Chapter 2
Nucleation

Cavitation is critically dependent on the existence of nucleation sites. Cavitation starts when these nuclei enter a low-pressure region where the equilibrium between the various forces acting on the nuclei surface cannot be established. As a result, bubbles appear at discrete spots in low-pressure regions, grow quickly to relatively large size, and suddenly implode as they are swept into regions of higher pressure. In most conventional engineering contexts, the prediction and control of nucleation sites is very uncertain even when dealing with a simple liquid like water. Here we present data on the nuclei distribution in more complex fluids, such as polymer aqueous solutions and blood.

2.1 Nucleation Models

Nucleation is the onset of a phase transition in a small region of a medium. The phase transition can be the formation of a tiny bubble in a liquid or of a droplet in saturated vapour. There are two main types of nucleation models: homogeneous nucleation and heterogeneous nucleation.

Homogeneous nucleation takes place in a liquid phase without the prior presence of additional phases (Fuerth 1941; Church 2002). It is a consequence of the distribution of thermal energy among the molecules comprising a volume of liquid. Because some molecules will be more energetic than others, random processes will occasionally produce groupings of higher energy molecules. If the average energy is high enough, such a grouping of molecules represents an inclusion consisting of gas and vapour in the bulk of the liquid. Because statistical fluctuations in the distribution of thermal energy occur continuously, the small gas or vapour inclusions are constantly forming and disappearing. Such cavitation nuclei are, however, unstable. A gas bubble will dissolve in an undersaturated solution and the effect of surface tension will cause it to dissolve in a saturated solution. In supersaturated solutions, a bubble can be in equilibrium because the tendency for the bubble to dissolve due to surface tension is opposed by the tendency for the bubble to grow by diffusion of gas into it. This equilibrium is unstable; the bubble will grow or dissolve depending on whether the perturbation increases or decreases the bubble's radius relative
to its equilibrium radius (Epstein and Plesset 1950). Therefore, a liquid would be free of bubbles after a short period of time. This does not imply that gas bubbles could not serve as cavitation nuclei. It does imply, however, that in order for gas bubbles to serve as cavitation nuclei, they must be stabilized at a size small enough to prevent their rising to the surface of the liquid, yet large enough so that they will grow when exposed to negative pressure as low as a few bars. In other words, a stabilization mechanism must exist for a gas bubble before it can act as a cavitation nucleus. Various types of stabilizing skins have been proposed. These skins usually consist of contaminants which somehow deposit themselves on the bubble’s surface and counteract the surface tension. Fox and Herzfeld (1954) proposed that surface active organic molecules could form a rigid skin around a gas bubble. This skin would be impermeable to gas diffusion and would be mechanically strong enough to withstand moderate hydrostatic pressures. Rather than the rigid skin of organic molecules proposed by Fox and Herzfeld, Yount (1979, 1982) has developed a stabilization theory in which the dissolution of gas bubbles is halted by a non-rigid organic skin. This so-called varying-permeability model, which employs a skin of surface-active molecules to stabilize the nucleus, has been mainly applied to bubble formation in supersaturated liquids. Although this model was originally used to explain bubble formation in gelatin upon rapid decompression, Yount noted that it can be applied to bubbles in water as well. It can also be applied to polymer solutions because polymers have surfactant properties. Surfactants present a barrier to mass transport and reduce the surface tension at a liquid-gas interface (Borwankar and Wassan 1983). Both mechanisms increase the stability of nuclei against dissolution (Porter et al. 2004). Furthermore, since surfactants are prevalent in biological systems, this model may be particularly important for applications involving decompression sickness and medical ultrasonics.

