Skins of varying permeability: A stabilization mechanism for gas cavitation nuclei

David E. Yount

Department of Physics and Astronomy, University of Hawaii, Honolulu, Hawaii 96822

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Numerous experiments suggest that bubble formation in water is initiated by preexisting gas nuclei. This is unexpected since gas phases larger than the order of 1 μm in radius ought to rise to the surface of a standing liquid, whereas smaller ones should dissolve rapidly via the outward diffusion of gas that results from surface tension. Several mechanisms for stabilizing gas nuclei have been proposed, but in each case there is experimental evidence to the contrary. In this article, a model is investigated in which stability is maintained by surface-active skins of varying gas permeability. Data on ultrasonic cavitation and on bubble formation by counter-diffusion indicate that such skins, if they exist, must be initially permeable. Quantitative comparisons with bubble counts obtained recently from supersaturated gelatin lead to the further conclusion that nuclear skins become effectively impermeable if the static pressure is raised rapidly by a sufficiently large amount. The surface area, length, and energy per skin molecule deduced from these comparisons are remarkably similar to those of known surfactants, such as lung extract, lecithin, and oleyl alcohol.

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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,[1-4] 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.[5,6] These are specific tests for gas nuclei, and it is therefore evident that the precocious onset of cavitation in water and in aqueous media generally must be due mainly to the presence of such nuclei, even though their origins and the mechanisms stabilizing them are poorly understood. Furthermore, solid particles or container walls with smooth surfaces[7] are not expected to be effective in initiating bubble formation at tensile, ultrasonic, or supersaturation pressures less than about 1000 atm.[8]

Several models for stabilizing gas nuclei have been proposed, but a brief review of the literature indicates that none is firmly established. Harvey *et al.*[5] have shown that cracks or fissures in solid surfaces can support gas phases, and this mechanism must be considered viable, whether or not crevices in particles or motes are the main instigator of bubble formation in any particular case. Evidence in favor of the crevice model is provided by the observation of Greenspan and Tschiegg[9] that the acoustic cavitation threshold in water can be raised from less than 1 atm to greater than 100 atm by passing samples through membrane filters of 0.2-μ pore diameter. Evidence to the contrary was obtained by Sirotyuk,[10] who found that the removal of solid particles from ordinary water increases the cavitation strength by only a factor of about 1.3. In the Appendix, we show that the crevice model, at least in its present state of development,[11-13] does not provide a satisfactory explanation of bubble counts made recently in supersaturated gelatin.[14]

Gas phases in elastic media, such as foam rubber, can be stabilized by the restoring forces of the surrounding medium,[15] but this mechanism is precluded in water and in lean gelatin mixtures[14,16,17] since the elasticity is negligible in comparison with the surface tension. Coulomb repulsion by surface ions of like charge has also been suggested,[18] but specific tests of the "ion model" indicate that the cavitation strength of water is independent of the conductivity k due to ions of dissolved substances, even when the value of k is varied by more than two orders of magnitude.[10]

Fox and Herzfeld[19] have proposed that nuclei may be stabilized by an organic skin which mechanically prevents the loss of gas by diffusion. As long as their skins remain impermeable and intact, such nuclei would recover fully from any cyclical change in ambient pressure. It follows that there should be a threshold crushing pressure—that necessary to crumble the skin—below which previously applied static pressure would have no effect on cavitation. This prediction proved to be inconsistent with subsequent experiments by Strasberg[11,20] which showed that the oneset of ultrasonic cavitation in water increases smoothly with crushing pressure, and Herzfeld[21] abandoned the model as a result. In addition, Plesset[7] has pointed out that nuclei grow quite readily by rectified diffusion in oscillating pressure fields, and Strauss and Kunkle[17] have shown that bubble formation can be induced by counterdiffusion, i.e., by switching from a slowly diffusing gas to a more rapidly diffusing gas at constant total pressure. These observations indicate that diffusion through the liquid-gas interface is not inhibited in the absence of crushing and that nuclear skins, if they exist, must be initially permeable.

In this article we investigate a model in which stability is maintained by surface-active skins of varying gas

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permeability. Our interest in this model is stimulated by an examination, outlined in Sec. I, of bubble formation data from supersaturated gelatin.[14] The new results, like those of Strasberg[11,20] and of Strauss and Kunkle[17] are incompatible with the predictions of Fox and Herzfeld[19] for gas-impermeable organic skins, but they suggest that skins of some type must be involved. The discussion of the gelatin data in Sec. I also serves to define the relevant experimental quantities and to place the theoretical material of Sec. II in an experimental context. In Sec. III it is shown that good agreement with the gelatin data can, in fact, be obtained with a suitable choice of skin model and model parameters. The nature and possible origins of gas cavitation nuclei are considered further in Sec. V, and the crevice model[5,11-13] is reviewed in the Appendix.

I. BUBBLE FORMATION IN SUPERSATURATED GELATIN

A portion of the data collected by Yount and Strauss[14] in supersaturated gelatin is shown in Fig. 1. Each gelatin sample, initially free of visible bubbles, is subjected to a particular pressure schedule, causing macroscopic bubbles to form. The samples are 4 mm deep, and bubbles are counted in the lower 3 mm, corresponding to a fiducial volume of 0.4 ml per sample. The raw data thus consist of bubble counts N and their respective pressure schedules. The relevance of these data to aqueous media generally is suggested by the observation[14] that 93% of the bubbles produced with a typical schedule could be eliminated by centrifuging the water before mixing it with gelatin crystals.

For these experiments, the supersaturation pressure is given by

$$p_{ss} = p_s - p_f\,, \tag{1}$$

and the crushing pressure by

$$p_{\text{crush}} = p_m - p_0\,, \tag{2}$$

where $p_0 = 1$ atm (absolute) $= 1.013 \times 10^6$ dyn/cm^2 is the mixing pressure, p_m is the maximum pressure, p_s is the pressure at which the sample is saturated prior to decompression, and p_f is the final pressure. For these tests, p_s and p_m are set equal. A schematic pressure schedule is included in the figure.

There are four data groups in Fig. 1 defined, respectively, by

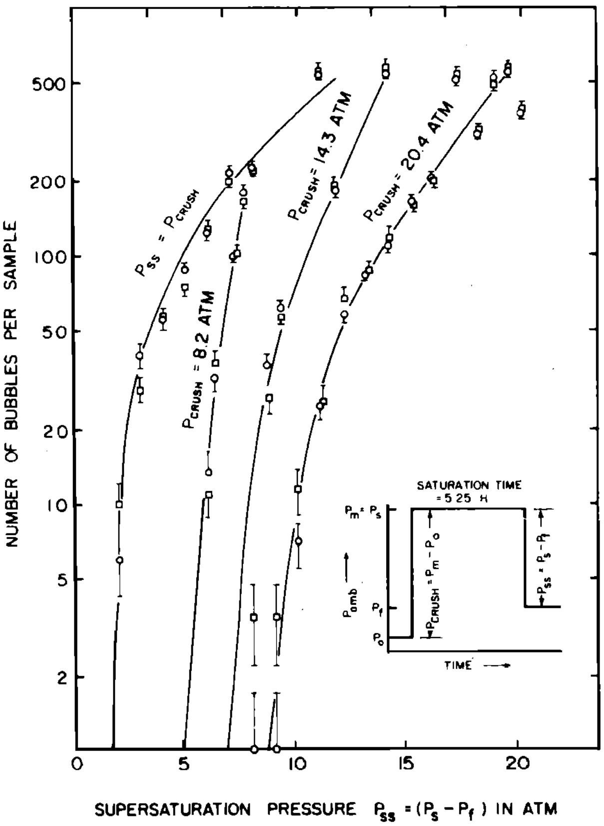

FIG. 1. Number of bubbles N per sample versus supersaturation pressure p_{ss} for data sets satisfying the respective four conditions: $p_{\text{crush}} = p_{ss}$, 8.2, 14.3, 20.4 atm. Good agreement with nearly all of the data points is obtained with the model summarized by Eqs. (20) and (21) in which nuclei are stabilized by skins of varying gas permeability. In the vicinity of $p_{\text{crush}} = p_{ss} = 20.4$ atm, the data points fall well below the model predictions, presumably because the thickness of the nuclear skin has not been taken into account.

