On the evolution, generation, and regeneration of gas cavitation nuclei

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Recently a new cavitation model has been proposed in which bubble formation in aqueous media is initiated by spherical gas nuclei stabilized by surface-active membranes of varying gas permeability. By tracking the changes in nuclear radius that are caused by increases or decreases in ambient pressure, the varying-permeability model has provided precise quantitative descriptions of several bubble counting experiments carried out with supersaturated gelatin. The model has also been used to calculate diving tables and to predict levels of incidence for decompression sickness in a variety of animal species, including salmon, rats, and humans. Although the phenomena involved are in some sense dynamic, the model equations, in their present form, are essentially static and can be derived by requiring mechanical or chemical equilibrium at each setting in a rudimentary pressure schedule. In this paper, we examine the time dependence of the evolution of an individual nucleus from one equilibrium state to another, and we then investigate a statistical process by which the equilibrium size distribution of an entire population of nuclei may be generated or regenerated.

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INTRODUCTION

Ordinary samples of sea water, tap water, or even distilled water form visible bubbles when subjected to tensile, ultrasonic, or supersaturation pressures as small as 1 atm. This is several orders of magnitude below the theoretical tensile strength of pure water, and it implies that cavitation must be initiated by processes other than modest changes in pressure and the random motion of water and gas molecules.

Numerous experiments have demonstrated that cavitation thresholds can be significantly raised by degassing or by a preliminary application of static pressure.[1,2] These are specific tests for stable gas nuclei. Furthermore, solid particles or container walls with smooth surfaces[3] are not expected to be effective in initiating bubble formation at tensile, ultrasonic, or supersaturation pressures less than about 1000 atm.[4,5]

The existence of stable gas nuclei is at first rather surprising. Gas phases larger than 1 μm in radius should float to the surface of a standing liquid, whereas smaller ones should dissolve rapidly due to the surface tension. In Refs. 6 and 7, the earlier proposals for coping with this dilemma are critically reviewed, and a new model, called the varying-permeability or VP model is introduced. The essence of the new model is that cavitation nuclei consist of spherical gas phases small enough to remain in solution and strong enough to resist collapse, the mechanical compression strength being provided by an elastic skin or membrane composed of surface-active molecules. VP skins are ordinarily gas permeable, but they can become impermeable if the ambient pressure is increased rapidly by a sufficiently large amount, typically exceeding 8 atm.

Section I is an outline of the varying-permeability model which serves as the starting point for the theoretical developments which follow. In Sec. II, we introduce accretion and deletion functions to describe the transport of surfactant molecules to and from the skin, and we then use these functions to investigate the time dependence of the changes in the radius of an individual nucleus that occur as a result of increases or decreases in ambient pressure. The same accretion and deletion functions are used again in Sec. III to explore a stochastic mechanism by which a population with an arbitrary initial size distribution might eventually achieve equilibrium at a constant external pressure. As discussed in Sec. IV, the equilibrium size distribution obtained from this analysis is of the same form as the primordial distributions extracted from bubble counting experiments in supersaturated gelatin.

I. THE VARYING-PERMEABILITY MODEL

Because of the surface tension γ, mechanical equilibrium of a spherical gas bubble of radius r can be achieved only when the internal pressure $p_{\rm in}$ is higher than the ambient hydrostatic pressure $p_{\rm amb}$. This situation is described by the Laplace equation,

$$p_{\rm in}=p_{\rm amb}+2\gamma/r \quad \text{(gas bubbles)}. \tag{1}$$

If the liquid surrounding the cavity is in diffusion equilibrium with an external gas mixture at $p_{\rm amb}$, a pressure increment of $p_{\rm in}-p_{\rm amb}=2\gamma/r$ will exist across the boundary of the cavity, and gas will tend to flow outward until the radius diminishes to zero.

In the varying-permeability model,[6,7] collapse of a spherical gas nucleus is prevented by the compression strength of an elastic skin or membrane composed of surface-active molecules. The skin pressure $2\Gamma/r$ can be added to the left-hand side of Eq. (1) to yield a new expression for mechanical equilibrium,

$$p_{\rm in}+2\Gamma/r=p_{\rm amb}+2\gamma/r \quad \text{(gas nuclei)}. \tag{2}$$

Alternatively, one can think of the skin compression Γ as the amount by which the surface tension is reduced by the surfactant molecules. The new surface tension, $\gamma' \equiv \gamma-\Gamma$, can be substituted for γ in Eq. (1).

The skin compression Γ is analogous to the "surface pressure" Π that is measured when an "insoluble monolayer" of surface-active molecules is spread across the liquid–gas interface in a Langmuir trough.[8] In a

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typical Π-A (surface pressure versus surface area) curve, the magnitude of Π increases as the monolayer area and hence the spacing between surfactant molecules are reduced. Eventually Π reaches a limiting value, and further reductions in surface area can be accommodated only by expelling surfactant molecules from the interface.

The Π-A curve assumed for Γ in the varying-permeability model is essentially a step function. "Small-scale" changes in nuclear radius—those associated with variations in the spacing of a fixed number of skin molecules—are neglected, and only "large-scale" changes—those associated with the accretion or deletion of skin molecules—are actually calculated. The small-scale changes are important conceptually because they permit a stable mechanical equilibrium near the calculated large-scale radius with the fixed number of skin molecules appropriate to that radius. All large-scale processes take place at the maximum skin compression γ_c, which is referred to as the "crumbling compression." Whereas the values of Π measured on flat interfaces rarely exceed the surface tension of the underlying substrate, γ_c must be larger than γ for a surfactant nucleus to survive. The greater compression strength required for the nuclear membrane is made plausible by the spherical geometry and small surface area.

Application of the varying-permeability model to predict bubble counts in supersaturated gelatin is based on the "ordering hypothesis."[6,7] Each gelatin sample is assumed to have the same initial distribution of nuclear radii, and the number of bubbles formed is equal to the number of nuclei larger than some minimum initial radius $r_0^{\min}$. The ordering hypothesis then states that nuclei are neither created nor extinguished when samples are subjected to a pressure schedule and that the initial ordering according to size is preserved. It follows that each bubble count is determined by the properties and behavior of a single critical nucleus and that a family of pressure schedules yielding the same bubble count N is characterized by the same critical radius $r_0^{\min}$ and by the same crumbling compression γ_c.