In heterogeneous nucleation small pockets of gas are stabilized at the bottom of the cracks or crevices found on hydrophobic solid impurities in the liquid (Strasberg 1959; Apfel 1970; Atchley and Prosperetti 1989). Liquids normally contain a large number of solid impurities with a very irregular surface consisting of grooves or pits (Crum 1979). As is schematically shown in Fig. 2.1, a crevice stabilized gas nucleus can have an interface that is concave towards the liquid. Due to surface tension, the pressure of the gas in the nucleus can therefore be less than the pressure in

**Fig. 2.1** The crevice model of nucleation: (a) Stabilization mechanism of nuclei. (b) Nucleus starts to grow into a bubble when the pressure in the surrounding liquid is reduced
the liquid, and if gas diffuses from the nucleus, so long as the contact line is pinned, the concavity will increase, reducing the pressure of gas. Hence such a nucleus can persist without dissolving completely into the liquid. The origin of such nuclei has been explained by considering the flow of a liquid onto a hydrophobic surface with crevices (Atchley and Prosperetti 1989). The crevice model is useful for explaining the hysteresis effect of pressurization on cavitation threshold (Crum 1980). The cavitation threshold increases because pressurization causes the crevice to shrink and gas diffuses into the surrounding liquid. After the pressure is released, a smaller pocket of gas exists in the crevice requiring a larger negative pressure to produce nucleation.

Another explanation of the origin and persistence of nuclei is that ordering of liquid molecules adjacent to solid surfaces leads to local hydrophobicity in regions of concavity of an otherwise non-hydrophobic surface (Mørch 2000). This explanation suggests that the resulting voids have interfaces which are convex toward the liquids, and that their persistence is due to a resonant behaviour forced by ambient vibrations.

Cavitation nuclei are not always permanently stabilized. Short-lived nuclei can also formed by radiation. Although many theories have been proposed to explain this phenomenon, the one that seems to have the most experimental support is the thermal spike model (Seitz 1958). In this model, a positive ion is created by the radiation-matter interaction. This ion quickly liberates its energy, generating neighbouring atoms that are thermally excited. If tension exists within the liquid, this region can produce a vapour bubble that expands and eventually results in a cavitation event.

Example: Classical Theory of Homogeneous Nucleation

According to classical theory of homogeneous nucleation (see, for example, Frenkel 1955), a nucleus is spontaneously generated as a result of density fluctuations in the metastable liquid phase in the form of a small vapour bubble of radius \( r \). A minimum reversible work required to form a nucleus of new phase depends on the radius of the bubble and arrives a maximum at the critical radius \( r_c \). The nucleation rate \( J \), which determines the average number of nuclei formed in a unit volume of the metastable phase per unit time, is proportional to the probability of having a critical nucleus

\[
J = J_0 \exp \left( -\frac{W_{\text{min}}}{k_B T} \right),
\]

where

\[
W_{\text{min}} = \frac{4}{3} \pi r_c^2 \sigma
\]

determines the nucleation barrier, which is equal to the minimum reversible work required to form a critical size nucleus, \( \sigma \) is the surface tension, \( k_B \) is the Boltzmann constant, and \( J_0 \) is a factor which does not depend on the critical radius \( r_c \) and changes only slightly with the depth of penetration into the metastable state. All
modifications introduced in the theory later do not change the general result of the classical theory given by Eqs. (1) and (2) and concern only details of calculations of the kinetic prefactor $J_0$ and the nucleation barrier $W_{\text{min}}$ in different cases of metastable states (see, for example, Debenedetti 1996).

In the classical theory of homogeneous nucleation the critical radius and the nucleation barrier can be calculated with the Gibbs equations (Landau and Lifshitz 1980)

\begin{align*}
  r_c &= \frac{2\sigma v}{\mu(P) - \mu'(P)}, \quad (3) \\
  W_{\text{min}} &= \frac{16\pi}{3} \frac{\sigma^3 v^2}{[\mu(P) - \mu'(P)]^2}, \quad (4)
\end{align*}

where $P$ is the bulk phase pressure, $v$ is a specific volume of the nucleus, and $\mu(P)$ and $\mu'(P)$ are the chemical potentials of the nucleus and of the metastable bulk fluid phase, respectively. A nucleus with radius less than a critical size $r_c$ requires energy for further growth and usually disappears without reaching the critical size. A nucleus with radius larger than $r_c$ grows freely with decrease of free energy, and a phase transition into a thermodynamically stable vapour phase takes place. Equations (3) and (4) can be applied for the formation of liquid droplets in supercooled vapour as well as for the formation of vapour bubbles in superheated liquid at moderate positive pressures and in the critical region. In metastable liquids at low temperatures considerable negative pressures are observed. In this case, Eqs. (3) and (4) are not more applicable. Particularly for large negative pressures the equations for $r_c$ and $W_{\text{min}}$ developed by Fisher (1948) can be used

