# Physik der Blasen:

Formeln und Literatur

# **Zusammenfassung von Thomas D. Kunkle**

# LIST OF ACRONYMS AND SYMBOLS

# Acronyms

ESP	Equilibrium Spreading Pressure
SS model	Surfactant Stabilized model
STP	Standard Temperature and Pressure
VP model	Varying Permeability model
msw	meters sea water
fsw	feet sea water

Symbol	Definition	Defining Equation	Units
A	Area per surfactant molecule	(4.18)	$cm^2$
$^{A}diff$	Area for diffusion per surfactant molecule	(4.52)	cm <sup>2</sup>
$A_{min}$	Minimum value of A	(4.25)	cm <sup>2</sup>
$A_O$	Cross-sectional area of a surfactant molecule	(4.19)	cm <sup>2</sup>
$A_1$	Surfactant area parameter	(4.22)	$cm^2$
Αγ	Molecular area at which ${\rm I\!I}$ is equal to $\gamma$	(4.88)	cm <sup>2</sup>
$B_{\mathcal{p}}$	First-order virial coefficient	(4.1)	cm <sup>2</sup> dyne <sup>-1</sup>
$B_1$	Surfactant dynamic parameter	(4.27)	dyne $sec^{1/2}$ cm <sup>-2</sup>
$c_p$	Second-order virial coefficient	(4.1)	cm <sup>4</sup> dyne <sup>-2</sup>
$C_1$	Surfactant compression parameter	(4.22)	dyne cm <sup>-1</sup>
$^{\mathcal{C}}j^{I}$	Inert gas uptake parameter of the $j$ th body structure	(6.18)	mole erg <sup>-1</sup> sec <sup>-1</sup>
D	Diffusion coefficient		$cm^2 sec^{-1}$
DZ	Thickness of the layers dividing the gelatin slab	(4.31)	cm
$D \wp$	Thickness of the shells dividing the nuclear domain	(4.44)	cm
$D_1$	Gas uptake constant	(4.37)	$cm^{-1}$
$E_{SOI}$	Molecular desorption energy		erg
f(r)	Rate of nuclear destruction	(5,20)	sec <sup>-1</sup>
F	Gas flux		mole cm <sup>-2</sup> sec <sup>-1</sup>

Symbol	<u>Definition</u>	Defining Equation	Units
g(r)	Initial distribution of gas in the nuclear domain; or	(1.8)	mole cm <sup>-3</sup>
	Rate of nuclear creation	(5.20)	sec-1 cm-4
H	Fraction of the nuclear surface available for gas diffusion	(4.52)	
k	Boltzmann constant		erg °K <sup>-1</sup>
n	Number of shells dividing the nuclear domain	(4.44)	v
n(r)	Distribution of nuclear radii	(2.3)	cm <sup>-4</sup>
N	Amount of gas; or	(1.2)	moles
	Number of bubbles per ml	,	cm <sup>-3</sup>
N(r)	Integral distribution of nuclear radii	(2.3)	cm <sup>-3</sup>
Nmol	Number of surfactant molecules	(4.62)	
$N_{tau}$	Number of layers dividing the gelatin slab	(4.31)	
p	Gas pressure	(1.1)	dyne cm <sup>-2</sup>
Pamb	Ambient pressure	(1.1)	dyne cm <sup>-2</sup>
$p_{amb}^{J}$	Absolute pressure at the jth point in the ambient pressure profile	(4.29)	dyne cm <sup>-2</sup>
Pcrush	Crushing pressure	(2.2)	dyne cm <sup>-2</sup>
$p_f$	Final pressure		dyne cm <sup>-2</sup>
$p_m$	Maximum pressure		dyne cm <sup>-2</sup>
$p_{\mathcal{S}}$	Saturation pressure		dyne cm <sup>-2</sup>
pss	Supersaturation pressure	(1.18)	dyne cm <sup>-2</sup>
$p_O$	Initial pressure		dyne cm <sup>-2</sup>
Pj*	Minimum supersaturation pressure required for bubble formation in the $j^{ ext{th}}$ body structure	(6.21)	dyne cm <sup>-2</sup>
p.¢	Probability of contacting the lth type of decompression sickness syndrome		dyno ca
$q_{j}$	Dummy variables defined for notation purposes:	(6.3) (4.72)	
	$q_{1} \equiv r$ $q_{2} \equiv p$ $q_{3} \equiv N$ $q_{4} \equiv \Pi$		