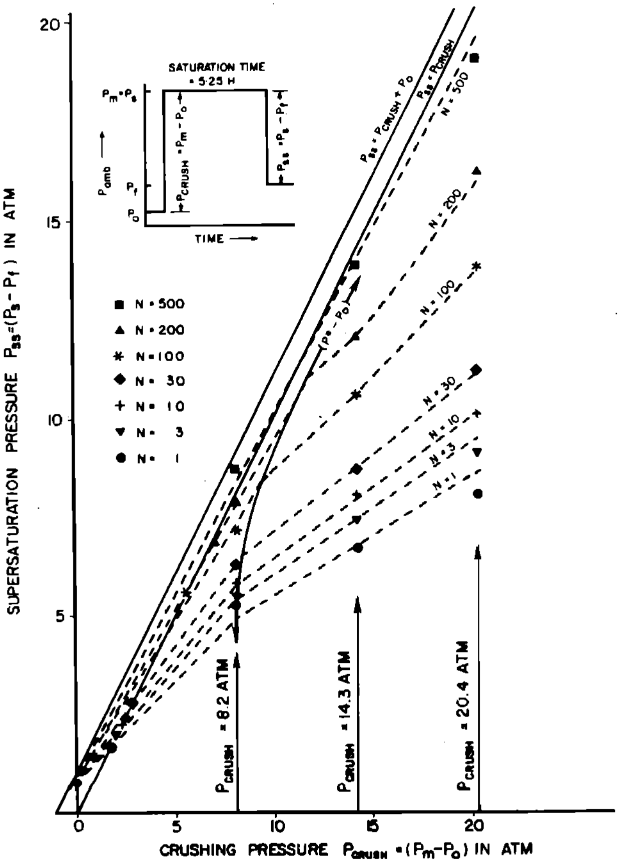

FIG. 2. Plot of p_{ss} versus p_{crush} for various numbers of bubbles N. The points for $p_{\text{crush}} = 8.2$ atm and 20.4 atm at $N = 500$ were obtained by extrapolation, and the rest were found by interpolation of the data in Fig. 1. A sudden decrease in slope occurs at $p_{\text{crush}} = p^* - p_0$, at which point the skin becomes impermeable. Subsequent increases in ambient pressure are resisted by a corresponding rise in the internal pressure, as well as by the eleasticity of the skin itself.

$$p_{\text{crush}} = p_{ss}, \tag{3a}$$

$$p_{\text{crush}} = 8.2 \text{ atm}, \tag{3b}$$

$$p_{\text{crush}} = 14.3 \text{ atm}, \tag{3c}$$

$$p_{\text{crush}} = 20.4 \text{ atm}. \tag{3d}$$

It is evident from the figure that the number of bubbles depends strongly on p_{crush}, as well as on p_{ss}. This is important since crushing is a specific test for gas nuclei. It is also worth noting that ultrasonic cavitation experiments ordinarily measure only bubble formation thresholds. That is, they determine acoustic cavitation pressures along the one-dimensional line $N \sim 1$ but do not explore the two-dimensional region $N \geq 1$, which is accessible in gelatin.

From the data in Fig. 1, combinations of p_{ss} and p_{crush} can be found that give a fixed bubble number: $N = 1$, $N = 3$, $N = 10$, etc. The results can then be replotted, as in Fig. 2, to yield p_{ss} versus p_{crush} for the values of N selected. One additional data point is shown in Fig. 2. This was obtained from samples originally at atmospheric pressure that were evacuated to negative gauge pressures until bubbles were seen. The formation threshold determined in this way,

$$(p_{\text{crush}},\ p_{ss},\ N) = (0 \text{ atm},\ 0.8 \text{ atm},\ 1 \text{ bubble}), \tag{4}$$

lies along the axis $p_{\text{crush}} = 0$ atm.

The data shown in Fig. 2 seem to trace out a family of curves possibly originating at a single point along the line $p_{ss} = p_{\text{crush}} + p_0$. For any value of N, p_{ss} increases smoothly with p_{crush}. This is in qualitative agreement with the ultrasonic cavitation findings of Strasberg,[11,20] and it further negates the gas-impermeable, organic-skin model of Fox and Herzfeld.[19,21] On the other hand, the curves in Fig. 2 are very simple and appear to be linear for modest values of p_{crush}: This feature of the data can be reproduced by skin models in which the membrane is initially permeable.

II. SKIN MODELS WITH VARYING PERMEABILITY

A. Basic concept

To establish a relationship between the structure of gas nuclei and the number of bubbles counted in a series of gelatin runs, we first assume that each sample has the same initial distribution of nuclear radii $f(r_0)$ and that N, the number of bubbles observed, is given by the number of nuclei larger than some minimum initial radius $r_0^{\min}$. This idea can be expressed by

$$N(r_0^{\min}) = \int_{r_0^{\min}}^{\infty} f(r_0)\,dr_0, \tag{5}$$

which contains the tacit assumptions that nuclei are not extinguished by the pressure schedule and that the initial ordering according to size is preserved. That is, if the nucleus "a" is smaller than the nucleus "b" at pressure p_0, then both nuclei are still present in the sample at pressure p_f, and nucleus "a" is still smaller than nucleus "b". This is referred to as the "ordering hypothesis."

At the end of the pressure schedule, there is a new distribution of nuclear radii $g(r_f)$ and a new radius $r_f^{\min}$ above which all nuclei in the sample will grow into macroscopic bubbles. The criterion for bubble formation is thus expressed in terms of $r_f^{\min}$, and the object of the calculation is to find $r_0^{\min}$ in terms of $r_f^{\min}$, so that $N(r_0^{\min})$ can be determined. The calculation is carried out in steps, and for each change in ambient pressure or in dissolved gas tension, one obtains an updated value for $r^{\min}$. For simplicity, we drop the superscript "min" in most of what follows, letting r_0, r_m, r_s, and r_f represent at pressures p_0, p_m, p_s, and p_f the radius of that limiting nucleus which barely exceeds the threshold for bubble formation at p_f.

B. The Love equation

Following Fox and Herzfeld,[19] we calculate changes in nuclear radius by applying the equation given by Love[22] 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 sum of the external pressures p_{out}. For small shell thicknesses δ, the result is

$$\partial r = (\partial p_{\text{in}} - \partial p_{\text{out}})r^2/3\eta a' p_{\text{in}}, \tag{6}$$

where for adiabatic processes, such as ultrasonic cavitation, η is the ratio of the specific heats for the gas, and for isothermal processes, such as the compressions and decompressions of Yount and Strauss,[14] η is equal to one.