Two independent derivations of the VP model have been proposed.[7] The first, following the gas-impermeable organic skin model of Fox and Herzfeld,[9] begins with the differential equation given by Love[10] for an elastic shell. It is assumed that the shell is bounded by spherical concentric surfaces and that it is held strained by a difference between the internal pressure p_{in} and the external pressure p_{out}. For a hydrophobic shell, p_{out} is just the right-hand side of Eqs. (1) and (2):

$$p_{\text{out}} = p_{\text{amb}} + 2\gamma/r \,. \tag{3}$$

The skin compression in Eq. (2) is identified as

$$\Gamma = \delta E/(1-\nu) \,, \tag{4}$$

where E is Young's modulus, ν is Poisson's constant, and δ is the "active skin thickness," i.e., the thickness of that portion of the skin which is capable of supporting a pressure gradient.[11] The assumption that Γ has a constant value γ_c for all large-scale changes in radius is equivalent to the assumption that the right-hand side of Eq. (4) is fixed. Integration of the Love equation[10] then yields the VP expressions for the changes in nuclear radius that occur during each step of a rudimentary pressure schedule.

The second derivation of the VP model[7] is thermodynamic or chemical, rather than mechanical. An auxiliary assumption requires that surfactant molecules be present not only in the skin, but also in a contiguous "reservoir." In effect, the reservoir is a materialization of the right-hand side of Eq. (2) with reservoir pressure

$$p_R = p_{\text{out}} \,, \tag{5a}$$

$$= p_{\text{amb}} + 2\gamma/r \,, \tag{5b}$$

while the skin may be regarded as a materialization of the left-hand side with small-scale skin pressure

$$p_S = p_{\text{in}} + 2\Gamma/r \,. \tag{5c}$$

The condition for small-scale mechanical equilibrium, $p_R = p_S$, is illustrated in Fig. 1(a). This condition could be satisfied by any reservoir which transmits the pressure $p_R = p_{\text{out}}$ to the skin-reservoir interface. Examples would be an attached surfactant droplet, a bulge in the skin, or a reservoir consisting of surfactant molecules dissolved in the surrounding liquid. For the sake of discussion, the skin and reservoir are visualized in the VP model as concentric shells of negligible thickness and hence of the same radius r. As shown schematically in Fig. 1(b), the reservoir is assumed to be outside the skin in contact with the li-

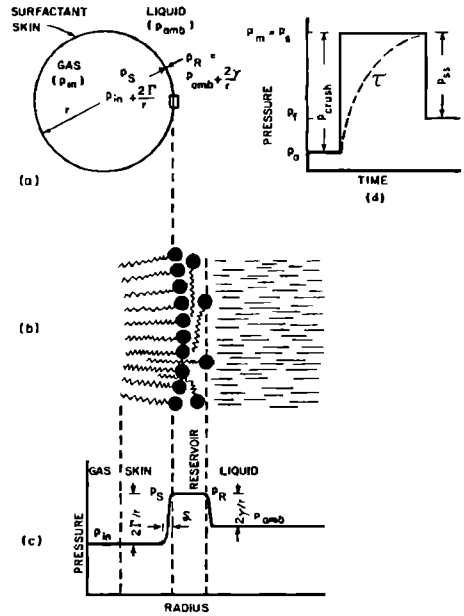

FIG. 1. Outline of the varying-permeability model. The spherical geometry and the condition for small-scale mechanical equilibrium, $p_R = p_S$, are illustrated in (a). A magnified view of the skin and the reservoir is shown in (b), and (c) is a plot of pressure versus radius indicating at what points p_{in}, p_S, p_R, and p_{amb} apply. The rudimentary pressure schedule in (d) consists of a rapid compression from p_0 to p_m, saturation of the sample at $p_m = p_s$, and a rapid decompression from p_s to p_f.

quid, and the skin is inside the reservoir in contact with the gas. The surfactant molecules composing the skin and the reservoir are hydrophobic, but those in the reservoir are not aligned and hence cannot support a pressure gradient. Fig. 1(c) is a plot of pressure versus radius in the vicinity of the skin and shows at what points the pressures p_{in}, p_S, p_R, and p_{amb} apply.

For the large-scale changes in radius actually calculated in the VP model, the magnitude of p_S is[7]

$$p_S = p_{in} + 2\gamma_C/r \,. \tag{5d}$$

However, the transport of surfactant molecules between the skin and the reservoir is described—not by setting p_S equal to p_R—but instead by requiring that the electrochemical potentials be equal in the two regions.

The electrochemical potential is taken to be[7]

$$\xi = \mu + kT\ln(\rho) + pv + Ze\psi \,, \tag{6}$$

where μ is the purely chemical potential, k is the Boltzmann constant, T is the absolute temperature, ρ is the molecular concentration or number density, p is the static pressure, v is the active volume occupied by one surfactant molecule, Ze is the effective charge of one surfactant molecule, and ψ is the electrostatic potential. In the reservoir we have[7]

$$\xi_R = \mu_R + kT\ln(\rho_R) + p_R v + (Ze\psi)_R \,, \tag{7a}$$

and in the skin we have[7]

$$\xi_S = \mu_S + kT\ln(\rho_S) + p_S v + (Ze\psi)_S \,, \tag{7b}$$

where v is assumed to have the same value in the two regions. Inserting Eqs. (5b) and (5d) into Eqs. (7a) and (7b) and setting ξ_R equal to ξ_S, we obtain[7]

$$p_{in} + 2\gamma_C/r - \beta = p_{amb} + 2\gamma/r \,, \tag{8a}$$

where β is defined by[7]

$$\beta = [kT\ln(\rho_R/\rho_S) + (\mu_R - \mu_S) + (Ze\psi)_R - (Ze\psi)_S] \,. \tag{8b}$$

To illustrate how changes in radius can be calculated from Eqs. (8a) and (8b), we shall briefly investigate what happens when a liquid sample containing VP nuclei is subjected to the rudimentary pressure schedule shown in Fig. 1(d). The schedule consists of a rapid compression from p_0 to p_m, saturation of the sample at $p_m = p_s$, and a rapid decompression from p_s to p_f. The term "rapid" means operationally that the process involves no change in the dissolved gas tension τ. Saturation at $p_m = p_s$ means that τ assumes the value p_s prior to decompression. The maximum over pressure or crushing pressure is then

$$p_{crush} \equiv (p_{amb} - \tau)_{max} \,, \tag{9a}$$

$$= (p_m - p_0) \,, \tag{9b}$$

and the maximum supersaturation is

$$p_{ss} \equiv (\tau - p_{amb})_{max} \,, \tag{10a}$$

$$= (p_s - p_f) \,. \tag{10b}$$

If we further assume that p_{crush} is not too large, e.g., it is less than 8 atm, then the nuclear skin will remain "permeable," and p_{in} will remain equal to τ and hence to p_0 during the initial compression. At the beginning of the compression, Eq. (8a) takes the form

