_i(t)$ is to estimate all fluid forces acting on the particle and to equate the total force F_i to $m_p du_i/dt$ (where m_p is the particle mass, i denotes the vector components). For incompressible and Newtonian fluid the basic equations to be solved are the continuity equation

$$\frac{\partial u_i}{\partial x_i} = 0$$

and the steady state Navier-Stokes equations

$$\rho\left(\frac{\partial u_i}{\partial x_j}\right) = -\frac{\partial p}{\partial x_i} - \rho \nu \frac{\partial^2 u_i}{\partial x_j \partial x_j}$$

where ρ and ν are the density and kinematic viscosity of the continuous phase.

Commonly the first force acting on the particles to be determine is the drag force. The classical Stokes solution for rigid spheres was modified for fluid spheres, such as the bubbles, to account the velocity distributions in both phases. For large Reynolds numbers (Re >> 1) the drag coefficient is $C_D = 48/Re$ and the experimental data showed that the drag curve for fluid particles deviates from that for rigid particles. Also, a circulating motion of the fluid inside the particles was observed due to external flow. Such bubbles with internal motions are classified as *circulating particles in contrast to rigid particles*. A bubble behaves as a rigid particle when it is covered with a surface film (contaminated systems) which prevents any internal motion or significant deformation of the bubble shape under normal and shearing stresses. When such film is not built on the bubble wall (purified systems) and inertial forces are not significant (low Reynolds number), the gas comprising the bubble has motion of its own and the bubble is a circulating particle. Heat and mass transfers to and from the immersed particles is observed and for the case of fluid particles these transfers are affected by the internal motion. The transfer rates from circulating particles were observed to be about five times larger than those from noncirculating "rigid" bubbles.

Beside the drag force, a buoyancy force also acts on the particles. By equating the drag and the buoyancy force on a bubble, a relationship between rise velocity and radius of the bubble can be determined (Batchelor, 1967). For large Reynolds numbers, when the viscosity is not important (i.e., large bubbles), the rise velocity is given by $V_r = gr^2/9\nu$. For small Reynolds numbers, when the viscosity is important (i.e., small bubbles), the rise velocity is $V_r = gr^2/3\nu$. This principle extends to a bubble radius of about 1.2 mm. For air bubbles in water this size may be taken as the dividing line between large and small bubbles. The

velocity of small bubbles is controlled by viscosity and surface tension. For large bubbles both, the relationship between the velocity and the radius and the vertical path of rising, are controlled by the turbulence. Therefore the three bubble shape regimes and their respective rising path appearance give three different regions of the bubble terminal velocity (Figure 2.4). These are: Streamline region (noted as I in the figure), covering the small bubble sizes (up to 1 mm) and characterized with fairly spherical bubbles with straight line path; Intermediate region (II in the figure), covering bubble sizes from 1 to about 3.5 mm and having ellipsoidal bubble shapes with zig-zag motion; Turbulent region (III in the figure), over large bubble sizes (from about 3.5 mm to 1 cm) with deformed bubbles and irregular rising path.

Figure 2.4   Flow regimes of bubble motion (from Soo, 1967) .

Note that when the bubbles are formed artificially some initial velocity may be added. And that velocities of successive bubbles are higher than that for single bubbles of the

same size, particularly in the range of 1 mm radius.

2.3.3 Bubble Clouds Dynamics

Higher concentration of bubbles in a flow forms a multiphase system. In the case of a bubbly mixture of the liquid and its vapors, the system has two phases and two components. More realistic notion for multiphase flow is a system having two phases and three components since virtually there is always some gas in real bubbles. The asymptotic states of a multiphase system are the *homogeneous* mixture when the dispersed phase (the bubbles) is uniformly distributed within the continuous phases (the liquid), and the *separated* flow when the two phases exist in two separate streams. While the two streams in a separate flow can travel at different velocities and the relative motion is a necessary part of the analysis, in well mixed homogeneous system with small particle sizes any significant relative motion is negligible. In absence of relative motion the governing mass and momentum conservation equations reduce to forms similar to those for a single-phase flow. However the effective mixture density ρ is taken into account