The parameter a' can be expressed in terms of Young's modulus E and Poisson's constant ν,

$$a' = 2\delta E/3\eta p_{\text{in}}(1-\nu). \tag{7}$$

For shallow samples, such as those used in the gelatin experiments,[14] the hydrostatic pressure can be neglected. The total pressure just outside the membrane is the sum of the ambient gas pressure p_{amb} and the liquid-membrane interface pressure, which we approximate by $2\gamma/r$, where γ is the liquid–gas surface tension. In making this approximation, we are, in effect, assuming that the membrane is perfectly hydrophobic.[7,8] This is reasonable for an "insoluble monolayer" having the general properties described by Gaines.[23] The external pressure is then given by

$$p_{\text{out}} = p_{\text{amb}} + 2\gamma/r, \tag{8a}$$

and the corresponding differential is

$$\partial p_{\text{out}} = \partial p_{\text{amb}} - 2\gamma\partial r/r^2. \tag{8b}$$

Our result for a' is smaller than that calculated by Fox and Herzfeld[19] by the numerical factor $(\frac{2}{3})/(\frac{3}{2}) = \frac{4}{9}$. Also, Fox and Herzfeld[19] do not include the term $2\gamma/r$ in Eq. (8a) or the corresponding term $-2\gamma\partial r/r^2$ in Eq. (8b).

Equation (6) can now be rewritten as

$$2(\Gamma - \gamma)(\partial r/r^2) = \partial p_{\text{in}} - \partial p_{\text{amb}}, \tag{9}$$

where the parameter

$$\Gamma \equiv \delta E/(1-\nu) \tag{10a}$$
$$= 3\eta a' p_{\mathrm{in}}/2$$

has the same dimensions as γ, namely, force/length or energy/area. We therefore refer to Γ as the "skin compression" and note that it is analogous to the "surface pressure" Π defined in standard texts.[23] Whereas Γ is applicable to spherical gas nuclei, measurements of Π are ordinarily made on horizontal surfaces and yield values less than or equal to the liquid–gas surface tension of the underlying substrate. To stabilize gas nuclei with permeable skins, it is usually necessary that Γ be greater than or equal to γ: We assume that this is possible and attribute a greater compression strength to the spherical geometry.

Next we assume that the skin compression Γ has a constant value γ_C for all calculations based on the Love equation. This is suggested by the observation that E and ν in Eq. (10a) are constant in macroscopic systems obeying Hooke's law and that the skin thickness δ would be effectively constant if, for example, the elastic properties of the membrane were determined by a single active layer, possibly associated with an inactive reservoir or bulk phase of surfactant molecules. We discuss this assumption in more detail in the last article of this section. Meanwhile, Eq. (9) can be rewritten

$$2(\gamma_C-\gamma)(\partial r/r^2) = \partial p_{\mathrm{in}} - \partial p_{\mathrm{amb}}, \tag{11}$$

where γ_C is referred to as the "crumbling compression" or as the "equilibrium spreading compression" depending upon whether the nucleus is contracting or expanding.

In applying Eq. (11), we are primarily interested in compressions and decompressions that are "rapid" or "hydraulic" in the sense that negligible gas diffuses into or out of the bulk sample while a change in ambient pressure is taking place. At distances comparable with the nuclear radius, however, there may be enough time for diffusion equilibrium to be maintained. If there is, the skin is considered to be "permeable," and if there is not, the skin is considered to be "impermeable." In other words, a skin is either permeable or impermeable in our model, and gradations in permeability and the possible dependence of permeability on compression rates, etc. are not taken into account.

In actual nuclei, the effects of a rapid compression are not fully developed until several minutes after the initial increase in ambient pressure has occurred.[14] Thus, the radius r^* or ambient pressure p^* which we use to characterize the onset of impermeability in the model are not rigorously linked to a definite time during the actual compression. Rather, these parameters serve as a measure of the overall effects of a fully developed compression. The nucleus acts as if it became impermeable at $p_{\mathrm{amb}} = p^*$, and the quantity of gas inside the nucleus is that which would be contained inside a cavity of radius r^* in diffusion equilibrium with the surrounding medium at the onset of impermeability.

For variations in p_{amb} such that the nuclear skin is effectively permeable, the internal pressure p_{in} remains equal to the tension τ of dissolved gas in the sample at the start of the process, and we have

$$\partial p_{\mathrm{in}} = 0 \quad \text{(for permeable variations in } p_{\mathrm{amb}}\text{)}. \tag{12}$$

Equation (11) then takes the form

$$2(\gamma_C-\gamma)(\partial r/r^2) = -\partial p_{\mathrm{amb}}$$
$$\text{(for permeable variations in } p_{\mathrm{amb}}\text{)}. \tag{13}$$

For changes in p_{amb} such that the nuclear skin is effectively impermeable, we evaluate p_{in} by assuming that the gas inside is ideal. The isothermal processes ($\eta = 1$) of Yount and Strauss[14] then give

$$p_{\mathrm{in}} = \tau^* r^{*3}/r^3, \tag{14a}$$
$$\partial p_{\mathrm{in}} = -(3\tau^* r^{*3}/r^4)\partial r \tag{14b}$$
$$\text{(for impermeable variations in } p_{\mathrm{amb}}\text{)},$$

where the constants τ^* and r^* are, respectively, the gas tension and the nuclear radius at the beginning of the impermeable process. Equation (11) becomes

$$[2(\gamma_C-\gamma) + (3\tau^* r^{*3}/r^2)](\partial r/r^2) = \partial p_{\mathrm{amb}} \tag{15}$$
$$\text{(for impermeable variations in } p_{\mathrm{amb}}\text{)}.$$

During saturation of the sample at $p_{\mathrm{amb}} = p_s$, $\partial p_{\mathrm{amb}}$ is zero. Meanwhile, the tension of τ of dissolved gas surrounding the nucleus is increasing from its initial value $\tau_0 = p_0$ to its saturation value $\tau_s = p_s$. Given the long times involved, it seems likely that p_{in} will equilibrate with the surrounding gas tension and hence increase to $\tau_s = p_s$. This raises the question: What happens to the nuclear radius as p_{in} increases from p_0 to p_s, while $p_{\mathrm{amb}} = p_s$ is constant?

A trial calculation using Eq. (11) with $\partial p_{\mathrm{amb}} = 0$ suggests that the nucleus might be fully restored as the sample becomes saturated at $p_{\mathrm{amb}} = p_s$, i.e., that $r_s = r_0$. If this were the case, the effect of crushing would be lost—in sharp disagreement with a number of experiments,[5,11,14] as well as with the data plotted in Fig. 1. A more direct indication that nuclear radii do not increase at $p_{\mathrm{amb}} = p_s$ is provided by special schedules having initial pressure spikes so that $p_m > p_s$. The resulting bubble counts (see Table I of Ref. 14) depend only upon p_{crush} and p_{ss} and not upon p_s *per se*. We are compelled to assume, therefore, that no change in radius takes place at p_s and that

$$r_s = r_m. \tag{16}$$

We discuss this assumption, as well as the related assumption $\Gamma = \gamma_C$, in more detail in the final article of this section.

Our criterion for bubble formation at the final pressure p_f is the Laplace condition

$$p_s - p_f \geq 2\gamma/r_f, \tag{17a}$$

which contains no reference to the skin and is equivalent to setting Γ equal to zero. That is, bubble formation occurs in our model without stretching or tearing the skin. This is plausible if skins are permeable during decompression, since a gas shell could easily form just outside the skin and continue to grow whenever p_{in} becomes larger than $p_{\mathrm{amb}} + 2\gamma/r$.

In contrast, the skins proposed by Fox and Herzfeld[19] are impermeable as long as they remain intact. Such skins might stretch and support a tension before breaking open, and this would inhibit bubble formation at p_f. To account for this possibility, Fox and Herzfeld[19] define a "tearing strength" or tearing tension, which is equivalent to setting Γ equal to $-\gamma_T$. The corresponding criterion for bubble formation is

$$p_s - p_f \geq 2(\gamma + \gamma_T)/r_f . \tag{17b}$$

C. Model equations

The mathematical basis of the varying-permeability model is summarized by Eqs. (13), (15), (16), and (17a). In this article, we apply these equations to a gas nucleus embedded in a shallow test sample that is subjected to the usual pressure schedule shown in Figs. 1 and 2. At the beginning of the schedule, the sample is in diffusion equilibrium at $p_{\text{amb}} = p_0$. We assume that the skin stabilizing the nucleus is initially gas permeable so that

$$p_{\text{in}}^0 = \tau_0 = p_{\text{amb}}^0 = p_0 , \tag{18}$$

where τ_0 is the initial value of the dissolved gas tension.