$$p_0 + 2\gamma_C/r_0^{min} - \beta_0 = p_0 + 2\gamma/r_0^{min} \,, \tag{11a}$$

and at the end of the compression, it can be written

$$p_0 + 2\gamma_C/r_m^{min} - \beta_m = p_m + 2\gamma/r_m^{min} \,. \tag{11b}$$

Setting β_m equal to β_0, we obtain the VP expression for the change in radius induced by a rapid, permeable compression from p_0 to p_m (Ref.7):

$$2(\gamma_C - \gamma)[(1/r_m^{min}) - (1/r_0^{min})] = p_{crush} \,. \tag{12}$$

A trial calculation[7] using either the Love equation[10] or Eq. (8a) with $\beta_s = \beta_m$ suggests that the nucleus would be fully restored during the saturation phase as p_{in} increases from p_0 to $p_s = p_m$. That is, r_s^{min} would be equal to r_0^{min}, and any effect of crushing would be lost. This is directly contradicted by experiment,[1,2] hence the empirical assumption is made that[7]

$$r_s^{min} = r_m^{min} \,. \tag{13}$$

Mechanical equilibrium can now be achieved by allowing Γ to "relax" to its initial small-scale value $\Gamma_s = \Gamma_0 = \gamma$, but thermodynamic equilibrium requires that β_s differ from $\beta_m = \beta_0$.[7] The equation for a rapid, permeable decompression from p_s to p_f is obtained from Eq. (8a) by setting $\beta_f = \beta_s$:

$$2(\gamma_C - \gamma)[(1/r_f^{min}) - (1/r_s^{min})] = -p_{ss} \,. \tag{14}$$

The criterion for bubble formation at p_f is the Laplace condition[7]

$$p_{ss} = 2\gamma/r_f^{min} \,. \tag{15}$$

When Eq. (15) is combined with Eqs. (12)–(14), one finds a linear relation between p_{ss} and p_{crush} (Refs. 6 and 7):

$$p_{ss} = [2\gamma(\gamma_C - \gamma)/r_0^{min}\gamma_C] + [p_{crush}(\gamma/\gamma_C)] \,. \tag{16}$$

Each bubble number N is now characterized by a single nucleus with parameters r_0^{min} and γ_C, and for permeable compressions, each isopleth of constant N is simply a straight line in a plot of p_{ss} vs p_{crush}.

The definition of β in Eq. (8b) suggests that β_0 in Eq. (11a) should have the same value for all nuclei in a given sample. This leads to the prediction[7] that γ_C, which is fixed for a particular nucleus throughout an arbitrary pressure schedule, will increase linearly with the initial nuclear radius r_0^{min}. The corresponding equation,[7]

$$\gamma_C = \gamma + (\beta_0/2)r_0^{min} \,, \tag{17}$$

should also be satisfied by the combinations of r_0^{min} and γ_C determined for various isopleths of constant N. This prediction has been confirmed by three separate gelatin experiments,[7,11,12] one of which[12] used filtered samples to obtain a model-independent determination of r_0^{min}.

The case in which p_{crush} exceeds the threshold for impermeability, $p^*_{crush} = p^* - p_0$, is treated in Ref. 7, which should also be consulted for a fuller discussion of the VP assumptions. In Ref. 11, the model is applied to "slow" compressions, and a finite skin thick-

ness δ is incorporated into the model and evaluated experimentally.

In the first applications of the varying-permeability model to decompression sickness,[13-16] one additional assumption has been made, namely, that isopleths of constant bubble number N are also lines of constant effective dose. The critical supersaturation p_{ss} needed to produce signs or symptoms in a given percentage of the subjects has then been calculated as a function of the exposure pressure $p_{\text{crush}} + p_0$ for various combinations of $r_0^{\min}$, γ_C, and p^*. The optimum values of these parameters determined *in vivo*[13-16] are similar to those obtained in gelatin.[7,11,12]

II. EVOLUTION OF NUCLEAR RADII IN THE VP REGIME

The main task of the varying-permeability model has been to describe the changes in nuclear radius that occur with increases or decreases in ambient pressure. In this section, we go one step beyond the original equilibrium formulation[7] and attempt to extract the time dependence of the nuclear radius as it progresses from one stationary value to another. As usual in the VP regime, we track a single critical nucleus characterized by an initial radius $r_0^{\min}$, a constant crumbling compression γ_C, and a fixed impermeability threshold p^*. We also focus our attention on the accretion and deletion of surfactant molecules by the skin—those processes which produce large-scale changes in radius, and we simplify the concomitant problem of the diffusing gas by assuming that the skin at any given moment is either completely permeable or impermeable.

The rates or probabilities per unit time for a nucleus of radius r to add or slough off skin molecules are given by the accretion and deletion functions χ and ϕ. The specific functions assumed for this analysis are

$$\chi = A \exp[(\gamma_C - \gamma)S/kT] X[(\rho_R - \rho_R^0)/\rho_R^0] \quad \text{(accretion)}, \tag{18a}$$

$$\phi = A \exp[(\gamma_C - \gamma)S/kT] X[(\rho_S - \rho_S^0)/\rho_S^0] \quad \text{(deletion)}, \tag{18b}$$

where the constant A will be referred to as the "pre-exponential factor,"[17] where S is the average surface area occupied by one skin molecule *in situ*,[7] and where

$$X = 4\pi r^2/S \tag{19}$$

is the total number of surfactant molecules in the skin. Both transport rates are proportional to the exposed surface area $4\pi r^2$ and hence to the number of skin molecules X. The concentrations ρ_R in the reservoir and ρ_S in the skin have appeared already in Eqs. (7a) and (7b), and ρ_R^0 and ρ_S^0 are simply the equilibrium values, i.e., the values for which χ and ϕ are assumed to be equal, not only to one another, but also to zero. At a later stage, we will make the approximation $\rho_R^0 \simeq \rho_S^0 \simeq \rho^0$ in the denominators of Eqs. (18a) and (18b), which is analogous to the VP approximation $v_R \simeq v_S \simeq v$ in Eqs. (7a) and (7b).

