Determination of the radii of gas cavitation nuclei by filtering gelatin

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(Received 6 June 1977; revised 15 November 1978)

We report an experiment in which the size distributions of the entities which initiate bubble formation in supersaturated gelatin are systematically altered by passing test samples through Nuclepore filters with nominal pore diameters of 0.4, 0.6, 0.8, 1.0, and 3.0 μm. The actual diameters range from +0% to −20% of the nominal values. The data are compared with a new model, described in the previous article, in which gas cavitation nuclei are stabilized by surface-active skins of varying gas permeability. Within the measurement resolution, the initial cutoff radii for bubble formation are the same as the respective filter-pore radii. This implies that the calculated radii are those of actual physical structures capable of initiating bubble formation in gelatin.

PACS numbers: 43.35.Ei, 43.25.Yw, 47.55.Bx

INTRODUCTION

The previous article describes a new model for stabilizing gas cavitation nuclei. The existence of such nuclei is inferred from experiments indicating that cavitation thresholds in aqueous media can be significantly raised by degassing or by a preliminary application of static pressure. This result is unexpected since gas phases larger than the order of 1 μ in radius ought to rise to the surface of a standing liquid, whereas smaller ones should dissolve rapidly via the outward diffusion that results from surface tension. The model confronts this dilemma by assuming that nuclei small enough to remain in suspension are stabilized by elastic skins or membranes which resist compression mechanically.

By comparing the predictions of different model types with data obtained recently from gelatin supersaturated with gas, it is found that nuclear skins must be initially permeable, a conclusion that is consistent with ultrasonic cavitation results. On the other hand, skins can become effectively impermeable if the ambient static pressure is increased rapidly by an amount that depends upon the initial nuclear radius and typically equals or exceeds 8.2 atm. Skins are permeable during decompression. In the same analysis, it is shown that the crevice model, at least in its present state of development, does not provide a satisfactory quantitative explanation for bubble counts in supersaturated gelatin.

Essentially, the varying-permeability model is a description of the way nuclear radii respond to changes in ambient pressure. For a given pressure schedule, one can calculate an initial minimum radius above which all nuclei originally in the sample will ultimately grow to form macroscopic bubbles. The number of bubbles counted is thus uniquely associated with a radius, and one can determine from a series of runs the initial integral radial distribution derived from the bubble counts and the pressure schedules via the model.

Granting that the varying-permeability model adequately summarizes the data from a particular batch of gelatin, hereafter referred to as gelatin batch A, one may still doubt that the model parameter is the radius of an actual physical entity. To explore this point further, we have carried out another type of experiment in which the initial size distribution of the objects that initiate bubble formation in gelatin is systematically altered by passing samples through highly uniform filters of different gauge. Ideally, we anticipate that a given filter will introduce a sharp cutoff in the physical distribution and that no nuclei of larger dimension will survive. A corresponding cutoff should then be observed in the calculated distribution derived from the bubble counts and the pressure schedules via the model.

The data and certain procedural details are given in Sec. I. The calculated radial distributions are presented and interpreted in Sec. II, and further implications are discussed in Sec. III.

I. EXPERIMENTAL RESULTS

The apparatus and procedures used in studying bubble formation in supersaturated gelatin are described elsewhere in detail. We mention here only the salient features and those respects in which the present experiment differs from the ones reported previously.

For this series of runs, a new batch, gelatin batch D, was prepared and stored in individual 10-ml aliquots by freezing. Bubble counts from a given batch are ordinarily reproducible within statistical errors calculated from the square root of the number of bubbles, but significant differences have been noted between batches even those mixed with the same stock of gelatin crystals.

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By the time this experiment was begun, the original supply of crystals was exhausted. Considerable difficulty was encountered in preparing a new batch that would give practical bubble yields. Gelatin batch D is thus a blend of two Knox gelatin stocks, one for which the yield was too high and another for which the yield was too low. Specifically, the high-yield stock gave 2190 bubbles per sample, and the low-yield stock gave six bubbles per sample for a test schedule in which samples were rapidly compressed from 1 atm (absolute) to 21.4 atm (absolute), held at 21.4 atm (absolute) for 5.25 h, and rapidly decompressed back to 1 atm (absolute). The same schedule gave 156 bubbles per sample in batch D, which is mixed from 80% high-yield and 20% low-yield crystals.

The fact that the blend yield is only about 7% of the high yield, when 80% of the blend crystals are from high-yield stock, indicates that the low-yield stock contains substances capable of eliminating nuclei that would ordinarily be present either in high-yield gelatin or in the distilled water with which low-yield samples were made. Thus these data are not inconsistent with the previous finding that although some nuclei are definitely associated with the gelatin crystals, the majority are present in the water used in mixing. Nuclei from the two sources appear to be indistinguishable and are assumed to be of the same type.