Symbol	<u>Definition</u>	Defining Equation	Units
r	Radius, measured to liquid-gas interface, of a bubble or nucleus	(1.1)	cm
12	Critical radius for bubble growth		
$r_{c}$	Initial radius of a bubble or nucleus	(1,20)	CM Cm
r <sub>O</sub> R	Gas constant	(1.16)	cm
$\overline{R}$			erg mole <sup>-1</sup> °K <sup>-1</sup>
л	Gas constant corrected for non-ideal gas behavior	(4.10)	erg mole <sup>-1</sup> °K <sup>-1</sup>
s	Steepness parameter	(4.89)	
S	Solubility	(1.5)	mole cm <sup>-1</sup> dyne <sup>-1</sup>
$^{S}j^{\mathcal{I}}$	Inert gas solubility of the $j^{ ext{th}}$ body structure	(6.19)	mole cm <sup>-1</sup> dyne <sup>-1</sup>
t	Time		sec
$t_j$	Elapsed time to the $j^{ ext{th}}$ point of the ambient pressure profile	(4.29)	sec
T	Temperature	(1.2)	° K
U	Gas concentration	(1.5a)	mole cm <sup>-3</sup>
$U_{\mathcal{O}}$	Equilibrium gas concentration	(1.5)	mole cm <sup>-3</sup>
$U_{j}$	Gas concentration in the $j^{th}$ shell of the nuclear domain; or	(4.43)	mole cm <sup>-3</sup>
	Gas concentration in the $j^{ extsf{th}}$ body structure	(6.17)	mole cm <sup>-3</sup>
$U_{j}^{I}$	Inert gas concentration in the $j^{ extsf{th}}$ body structure	(6.18)	mole cm <sup>-3</sup>
V	Volume	(1.2)	cm <sup>3</sup>
$\overline{V}$	Volume corrected for non-ideal gas behavior	(4.10)	cm <sup>-3</sup>
$v_j$	Volume of the $j^{th}$ shell in the nuclear domain; or	(4.47)	$cm^3$
	Volume of evolved gas in the $j^{ ext{th}}$ body structure	(6.2)	$cm^3$
$W_j$	Gas concentration in the $j^{\text{th}}$ layer of the gelatin slab	(4.32)	mole cm <sup>-3</sup>
α	Gas-permeability coefficient	(1.4)	${\rm cm~sec^{-1}}$
Υ	Surface tension	(1.1)	dyne cm <sup>-1</sup>
δ	Accuracy parameter	(4.72)	
$\Delta p$	Pressure reduction		dyne cm <sup>-2</sup>
Δη	Increment in radius	(4.71)	cm

Symbol	<u>Definition</u>	Defining Equation	Units
$\Delta t$	Length of time step	(4.71)	sec
$\Delta t_j$	Set of maximum time steps	(4.73)	sec
κ	Nuclear growth rate constant	(5.15)	sec <sup>-1</sup>
ξ	Slope constant	(4.86)	dyne cm <sup>-1</sup>
Π	Surface pressure of the surfactant	(4.6)	dyne cm <sup>-1</sup>
$\Pi_{max}$	Maximum value of N	(4.27)	dyne cm <sup>-1</sup>
ρ	Radial variable		cm
Pmax	Radius of the nuclear domain	(4.41)	cm
σ	Thermodynamic fluctuation in area	(5.1)	${\tt cm}^2$
τ	Gas tension	(1.5)	dyne cm <sup>-2</sup>
$^{ au}j$	Gas tension in the $j^{ extsf{th}}$ body structure	(6.17)	dyne cm <sup>-2</sup>
ś	Fraction of fluctuations that uniformly increase the area of a diffusion-window	(5.2)	
F	Fraction of surfactant molecules available for diffusion	(5.11)	