Next there is a rapid increase in ambient pressure, and if the crushing pressure $p_{\text{crush}} = p_m - p_0$ exceeds some critical level $p^* - p_0$, the skin becomes effectively impermeable. By integrating the left-hand side of Eq. (13) from r_0 to r^* and the right-hand side from p_0 to p^*, we obtain

$$2(\gamma_C - \gamma)[(1/r^*) - (1/r_0)] = p^* - p_0 \tag{19a}$$

(for the permeable compression from $p_{\text{amb}} = p_0$ to $p_{\text{amb}} = p^*$).

By integrating the left-hand side of Eq. (15) from r^* to r_m and the right-hand side from p^* to p_m, we find for $\tau^* = p_0$:

$$2(\gamma_C - \gamma)[(1/r_m) - (1/r^*)] = p_m - p^* + p_0[1 - (r^*/r_m)^3] \tag{19b}$$

(for the impermeable compression from $p_{\text{amb}} = p^*$ to $p_{\text{amb}} = p_m$).

Impermeability may occur when the skin molecules are so tightly packed that negligible gas diffuses between them during times of interest, e.g., 100 s for the rapid compressions considered here. Such a condition would be relieved immediately by small reductions in ambient pressure, and we therefore assume that all decompressions are permeable. Recalling that r_s is equal to r_m from Eq. 16, we integrate the left-hand side of Eq. (13) from r_s to r_f and the right-hand side from p_s to p_f. The result is

$$2(\gamma_C - \gamma)[(1/r_f) - (1/r_s)] = p_f - p_s \tag{19c}$$

(for the permeable decompression from $p_{\text{amb}} = p_s$ to $p_{\text{amb}} = p_f$).

Equations (16), (17a) (with the "equals" sign), (19a), (19b), and (19c) can be combined to yield

$$p_{ss} = [2\gamma(\gamma_C - \gamma)/r_0\gamma_C] + [p_{\text{crush}}(\gamma/\gamma_C)], \tag{20}$$

for the ever-permeable region $p_{\text{crush}} = p_m - p_0 \leq p^* - p_0$, and

$$p_{ss} = [2\gamma(\gamma_C - \gamma)/r_0\gamma_C] + \{[p_m - p_0(r^*/r_m)^3](\gamma/\gamma_C)\} \tag{21}$$

for the permeable-impermeable-permeable region $p_{\text{crush}} = p_m - p_0 > p^* - p_0$. An equivalent form of Eq. (21) is

$$p_{ss} = \frac{2\gamma(\gamma_C - \gamma)}{r_0\gamma_C} + \frac{(p^* - p_0)\gamma}{\gamma_C} + \frac{(p_m - p^*)\gamma}{\gamma_C[1 + (\bar{r}/B)]} , \tag{22a}$$

where

$$\bar{r} \equiv r^*(r^*/r_m) , \tag{22b}$$

$$B \equiv 2(\gamma_C - \gamma)/\{p_0[(r^*/r_m) + 1 + (r_m/r^*)]\} . \tag{22c}$$

D. Equilibrium considerations

In this article, we reexamine the assumptions $\Gamma = \gamma_C$ and $r_s = r_m$ from the points of view of thermodynamic and mechanical equilibrium. In the process, we obtain an alternative derivation of the model equations and gain further insight into the sense in which the varying-permeability model may be considered to approximate the behavior of actual nuclei.

Previously we have calculated "large-scale" changes in nuclear radius—changes that occur through an increase or decrease in the number of interfacial surfactant molecules—by applying the equation given by Love[22] for a spherical shell. One might expect, however, that the transport of such molecules from one phase to another would be governed by thermodynamic, rather than purely mechanical considerations. In our case, thermodynamic equilibrium can be specified by assuming that there are only two phases, the skin and the reservoir, and by setting their electrochemical potentials equal.

The electrochemical potential is given by

$$\xi = \mu + kT \ln(\rho) + pv + Ze\psi , \tag{23a}$$

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 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

$$\xi_R = \mu_R + kT \ln(\rho_R) + p_R v + (Ze\psi)_R , \tag{23b}$$

and in the skin we have

$$\xi_S = \mu_S + kT \ln(\rho_S) + p_S v + (Ze\psi)_S , \tag{23c}$$

where we have assumed that v is the same in the two phases.

Next we assume that the reservoir and skin are concentric spherical shells of negligible thickness, and hence of the same radius. The reservoir is outside the nucleus in contact with the liquid, and the skin is inside the reservoir in contact with the gas. Unlike the skin, the reservoir cannot support a pressure gradient, and it passively transmits the external pressure p_{out} from the liquid to the skin. The pressure of the reservoir is

$$p_R = p_{\mathrm{amb}} + 2\gamma/r\,, \tag{24a}$$

and the pressure in the skin is

$$p_S = p_{\mathrm{in}} + 2\gamma_C/r\,. \tag{24b}$$

Inserting these expressions for p_R and p_S into Eqs. (23b) and (23c) and setting ξ_R equal to ξ_S, we obtain

$$p_{\mathrm{in}} + 2\gamma_C/r - \beta = p_{\mathrm{amb}} + 2\gamma/r\,, \tag{25a}$$

where β is given by

$$\beta \equiv [kT \ln(\rho_R/\rho_S) + (\mu_R - \mu_S) + (Ze\psi)_R - (Ze\psi)_S]/v\,. \tag{25b}$$

Assuming that β and γ_C are constant for a given nucleus, we can differentiate Eq. (25a) to obtain the Love equation in the form of Eq. (11). Conversely, β may be regarded as the constant of integration that results from solving Eq. (11). The constant of integration is not zero with respect to large-scale changes in radius because these are determined by thermodynamic, rather than by mechanical equilibrium. The criterion for bubble formation [Eq. (17a)] can also be obtained from Eq. (25a) simply by deleting all references to the skin, i.e., by setting γ_C and β equal to zero.

Initially at $p_{\mathrm{in}} = p_{\mathrm{amb}} = p_0$, Eq. (25a) becomes

$$p_0 + 2\gamma_C/r_0 - \beta_0 = p_0 + 2\gamma/r_0\,, \tag{26a}$$

which can be satisfied if we set

$$\beta_0 = 2(\gamma_C - \gamma)/r_0\,. \tag{26b}$$

Similarly, after a rapid, permeable compression from $p_{\mathrm{amb}} = p_0$ to $p_{\mathrm{amb}} = p^*$, we have

$$p_0 + 2\gamma_C/r^* - \beta^* = p^* + 2\gamma/r^*\,, \tag{27a}$$

$$\beta^* = 2(\gamma_C - \gamma)/r^* - (p^* - p_0)\,. \tag{27b}$$

If we now set β^* equal to β_0, we obtain the model expression [Eq. (19a)] for a rapid, permeable compression from $p_{\mathrm{amb}} = p_0$ to $p_{\mathrm{amb}} = p^*$.