Qualitatively, gelatin batch D is similar to gelatin batch A, but there are some quantitative differences. The surface tensions, determined from the contact angle and from the height of the sol in a capillary tube, are, respectively,

\[ y = (51 \pm 5) \text{dyn/cm (gelatin batch A),} \quad (1a) \]

\[ y = (55 \pm 5) \text{dyn/cm (gelatin batch D).} \quad (1b) \]

These agree within the assigned errors, and we have elected to continue using the former value in the analysis of both data sets.

The viscosity of gelatin sol \( \eta_{\text{gel}} \) depends upon the degree of gelatin, as well as upon the temperature. Values measured with a commerical viscometer in gelatin batch D at 23°C ranged from 4 to 10 times the viscosity of water. This gives

\[ 0.04 \leq \eta_{\text{gel}} \leq 0.10 \text{ dyn-s/cm}^2 \text{ at 23°C.} \quad (1c) \]

Shortly before each run, the contents of one aliquot were thawed, and appropriate fractions were passed through various Nuclepore filters at room temperature. The nominal pore diameters were 0.4, 0.6, 0.8, 1.0, and 3.0 μm, and the actual diameters ranged from +0% to -20% of the nominal values. The central values of the pore radii \( r_p \) are then 0.18, 0.27, 0.36, 0.45, and 3.0 μm with a range of ±10%.

Each gelatin sample, initially free of visible bubbles, was subjected to a particular pressure schedule, causing macroscopic bubbles to form. The samples were 4 mm deep, and bubbles were counted in the lower 3 mm. This results in a fiducial volume of about 0.4 ml per sample. The measured fiducial volumes of the glass counting chambers used in previous experiments were identical to one another within ±3%, but only two of these have survived. In the present experiment, four new chambers were also used, and their respective bubble counts have been corrected to correspond to the standard fiducial volume. The raw data thus consist of the bubble counts \( N \) and their respective pressure schedules, fiducial volumes, and filter-pore radii \( r_p \).

The data obtained from gelatin batch D with no-filter and with the 1.35-μ filter are shown in Fig. 1. The supersaturation pressure is given by

\[ P_{\text{sat}} = P - P_0, \quad (2a) \]

and the crushing pressure by

\[ P_{\text{crush}} = P_{\text{sat}} - P_0, \quad (2b) \]

where \( P_0 = 1 \text{ atm (absolute)=} 1.013 \times 10^5 \text{ dyn/cm}^2 \) is the mixing pressure, \( P_\infty \) is the maximum pressure, \( P_0 \) is the pressure at which the sample is saturated prior to decompression, and \( P_\infty \) is the final pressure. The time allowed for saturation at \( P_0 \) is 5.25 h, while the calculated saturation time constant (\( e^{t/\tau} \)) at the bottom of a sample is 74 min. For all of the runs reported in this article, \( P_0 \) and \( P_\infty \) are set equal. A pressure schedule illustrating these relationships is included in Fig. 1.

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

\[ P_{\text{crush}} = P_{\text{sat}} \quad (3a) \]

\[ P_{\text{crush}} = 8.2 \text{ atm} \quad (3b) \]

\[ P_{\text{crush}} = 13.6 \text{ atm} \quad (3c) \]

\[ P_{\text{crush}} = 20.4 \text{ atm} \quad (3d) \]

At most pressure settings, bubble counts from two or more samples have been combined. The new results confirm the strong dependence of bubble number \( N \) on the crushing pressure \( P_{\text{crush}} \) observed in gelatin batch A. This is important since crushing is a specific test for gas nuclei.

Following Ref. 1, we obtain from the data in Fig. 1, combinations of \( P_{\text{sat}} \) and \( P_{\text{crush}} \) that give a fixed bubble number: \( N = 0.1, 1.0, 10, 30, 100, 200 \) per sample. The results are replotted in Fig. 2 to yield \( P_{\text{sat}} \) versus \( P_{\text{crush}} \) for the values of \( N \) selected. One additional data point is shown in Fig. 2. This was found by evacuating samples originally at atmospheric pressure to negative gauge pressures until bubbles were seen. The formation threshold determined in this way,

\[ (P_{\text{crush}}, P_{\text{sat}}, N) = (0 \text{ atm}, 0.8 \text{ atm}, 1 \text{ bubble}) \quad (4a) \]

is identical to that in gelatin batch A, and it appears along the axis \( P_{\text{crush}} = 0 \text{ atm.} \)