The quantity

$$\Delta E_{\gamma'} \equiv \gamma' S, \tag{20a}$$

$$= -(\gamma_C - \gamma)S, \tag{20b}$$

which appears with a negative sign in the exponential factors of the transport functions, is the activation energy required to add one skin molecule. In the absence of a skin, γ_C is equal to zero, and the activation energy becomes

$$\Delta E_{\gamma} \equiv \gamma S, \tag{21}$$

which is just the surface energy needed to expand the liquid–gas interface by the area S. Since $(\gamma_C - \gamma)$ is constant for a given nucleus in the VP regime, it is convenient at this point to define the exponential activation amplitude as

$$A' = A \exp[(\gamma_C - \gamma)S/kT] \tag{22}$$

and rewrite Eqs. (18a) and (18b) more simply as

$$\chi = A' X(\rho_R - \rho_R^0)/\rho_R^0 \quad \text{(accretion)}, \tag{23a}$$

$$\phi = A' X(\rho_S - \rho_S^0)/\rho_S^0 \quad \text{(deletion)}. \tag{23b}$$

Solving for the molecular concentrations in Eqs. (7a) and (7b), we obtain:

$$\rho_R = \exp\{[\xi_R - \mu_R - (\text{Ze}\psi)_R - p_R v]/kT\}, \tag{24a}$$

$$\rho_R^0 = \exp\{[\xi_R - \mu_R - (\text{Ze}\psi)_R - p_R^0 v]/kT\}, \tag{24b}$$

$$\rho_S = \exp\{[\xi_S - \mu_S - (\text{Ze}\psi)_S - p_S v]/kT\}, \tag{24c}$$

$$\rho_S^0 = \exp\{[\xi_S - \mu_S - (\text{Ze}\psi)_S - p_S^0 v]/kT\}, \tag{24d}$$

where the quantities ξ_R, ξ_S, μ_R, μ_S, $(\text{Ze}\psi)_R$, and $(\text{Ze}\psi)_S$ are assumed to be independent of the pressures p_R and p_S. The respective normalized density increments are then

$$(\rho_R - \rho_R^0)/\rho_R^0 = \exp[-(p_R - p_R^0)v/kT] - 1, \tag{25a}$$

$$(\rho_S - \rho_S^0)/\rho_S^0 = \exp[-(p_S - p_S^0)v/kT] - 1. \tag{25b}$$

We will now show that the arguments of the exponents in Eqs. (25a) and (25b) are much less than one for pressure excursions below, for example, 100 atm. The active volume is defined by

$$v = \delta S. \tag{26}$$

The measured value of the active skin thickness is[11]

$$\delta \simeq 2.5 \text{ Å}, \tag{27}$$

and the area per skin molecule averaged over three experiments is[7,11,12]

$$S \simeq (65 \text{ Å}^2 + 45 \text{ Å}^2 + 48 \text{ Å}^2)/3, \tag{28a}$$

$$\simeq 53 \text{ Å}^2. \tag{28b}$$

The magnitude of the active volume is then

$$v \simeq 132 \text{ Å}^3, \tag{29}$$

and the numerators inside the exponents of Eqs. (25a) and (25b) are less than

$$(100 \text{ atm})(132 \text{ Å}^3) \simeq 1.33 \times 10^{-14} \text{ ergs}. \tag{30}$$

This is small compared to the denominators,

$$kT \simeq 4.14 \times 10^{-14} \text{ ergs} \tag{31}$$

at 300 °K, and hence we may expand the exponents and make the approximations:

$$(\rho_R-\rho_R^0)/\rho_R^0\simeq-(p_R-p_R^0)v/kT\,, \tag{32a}$$

$$(\rho_S-\rho_S^0)/\rho_S^0\simeq-(p_S-p_S^0)v/kT\,, \tag{32b}$$

$$\chi\simeq-A'X(p_R-p_R^0)v/kT\ \text{(accretion)}, \tag{33a}$$

$$\phi\simeq-A'X(p_S-p_S^0)v/kT\ \text{(deletion)}. \tag{33b}$$

To illustrate the use of χ and ϕ in the VP regime, we shall consider one transition in detail and give only the results for the others. The relevant pressures for a permeable compression from p_0 to p^* can be obtained from Eqs. (5b) and (5d):

$$p_R=p^*+2\gamma/r\,, \tag{34a}$$

$$p_R^0=p_0+2\gamma/r_0^{\min}\,, \tag{34b}$$

$$p_S=p_0+2\gamma_C/r\,, \tag{34c}$$

$$p_S^0=p_0+2\gamma_C/r_0^{\min}\,, \tag{34d}$$

where $r=r(t)$ is the magnitude at time t of the nuclear radius as it decreases from $r_0^{\min}$ to $r_{\min}^*$.

The rate of change of the number of skin molecules dX/dt is just the difference between the accretion and deletion functions χ and ϕ:

$$\frac{dX}{dt}=\chi-\phi\,. \tag{35}$$

A second expression for dX/dt can be found by differentiating Eq. (19):

$$\frac{dX}{dt}=\frac{8\pi r}{S}\frac{dr}{dt}\,. \tag{36}$$

To obtain a differential equation for $r(t)$, we first replace X in Eqs. (33a) and (33b) with $4\pi r^2/S$ from Eq. (19). We then substitute for p_R, p_R^0, p_S, and p_S^0 using Eqs. (34a)–(34d) and equate the expressions for dX/dt in Eqs. (35) and (36). This gives

$$\frac{dr}{dt}=\frac{A'vr}{2kT}\left[-(p^*-p_0)+2(\gamma_C-\gamma)\left(\frac{1}{r}-\frac{1}{r_0^{\min}}\right)\right]. \tag{37}$$

Finally, with the help of Eq. (12), we express the applied pressure increment $p_{\text{crush}}=p^*-p_0$ in terms of the equilibrium radii, $r_0^{\min}$ at the beginning and $r_{\min}^*$ at the end of the transition. The result is

$$\frac{dr}{dt}=\frac{A'vr(\gamma_C-\gamma)}{kT}\left(\frac{1}{r}-\frac{1}{r_{\min}^*}\right). \tag{38}$$