# CHAPTER 1. INTRODUCTION

Nucleation in supersaturated fluids is the process which permits some or all of the excess gas present to evolve into bubbles. It is usually illustrated by the familiar example of bubble formation in carbonated beverages such as champagne or tonic water. When such a beverage is uncorked, bubbles form both on the walls of the container and within the liquid itself. They quickly grow in size as gas diffuses into them from the surrounding fluid, and as they grow, they float rapidly to the surface where they dissipate. Eventually, all of the excess gas is released, either into bubbles or by diffusion through the surface, at which time bubble formation and growth cease and the beverage becomes "flat."

This example illustrates two fundamental characteristics of the nucleation process: that critical supersaturation is required to form bubbles and that this critical pressure is surprisingly small. The second point is of particular significance because, as will be discussed later in this chapter, the supersaturation pressure required for bubble nucleation in a pure fluid is expected to be greater than 1,000 bar. Evidently, the bubbles observed to form in common fluids at modest supersaturation pressures do not form de novo, but instead arise at "weak points" in the fluid that serve as cavitation nuclei.

In this chapter the relationship between bubble formation and cavitation nuclei will be systematically explored. The first section introduces definitions and physical concepts concerning the physics of gas bubbles that will be used throughout the remainder of the text. The second section outlines the theory of homogeneous nucleation, which describes the process by which bubbles are formed within pure fluids by thermodynamic fluctuations. The final section establishes the existence of cavitation nuclei by showing that real fluids do not behave as ideal pure fluids should and must therefore contain impurities responsible for the precocious bubble formation.

## 1.1. Bubble definitions and concepts

The analysis of experimental and theoretical work concerning gas phase nucleation in fluids often requires precise knowledge of the nature of bubbles. In this section an introduction to the physics of gas bubbles is presented and definitions, concepts, and equations that will be used for future work are developed.

A "bubble" in a fluid is defined to be a spherical gas cavity characterized by the mechanical equilibrium of the internal gas pressure and the sum of the ambient pressure and the fluid surface pressure,

$$p = p_{amb} + 2\gamma/r , \qquad (1.1)$$

where p is the internal gas pressure,  $p_{amb}$  is the ambient pressure,  $\gamma$  is the liquid-gas surface tension, and r is the bubble radius. This equation by itself does not provide sufficient information to calculate the size of the bubble. An equation of state for the internal gas is needed to establish a relationship between the internal pressure, the bubble radius, and the amount of gas. A particularly simple equation of state is the ideal gas law

$$pV = NRT$$
, (1.2)

where V is the volume of the bubble, N is the amount of gas contained in the bubble, R is the universal gas constant, and T is the absolute temperature. Combining equations (1.1) and (1.2) yields the cubic equation

$$4\pi(p_{amb}r^3 + 2\gamma r^2) = 3NRT$$
, (1.3)

which may be solved for r if the values of N,  $p_{amb}$ , and  $\gamma$  are known.

The amount of gas contained in a bubble is not necessarily constant; it can vary due to gas diffusion. Thus, mechanical equilibrium does not imply diffusion equilibrium. The rate of gas transport is determined by the difference equation

$$\frac{dN}{dt} = 4\pi r^2 \alpha [U(r) - U_O] , \qquad (1.4)$$

where U(r) is the concentration of gas in the fluid just beyond the liquid-gas dividing surface,  $U_O$  is the concentration necessary to establish equilibrium with the gas in the bubble, and  $\alpha$  is a constant of proportionality. The function  $U(\rho)$  is defined to be the gas concentration in the fluid at a radial distance  $\rho$  from the center of the bubble, which is assumed to be spherically symmetric. The value of  $U(\rho)$  is related to the solubility of the gas, S, through Henry's law