\begin{align*}
  r_c &= -\frac{2\sigma}{P}, \quad (5) \\
  W_{\text{min}} &= \frac{16\pi}{3} \frac{\sigma^3}{P^2}. \quad (6)
\end{align*}

However, these equations in turn fail at zero and small positive pressures where they give an unphysical divergence $r_c \to \infty$ and $W_{\text{min}} \to \infty$. A better result in this region can be obtained with the theory developed by Blander and Katz (1975). They obtained that the nucleation barrier $W_{\text{min}}$ is defined by Eq. (2), and found for the critical radius

\begin{equation}
  r_c = \frac{2\sigma v}{P V - P} \approx \frac{2\sigma}{(P^* - P) \delta}, \quad (7)
\end{equation}

where $P^*$ is the saturation pressure at given temperature $T$. The correction factor $\delta$ takes into account the effect of the pressure $P$ in the metastable liquid on the vapour pressure $p_v$ in the nucleus and is given by the equation
\[ \delta \approx 1 - \frac{\rho_V}{\rho_L} + \frac{1}{2} \left( \frac{\rho_V}{\rho_L} \right)^2, \quad (8) \]

where \( \rho_L \) is the density of the liquid and \( \rho_V \) the density of the vapour. Equations (7) and (8) are accurate for values of \( P \) at least up to 0.1 MPa, but are not valid in the critical region where the ratio \( \rho_V/\rho_L \approx 1 \) is not small and analytical expansion (8) is not more applicable.

In the theory of homogeneous nucleation the mean time of formation of a critical nucleus in a volume \( V \)
\[ t_M = (JV)^{-1} \quad (9) \]
determines the lifetime of the metastable state. The homogeneous nucleation limit of the metastable state is determined as a locus of the constant lifetime \( t_M = \text{const.} \)

2.2 Nuclei Distribution

The basic questions we want to answer in this section are how big are the nuclei and how many are these of each size. Data are presented for water, various polymer solutions, and blood. No information is available in the literature for the case of synovial liquid and saliva.

2.2.1 Distribution of Cavitation Nuclei in Water

Several methods have been used to investigate the distribution of cavitation nuclei in water. Yilmaz et al. (1976) and Ben-Yosef et al. (1975) used the light scattering method, Gates and Bacon (1978) used a holographic technique, while Gavrilov (1969) used acoustic methods. Measurements of nuclei distribution using a Coulter counter were performed by Ahmed and Hammitt (1972), Pynn et al. (1976) and Oba et al. (1980). The Coulter counter detects change in electrical conductance of a small aperture as fluid containing cavitation nuclei is drawn through. A typical apparatus has one or more microchannels that separate two chambers containing electrolyte solutions. When a nucleus flows through one of the microchannels, it results in the electrical resistance change of the liquid filled microchannel. This resistance change can be recorded as voltage pulses, which can be correlated to the size of cavitation nuclei. Another direct measurement of the presence of cavitation nuclei is achieved when a liquid sample is passed through a region of known low pressure. Nuclei with radii that exceed a certain value radius will cavitate. The event rate of these cavitating bubbles can then be counted by visual observations. Moreover, when a cavitating bubble is convected to a region of higher pressure downstream, it will collapse producing an acoustic emission. The noise pulses can be detected and counted, giving another independent measurement of the nuclei. Devices that measure nuclei through inducing cavitation events are called cavitation susceptibility meters (Chambers et al. 1999).
Some attempts were made to obtain a relationship that describes the distribution of cavitation nuclei in water. Gavrilov (1969) reported that the number of bubble nuclei is inversely proportional to the nuclei radius. Ahmed and Hammitt (1972) indicated that the distribution of cavitation nuclei can be described by