Two more data points, not plotted in Fig. 2, were taken in an effort to trace the line \( N = 1 \) into the region \( P_{\text{crush}} < 0 \), where it intersects the line \( P_{\text{sat}} = P_{\text{crush}} + P_0 \) at the point

\[ (P_{\text{crush}}, P_{\text{sat}}, N) = (-0.37 \text{ atm}, +0.63 \text{ atm}, 1 \text{ bubble}) \quad (4b) \]
The new points

\[
(p_{\text{crush}}, p_{ss}, N) = [-0.13 \text{ atm}, +0.84 \text{ atm},
(1.3 \pm 0.4) \text{ bubbles}],
(4c)
\]

\[
(p_{\text{crush}}, p_{ss}, N) = [-0.37 \text{ atm}, +0.58 \text{ atm},
(0.25 \pm 0.25) \text{ bubbles}],
(4d)
\]

are consistent with this intersection and confirm that the region \(p_{\text{crush}} < 0\) is physically meaningful and accessible to experimental study. (By definition, \(p_{\text{crush}} = p_m - p_0\) is negative if the pressure is lowered from \(p_0\) to \(p_m = p_a\) and held there for 5.25 h before being lowered again to \(p_f\).) The same intersection was found in gelatin batch A.

For each filter, we have collected data of the four types defined by Eqs. (3a)-(3d). The analysis for \(p_{\text{crush}} = p_{ss}\) is remarkably simple, and these measurements are also the most sensitive since the rapid variation of \(N\) with \(p_{ss}\), seen in Fig. 1 for \(p_{\text{crush}} = 8.2, 13.6, 20.4 \text{ atm}\), tends to mask the effect being investigated.

For the sake of brevity and clarity, therefore, we note the consistency of the entire data sample, both internally and with the varying-permeability model, and we discuss in detail only the results for \(p_{\text{crush}} = p_{ss}\). These are shown in Fig. 3 along with the corresponding values for unfiltered gelatin, taken from Fig. 1.

Within the statistical errors assigned, there appears to be no difference between the no-filter points and those found with filters of pore radius \(r_a = 1.35 \mu\). A comparison of matching sets of data gives a statistically insignificant difference of \((1.5 \pm 2.6)\%\), where the no-filter set yields the higher value. Evidently, the number of nuclei present in the original sample with physical radii larger than 1.35 \(\mu\) was negligible.

The curves in Fig. 3 for pore radii of 0.18, 0.27, 0.36, and 0.45 \(\mu\) lie significantly lower than the no-filter results, and their thresholds are systematically displaced to higher values of the supersaturation pressure \(p_{ss}\). Since the value \(r_{\text{min}}^{p_{ss}}\) of the minimum radius for bubble formation at the final pressure \(p_f\) varies inverse-
of filtration and that no nuclei remain in the sol after the first stage will survive the passage through subsequent filters of the same gauge. As far as this test is concerned, the operation of the filters is ideal.

In the second test, a relatively large volume of gelatin was passed through the same filter, and samples of the filtrate were drawn off at specified intervals and subjected to the same pressure schedule as was used in the first test. Here it should be noted that we were not able to pass significant quantities of gelatin solution through Nuclepore filters of 0.2-μm nominal diameter (0.09-μm pore radius with a range of ±10%). Similarly, filters with pore radii of 0.18, 0.27, 0.36, and 0.45 μm clogged after passing definite "limiting volumes" of, respectively, 1.9, 4.9, 8.5, and 15.8 ml. Since the number of pores in such a filter is many orders of magnitude larger than the number of gas nuclei, clogging must have been due to gelatin constituents other than gas nuclei.

The main result of the second test, evident in Fig. 4, is that the number of nuclei per sample decreases significantly with increasing filtrate volume. In this respect, the operation of the filters was not ideal. We believe the phenomenon is due to partial clogging of the filter pores, and a quantitative explanation is developed in Appendix A. It is already clear, however, that for ordinary samples, which are taken from the first 0.5 ml of filtrate, the losses indicated in Fig. 4 are too small to account for the large decrease in bubble number seen with decreasing pore radius at high p. Figure 4 was obtained with the 0.45-μm filter, but this conclusion holds also for the 0.36, 0.27, and 0.18-μm filters.