Integration of Eq. (38) yields the familiar expression for an exponential decay,

$$r(t)=r_{\min}^*+(r_0^{\min}-r_{\min}^*)\exp(-t/\sigma^*)\,, \tag{39a}$$

where the constant of integration has been chosen so that $r(0)$ is equal to $r_0^{\min}$ and $r(\infty)$ is equal to $r_{\min}^*$. The time constant,

$$\sigma^*=(2kT/A'v)[r_{\min}^*/2(\gamma_C-\gamma)]\,, \tag{39b}$$

can be rewritten as

$$\sigma^*=(2kT/A'v)(1/\beta_0)(r_{\min}^*/r_0^{\min}) \tag{39c}$$

by substituting from Eq. (17). The ratio $r_{\min}^*/r_0^{\min}$ is independent of the nuclear radius and can be replaced by using Eqs. (12) and (17). The final result for the permeable region $p_{\text{crush}}=p_m-p_0\leqslant p_{\text{crush}}^*=p^*-p_0$ is

$$\sigma^*=(2kT/A'v)/(p_m-p_0+\beta_0)\,, \tag{39d}$$

$$=(2kT/A'v)/(p_{\text{crush}}+\beta_0)\,. \tag{39e}$$

For a rapid compression in the impermeable region $p_{\text{crush}}\geqslant p_{\text{crush}}^*$, the radius decreases from $r_{\min}^*$ to $r_m^{\min}$ according to the equations

$$r(t)=r_m^{\min}+(r_{\min}^*-r_m^{\min})\exp(-t/\sigma_m)\,, \tag{40a}$$

$$\sigma_m=2kTr_m^{\min}/[A'v2(\gamma_C-\gamma)]\,, \tag{40b}$$

$$=(2kT/A'v)(1/\beta_0)(r_m^{\min}/r_0^{\min})\,, \tag{40c}$$

$$=(2kT/A'v)/[p_m-p_0(r_{\min}^*/r_m^{\min})^3+\beta_0]\,. \tag{40d}$$

It can be shown by solving[18] the cubic Eq. (19b) in Ref. 7 and by making the usual substitution for $(\gamma_C-\gamma)$ via Eq. (17) that $r_{\min}^*/r_m^{\min}$ in Eq. (40d) is independent of the radius and is a function only of the pressures p_0, p^*, and p_m.

For a rapid, permeable decompression from p_s to p_f, the radius increases from $r_s=r_m$ to r_f according to the equations

$$r(t)=r_f^{\min}+(r_s^{\min}-r_f^{\min})\exp(-t/\sigma_f)\,, \tag{41a}$$

$$\sigma_f=2kTr_f^{\min}/[A'v2(\gamma_C-\gamma)]\,, \tag{41b}$$

$$=(2kT/A'v)(1/\beta_0)(r_f^{\min}/r_0^{\min})\,. \tag{41c}$$

For the case in which the original compression p_{crush} lies entirely within the permeable region, Eq. (12) may be used to rewrite Eq. (41c) as

$$\sigma_f=(2kT/A'v)/(p_{\text{crush}}-p_{ss}+\beta_0)\,. \tag{41d}$$

We shall now interpret the pre-exponential factor A and the exponential activation amplitude A' by comparing our "diffusion equation," $dX/dt=\chi-\phi$, with Fick's law,[17]

$$\frac{dn}{dt}=-\frac{D\Lambda\Delta\rho}{\Delta r}\,, \tag{42a}$$

where D is the self-diffusion coefficient and dn/dt is the net rate at which the molecules of interest diffuse across an area Λ as a result of a density gradient $\Delta\rho/\Delta r$. Identifying dn/dt as $-dX/dt$ and setting $\Lambda=4\pi r^2$, we can express Eq. (42a) as

$$\frac{dX}{dt}=\frac{D4\pi r^2\Delta\rho}{\Delta r}\,. \tag{42b}$$

Meanwhile, substituting Eqs. (18a), (18b), and (19) into Eq. (35), we obtain

$$\frac{dX}{dt}=A\exp\left(\frac{(\gamma_C-\gamma)S}{kT}\right)X\left[\left(\frac{\rho_R-\rho_R^0}{\rho_R^0}\right)-\left(\frac{\rho_S-\rho_S^0}{\rho_S^0}\right)\right]. \tag{43a}$$

We next let $(\rho_R-\rho_R^0)$ equal $\Delta\rho_R$ and $(\rho_S-\rho_S^0)$ equal $\Delta\rho_S$, and we then make the approximation $\rho_R^0\simeq\rho_S^0\simeq\rho^0$. Equation (43a) becomes

$$\frac{dX}{dt}=A\exp\left(\frac{(\gamma_C-\gamma)S}{kT}\right)\frac{4\pi r^2}{S}\frac{\Delta\rho}{\rho_0}\,, \tag{43b}$$

where $\Delta\rho=(\Delta\rho_R-\Delta\rho_S)$ is the net density increment.

Comparing Eqs. (42b) and (43b), we find

$$A = D\rho_0 S/\Delta r\,, \tag{44a}$$

$$A' = (D\rho_0 S/\Delta r)\exp[(\gamma_C - \gamma)S/kT]\,. \tag{44b}$$

Setting $\rho_0 v$ equal to one and taking the self-diffusion coefficient to be[17]

$$D = kT/4\pi\eta R\,, \tag{45}$$

where η is the viscosity and R is the radius of the diffusing molecule, assumed to be spherical, we have finally

$$(2kT/A'v) = (8\pi\eta R\,\Delta r/S)\exp[-(\gamma_C - \gamma)S/kT]\,. \tag{46}$$

This section can be summarized by saying that the transition from one equilibrium state to another in the VP regime is via an exponential decay law. For a given transition, the time constants for different nuclei vary inversely with the exponential activation amplitude A', and they depend explicitly upon the radius and the temperature solely through the exponential activation energy factor $\exp[(\gamma_C - \gamma)S/kT]$. [We use the word "explicitly" because the viscosity η in Eq. (46) is also a function of temperature.] Different transitions are characterized by different time constants and tend to decrease as the magnitudes of the pressure changes increase.

III. STOCHASTIC GENERATION AND REGENERATION OF THE PRIMORDIAL SIZE DISTRIBUTION

In the previous section, we investigated the time dependence of the radius of an individual nucleus subjected to an increase or a decrease in ambient pressure. We now consider, at constant ambient pressure, a statistical process by which the equilibrium size distribution of an entire population of nuclei may be generated or regenerated.

To be definite, we assume that p_{amb} is equal to p_0. (The final results are independent of this choice.) We further assume that each nucleus and its surrounding medium are in diffusion equilibrium. It follows that p_{in} is equal to the dissolved gas tension τ, which is equal to p_0. Mechanical equilibrium of a nucleus of radius r is then expressed by the relations

$$p_S = p_R\,, \tag{47a}$$

$$p_0 + 2\Gamma/r = p_0 + 2\gamma/r\,, \tag{47b}$$

where the skin compression Γ has a small-scale value of γ and is thus independent of the radius r.