\[ N(v) = \frac{pV}{4.838 \sigma v^{2/3} + pv}, \]  

where \( N(v) \) is the number of nuclei of volume \( v \), \( V \) the total gas content, \( \sigma \) the surface tension, and \( p \) is the ambient pressure. If \( 4.838 \sigma v^{2/3} \ll pv \) then \( N(v) \propto d^{-3} \), and if \( 4.838 \sigma v^{2/3} \gg pv \) then \( N(v) \propto d^{-2} \), where \( d \) is the gas nuclei diameter. Shima et al. (1985) indicated that, in the range 2 \( \mu \)m < \( d \) < 20 \( \mu \)m, the gas nuclei distribution in water can be described by

\[ N(d) = \frac{M}{d^n}, \]  

where \( M \) is a constant. They found that the values of the exponent \( n \) lies between 2 and 4, in agreement with the results of Gavrilov (1969) who indicated \( n = 3.5 \). In a later study, Shima and Sakai (1987) obtained a more general equation for the size distribution of bubble nuclei in the form:

\[ N(r) = \frac{M}{r^n e^{-\frac{nK}{2} (\ln r - \ln \alpha)^2}}, \]  

where \( r \) is the nuclei radius and \( M, n, K, \) and \( \alpha \) are constants. They found good agreement with the experimental results reported by Ahmed and Hammitt (1972), Ben-Yosef et al. (1975), and Klaestrup-Kristensen et al. (1978).

### 2.2.2 Distribution of Cavitation Nuclei in Polymer Solutions

Oba et al. (1980) and Shima et al. (1985) have measured the distribution of cavitation nuclei in water and various polymer solutions using a Coulter counter. They indicated that the size range of the nuclei is from 2 to 50 \( \mu \)m in radius, and the number of small nuclei below 7 \( \mu \)m represents more than 50% from the total number of nuclei.

Oba et al. (1980) investigated the influence of polyethylene oxide concentration on the nuclei size distribution (Fig. 2.2). They found that the number of nuclei increases with the polymer concentration for nuclei diameters smaller 14 \( \mu \)m. For a diameter of about 12 \( \mu \)m, the number of bubble nuclei is one order of magnitude larger than in the case of water. However, for nuclei diameters larger than 14 \( \mu \)m, a significant reduction of the number of cavitation nuclei was observed. For a diameter of 35 \( \mu \)m, the number of nuclei in the 100 ppm polyethylene solution is one order of magnitude smaller than in the case of water.
Shima et al. (1985) measured the cavitation nuclei distribution, in the range 2–20 μm, in three polymer aqueous solutions, namely a 100 ppm polyethylene oxide (Polyox) aqueous solution, a 2,000 ppm hydroxyethylcellulose aqueous solution, and a 50 ppm polyacrylamide aqueous solution (Fig. 2.3). For nuclei diameters larger than 3 μm they also found a decrease of the number of bubble nuclei in comparison to the case of water. The largest reduction was observed in the polyacrylamide and polyethylene solutions, while the results obtained in the hydroxyethylcellulose solution are almost similar to the case of water. They also indicated that the scaling law between the number of bubble nuclei and the nuclei diameter is not affected by the polymer additives.

2.2.3 Cavitation Nuclei in Blood

The first attempts to detect cavitation in blood within the abdominal aorta of dogs exposed in vivo to lithotripsy have not proved successful although cavitation was observed in blood under in vitro conditions (Williams et al. 1988). Similar observations have been made by Deng et al. (1996).

Lee et al. (1993) investigated bubble formation in the inferior vena cavae of dead rats after 6–15 h exposures to air at 12.3 MPa and decompression to 0.1 MPa at 1.36 MPa/min. Bubbles were detected by light microscopy, buoyancy, and underwater dissection. No bubbles were formed in 42 blood-filled vena cavae that were
isolated from the minor circulation by ligatures, but bubbles were always observed in unisolated vena cavae. Their results indicate that nuclei are not present in blood, even at supersaturations that are significantly higher than those experienced in vivo. One explanation for this result is that the continuous filtration of impurities by the body allows the presence of cavitation nuclei in only minute amounts, and only in particular sites. This observation concurs with the finding that the cavitation threshold for water doubles upon filtration to 2 μm (Greenspan and Tschiegg 1967).