$$\rho = \sum_n \alpha_n \rho_n$$

where α_n is the volume fraction of each of the n components or phases whose individual densities are ρ_n. The analysis can follow two paths. Along the first path, the continuity and momentum equations for the homogeneous mixture as a whole in the absence of viscous

effects are used in the form

$$\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial x_j}(\rho u_j) = 0$$

$$\frac{\partial}{\partial t}(\rho u_i) + \frac{\partial}{\partial x_j}(\rho u_i u_j) = -\frac{\partial p}{\partial x_i} + \rho g_i$$

In addition, a barotropic relation, $p = f(\rho)$ and its associated sonic speed $c = (dp/d\rho)^{1/2}$ are

sought. The result relates the sonic speed, c, and the air volume fraction, α, in the liquid, and

reveals the most remarkable feature of the gas/liquid systems: the sonic velocity can be much

smaller (as low as 20 m s^{-1}) than that in each of the mixture components. The second path

is followed when the barotropic relation for the mixture can not be established. Then the

continuity and momentum equations are written in terms of the volume of individual bubbles

$V_b = 4/3 \pi r^3$ rather than the mixture density ρ:

$$\rho_L \frac{Du_i}{Dt} = -(1 + N_b V_b) \frac{\partial p}{\partial x_i}$$

$$\frac{\partial u_i}{\partial x_i} = \frac{N_b}{(1 + N_b V_b)} \frac{DV_b}{Dt}$$

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where N_b is the number of bubbles per unit volume and $D/Dt = \partial/\partial t + u_i\partial/\partial x_i$. The relation

between the pressure p and the bubbles volume V_b is assured by the Rayleigh-Plesset

equation. This system of equations can be solved for the unknown $p(x_i, t)$, $u_i(x_i, t)$ and

$V_b(x_i,t)$ and physically gives the history of the size of individual bubbles as they progress in

the flow and the interactions between them. The significant change of the sound propagation

speed and acoustic attenuation are also obtained using this approach, however, this time the

effect of the individual bubble dynamics on the behavior of a homogeneous bubble mixture

is revealed.

This approach is used when the effect of the individual bubble dynamics on the

dynamics of a finite cloud of bubbles is of interest. The analysis of the collective dynamics

of bubble clouds seeks the response of the cloud to a small perturbation in the pressure at

infinity, p_∞. The result determines the bubbles radii $r(x_i,t)$, velocities $u (x_i,t)$ and pressure

$p(x_i,t)$ in terms of the initial bubble radii r_0 and cloud size A_0, the number of bubbles N_b in

the cloud and the amplitude and frequency of the perturbation. It shows that the cloud has

a number of natural frequencies (the term natural frequency is introduced in §2.4) and modes

of oscillation. If the perturbation amplitude is zero the cloud would have oscillations only at

its natural frequencies. The lowest natural frequency of the cloud ω_{low} can be related with the

mean void fraction $\alpha_0 = N_b V_{b0}/(1+N_b V_{b0})$, where V_{b0} is the initial bubble volume, as

$$\omega_{low} = \omega_N \left[1 + \frac{4}{3\pi^2} \frac{A_0^2}{R_0^2} \frac{\alpha_0}{1 - \alpha_0}\right]^{-1/2}$$

Hence, the natural frequencies of the cloud will extend to frequencies much smaller than the

individual bubble frequency, ω_N, if the initial void fraction, α_0, is much larger than the square of the ratio of bubble size to cloud size, $\alpha_0 >> (R_0/A_0)^2$. If the reverse is the case, $\alpha_0 << (R_0/A_0)^2$, all the natural frequencies of the cloud are contained in a small range just below ω_N.