After a rapid, impermeable compression from $p_{\mathrm{amb}} = p^*$ to $p_{\mathrm{amb}} = p_m$, we have

$$p_0(r^*/r_m)^3 + 2\gamma_C/r_m - \beta_m = p_m + 2\gamma/r_m\,, \tag{28a}$$

$$\beta_m = 2(\gamma_C - \gamma)/r_m - [p_m - p_0(r^*/r_m)^3]\,. \tag{28b}$$

Setting β_m equal to β^*, we find the model expression [Eq. (19b)] for a rapid, impermeable compression from $p_{\mathrm{amb}} = p^*$ to $p_{\mathrm{amb}} = p_m$.

We now require that r_s be equal to r_m in accordance with Eq. (16) and write the thermodynamic equilibrium following saturation at $p_{\mathrm{amb}} = p_s$ as

$$p_s + 2\gamma_C/r_s - \beta_s = p_s + 2\gamma/r_s\,, \tag{29a}$$

$$\beta_s = 2(\gamma_C - \gamma)/r_s\,. \tag{29b}$$

Evidently, β_s is not equal to $\beta_0 = \beta^* = \beta_m$, and we have changed the constant of integration at $p_{\mathrm{amb}} = p_s$ rather than the radius $r_s = r_m$. However, β_s is of the same form as β_0, and in this sense the constant of integration has been "restored" or "updated" at $p_{\mathrm{amb}} = p_s$ rather than the radius.

Following a rapid, permeable decompression from $p_{\mathrm{amb}} = p_s$ to $p_{\mathrm{amb}} = p_f$, we have

$$p_s + 2\gamma_C/r_f - \beta_f = p_f + 2\gamma/r_f\,, \tag{30a}$$

$$\beta_f = 2(\gamma_C - \gamma)/r_f - (p_f - p_s)\,. \tag{30b}$$

Requiring that β_f be equal to β_s, we obtain the model expression [Eq. (19c)] for a rapid, permeable decompression from $p_{\mathrm{amb}} = p_s$ to $p_{\mathrm{amb}} = p_f$.

It is by now evident that we can derive all of the varying-permeability model equations for large-scale changes in nuclear radius, including the criterion [Eq. (17a)] for bubble formation at p_f, by requiring that surfactant molecules in the reservior and in the skin be in thermodynamic equilibrium. The new derivation is consistent with the earlier one in the sense that none of the original assumptions have been violated and the Love equation [Eq. (11)] can be obtained at any pressure $p_{\mathrm{amb}} = p_0$, p^*, p_m, p_s, and p_f by rewriting the corresponding equation for thermodynamic equilibrium in terms of p_{in} and p_{amb} and by differentiating.

A curious feature of the thermodynamic point of view is that β, as defined by Eq. (25b), would seem to be independent of radius, whereas β_0 in Eq. (26b) appears to be a function of r_0. If we now assume that β_0 is not only constant for a given nucleus but the same constant for all nuclei at $p_{\mathrm{amb}} = p_0$, we obtain the intriguing prediction that γ_C will increase linearly with r_0:

$$\gamma_C = \gamma + (\beta_0/2)r_0\,. \tag{31}$$

"Small-scale" changes in radius are those which can be brought about merely by varying the spacing between a fixed total number of exposed skin molecules, i.e., between a fixed number of surfactant molecules in the active layer. Such changes are neglected in the calculations, but they play an essential role in the model. In particular, Γ is variable for small-scale changes in radius, and this permits a stable mechanical equilibrium near the calculated large-scale radius with the fixed number of skin molecules appropriate to that radius.

The general expression for mechanical equilibrium is

$$p_{\mathrm{in}} + 2\Gamma/r = p_{\mathrm{amb}} + 2\gamma/r\,, \tag{32a}$$

where all of the properties of the skin and the reservoir are now incorporated into the skin compression Γ. Equation (32a) is perhaps obvious by inspection, and it can be obtained from Eq. (25a) by setting

$$2\Gamma/r = 2\gamma_C/r - \beta\,. \tag{32b}$$

At the respective pressures $p_{\mathrm{amb}} = p_0$, p^*, p_m, p_s, and p_f, we have:

$$\Gamma_0 = \gamma\,, \tag{33a}$$

$$\Gamma^* = \gamma_C - (\gamma_C - \gamma)(r^*/r_0)\,, \tag{33b}$$

$$\Gamma_m = \gamma_C - (\gamma_C - \gamma)(r_m/r_0)\,, \tag{33c}$$

$$\Gamma_s = \gamma\,, \tag{33d}$$

$$\Gamma_f = \gamma_C - (\gamma_C - \gamma)(r_f/r_s)\,. \tag{33e}$$

A plausible criterion for bubble formation in the small-scale or mechanical-equilibrium regime is that Γ_f should be less than or equal to zero. Equation (33e) then

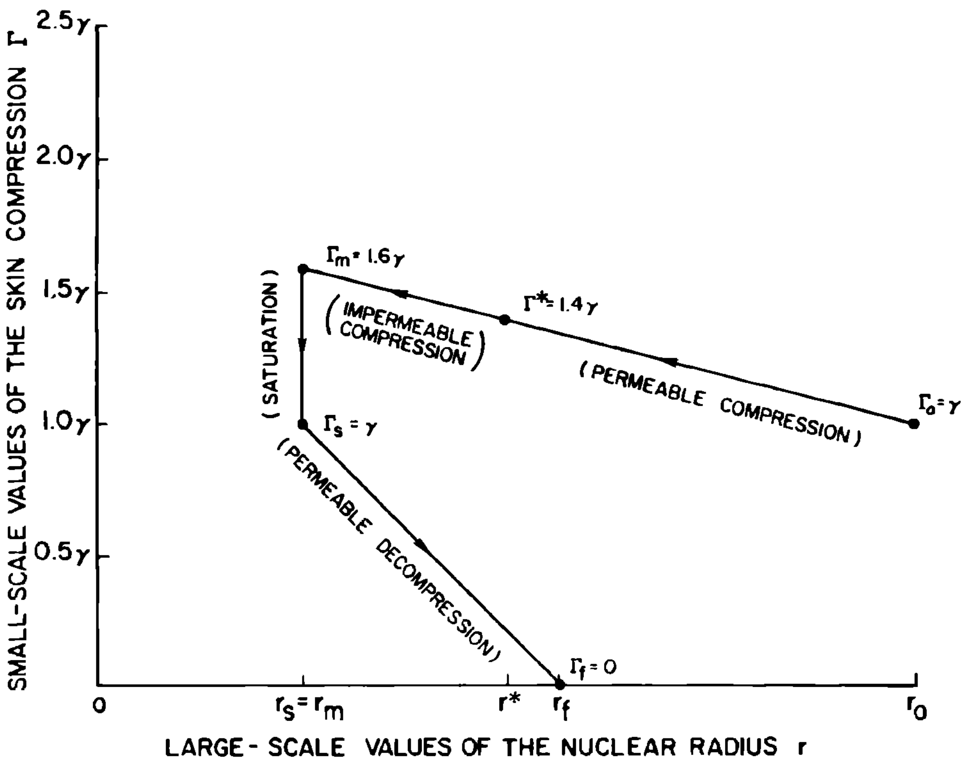

FIG. 3. Small-scale behavior of the skin compression Γ versus the large-scale radius r for the hypothetical case $\gamma_C = 1.8\gamma$, $r^* = r_0/2$, and $r_s = r_m = r^*/2$. Whereas Γ is treated as a constant in calculations of the large-scale radii, mechanical equilibrium is maintained by allowing small-scale variations in Γ as shown here.

gives

$$2(\gamma_C - \gamma)/r_s \geq 2\gamma_C/r_f . \qquad (34)$$

Substituting this result into Eq. (19c), we obtain the usual Laplace condition for bubble formation given in Eq. (17a). The small-scale behavior of **Γ** described by Eqs. (33a)–(33e) is illustrated schematically in Fig. 3 for the case: $\gamma_C = 1.8\,\gamma$, $r^* = r_0/2$, and $r_s = r_m = r^*/2$, where $r_f = 2.25$ was calculated from Eq. (34).