More recently, Chambers et al. (1999) investigated the nuclei characteristics of blood using a cavitation susceptibility meter in an ex vivo sheep model. This hydrodynamic method measures the nuclei threshold pressure by subjecting the fluid to a certain characterized flow. All nuclei with a critical pressure higher than the minimum pressure within the device will cavitate, and the number of activated nuclei was determined by counting the cavitation events. The nuclei concentration of blood was measured to be at most 2.7 nuclei per litre and the authors estimated that the radius of the nuclei is on the order of 0.3 μm. However, they noted that these values may be even lower in an in vivo situation.

Chappel and Payne (2006) suggested that cavitation nuclei could originate from tissues or microcapillaries and migrate into blood circulation. The contact between adjoining endothelial cells on the capillary walls could be a site for crevice nuclei. The effect of muscular contraction on crevices might be expected to squeeze the gas pocket and potentially cause the release of bubbles. While the concept of in
vivo hydrophobic crevices remains a theoretical possibility, none have yet been identified. No bubble formation was observed when isolated endothelium in contact with blood was decompressed (Lee et al. 1993). The extravascular space could be an alternative location: as extravascular gas nuclei expand, they might rupture capillaries, thereby seeding the blood with gas (Vann 2004).

It has been also suggested that musculoskeletal activity could generate surface-active molecules that stabilize the nuclei and increase their lifetime (Hills 1992). On the other hand, there have been studies that demonstrate the beneficial effect of surfactants on bubble elimination. The addition of surfactants to blood makes it feasible to manipulate interfacial stresses and prevent or reduce formation of the adhesion responsible for trapping intravascular gas bubbles. In vivo studies have shown that the addition of surfactants favorably alters the patterns of deposition and accelerate the rates of clearance of bubbles (Suzuki et al. 2004). While surfactants could play a role first in nuclei stabilization, they could also be involved at last in vascular bubble elimination.

2.3 Tensile Strength

It is important to realise that cavitation is not necessarily a consequence of the reduction of pressure to the liquid’s vapour pressure, the latter being the equilibrium pressure, at a specified temperature, of the liquid’s vapour in contact with an existing free surface. Cavity formation in a homogeneous liquid requires a stress sufficiently large to rupture the liquid. This stress represents the tensile strength of the liquid at that temperature (Brennen 1995; Trevena 1987; Young 1989).

Several methods have been employed to obtain the tensile strength of water. The first to be used was the Berthelot tube technique: a vessel is filled with liquid water at high temperature and positive pressure, then sealed and cooled down at constant volume. The liquid sample follows an isochore and is brought to negative pressure. Berthelot claimed that he had reached –5 MPa in a glass ampoule completely filled with pure water (Berthelot 1850). Another method was designed by Briggs (1950): by spinning a glass capillary filled with water, he obtained a minimum value of the tensile stress of –27.7 MPa at 10°C; the tension falls to a much smaller value at lower temperature (down to –2 MPa at 0°C). Shock tube and bullet piston experiments generate negative pressure by reflection of a compression wave travelling in water at an appropriate boundary. This type of experiments has been reconsidered several times and the presently accepted results are around –10 MPa (Williams and Williams 2000). It is worth noting here that even larger values of the tensile strength of water were obtained. Zheng et al. (1991) used an improved version of the static Berthelot method by using synthetic water inclusions in quartz. A quartz crystal with cracks is autoclaved in the presence of liquid water. Water fills the cracks which then heal at high temperature, thus providing low density water in a small Berthelot tube. They reported a maximum tension of –140 MPa at 43°C. This result is similar to that obtained by Roedder (1967) who reached –100 MPa with water inclusions in natural rocks.
Despite numerous studies, the precise role of non-Newtonian properties in determining cavitation threshold remains unclear. Most previous work in this area has considered polymer solutions – fluids made non-Newtonian by polymeric additives (Trevena 1987). Under conditions of dynamic stressing by pulses of tension there is evidence that polymer additives can lower cavitation threshold. An example has been reported by Sedgewick and Trevena (1978) who studied the cavitation properties of water containing polyacrylamide additives by the bullet-piston reflection method. Williams and Williams (2000) have shown that the latter method, which involves the conversion of a compressional pulse to a rarefaction at the free surface of a column of liquid, provides realistic estimates of tensile strength for water and other Newtonian fluids (Williams and Williams 2002).