2.4 Bubble Acoustics

The response of a bubble to a continuous, oscillating pressure field is the domain of acoustic cavitation. The acoustic cavitation has two important characteristics. One is that generally it is a non-linear process manifested in non-proportional changes of the bubble radius with the sound pressure. The second is that the high compressibility of the gas bubbles leads to a gaining of much potential energy when the bubbles expand and to concentration of kinetic energy when the bubbles collapse. This transformation of low energy density sound wave into a high energy collapsing bubble, or the concentration of the energy into a very small volume produces very high pressures and temperatures which can erode solids, initiate chemical reactions and produce luminescence. One useful classification of the subject uses the magnitude of the bubble radius oscillations in response to the imposed fluctuating pressure field. Accordingly, three regimes can be distinguished: 1) For very small pressure amplitude the response is linear. The first step in the linear analysis is to identify the

natural frequency of an oscillating bubble. 2) The response of a bubble will begin to be affected by the nonlinearities in the governing equations, particularly the Rayleigh-Plesset equation, as the amplitude of oscillation increases. Nevertheless, the bubble may continue to

oscillate stably. Such situations are referred as *stable acoustic cavitation* and the bubbles oscillate for many sound wave periods. 3) There are circumstances when the change in bubble size during a single cycle of oscillation become so large (several orders of magnitude) that the bubble undergoes an explosive growth, and then violent collapse similar to the collapse in a liquid in rest. Such bubble response to the outer pressure field is termed *transient acoustic cavitation*. These three situations follow with increasing the amplitude of oscillation, but there are also other factors that can affect the bubble response to be stable or transient. One of the factors is the relationship between the frequency ω of the imposed oscillations (i.e., the sound frequency) and the natural frequency of the bubble ω_N. Another factor is the relationship between the pressure oscillation amplitude p_{osc} and the mean pressure of the continuous phase $|p_\infty|$. For example, if $p_{osc} < |p_\infty|$, the bubble is never under tension and will not cavitate. Factor affecting the bubble response is also the content of the bubble: predominantly vapor or gas. Gas-filled bubbles are prone to stable oscillations while bubbles which contain mostly vapor more readily exhibit transient acoustic cavitation.

In order to find the natural frequency of a bubble the linearized solution of the Rayleigh-Plesset equation is considered. The pressure in the liquid far from the bubble, p_∞, is the sum of the mean pressure $|p_\infty|$ and small oscillatory pressure of amplitude p_{osc} and frequency ω

$$p_\infty = |p_\infty| + Re[p_{osc}e^{j\omega t}]$$

where $Re[\cdot]$ denotes the real part of a complex number. The linear response of the bubble

will be the sum of some equilibrium size r_e at pressure $|p_\infty|$ and bubble radius oscillation φ (generally a complex number)

$$r = r_e (1 + Re[\varphi e^{j\omega t}]).$$

From the Rayleigh-Plesset equation the frequency at which the maximum amplitude (or peak or resonant response) of the bubble radius occurs, ω_p, can be found:

$$\omega_p = [\frac{3(|p_\infty| - p_V)}{\rho_L r_e^2} + \frac{4\gamma}{\rho_L r_e^3} - \frac{8v_L^2}{r_e^4}]^{1/2}$$

The resonant frequency ω_p is an important quantity in any bubble dynamic problem. It is function of the pressure difference ($|p_\infty|$ - p_V), the equilibrium bubble radius r_e and the liquid properties. For small bubbles the viscous and surface tension terms dominate and the resonant frequency is almost independent on the pressure. For large bubbles the viscous influence become negligible and ω_p depends on ($|p_\infty|$ - p_V) . The natural frequency, ω_N, is defined as the value of the resonant frequency, ω_p, for zero damping, which is represented by the viscous terms:

$$\omega_N = [\frac{1}{\rho_L r_e^2} \{3(|p_\infty| - p_V) + 4 \frac{\gamma}{r_e}\}]^{1/2}$$

For the typical nuclei commonly found in water, 1 to 100 μm, the natural frequencies are of order 5 to 25 kHz.