We can summarize this section by noting that the varying-permeability model, derived originally from the differential equation given by Love,[22] is compatible with thermodynamic equilibrium, which governs the transport of surfactant molecules between the reservior and the skin, and mechanical equilibrium, which determines the spacing between skin molecules whose total number is fixed. For large-scale or thermodynamic changes in radius, the skin compression Γ is effectively constant for a given nucleus, but its value is predicted by Eq. (31) to increase linearly with the initial radius r_0. For small-scale or mechanical changes in radius, the skin compression varies within the range $0 \leq \Gamma \leq \gamma_C$, assuming the value 0 at the onset of bubble formation.

III. COMPARISON WITH EXPERIMENT

In a plot of p_{ss} versus p_{crush}, such as Fig. 2, Eq. (20) yields a family of straight lines with variable slope $\partial p_{ss}/\partial p_{\text{crush}} = \gamma/\gamma_C \leq 1$. At the onset of impermeability, the internal pressure p_{in} begins to rise, and the nucleus becomes more resistent to further crushing. This is most easily seen in Eq. (22a), where impermeability reduces the slope by the factor $1/[1+(\bar{r}/B)]$. The intercepts at $p_{\text{crush}} = 0$ increase with decreasing initial radius r_0, and thus with increasing bubble number N. Qualitatively, then, the model is in agreement with the data in Figs. 1 and 2, and a quantitative comparison should now be attempted.

In this analysis, we assume that r_0, γ_C, and p^* are constant for a given bubble number N, but we allow all three to have different values for different N. The air-liquid surface tension has been measured in gelatin and is given by[14]

$$\gamma = (51 \pm 5)\,\text{dyn/cm}. \qquad (35)$$

The radii r^*, $r_s = r_m$, and r_f are calculated from Eqs. (19a), (19b), and (19c), respectively, and in that order. The supersaturation pressure p_{ss} is then determined as a function of the crushing pressure p_{crush} using Eq. (20) in the permeable region $p_{\text{crush}} \leq p^* - p_0$ and Eq. (21) or Eqs. (22a–22c) in the impermeable region $p^* - p_0 < p_{\text{crush}}$. The process is repeated until an optimum set of the three model parameters r_0, γ_C, and p^* has been found for each value of N.

The results of the model calculations are indicated by the solid lines in Fig. 1 and by the dashed lines in Fig. 2. Also shown in Fig. 2 is the impermeability threshold $p^* - p_0$, which exceeds 8 atm in all cases and increases with increasing N and hence with decreasing r_0. The predictions are not very sensitive to this parameter, and for simplicity we have required that values of $p^* - p_0$ for different N lie on a smooth curve.

In Fig. 4, combinations of γ_C/γ and r_0 are plotted for each bubble number N. The values of the initial radius shown in this figure are in the range

$$0.08\ \mu \leq r_0 \leq 0.59\ \mu . \qquad (36)$$

The corresponding skin compressions satisfy the inequalities

$$57\ \text{dyn/cm} \leq \gamma_C \leq 98\ \text{dyn/cm}. \qquad (37)$$

The data are in good agreement with the linear relation

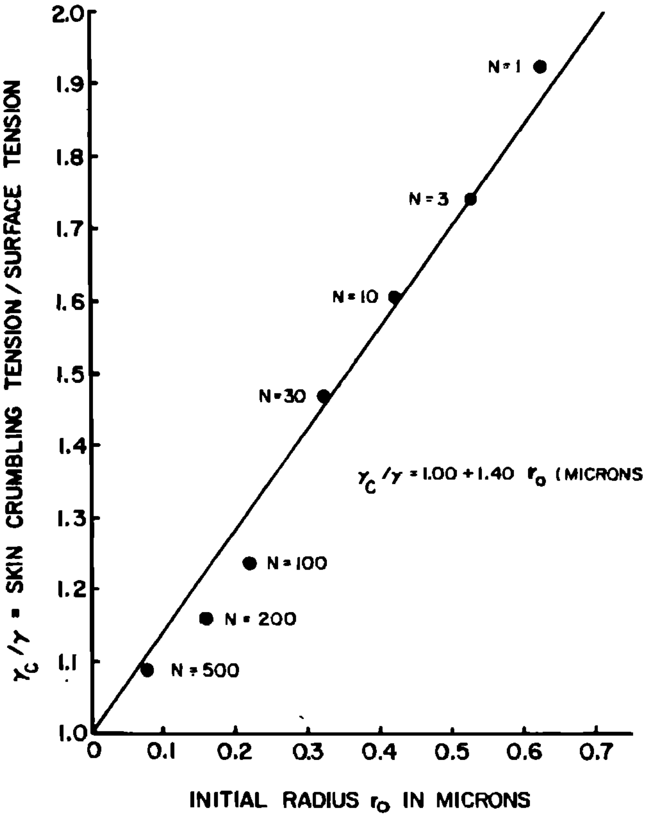

FIG. 4. Reciprocal of the initial slope $\partial p_{ss}/\partial p_{\text{crush}} = \gamma/\gamma_C$ versus the initial radius r_0 for the dashed curves in Fig. 2. A linear dependence of γ_C/γ upon r_0 is predicted in Eq. (31) from thermodynamic-equilibrium considerations.

$$\gamma_C/\gamma = 1.00 + 1.40 r_0 , \tag{38}$$

where r_0 is expressed in microns. Equation (38) can be rewritten as

$$\gamma_C = \gamma + 1.40 \gamma r_0 , \tag{39a}$$

which becomes identical to Eq. (31) if we set

$$\beta_0 = 2.80 \gamma / \mu \tag{39b}$$

$$\simeq 143 \text{ dyn/cm-}\mu . \tag{39c}$$

The initial radial distribution $N(r_0^{\min})$ derived from this analysis is plotted in Fig. 5 with the horizontal scale contracted by $\frac{1}{5}$ to permit the radial distributions at $p_{\text{amb}} = p_0 = 1$ atm absolute and at $p_{\text{amb}} = p_m = 9.2$, 15.3, and 21.4 atm (absolute) to be shown clearly on the same graph. A good empirical parameterization of the initial distribution is given by

$$N(r_0^{\min}) = 1200 \exp(-r_0^{\min}/0.088 \mu) \tag{40}$$

nuclei or bubbles per 0.4-ml sample.

The distributions for $p_{\text{amb}} = p_m = 9.2$, 15.3, and 21.4 atm absolute are obtained by applying the relevant model equations to Eq. (40), rather than to the individual points. By smoothing the data in this way, we can see more clearly the effect of each pressure change. Evidently, the variations in radius are truly "large-scale" in this model and often exceed a factor of ten. Small-scale changes, for which by definition the number of skin molecules is fixed, are limited to a few tens of percent in typical surfactants subjected to compressions for which the "surface pressure" Π is in the vicinity of the surface tension γ.[24–26] Within the plotting accuracy, the original exponential form is preserved, and only the slope and intercept at zero radius are affected. The radial distribution at $p_{\text{amb}} = p^*$ appears to have no special significance and differs from the curves for $p_{\text{amb}} = p_m = 9.2$, 15.3, and 21.4 atm (absolute) only because p^* is not a constant.