$$U(\rho) = S\tau(\rho) , \qquad (1.5a)$$

where  $\tau$  is "gas tension." In a "diffusion-equilibrated" fluid the gas tension is equal to the gas pressure,  $\tau=p$ , while in a "saturated" fluid the gas tension is equal to the ambient pressure,  $\tau=p_{amb}$ . The value of  $U_O$  is therefore determined by the equation

$$U_O = Sp . ag{1.5b}$$

Equation (1.3) may be differentiated to yield the relationship between differential changes in r,  $p_{amb}$ , and N, namely

$$dr = \left[\frac{3RT}{4\pi r^2} dN - r dp_{amb}\right] / \left[3p_{amb} + 4\gamma/r\right], \qquad (1.6)$$

where it is assumed that the temperature is constant. Dividing by dt and substituting from equations (1.4) and (1.5b) yields

$$\frac{dr}{dt} = \left\{ 3RT\alpha [U(r,t) - Sp] - r \frac{dp_{amb}}{dt} \right\} / \left( 3p_{amb} + 4\gamma/r \right). \tag{1.7}$$

This equation allows the bubble radius to be calculated at any time, given an initial size and the values of U(r,t) and  $p_{cmh}(t)$ .

The value of U(r,t) must be known before equation (1.7) can be solved. The concentration  $U(\rho,t)$  is determined by the Fickian diffusion equation

$$\frac{\partial U}{\partial t} = D\nabla^2 U + \hat{v} \cdot \nabla U , \qquad (1.8a)$$

where D is the diffusion constant and  $\vec{v}$  is the velocity of the fluid. Solutions of equation (1.8a) must also satisfy the boundary conditions

$$\lim_{\rho \to \infty} U(\rho, t) = S\tau(t) , \qquad (1.8b)$$

where  $\tau(t)$  is the ambient gas tension, where  $U(\rho,t)$  satisfies the equation

$$D \left. \frac{\partial U(\rho,t)}{\partial \rho} \right|_{P} = \alpha [U(P,t) - Sp(t)] , \qquad (1.8c)$$

and where the initial concentration is

$$U(\rho, 0) = g(\rho) . \tag{1.8d}$$

Because the variables p(t) and r(t) occur in equation (1.8), while  $U(\rho,t)$  occurs in equation (1.7), these equations are mathematically coupled and must be solved simultaneously. Exact solutions to this system, if they exist at all, are probably too formidable for practical use. Hence, numerical methods must be employed or simplifying assumptions made.

One set of simplifying assumptions, first applied to bubbles by Epstein and Plesset (1950), is that the transport term  $\vec{v} \cdot \nabla U$  in equation (1.8a) may be neglected, and that the exchange of gas across the liquid-gas dividing surface is sufficiently fast that the fluid just outside the dividing surface is nearly in equilibrium with the internal gas,

$$U(r,t) \simeq Sp(t) . ag{1.9}$$

Epstein and Plesset (1950) found that the initial concentration gradient at the interface is then given by the equation

$$\frac{\partial U(\rho,t)}{\partial \rho} \bigg|_{\mathcal{P}} = S(p_{amb} - p)/r . \tag{1.10}$$

Comparison of this equation with equation (1.8c) shows that this result will be correct only if the inequality

$$S \frac{2\gamma}{r^2} < \frac{\alpha}{D} \left[ U(r) - Sp(\theta) \right] \tag{1.11}$$

is satisfied. Because the left-hand side of equation (1.11) diverges as r goes to zero, the assumption in equation (1.9) must fail for small bubbles. By assuming that equation (1.9) is valid to 10 percent, the radius of the smallest bubble to which this approximation may be accurately applied can be computed. The result is

$$r_{min} = 10 \frac{D}{\alpha} , \qquad (1.12a)$$

where  $p_{amb}$  is taken to be zero. Substituting the values for D and  $\alpha$  from Table 4.2 for nitrogen in water, the following numerical value is obtained:

$$r_{min} = 5.3 \times 10^{-2} \text{ cm}$$
 (1.12b)

For bubbles larger than this radius, the gas flux is limited by the rate at which gas diffuses through the liquid and is said to be "diffusion-limited." For bubbles smaller than this size, the flux is limited by the rate of gas transport across the liquid-gas interface, and the flux is said to be "perfusion-limited." Evidently, the approximation in equation (1.9) is correct in the diffusion-limited case.