There are three primary contributions to the damping of bubble oscillations, namely that due to liquid viscosity, that due to liquid compressibility through acoustic radiation, and that due to thermal conductivity. These are usually presented as three additive contributions to a total damping coefficient δ which is employed in the Rayleigh-Plesset equation in the place of the liquid viscosity μ_L:

$$\delta = \mu_L + \delta_T + \delta_R$$

The relative magnitude of the three components of damping are quite different for different bubble radii r_e (Figure 2.5). The viscous dissipation in the bulk liquid, μ_L, dominates for very small bubbles; the thermal component, δ_T, coming from irreversible

Figure 2.5   Sound damping coefficients for an air bubble (from Clay and Medwin, 1977). Note the dual abscissa.

heat loss associated with isothermal compression near the bubble wall, is important for bubble size range of practical interest; the re-radiation component, δ_R, emerging from the scattering

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of the sound in all directions when the sensing sound impulse strikes the bubbles and causes its radial oscillation, dominates only for bubbles larger than 1 cm.

When the perturbation of the bubble radius, φ, is small the response is linear. However, at larger perturbations nonlinear effects take place. One of these is the observation of bubble responses at not only harmonics frequencies higher than the perturbation frequency ω (superharmonics) but also at frequencies less than ω (subharmonics). As the amplitude of excitation increases both super- and subharmonic frequencies become more prominent. These different kinds of response occur depending on whether ω is greater or less than the natural frequency of the bubble. Another nonlinear effect, the mass transfer of dissolved gas between the liquid and the bubble, is called rectified mass diffusion. During the oscillation of the bubble radius with the sound wave, gas is flowing in and out of the bubbles in the positive and negative cycles, respectively. However, as during expansion the bubble surface is larger and the interface thinner than those during contraction, there is a net flux of gas into the bubbles. So, this effect would be added to the bubble growing by the inertial forces and would cause growth even in liquid nonsaturated with gas. A third kind of nonlinear effect is the force experienced by a bubble in an acoustic field due to the finite wavelength of the sound waves, called Bjerknes force. This force causes a migration of the bubble in a stationary sound field, so that the bubble will go to and from different points along the sound wave profile, respectively different pressures. As a consequence the bubble may start to grow by rectified diffusion which may not otherwise occur.

2.5   Bubble Optics

Another vast field of study related to the particles, including bubbles, and cloud of particles is their interaction with the light. In this case processes such as absorption, emission, and scattering are considered. The Mie theory analyzes the intensity of scattered radiation by a single spherical particle. In a space containing only a few particles the scattered intensity is nearly equal to the scattered intensity from a single particle multiplied by the number of particles. For denser mixtures multiple scattering becomes important. The scattering from air-filled bubbles in water can be generally described with the Mie theory for scattering of plane electromagnetic wave by a dielectric sphere. The scattering from bubbles include three phenomena: 1) light is deviated from its line on propagation (diffraction); 2) light penetrates the particle and emerges with or without one or more internal reflections (refraction); and 3) light is reflected externally. The diffraction is independent on the particle composition, whereas the refraction and reflection are determined by the refractive index of the particle, hence their composition. Particle size is the major parameter in the scattering. The influence of the shape was also studied. The diffraction pattern and external reflection from irregular randomly oriented particles are similar to those produced by spherical particles since the projected area and the probability for reflection from all angles of incidence are equal. Bubbles in water have the so called critical scattering region, Figure 2.6. Only the rays with incident angle of $\theta = 0^\circ$ pass through the bubble unchanged. For all incident angles θ from 0 to some critical value $\theta_c = \arcsin(1/1.33) = 48.8^\circ$ the rays deviate from the forward direction of propagation. The light incident at angles greater than θ_c is totally reflected.

Figure 2.6   Ray paths through an air bubble from a parallel light source
             (from Walsh and Mulhearn, 1987) .