As a first approximation, p_S and p_R remain fixed and equal to one another in the statistical regime. There are, however, small fluctuations in p_S and p_R associated with the random accretion or deletion of individual skin molecules. We estimate these pressure changes by dividing the accretion energy $\Delta E_\gamma = -(\gamma_C - \gamma)S$ in Eqs. (20a) and (20b) by the total active skin volume $Xv = \delta 4\pi r^2$ to obtain

$$-(p_S - p_S^0) \simeq -(p_R - p_R^0)\,, \tag{48a}$$

$$\simeq (\gamma_C - \gamma)S/\delta 4\pi r^2\,, \tag{48b}$$

$$\simeq (\gamma_C - \gamma)/\delta X\,. \tag{48c}$$

The random fluctuations in the radius r and in the total number of skin molecules X are accompanied by variations in the crumbling compression γ_C. This is a significant departure from the VP regime, in which each gas nucleus is characterized by a fixed initial radius r_0 and hence by a constant γ_C. From Eqs. (17) and (19) we have

$$\gamma_C = \gamma + (\beta_0 r/2)\,, \tag{49a}$$

$$= \gamma + \beta_0 (XS/\pi)^{1/2}/4\,, \tag{49b}$$

where, as usual, β_0 is a property of the population as a whole and has the same value for all VP nuclei in the sample.

Substitution of Eqs. (49a) and (49b) into Eqs. (48b) and (48c) gives

$$-(p_S - p_S^0) \simeq -(p_R - p_R^0)\,, \tag{50a}$$

$$\simeq \beta_0 S/\delta 4\pi r\,, \tag{50b}$$

$$\simeq \beta_0 (S/\pi X)^{1/2}/4\delta\,. \tag{50c}$$

The accretion and deletion functions in Eqs. (33a) and (33b) are now both positive and equal, and they can be written

$$\chi = \phi\,, \tag{51a}$$

$$\simeq A\alpha_0 X^{1/2}\exp(\alpha_0 X^{1/2})\,, \tag{51b}$$

where the exponent is obtained from the activation amplitude A' in Eq. (22), where α_0 is defined by

$$\alpha_0 = \beta_0 (S/\pi)^{1/2} v/4\delta kT\,, \tag{51c}$$

$$= \beta_0 (S/\pi)^{1/2} S/4kT\,, \tag{51d}$$

and where $\alpha_0 X^{1/2}$ is equal to $(\gamma_C - \gamma)S/kT$.

Guided by a derivation given in Ref. 19, we now let $F(X,t)$ represent the number of gas nuclei of "size" X at time t. By definition, the probability for accreting a skin molecule in the time element dt is $\chi(X)dt$, and the probability for deleting a skin molecule in the time element dt is $\phi(X)dt$. Treating F as a discrete function of the discrete variable X, we find (for $X \pm 1$)

$$\frac{dF(X,t)}{dt} = [F(X+1,t)\phi(X+1) - F(X,t)\phi(X)] - [F(X,t)\chi(X) - F(X-1,t)\chi(X-1)]\,. \tag{52}$$

Approximating the discrete quantities F and X by a continuous function F of the continuous variable X, we have

$$\frac{\partial F(X,t)}{\partial t} = \frac{\partial[\phi(\xi)F(\xi,t)]}{\partial \xi}\bigg|_{\xi = X+1/2} - \frac{\partial[\chi(\xi)F(\xi,t)]}{\partial \xi}\bigg|_{\xi = X-1/2}\,. \tag{53}$$

Since

$$\frac{\partial[\phi(\xi)F(\xi,t)]}{\partial \xi}\bigg|_{\xi = X+1/2} \simeq \frac{\partial[\phi(X)F(X,t)]}{\partial X} + \frac{1}{2}\frac{\partial^2[\phi(X)F(X,t)]}{\partial X^2}\,, \tag{54a}$$

$$\frac{\partial[\chi(\xi)F(\xi,t)]}{\partial \xi}\bigg|_{\xi = X-1/2} \simeq \frac{\partial[\chi(X)F(X,t)]}{\partial X} - \frac{1}{2}\frac{\partial^2[\chi(X)F(X,t)]}{\partial X^2}\,, \tag{54b}$$

we obtain[19]

$$\frac{\partial F}{\partial t} \simeq \frac{\partial(\phi F)}{\partial X} - \frac{\partial(\chi F)}{\partial X} + \frac{1}{2}\frac{\partial^2(\phi F)}{\partial X^2} + \frac{1}{2}\frac{\partial^2(\chi F)}{\partial X^2} . \quad (55)$$

We now seek a stationary distribution $F(X)$ such that $\partial F/\partial t$ in Eq. (55) will be equal to zero for the accretion and deletion functions χ and ϕ given in Eqs. (51a)–(51d). It is easily shown by direct substitution that the expression

$$F(X) = (\tfrac{1}{2})N_0\alpha_0 X^{-1/2}\exp(-\alpha_0 X^{1/2}) \quad (56)$$

meets these requirements. The number of nuclei larger than $X_0^{\min}$ is given by the integral distribution

$$N(X_0^{\min}) = \int_{X_0^{\min}}^{\infty} F(X)dX , \quad (57a)$$

$$= N_0\exp[-\alpha_0(X_0^{\min})^{1/2}] , \quad (57b)$$

and the number larger than $r_0^{\min}$ is given by the integral distribution

$$N(r_0^{\min}) = N_0\exp[-\beta_0 S r_0^{\min}/2kT] , \quad (58a)$$

$$= N_0\exp[-(\gamma_C - \gamma)S/kT] . \quad (58b)$$

We end this section by examining the time dependence of an arbitrary distribution $G(X,t)$ as it approaches the stable solution $F(X)$ given by Eq. (56). Letting $\Delta(X,t)$ be the difference between $G(X,t)$ and $F(X)$, we can write

$$G(X,t) = F(X) + \Delta(X,t) . \quad (59)$$

To separate the variables X and t, we express Δ as a product of two functions,

$$\Delta(X,t) = T(t)Y(X) , \quad (60)$$

and replace F in Eq. (55) by $G(X,t)$ in Eqs. (59) and (60). The result is

$$\frac{1}{T}\frac{\partial T}{\partial t} = \frac{1}{Y}\frac{\partial^2\phi Y}{\partial X^2} , \quad (61)$$

where $\phi = \chi$ is given by Eqs. (51a)–(51d).