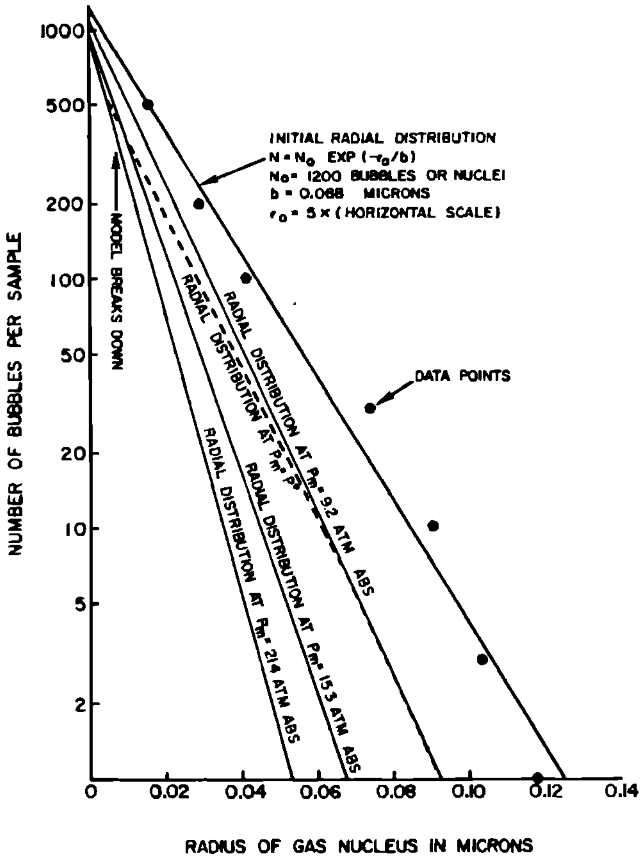

FIG. 5. Integral distributions of nuclear radii for various ambient pressures: 1.0, 9.2, 15.3, and 21.4 atm (absolute). For 1.0 atm (absolute) (r_0), the horizontal scale has been contracted by 1/5 to permit all of the distributions to be shown clearly on the same graph. Within the errors suggested by the scatter of the experimental points, all distributions are exponential except that at the variable pressure p^*.

IV. DISCUSSION

Having demonstrated that the varying-permeability model provides an excellent parameterization of a rather extensive and comprehensive data sample, we now attempt to extract from the equations as much additional information as we can concerning the possible origins and nature of gas cavitation nuclei. An important question, which we shall address first, is whether or not there are substances in nature with the general properties that we have attributed to our skin molecules.

In Chap. 4 of his book on insoluble monolayers, Gaines[23] notes that in certain cases, surface-active molecules originally present in a bulk phase, such as a droplet, will spontaneously leave the bulk phase and spread out across a liquid–gas interface to form a stable monolayer. Assuming there is enough material, spreading will occur until the "surface pressure" Π has risen to the "equilibrium spreading pressure," which Gaines denotes by ESP. For some materials, especially those whose bulk phase is a liquid of fairly low viscosity under the experimental conditions, collapse of a monolayer occurs at the ESP, and the film cannot be compressed above this pressure. This is precisely our assumption that Γ has the same value whether the surfactant–liquid interface is contracting or expanding, i.e., whether the sample containing the nucleus is subjected to a compression or a decompression.

On a molecular level, constant Γ implies a constant energy per exposed skin molecule, just as constant γ implies a constant energy per surface water molecule. This is at the heart of the large-scale, thermodynamic approximation in which the forces between surfactant molecules are assumed to be attractive, short-range, and essentially constant, and in which the work done in changing the spacing between a fixed number of skin molecules is neglected.

The rate at which a monolayer spreads across a liquid–gas interface is, for our purposes, practically instantaneous. For example, oleic acid has been observed to spread radially from a bulk phase at a rate of 10 cm/s.[23,27] The time that would be required to surround a nucleus of radius $r \sim 1\ \mu$ is of the order 10^{-7} s. ESP magnitudes appear also to be quite promising. For example, oleyl alcohol at room temperature has an ESP of 30 dyn/cm and satisfies the condition that the collapse pressure is equal to the ESP.[23,28] It is highly plausible that there are substances with an equilibrium spreading compression γ_C that is larger than the surface tension of water (about 72 dyn/cm) when the surfactant molecules are arranged on a spherical surface.

Gaines points out that in order for spontaneous spreading to occur, it must lead to a reduction of the free energy of the system. The implication for our model is that the surfactant molecules are more tightly bound to the skin than they are to the bulk phase. An equivalent statement in our notation is that β defined by Eq. (25b) should be greater than zero. Metastable states are also quite common among monolayers, indicating the presence of potential barriers that can inhibit molecules from being transported freely from one phase to another. These observations suggest that our distinction between large-scale thermodynamic equilibrium, which determines the number of surfactant molecules at the interface, and small-scale mechanical equilibrium, which determines their spacing, is valid. The existence of metastable states would also account for the inference that nuclei do not expand when the sample is being saturated at $p_{\mathrm{amb}} = p_s$ or, more generally, when p_{in} is less than or equal to p_{amb}. These are all cases in which mechanical equilibrium can be maintained in the vicinity of a fixed large-scale radius r by allowing the skin compression to assume a small-scale, metastable value in the range $\gamma \leq \Gamma \leq \gamma_C$.

As can be seen in Fig. 1, the varying-permeability model works well everywhere except at the highest values of p_{crush} and p_{ss}. The fact that the model itself is breaking down can best be appreciated by noting that for $p_{ss} = p_{\mathrm{crush}} > 14$ atm, the bubble counts actually decrease with increasing pressure. (The ratio of the bubble count at 20.4 atm to that at 14.3 atm is 0.790 ± 0.017.[14]) This is logically inconsistent with Eq. (5) since r_0^{min} decreases with increasing $p_{ss} = p_{\mathrm{crush}}$, and the number of nuclei above r_0^{min} should therefore increase monotonically. The nuclei in question have radii $r_0^{\mathrm{min}} \lesssim 0.07\ \mu$ and $r_m^{\mathrm{min}} = r_s^{\mathrm{min}} \lesssim 50$ Å. The latter is comparable with the thicknesses of typical monolayers, which range from 5 to 50 Å. (See Ref. 23, p. 112.) It is plausible, therefore, that the model breaks down at high p_{ss} and p_{crush} because the assumptions that $\delta \ll r^{\mathrm{min}}$ and that nuclei are not extinguished are violated. If this interpretation is correct, then the length of a typical skin molecule *in situ* satisfies the restriction

$$\delta \lesssim 50\ \text{Å}, \tag{41}$$

and nuclei are destroyed or become otherwise inaccessible when $r \sim \delta$. Since a breakdown is expected at this level, its observation is evidence: (1) that the level is actually reached, (2) that large-scale decreases in radius actually occur during compression, and (3) that large-scale increases in radius occur during decompression.

The exponential in Eq. (40) resembles the Boltzmann distribution

$$N = N_0 \exp(-E/kT), \tag{42}$$

where E is an energy, k is the Boltzmann constant, and T is the absolute temperature. In an attempt to find a correspondence, we solve Eq. (38) for r_0 and substitute into Eq. (40) to obtain

$$N = 1200 \exp[-(\gamma_C - \gamma)S/kT] \quad \text{nuclei or bubbles per sample}, \tag{43}$$

where

$$S \equiv kT/(1.40 \times 0.088\,\gamma) \tag{44a}$$

is the unknown unit of surface area to which the correspondence may apply. For $T = 294\,^{\circ}\mathrm{K}$ and $\gamma = 51$ dyn/cm, we have

$$S = 65\ \text{Å}^2. \tag{44b}$$

It should be emphasized that Eq. (44b) is an experimental number calculated from the absolute temperature T, the surface tension γ, the slope in Fig. 4 (which is essentially the thermodynamic equilibrium parameter β_0), and the slope in Fig. 5. *A priori* there is nothing in the model that determines the value of any of these quantities. Yet the result is typical of the area per molecule occupied by known surfactants. For example,[26] when a monolayer of a certain phosphoglyceride is maximally compressed, each molecule occupies an area of about 75 Å^2. Gaines[23] (p. 186) suggests an area near 20 Å^2 per molecule for fatty acids and 36–45 Å^2 for sterols. He also plots[23] (p. 257) data of van Deenen *et al.*[29] which suggest a range of 35–60 Å^2 for typical synthetic phospholipids. Furthermore, the related quantity, $S = kT/\gamma = 8$ Å^2, is about the surface area that would be filled by one water molecule. Thus we associate S

with the interfacial area taken up by one skin molecule.