2.6   Temperature Effect

Temperature can influence the single-bubble dynamics significantly in some circumstances. It is seen from the generalized Rayleigh-Plesset equation (§ 2.3.1, p. 18) that thermal effects would occur if the temperatures in the bubble and the liquid, T_b and T_∞, are significantly different since the vapor pressure p_V would be different at the both temperatures. Often this difference, $(T_b(t) - T_\infty)$, is negligible and then the bubble wall motion would be inertially controlled, i.e. governed only from the first and third terms in left-hand side of the equation. But there are circumstances in which the temperature difference is important and the effects caused by this difference dominate the bubble dynamics. Bubble growth and collapse are then thermally controlled. To evaluate how the departure of the bubble temperature T_b from the liquid temperature T_∞ influences the bubble dynamics, it is necessary to determine the relation between the temperature difference $(T_b - T_\infty)$ and the bubble radius changes $r(t)$. From the energy balance equation it is possible to obtain relation between the bubble radius $r(t)$ and the temperature gradient at bubble wall $(\partial T/\partial x_i)_{xi = r}$. Then, relation between $(\partial T/\partial x_i)_{xi=r}$ and $(T_b - T_\infty)$ can be found by solving the heat diffusion equation; but, no

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exact analytical solution exists. The approximate solution, confined for the cases in which the thickness of the thermal boundary layer surrounding the bubble is small compared with the bubble radius, provides a result which shows the bubble dynamic behavior is strongly dependent on thermodynamic parameters.

The net result of the thermally controlled bubble growth is that after some critical moment when the thermal term of the Rayleigh-Plesset equation becomes important, the bubble radius would increase more slowly. That is, the thermal effects would inhibit the bubble growth.

Thermal effects are negligible for most of the collapse phase, however, they play a very important role in the final stage of collapse when the bubble contents are highly compressed by the inertia of the inrushing liquid. The elapsed time for this process is very short (in order of microseconds) and hence the gas in the bubble behaves adiabatically. But, despite the small elapsed time, heat transfer between the liquid and the gas is significant because there are extremely high temperature gradients on short distances (e.g., from the bubble wall to its center the temperature difference may be 3400°K and after 2 μs the interface temperature may drop to 300°K) .

For the cases of bubble dynamics in a flow, the temperature influence is revealed through convection and Marangoni effect. The Marangoni effect, caused by gradients in the temperature (or surfactant concentration, §2.7.2), creates gradients of surface tension γ over the bubble surface. The surface tension decreases linearly with the temperature and the controlling property dγ/dT is identifiable. The surface tension gradient

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creates in a certain direction a flow tangential to the bubble surface and shear stress in opposite direction is required in order for the surface to remain in equilibrium. Such a shear stress, however, would modify the boundary conditions necessary for the validity of the Rayleigh-Plesset equation solution, hence altering the flow and forces acting on the bubbles. Indeed, a Marangoni force, $2\pi r^2 (d\gamma/dx)$, acting on the bubble should be added to the drag force in the direction of decreasing surface tension. Thus, the presence of a temperature gradient in some direction x, dT/dx, would lead to an additional force on the bubble of magnitude $2\pi r^2 (-d\gamma/dT)(dT/dx)$ in direction of the warmer fluid since the surface tension decreases with temperature.

The convection, caused by the relative motion between the bubble and the liquid, usually enhances the rate of heat transfer to the interface of the bubble and hence affects the dynamics of thermally controlled growth. The enhancement of heat transfer rate is normally represented by a Nusselt number, Nu, defined as the ratio of the actual heat transfer rate to the rate of heat transfer by conduction and is introduced in the thermal term in the Rayleigh-Plesset equation. Then the relationship between Nu and the Péclet number, Pe, is sought. (The Peclet number is defined as $Pe = ur/\alpha_L$, where u is the typical translational velocity of the bubble relative the liquid, and α_L is the thermal diffusivity of the liquid.) The exact form of this relationship is not known, but in many convective heat transfer problems it takes the form

$$Nu = 1 \qquad \text{for } Pe \ll 1$$

$$= C \, Pe^m \quad \text{for } Pe \gg 1,$$

where C is a constant of order 1, m < 1. Also, the form of the relative velocity u should be assumed. It could be due to the buoyancy, to the pressure gradients caused from the acceleration of the liquid, or to the presence of a solid boundary nearby. Estimates for different cases show that the convective heat transfer may delay or even eliminate the thermal inhibition on the bubble growth and the inertial controlled growth would continue indefinitely.