A useful approximation for perfusion-limited bubbles is that the diffusion of gas in the liquid is much faster than the transport across the interface. In this case  $\mathcal{U}(r,t)$  is nearly equal to the gas concentration at a large distance from the bubble.

$$U(r t) = \lim_{\rho \to \infty} U(\rho, t) = S\tau(t) . \qquad (1.13)$$

This approximation is also valid for a bubble in a stirred fluid or for a rapidly moving bubble. Substitution of equation (1.13) into equation (1.7) yields

$$\frac{dr}{dt} = \left[ 3RT\alpha S \left( \tau - p_{amb} - \frac{2\gamma}{r} \right) - r \frac{dp_{amb}}{dt} \right] / \left( 3p_{amb} + 4\gamma/r \right) . \tag{1.14}$$

This equation approximates the dynamic evolution of a perfusion-limited bubble. It should be noted from equation (1.8a) that the rate of gas transport in a spherical coordinate system depends on the term  $(\partial^2 U/\partial \rho^2) + (2/\rho)(\partial U/\partial \rho)$ , and that the ratio of the perfusion rate to the diffusion rate for a fixed concentration gradient is thus proportional to r. This indicates that the approximation in equation (1.13) is better for smaller bubbles, and that equation (1.14) becomes increasingly more accurate as the bubble size decreases.

# 1.1.1. Bubbles in saturated fluids

A particularly instructive application of equation (1.7) is to a bubble in a saturated fluid held at a constant ambient pressure. In this case the derivative  $dp_{amb}/dt$  is zero,  $\tau(t)$  is equal to  $p_{amb}$ , and  $g(\rho)$  is taken to be equal to  $Sp_{amb}$ . The diffusion-limited case of this problem has been considered by Epstein and Plesset (1950), Fox and Herzfeld (1954), Bernd (1963), and Yang and Liang (1972). The calculations of Epstein and Plesset indicate that a bubble having an initial radius of 100  $\mu$ m will completely dissolve in water at STP in 5.88 x seconds.

For perfusion-limited bubbles, equation (1.14) may be employed in the form

$$\frac{d\mathbf{r}}{dt} = -\left[6RT\alpha S\gamma/r\right]/\left[3p_{amb} + 4\gamma/r\right] . \tag{1.15}$$

This equation can be immediately integrated to yield

$$(\alpha SRT)t = \frac{p_{amb}}{4\gamma} (r_O^2 - r^2) + \frac{2}{3} (r_O - r) ,$$
 (1.16)

where  $r_{\mathcal{O}}$  is the initial radius of the bubble. As can be seen from equation (1.15), if  $\gamma$  is not equal to zero, then the bubble is unstable and will contract until it is extinguished. The physical cause of this contraction is the diffusion of the internal gas into the surrounding fluid, a process driven by the inequality between the internal gas pressure p and the ambient gas tension  $\tau$ . A necessary requirement for the stability of a bubble in a saturated fluid is that the surface pressure vanishes. This can occur only if the surface tension is zero or the radius is infinite. Since both of these possibilities must be ruled out for real bubbles, it is concluded that all bubbles that exist in saturated fluids are unstable and will eventually collapse. The lifetime of a small bubble can be calculated from equation (1.16) by setting r to zero and solving for t:

$$t = \left(\frac{p_{amb}}{4\gamma} r_o^2 + \frac{2}{3} r_o\right) / \alpha SRT . \tag{1.17}$$

## 1.1.2. Growth of bubbles in supersaturated fluids

When the concentration of gas dissolved in a fluid is larger than the equilibrium value, the fluid is said to be "supersaturated." Mathematically, this means that  $\tau$  is greater than  $p_{cmb}$ . The difference between the gas tension and the ambient pressure is defined as the supersaturation pressure

$$p_{SS} = \tau - p_{cmb} . \tag{1.18}$$

The growth rate of a small bubble in a supersaturated fluid held at constant ambient pressure may be found by substituting equation (1.18) into equation (1.14) to yield

$$\frac{dr}{dt} = \alpha SRT(p_{SS} - 2\gamma/r)/(p_{amb} + 4\gamma/3r) . \qquad (1.19)$$