The experimental arrangement used by Williams and Williams (2002) consists of a cylindrical, stainless steel tube closed at its lower end by a piston (Fig. 2.4a). The piston’s lower surface is coupled to a stun-gun which generates a pressure pulse in a column of liquid within the tube. The upper flange connects the tube to a regulated oxygen-free nitrogen supply and a pressure gauge. Pressure changes within the liquid are monitored using three dynamic pressure transducers mounted

![Figure 2.4](image_url)

**Fig. 2.4** The bullet-piston method for estimating the tensile strength of liquids. (a) Schematic of the cavitation threshold apparatus. (b) Pressure record obtained from a pressure transducer in an experiment on a sample of distilled water. (c) Cavitation threshold of distilled water. Reproduced with permission from Williams and Williams (2002). © IOP Publishing Ltd
in mechanically isolated ports in the wall of the tube. The main features of a typical pressure record obtained from a pressure transducer in an experiment on a sample of distilled water are shown in Fig. 2.4b, in which the data are presented in terms of transducer output in unscaled ADC units (positive values correspond to positive pressure and vice versa). A pressure pulse (feature “1” in Fig. 2.4b) is followed immediately by a tension pulse (“2”) and thereafter the record comprises “secondary” pressure-tension cycles (“3–4”, “5–6”, etc.) associated with cavitation activity. The method involves regulating a static pressure, \( P_s \), in the space above the liquid, \( P_s \) being increased gradually in a series of dynamic stressing experiments. From the dynamic pressure records a measurement is made of the time delay, \( \tau_i \), between the peak incident pressure (“1” in Fig. 2.4b) and the first pressure pulse arising from cavity collapse (“3” in Fig. 2.4b). Under tension, cavities grow from pre-existing nuclei within the liquid and eventually collapse and rebound, emitting a pressure wave into the liquid as they do so. Hence the interval \( \tau_i \), which encompasses the attainment of maximum cavity radius and its subsequent decrease to a minimum value, is reduced by increasing \( P_s \) (\( \tau_i \) therefore provides a convenient measure of cavitation activity). The experiment involves the transmission of tension by the liquid to the face of the piston and it follows that in the case of experiments in which cavitation is detected, the magnitude of the tension transmitted by the liquid is sufficient to develop a transient, net negative pressure in the presence of a background static pressure \( P_s \). Thus an estimate of the magnitude of tension capable of being transmitted by the liquid can be obtained from a knowledge of \( P_s \). The time delay, \( \tau_o \), between pulses corresponding to “1” and “2” in Fig. 2.4b represents the time required for the upward travelling pressure wave to return, as tension, to the lower transducer location. It also represents the smallest time interval for which a cavity growth-collapse cycle could occur (given that a bubble would have to grow and collapse infinitely quickly in order that \( \tau_i = \tau_o \)). Thus the tensile strength can be estimated by extrapolation of the data in Fig. 2.4c to that value of the pressure \( P_s \) at which \( \tau_i = \tau_o \), this condition representing the complete suppression of cavitation.

Bullet-piston work has demonstrated a reduction of liquid effective tensile strength in non-Newtonian polymer solutions, the reduction increasing with increasing polymer concentration (Williams and Williams 2002). However, when this system was investigated using an ab initio technique, the cavitation threshold was found to be increased by the same polymer additive (Overton et al. 1984; Brown and Williams 2000). When subjected to quasi-static stressing (in a modified Berthelot tube) the presence of polymer made no discernible difference to the effective tensile strength of the liquid (Trevena 1987).

References


References