2.7   Surfactant Effect

2.7.1   Influence of the Surfactants on Bubble Characteristics

Bubble formation, stability and velocity are strongly influenced by the presence of surface active material (surfactant), or by the purity of the system.

The comparison of the data on bubble terminal velocities from different investigators reveals a wide spread in the data which results from experimental scatter, but the greatest cause is the bubble surface contamination. Experimental terminal velocities for air bubbles rising in water are gathered by Clift et al. (1978) in Figure 2.7. In the figure the ellipsoidal regime and adjacent parts of the spherical and spherical-cap regimes of bubbles shape are presented with two curves: a curve for pure water and for contaminated water. Both curves converge for small (spherical) bubbles, since even purified water tends to contain

Figure 2.7   Terminal velocity of air bubble in water (from Clift et al., 1978) .

sufficient surfactant to cover completely small areas with a film, and for large (spherical-cap)

bubbles, since surface tension forces cease to be important. Surface-active contaminants

affect the rise velocity most strongly in the ellipsoidal range. At very low concentrations of

the surface active agent, this effect is almost not observable. As the concentration of the

surfactant is increased, a marked decrease in terminal velocity takes place for particles with

diameter in the range 1 - 7 mm. This implies that the terminal velocity may never reach steady

state and may pass through a maximum. At relatively high surfactant concentrations the

terminal velocity becomes independent of the surfactant concentration again.

Very few workers have succeeded in eliminating all surface-active

contaminants from their systems. Moreover, the type and concentration of contaminants

present have seldom been characterized. Lastly, as Figure 2.7 shows, the careful purification of a system has little effect for small and large bubbles. Based on the available evidence, the following conclusions may be drawn:

1) Surfactants tend to damp out internal motion by rendering the interface rigid. The influence of surfactant is most significant for low values of the ratio bubble viscosity/bulk liquid viscosity, since at large values of this ratio the viscous resistance of the internal fluid limits internal motion even for pure system.

2) Surfactants have the greatest influence on terminal velocity near the point of transition from rectilinear to oscillating motion. The reason is that the internal circulation can drastically alter the wake structure of a fluid particle.

3) Surfactants play a particularly important role in high surface tension systems (e.g. air/water) since the surface tension reductions are largest for these systems.

4) Most of the experimental results in the literature are for contaminated bubbles. It is difficult to eliminate the surface-active substances in systems of practical importance, thus the surfactant presence is not a serious limitation.

It is interesting then to understand why and how the surface active materials change the solutions properties and cause these significant effects.

2.7.2   Surfactant Nature and Action

A surface-active agent is a substance that, when present at low concentration in a system, has the property of adsorbing onto the surfaces and interfaces of the system and of altering to a marked degree the surface or interfacial free energies (surface tension) of those surfaces (or interfaces) . (There is a strict differentiation between surface and interface in the theory of the interfacial phenomena: the term *interface* indicates the boundary between any two phases; the term *surface* denotes the interface where one phase is a gas, usually air.)

It is recognized that important physical, chemical, and electrical properties of matter confined to phase boundaries are often profoundly different from those of the same matter in bulk. For many systems, even those containing a number of phases, the fraction of the total mass that is localized at phase boundaries (interfaces, surfaces) is so small that the contribution of these "abnormal" properties to the general properties and behavior of the system is negligible. There are, however, circumstances under which these "different" properties play a significant role. One such circumstance is when the phase boundary area is so large relative to the volume of the system that a substantial fraction of the total mass of the system is present at the boundaries (e.g., in all sorts of dispersions, such as emulsions, colloids) . In this circumstance surfactant can always be expected to play a major role in the system. Another such circumstance is when the phenomena occurring at phase boundaries are so unusual relative to the expected bulk phase processes that the entire behavior of the system is determined by the interfacial processes (e.g., corrosion, detergency, or flotation) .