This equation demonstrates the existence of a "critical radius for bubble growth" defined by

$$r_{\mathcal{C}} = 2\gamma/p_{\mathcal{SS}} . \tag{1.20}$$

A bubble larger than this critical radius will grow, while one smaller than this size will contract until it vanishes. If the gas tension is assumed to be constant, then equation (1.19) can be integrated to yield

$$r_{c}\left(\frac{2}{3} + \frac{p_{cmb}}{p_{ss}}\right) \ln\left(1 - \frac{r}{r_{c}}\right) + \frac{p_{cmb}}{p_{ss}} r = (\alpha SRT)t + K ; r < r_{c}$$
 (1.21a)

or

$$r_{\mathcal{C}}\left(\frac{2}{3} + \frac{p_{amb}}{p_{ss}}\right) \ln\left(\frac{r}{r_{\mathcal{C}}} - 1\right) + \frac{p_{amb}}{p_{ss}} r = (\alpha SRT)t + K ; r > r_{\mathcal{C}}$$
 (1.21b)

where the constant of integration must be chosen to satisfy the initial condition that  $r(\theta)$  is equal to  $r_{\theta}$ .

# 1.2. The nucleation of bubbles in pure fluids

The minimum supersaturation pressure required to induce bubble formation within a pure fluid can be calculated using the theory of homogeneous nucleation. This theory estimates the probability of creating a bubble of a particular radius via random molecular motion; the corresponding supersaturation pressure is determined from equation (1.20). The problem of computing the minimum supersaturation pressure is therefore converted into the task of estimating the size of the largest bubble that can be formed by thermodynamic fluctuations. This theory was first proposed by Becker and Döring (1935) and is described in detail in standard texts such as Frenkel (1946) and Landau and Lifshitz (1938).

The cornerstone of the theory of homogeneous nucleation is the use of the Boltzmann equation to determine the relative probability of the spontaneous creation of a bubble due to random molecular motion. If the formation energy of a bubble is E, then the relative probability of its de novo occurrence at any particular point in the liquid is given by the equation

$$p = e^{-E/kT} . (1.22)$$

The formation energy is the difference in energy between a spherical volume of fluid and a bubble of equal size. Two terms contribute to this energy differential. The first is the free surface energy of the newly formed liquid-gas interface, given by Landau and Lifshitz (1938) as

$$E_1 = 4\pi r^2 \gamma . \tag{1.23}$$

The second is the difference in internal energy between the gas in the bubble and that dissolved in an equal volume of fluid. Assuming an ideal gas, this energy is

$$E_2 = - (N - N_{fluid})RT \tag{1.24}$$

where  $N_{fluid}$  is the number of moles of gas dissolved in the fluid. Using equations (1.2) and (1.5), equation (1.24) becomes

$$E_2 = -\frac{4}{3} \pi r^3 (p_{anb} + 2\gamma/r - \tau SRT) . \qquad (1.25)$$

For the case of nitrogen in water at room temperature, the product SRT is  $1.64 \times 10^{-2}$ . As can be seen from the final results of this calculation, the  $2\gamma/r$  term normally dominates in this expression. Therefore, the total formation

energy is given approximately by

$$E = \frac{4}{3} \pi r^2 \gamma . \tag{1.26}$$

It should be noted that this energy is not equal to the work done in the expansion of a pre-existing bubble through a continuum of equilibrium states.