The two sides of Eq. (61) are independent functions of t and of X, respectively. It follows that both sides must be equal so some constant, which we take to be $-\lambda$. Integration of the time-dependent equation

$$\frac{\partial T}{\partial t} = -\lambda T \quad (62)$$

yields

$$T = C\exp(-\lambda t) , \quad (63)$$

where C is also a constant. The X equation, meanwhile, can be written

$$\phi\left(\frac{\partial^2 Z}{\partial X^2}\right) = -\lambda Z , \quad (64a)$$

where

$$Z(X) = \phi Y . \quad (64b)$$

Rather than attempt to solve Eq. (64a) explicitly, we shall make some general observations about the nature of the solution. First, we note that Eq. (64a) is of the Sturm–Liouville form[20]

$$d\left[q(X)\left(\frac{dZ}{dX}\right)\right]\Big/dX + u(X)Z = -\lambda p(X)Z . \quad (65)$$

The coefficients in our case are $q(X)=1$, $u(X)=0$, and $p(X)=1/\phi$, where $q(X)$ and $p(X)$ are positive over the entire range $0<X<\infty$. It follows for suitable boundary conditions and normalization N_0 [the actual choices will depend on the initial distribution $G(X,0)$] that Eq. (64a) has an infinite set of eigenvalues λ_n that are real and positive and that the eigenfunctions Z_n associated with λ_n are orthogonal and form a complete set.

The time-dependent difference function $\Delta(X,t)$ can now be expressed formally as a linear combination of the normal modes,

$$\Delta(X,t) = \sum_{n=1}^{\infty} C_n Z_n(X)\exp(-\lambda_n t) , \quad (66a)$$

and the constant coefficients C_n can, in principle, be evaluated from the initial condition

$$\Delta(X,0) = G(X,0) - F(X) , \quad (66b)$$

$$= \sum_{n=1}^{\infty} C_n Z_n(X) . \quad (66c)$$

The implication of this analysis is that an arbitrary initial distribution $G(X,0)$ approaches the appropriately normalized stable distribution $F(X)$ via the exponential decay of the normal modes of the difference function $\Delta(X,t) = G(X,t) - F(X)$.

IV. DISCUSSION

In this paper, we have attempted to gain a deeper understanding of gas cavitation nuclei by investigating two time-dependent extensions of the varying-permeability model. The main piece of evidence in favor of these extensions is the primordial integral size distribution,[7]

$$N(r_0^{\min}) = N_0\exp(-r_0^{\min}/b) , \quad (67)$$

which is equivalent to Eqs. (57b), (58a), and (58b). Whereas Eq. (67) was first deduced[7] and later verified[11,12] by treating $r_0^{\min}$ as an adjustable parameter in a VP analysis of bubble counts made in supersaturated gelatin, one of the subsequent experiments[12] used filtered gelatin samples to measure $r_0^{\min}$ directly. Data from this experiment confirm Eq. (67), which we therefore regard, not only as empirical, but also as model independent.

In deriving Eq. (67) *a posteriori*, we have chosen accretion and deletion functions, χ and ϕ in Eqs. (51a)–(51d), which satisfy the equilibrium condition $\partial F/\partial t = 0$ in Eq. (55). Our choices are "trivial" in the sense that both of the products χF and ϕF are constant, and all of the derivatives on the right-hand side of Eq. (55) are zero. Trivial though they may be, our transport functions are neither simple nor manifestly wrong. For one thing, given the complexity of $F(X)$ in Eq. (56), it is difficult to find other expressions for χ and for ϕ which will yield $\partial F/\partial t = 0$. Our functions do this to all orders. Equally important, we have shown that our candidates for χ and ϕ follow naturally from the varying-permeability model and can also describe

the accretion and deletion of skin molecules in the VP regime.

One consequence of using the same transport functions in both of these model extensions is that the exponential activation energy factor, $\exp(-\Delta E_\gamma/kT) \equiv \exp[+(\gamma_C-\gamma)S/kT]$ in Eqs. (18a) and (18b), appears in the denominator of the VP time constants. That is, all of the time constants are multiplied by $\exp[-(\gamma_C-\gamma)S/kT]$. An analogous factor appears in the Arrhenius expression for the rate constant of an "elementary" chemical reaction.[17] The rate constant is the reciprocal of our time constant σ, hence the argument in our exponent has the opposite sign. In other words, whereas the exponential factor is required in the transport functions to generate the primordial size distribution *a posteriori*, it is expected *a priori* to appear in the VP time constants if we view these transitions as being elementary chemical reactions with the usual temperature dependence.

To obtain some idea of the magnitude of the VP time constants, we evaluate the quantity $8\pi\eta R\Delta r/S\beta_0$ for $\eta=10$ dyn-s/cm^2 (similar to castor oil at 20°C), $\Delta r=30$ Å (the length of a surfactant molecule), $S=65$ Å^2 from Ref. 7, $R\simeq(3S\Delta r/4\pi)^{1/3}\simeq 9$ Å, and $\beta_0=1.43\times10^{-6}$ dyn/cm^2 from Ref. 7. The result is 0.8×10^{-3} s. The factor $\exp[-(\gamma_C-\gamma)S/kT]$ in Eq. (46) varies by three orders of magnitude in the gelatin experiments,[2,11,12] i.e., from the order of 1 to the order of 10^{-3}. Our analysis suggests, therefore, that the VP time constants range from 10^{-3} to 10^{-6} s.

The VP time constants depend on the nuclear radius via the exponential factor and the relation $(\gamma_C-\gamma)=\beta_0 r_0^{\min}/2$ from Eq. (17). This is surprising because it means that large nuclei would evolve and equilibrate more rapidly than small ones. The opposite would be true if the rates were controlled by gaseous diffusion. Since the VP time constants (10^{-3} to 10^{-6} s) are very short in comparison with the times required for an ordinary gas bubble to collapse [about 4 s at an initial radius of 0.5 μm (Ref. 21)], we expect that diffusion would indeed be the dominant process for the size range (e.g., 0.01 to 0.7 μm) explored in the gelatin experiments.[2,11,12] The presence of a skin on a gas bubble would reduce the rates for diffusion even further.

It seems, therefore, that the end point of a VP transition is determined by surface chemistry, while the actual rate is determined by gaseous diffusion. An important corollary is that the surfactant molecules react quickly enough so that the skin of an intact VP nucleus will track any changes in nuclear radius that result from gaseous diffusion. On the other hand, the VP time constants would be expected to play a role in acoustic cavitation where oscillatory changes in the ambient pressure and hence in the equilibrium nuclear radius can easily occur in times shorter than 10^{-3} s.