What makes a substance to act as a surfactant is its molecular structure. The surfactants have the so called *amphipathic* structure, which means that their molecules consist of two chemical groups called *lyophobic* and *lyophilic* groups; for aqueous solutions these

groups are respectively *hydrophobic* and *hydrophilic*. The two groups have radically different behavior relative to the molecules of the solvent in which the surfactant is: the lyophobic group has very little attraction for the solvent molecules, while the lyophilic group has strong attraction for the solvent. When a surface-active agent is dissolved in a solvent two processes occur. On the one hand, the presence of the lyophobic group in the interior of the solvent causes a distortion of the solvent liquid structure thus increasing the free energy of the system. For example, the increase of the free energy of a water/surfactant solution means that less work is needed to bring a surfactant molecule to the surface in comparison with the work for a water molecule. The surfactant therefore concentrates at the surface. Once the surfactant is adsorbed on the surface it decreases the interfacial free energy, or the surface tension. (Note that there is a difference between the terms *free energy* of the system and *interfacial free energy* of the surface.) Alternately less work is required to create a unit area of the interface or to expand it by a unit area. On the other hand, the presence of lyophilic group prevents the surfactant from being expelled completely from the solvent as a separate phase. Also, the lyophilic group provides the most gradual possible transition from the one phase to the other by its orientation toward the liquid phase while the lyophobic groups orientation is away from it. As an ultimate result, the amphipathic structure of the surfactant causes 1) concentration of the surfactants at the surfaces, 2) reduction of the surface tension of the solvent, and 3) orientation of the molecules within the surface layer.

The lyophobic group is usually a long-chain hydrocarbon residues contained in all kind of fatty acids. The lyophilic group is an ionic, or highly polar, group. In addition, the chemical composition that makes a group to be suitable for the lyophobic or lyophilic portions of the surfactant molecule vary with the nature of the solvent and the conditions of use. In a highly polar solvent such as water, hydrophobic group may be a hydrocarbon or fluorocarbon, whereas in a less polar solvent only some of these may be suitable, e.g., only fluorocarbon is suitable to be a lyophobic group in polypropylene glycol as a solvent. As the temperature and use conditions (e.g., presence of electrolyte or organic additives) vary, modification of the structure of the lyophobic and lyophilic groups may become necessary in order to maintain surface activity at a suitable level.

The addition of neutral electrolyte (such as NaCl, KBr) to an aqueous solution increases its ionic strength. In such a solution the adsorption of the surfactant molecules to the surfaces is enhanced because the repulsion between the oriented ionic molecules at the surface decreases. The oriented ionic molecules of the surfactant repulse the ions of the electrolyte and keep them at some small distance from the surface layer. Consequently, the concentration of ions as Na^+ and Cl^- in the interfacial layer is slightly less than in the bulk solution (Scott, 1986). This is termed as *negative* adsorption and characterizes the surface activity of *inorganic* salts: they slightly increase the surface tension of the solution instead of decreasing it as the "true" surfactant. The effect of increasing of surface tension of a solution by inorganic salts is generally very weak and even small amount of organic additives would suppress it and the general trend of the surfactant action – to reduce the surface tension – would prevail.

Surfactants usually act to reduce interfacial free energy (the surface tension) rather than to increase it, although there are occasional counter-examples, as it was mentioned above. The typical variation of surface tension with changes of the surfactant concentration, known as a Gibbs effect, is given in Figure 2.8. Initially, at very small surface concentrations, for which the molecules of the surfactant are still further apart, the surface tension reduction is almost unnoticeable. As the surfactant concentration increases and its molecules become sufficiently close packed to interact, the surface tension decreases more quickly until reaches

Figure 2.8   The variation of surface tension with surfactant concentration
                  (from Scott, 1986) .