The constant of proportionality occurring in equation (1.22) may be estimated by assuming that bubbles are the only permissible energy fluctuations, and that the integral sum of all such fluctuations is unity. This yields

$$C = 1/\int_{0}^{\infty} e^{-\frac{4}{3} \pi r^{2} \gamma / kT} dr = 4\sqrt{\gamma / 3kT} . \qquad (1.27)$$

The absolute probability of creating a bubble larger than radius r can now be found by integrating equation (1.22) over all radial values larger than r,

$$P(r) = 4\sqrt{\gamma/3kT} \int_{0}^{\infty} e^{-\frac{4}{3}\pi\xi^{2}\gamma/kT} d\xi \simeq \frac{1}{2\pi r\sqrt{\gamma/3kT}} e^{-\frac{4}{3}\pi r^{2}\gamma/kT}$$
(1.28)

This last equation gives the absolute probability of finding a bubble larger than a certain radius at a particular location in the fluid. The number of independent points in a unit volume of fluid in which a bubble of radius r may form is given roughly by

$$n = 1/\frac{4}{3} \pi r^3 . {(1.29)}$$

The formation time of a bubble is determined approximately by the time interval required for a molecule moving at the velocity of sound to cross the bubble,

$$t_{cross} \approx 2r/v_{sonic}$$
 (1.30)

The total rate of formation of bubbles larger than radius r is therefore given by

$$N(r) \approx nP/t_{cross} \approx \frac{3v_{sonic}}{16\pi\sqrt{\gamma/3kT}} \frac{1}{r^5} e^{-\frac{4}{3}\pi r^2\gamma/kT}$$
(1.31)

The critical radius corresponding to a formation rate of one bubble per ml per second in water ( $\gamma = 72~dyne/cm$ ,  $v_{sonic} \approx 10^5~cm/sec$ ) is about 1.0 nm. This radius corresponds to a threshold supersaturation pressure of over 1,400 bar. It should be noted that raising r to 1.1 nm lowers the formation rate by nine orders of magnitude, and that the threshold pressure is therefore very sharply defined.

The threshold supersaturation pressure for pure water determined using equation (1.31) is much larger than the tensile strength, which has been computed by Apfel (1970) to be about 1,400 bar. This difference arises because the  $E_2$  energy term was included in the bubble formation energy while Apfel used only the  $E_1$  term. The physical difference between the two treatments is that Apfel computed the probability of the occurrence of a vapor cavity while equation (1.31) gives the probability of the occurrence of a true bubble. Because equation (1.20) has been used to convert from a radius to a critical supersaturation pressure, and because this equation is based on the validity of the defining equation (1.1), it is clearly necessary that the energy  $E_2$  be included in the formation energy. Since the threshold supersaturation pressure of the gas-liquid system is larger than the tensile strength of the pure liquid, saturating a fluid with an inert gas evidently does not alter its tensile strength.

# 1.3. The existence of cavitation nuclei

The theory of homogeneous nucleation outlined in the previous section works well for certain very pure liquids. Apfel (1971) showed, for example, that the measured tensile strengths of ether and n-hexane are close to the theoretical levels. In most fluids, however, the critical supersaturation pressure for bubble formation is well below the expected value. In water at room temperature the predicted cavitation threshold is found from equation (1.31) to be about 2,100 bar. The highest threshold actually observed in water of extreme purity was found by Hemmingsen (1970) to be 270 bar. Samples of common tap water cavitate at ultrasonic and supersaturation pressures of less than one bar, a result which is more than three orders of magnitude below the theoretical prediction. Yount and Strauss (1976) reported that weak gelatin mixtures will cavitate when decompressed by 0.83 bar, while the onset of decompression sickness in humans was found by Gray (1944) to occur at 0.6 bar. It is evident that the bubbles formed in common fluids at modest supersaturation pressures do not originate de novo from thermodynamic fluctuations within the liquids. Therefore, the bubbles must arise from weak spots in the fluids that are associated with the impurities known as "cavitation nuclei."

This argument for the existence of cavitation nuclei has been known since the time of Becker and Döring (1935). Its relevance to decompression sickness in humans was first pointed out by Harvey et al. (1944). In the remainder of this publication are reported the results of experimental and theoretical studies designed to elucidate the physical properties of the cavitation nuclei that occur in common fluids, including animal tissue.

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