The net energy stored in the area S when the skin is compressed from its initial small-scale equilibrium value γ to its maximum or large-scale value γ_C can be calculated from Eqs. (35), (37), and (44b):

$$0.024 \text{ eV} \leq (\gamma_C - \gamma)S \leq 0.19 \text{ eV}. \tag{45}$$

The product of β_0 times the volume v per skin molecule satisfies the inequality

$$\beta_0 v = \beta_0 S\delta \lesssim 0.003 \text{ eV}. \tag{46}$$

This may be a measure primarily of the difference in chemical potential $\mu_R - \mu_S$ between the reservoir and the skin phases.

The Boltzman factor is associated here with individual skin molecules, rather than with the aggregate. This suggests that nuclei originate from collapsing bubbles that have accumulated on their surfaces a store of materials of greater or lesser surface activity. The process of collapse is selective, and weakly bound molecules are sloughed off. At a certain radius r_0, the surface residue successfully resists the collapse by opposing it with a skin compression Γ that is greater than or equal to the surface tension γ. If, on the contrary, nuclei began with a few molecules and grew by a process of random accretion, then the probability of finding nuclei with a particular radius would depend upon the total number of skin molecules involved.

ACKNOWLEDGMENTS

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APPENDIX: THE CREVICE MODEL

Strasberg[11] has noted that the theoretical predictions are qualitatively similar for "air trapped in cracks in the surface of suspended solids, and air bubbles surrounded by rigid permeable skins of organic impurities." He further states, in reference to his own work on ultrasonic cavitation in tap water, "It seems impossible to distinguish between the two types of nuclei by measurements of the type conducted in the present experiment." We shall now demonstrate that the two models can be distinguished quantitatively and that the crevice model, at least in its present state of development,[5,11-13] is inconsistent with the data on bubble formation in supersaturated gelatin.[14]

In proposing the crevice model, Harvey *et al.*[5] emphasized the notion of a critical radius for bubble formation in supersaturated media, essentially r_f in our Eq. (17a), but they did not calculate the changes in radius that occur during compression and decompression. Albano[13] has investigated a variety of crevice geometries and liquid-gas interfaces ("calotte") in supersaturated water, blood, and animal tissue. However, Albano did not distinguish between advancing and receding contact angles and thus concluded (incorrectly) that gas phases in simple cones, such as those considered by Harvey *et al.*,[5] by Strasberg,[11] and by Apfel,[12] "would dissolve immediately with increase in pressure." Nor did Albano derive any equations relating supersaturation pressure to previously applied static pressure. Apfel's calculations[12] were carried out for ultrasonic cavitation, and he states, "Furthermore, our model does not attempt to deal with the saturation or supersaturation problem, because in this case, a bubble may extend in some ill-defined way from the crevice."

We are left with Strasberg's equation[11]

$$p_a = p_f + A_1 p_m - A_2 p_s, \tag{A1}$$

where A_1 and A_2 satisfy the inequalities $(A_1+1) > A_2 > A_1 > 1$, and where $p_a = 0$ is the acoustic pressure amplitude. For $p_f = p_0$ ($p_{\text{crush}} = p_{ss}$), we find

$$p_{ss} = p_0[(A_1+1) - A_2]/A_2 + p_{\text{crush}}(A_1/A_2), \tag{A2}$$

which becomes identical to our Eq. (20) for the ever-permeable region if we put

$$A_1/A_2 = \gamma/\gamma_C < 1, \tag{A3a}$$

$$p_0[(A_1+1) - A_2]/A_2 = 2\gamma(\gamma_C - \gamma)/r_0\gamma_C > 0. \tag{A3b}$$

This confirms Strasberg's observation (at least for $p_f = p_0$) that the crevice model is qualitatively indistinguishable from a permeable-skin model. However, if we solve for A_1 and A_2 and substitute the experimental results for r_0 and γ_C given by Eqs. (36) and (37), we find:

$$A_1 = \gamma/\{(\gamma_C - \gamma)[(2\gamma/p_0 r_0) + 1]\}, \tag{A4a}$$

$$A_2 = \gamma_C/\{(\gamma_C - \gamma)[(2\gamma/p_0 r_0) + 1]\}, \tag{A4b}$$

$$0.40 \lesssim A_1 \lesssim 0.63, \tag{A5a}$$

$$0.70 \lesssim A_2 \lesssim 0.77. \tag{A5b}$$

In other words, Eq. (A2) will give a good description of the gelatin data for $p_{\text{crush}} = p_{ss}$ in the permeable region, and the inequalities $(A_1+1) > A_2 > A_1$ will be satisfied. However, the data are incompatible with the inequalities $A_2 > 1$ and $A_1 > 1$. Furthermore, the crevice model provides no explanation for the change in slope $\partial p_{ss}/\partial p_{\text{crush}}$, at $p_{\text{crush}} = p^* - p_0$ in Fig. 2 or the decrease in bubble count for $p_{\text{crush}} \gtrsim 14$ atm in Fig. 1.

Strasberg[11] found an increase in cavitation threshold from about 0.5 atm to about 1.5 atm for samples of tap water that had "aged" for 2 days. Strasberg states that the most reasonable explanation for this phenomenon is the slow rise of gas nuclei because of their buoyancy, and he calculates that spherical nuclei with radii larger than about 1 μ would be lost. Since compression and decompression amplitudes are equal for acoustic cavitation and since Γ, defined by Eq. (10a), is independent of the ratio of specific heats η, the varying-permeability model can be compared with Strasberg's data simply by putting $p_{\text{crush}} = p_{ss} = p_a$. Our own results in Fig. 2 indicate that points satisfying the first equality lie entirely within the ever-permeable region. Setting $p_{crush}=p_{ss}=1.5$ atm and $\gamma=72$ dyn/cm for water, we obtain from Eq. 20 $r_0=0.95$ μ, in excellent agreement with Strasberg's result. It seems unlikely that gas nuclei embedded in a random assortment of solid particles would either float to the surface or sink to the bottom of a standing liquid in such a systematic and predictable way.

Greenspan and Tschiegg[9] observed that the acoustic cavitation threshold in water could be raised from less than 1 atm to greater than 100 atm by passing samples through membrane filters of 0.2-μ pore diameter. This could be interpreted as evidence for the crevice model. Clearly such a filter would also eliminate spherical gas phases with outer physical radii larger than about 0.1 μ. The acoustic amplitude needed to reach $r_0=0.1$ μ is about 10 atm in gelatin, but it exceeds 14 atm in water because the surface tension is higher. Given the uncertainties in this comparison, it is plausible that any spherical gas nuclei in water which pass through a filter of 0.2-μ pore diameter would be driven into the "model breakdown region" during compression and would become inaccessible to further study by the acoustic method.

Since the crevice model is technically viable[5] and since dust particles with irregular surfaces must ordinarily be abundant, it is possible that some gas phases are, in fact, held together by this means. Cavitation in organic solvents, for example, could be initiated primarily by cracks in motes, while bubble formation in gelatin and probably also in water appears to be due mainly to gas nuclei stabilized by skins of varying permeability.

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