The stochastic and VP time constants are related via the transport functions χ and ϕ and vary inversely as the driving pressures, typified, respectively, by $\beta_0 S/\delta 4\pi r$ in Eq. (50b) and by β_0 in Eqs. (39c), (40c), and (41c). Scaling the VP time constants (10^{-6} to 10^{-3} s) by the ratio $\beta_0/(\beta_0 S/\delta 4\pi r)=\delta 4\pi r/S$ (which varies from 48 to 3381 for $\delta=2.5$ Å, $S=65$ Å^2, and 100 Å $< r <$ 7000 Å), we obtain a range of from 3.4×10^{-3} to 4.8×10^{-2} s for the accretion or deletion of one skin molecule. For a nucleus to migrate from a small to a large radius, or vice versa, a net exchange of about $X=4\pi r^2/S$ molecules would be required. For $r=7000$ Å and $S=65$ Å^2, this gives a factor of 9.4×10^6 and a range of 3.1×10^4 to 4.5×10^5 s. The time required for a stochastic transition may then be of the order of 10–100 h.

The general picture of gas cavitation nuclei that emerges from this investigation is rather similar to that outlined in Ref. 7. Nuclei may originate from collapsing bubbles which accumulate on their surfaces a store of surface-active molecules. At some point, probably within a few minutes or even seconds, the density of these molecules becomes sufficient to resist the collapse and stabilize the spherical gas volume at some initial radius r_0. Subsequent stochastic fluctuations in the number of skin molecules result eventually in the equilibrium size distribution $N(r_0^{\min})$ given in Eq. (67).

The equilibrium distribution, once established, can be distorted in various ways. Most of these fall under the rubric "denucleation." For example, a test sample can be partially denucleated by filtration, i.e., by cutting off the primordial distribution at the filter-pore radius r_p.[12] Another standard method is to add detergent[1,2] or other substances[11] which presumably operate by changing $(\mu_R-\mu_S)$ and hence β_0 in Eq. (58a). Pressure increments can be used to increase or decrease the radii of all nuclei in the sample, preserving the exponential, but changing its slope. A dependence on temperature is also predicted.

Given sufficient time and suitable conditions, it should be possible to regenerate the equilibrium distribution stochastically. If one waits long enough after filtration, nuclei larger than r_p should reappear. Similarly, since the theoretical equilibrium distribution is independent of ambient pressure the effects of pressure changes, such as those treated in the varying-permeability model, should eventually be erased. This provides a means by which the distribution $N(r_s^{\min})$ at $p_{amb}=p_m=p_s$ could eventually return to the initial distribution $N(r_0^{\min})$ which existed at $p_{amb}=p_0$.

Direct evidence for the stochastic generation and regeneration mechanisms proposed here and in Ref. 7 has recently been obtained by Johnson and Cooke.[22] These authors injected air bubbles into seawater and observed that although some bubbles dissolved completely, others stopped decreasing in size abruptly and remained as microbubbles apparently stabilized by films. Originally, the radial distribution ranged up to 7 μm and peaked at around 2 μm. During the first 4 h, there was little change in this distribution. After 22 h, although there was little reduction in the number, the microbubbles were generally smaller, and the radial distribution resembled a decaying exponential, cut off at the microscope resolution, about 0.3 μm. There is also some evidence for the regeneration of gas cavita-

tion nuclei *in vivo*, e.g., for a loss of decompression tolerance in striking or vacationing caison workers,[23] but other mechanisms, such as ingestion of nuclei or nucleation by cosmic rays,[24] may be involved.

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[1]E. N. Harvey, D. K. Barnes, W. D. McElroy, A. H. Whiteley, D. C. Pease, and K. W. Cooper, J. Cell. Comp. Physiol. 24, 1–22 (1944).
[2]D. E. Yount and R. H. Strauss, J. Appl. Phys. 47, 5081–5088 (1976).
[3]M. S. Plesset, ASME Fluids Engineering and Applied Mechanics Conference, Evanston, IL, 15–25, 1969 (unpublished).
[4]D. E. Yount and T. D. Kunkle, J. Appl. Phys. 46, 4484–4486 (1975).
[5]T. D. Kunkle and D. E. Yount, in *Sixth Symposium on Underwater Physiology*, edited by M. B. Kent (FASEB, Bethesda, 1975), pp. 459–467.
[6]D. E. Yount, T. D. Kunkle, J. S. D'Arrigo, F. W. Ingle, C. M. Yeung, and E. L. Beckman, Aviat. Space Environ. Med. 48, 185–191 (1977).
[7]D. E. Yount, J. Acoust. Soc. Am. 65, 1429–1439 (1979).
[8]G. L. Gaines, Jr., *Insoluble Monolayers at Liquid–Gas Interfaces* (Interscience, New York, 1966).
[9]F. E. Fox and K. F. Herzfeld, J. Acoust. Soc. Am. 26, 984–989 (1954).
[10]A. E. H. Love, *The Mathematical Theory of Elasticity* (Dover, New York, 1944), Reprint 4th ed., p. 142.
[11]D. E. Yount and C. M. Yeung, J. Acoust. Soc. Am. 69, 702–708 (1981).
[12]D. E. Yount, C. M. Yeung, and F. W. Ingle, J. Acoust. Soc. Am. 65, 1440–1450 (1979).
[13]D. E. Yount, in *Decompression Theory*, edited by T. E. Berghage (Undersea Medical Society, Inc., Bethesda, 1978), pp. 143–160.
[14]D. E. Yount, Aviat. Space Environ. Med. 50, 44–50 (1979).
[15]D. E. Yount and D. A. Lally, Aviat. Space Environ. Med. 51, 544–550 (1980).
[16]D. E. Yount, Undersea Biomed. Res. 8, 199–208 (1981).
[17]I. N. Levine, *Physical Chemistry* (McGraw–Hill, New York, 1978), pp. 442–502.
[18]*Handbook of Chemistry and Physics*, edited by C. D. Hodgman *et al.* (The Chemical Rubber Publishing Co., Cleveland, 1962), 44th ed., p. 320.
[19]K. H. Dieter, IEEE Trans. Bio-Med. Eng. BME 14, 124–146 (1967).
[20]R. P. Agnew, *Differential Equations* (McGraw–Hill, New York, 1942), pp. 257–268.
[21]P. S. Epstein and M. S. Plesset, J. Chem. Phys. 18, 1505–1509 (1950).
[22]B. D. Johnson and R. C. Cooke, Science 213, 209–211 (1981).
[23]D. N. Walder, in *Proceedings of the Third International Biometeorological Congress*, Pau (S. France) (Pergamon, Oxford, 1963), pp. 350–359.
[24]D. Sette and F. Wanderlingh, Phys. Rev. 125, 409–417 (1962); J. Acoust. Soc. Am. 41, 1074–1082 (1967).