its lower limit. At this critical surfactant concentration value the adsorbed layer is densely packed having thickness of order one molecule. The reduced surface tension facilitates the creation of a new or expansion of the existing interface which eventually leads to rupturing of the film. The tendency of rupturing the film is opposed by the film *surface dilational elasticity*, ϵ, which quantifies the resistance of the surface layer to mechanical disturbances. The film elasticity gives a measure of the ability of the film to adjust its surface tension in an

instant of stress. Referring to Figure 2.8 again, the film elasticity is defined by the negative slope of the curve: $\epsilon = d\gamma/d(lnA)$, where A is the surface area per surfactant molecule. For clean surfaces without surfactant the dilational elasticity is zero (no slope), then it increases to some maximum value (the steepest portion of the curve) with the concentration of the surfactant and finally becomes zero again when the surfactant is densely packed. When the elasticity is zero the film is prone to rupturing. Otherwise a mechanism of stabilizing the film is set at work. When a local spot in the film thins and stretches (for example, through a drainage by gravity, temperature changes or surfactant concentration variations), and the area of the film in that region increases, the surface tension increases from γ_1 to γ_2 (Figure 2.9)

Figure 2.9   Mechanism for restoring of a stretched surface active film
               (from Rosen, 1978) .

and a gradient of the tension ($\gamma_2 - \gamma_1$) is set up (Marangoni effect) that causes the liquid to flow toward the thinned spot from the thicker portion around it. In this way further thinning of the film is prevented, even "healed" by the surface transport of underlying material. So, the interplay between the two effects, Gibbs and Marangoni, stabilizes surface active films having some dilatational elasticity. The stabilization of films is affected by the difference in the relative solubilities of the chemical species involved, which would leads to difference in the mechanical properties of the film adsorbed (Garrett, 1967) . The films composed of

predominantly soluble surface active material forms more fluid surface layers for which adsorbing and desorbing from an interface is easy. Thus they constantly furnish stabilizing molecules to the interfaces and protect it against rupture. However, with an increase of the surfactant concentration the soluble material is displaced by a more insoluble one and the film becomes more brittle, i.e., the mechanical properties of the surface become less elastic and rupture of the film is more likely.

2.7.3   Foam

According to foaming theory, foam is produced when gas is introduced beneath the surface of a liquid that expands to enclose it with a film (Rosen, 1978). One type of foam is the mixture of gas particles separated by rather thick liquid films (Adamson, 1982); this is well exemplified by bubble clouds. The second type of foam contains mostly honeycomb-shaped bubbles of gas separated by thin films called *lamellae*. Good example of it is the foam lasting on the sea surface after the breaking of waves. Absolutely pure liquids do not foam. Gas bubbles introduced beneath the surface of an absolutely pure liquid rupture immediately when they touch each other or dissolve. For true foaming to occur the presence of surfactant that can be absorbed on the bubble interface to form a film resisting the excessive thinning of the lamella is required. Therefore, the film elasticity ϵ, defined in §2.7.2, is a necessary condition for a system to produce foam. The foam will be *persistent,* with lifetime measured in hours even days, when the actions of the Gibbs and Marangoni effects are balanced at given surfactant concentration and prevent the rupture of the lamella

after most of the liquid has drained out of it. *Transient* foam, with a lifetime less than a minute, exhibits a specific maximum as the concentration of the surfactant is varied. This common observation is explained by the Gibbs effect: the stabilizing mechanism, allowed by the film elasticity, is significant only within a certain concentration range of the solute (the sloped region of the curve in Figure 2.8), hence for these surfactant concentrations the foam will be stabilized. Out of this range, at very low and at too high surfactant concentrations, the change of the surface tension will be small and the gradient will be insufficient to prevent the thinning and stop eventual rupture of the film. The foaming properties of solutions can be modified greatly by the presence of organic materials: solutions that show excellent foaming properties can be converted to low- or nonfoaming materials and vice versa. The principle is that organic materials increase the rate of attainment of surface tension equilibrium, or because the critical value for the surfactant concentration is lowered.