II. COMPARISON WITH THE VARYING-PERMEABILITY MODEL

Following Ref. 1, we have compared the data in Figs. 1, 2, and 3 with a composite model in which nuclear skins are initially permeable and become impermeable if p is exceeded by some critical value p -p. All skins are permeable during decompression, and any changes in radius which might occur while the ambient pressure is set at p are assumed to be negligible. For the ever-permeable region p =p , the model yields

\[ P = P_m - P_0 - P \]

where p is the "crumbling compression," i.e., the maximum value of the "skin compression" P, and where p is again the minimum value of the initial radius r at which pressure the skin becomes impermeable. Subsequent increases in ambient pressure are resisted by a corresponding rise in the internal pressure, as well as by the elasticity of the skin itself.

ly with supersaturation pressure, the absence of bubbles at small p is indicative of an absence of gas nuclei with large r. This, in turn, implies an absence of gas nuclei with large initial radii r. Qualitatively then, each of the small-gauge filters appears to eliminate gas nuclei larger than some initial cutoff radius, and the ordering of cutoff radii and their corresponding filter-pore radii are the same.

Ideally, each filter would eliminate all of the nuclei in the sample with initial radii r larger than the pore radius r, and none of the nuclei with smaller radii. Since the number of nuclei with initial radii between two successive pore radii is fixed, the corresponding bubble counts would differ by a constant number. The data shown in Fig. 3 do not satisfy this condition. We have therefore carried out two additional tests in an effort to understand the operation of the filters better.

In the first test, gelatin sol was passed repeatedly through filters of the same pore radius r. A new filter was used for each passage, and a portion of the filtrate was drawn off and subjected to the schedule: p = 1 atm (absolute), p = p = 14.6 atm (absolute) for 5.25 h, p = 1 atm (absolute). The results, summarized in Table I, indicate that nuclei are lost only during the first stage
$p_m$: The magnitude of $r_m^{*\text{mix}}$ can be calculated directly from the relation

$$2(y_C - y) \left( \frac{1}{r_m^{\text{mix}}} - \frac{1}{r_m^{\text{mix}}} \right) = p^* - p_0,$$

(6b)

The magnitude of $r_m^{\text{mix}}$ can be found by iterating the equation

$$2(y_C - y) \left( \frac{1}{r_m^{\text{mix}}} - \frac{1}{r_m^{\text{mix}}} \right) = p_m - p^* + p_0 \left[ 1 - \left( r_m^{*\text{mix}} / r_m^{*\text{mix}} \right)^3 \right].$$

(6c)

Evidently the three-parameter ($r_0^{*\text{mix}}, y_C, p^*$) permeable–impermeable–permeable Eqs. (6a)–(6c) reduce to the two-parameter ($r_0^{*\text{mix}}, y_C$) ever-permeable Eq. (5) for $p_m = p^*$, and the later may be considered a special case of the former.

In applying the varying-permeability model to gelatin batch A, it was found that all of the data points satisfying Eq. (3a) ($p_{\text{crush}} = p_m$) were in the ever-permeable region $p_{\text{crush}} < p^* - p_0$. This appears also to be true of gelatin batch D, as can be seen in Fig. 2. Since all of the filter results in Fig. 3 satisfy Eq. (3a), they can be analyzed using only Eq. (5). Solving Eq. 5 for $r_0^{*\text{mix}}$ with $p_{\text{crush}} = p_m$, we obtain

### TABLE I. Multiple filtration test. The filter–pore radius is given in parenthesis, and the number of successive filtrations is indicated by the exponent.

<table>
<thead>
<tr>
<th>Filter</th>
<th>Bubble count</th>
<th>Filter</th>
<th>Bubble count</th>
<th>Filter</th>
<th>Bubble count</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(1.35)^1$</td>
<td>$202.6 \pm 6.4$</td>
<td>$(0.45)^1$</td>
<td>$112.8 \pm 4.2$</td>
<td>$(0.36)^1$</td>
<td>$73.8 \pm 3.5$</td>
</tr>
<tr>
<td>$(1.35)^2$</td>
<td>$227.9 \pm 15.1$</td>
<td>$(0.45)^2$</td>
<td>$110.2 \pm 10.5$</td>
<td>$(0.36)^2$</td>
<td>$66.9 \pm 8.2$</td>
</tr>
<tr>
<td>$(1.35)^3$</td>
<td>$202.5 \pm 14.2$</td>
<td>$(0.45)^3$</td>
<td>$130.5 \pm 11.4$</td>
<td>$(0.36)^3$</td>
<td>$76.3 \pm 8.7$</td>
</tr>
<tr>
<td>$(1.35)^4$</td>
<td>$208.4 \pm 14.4$</td>
<td>$(0.45)^4$</td>
<td>$106.6 \pm 10.3$</td>
<td>$(0.36)^4$</td>
<td>$50.7 \pm 8.8$</td>
</tr>
</tbody>
</table>

FIG. 3. Number of bubbles per sample versus supersaturation pressure $p_m = p_{\text{crush}}$ for filtered and unfiltered gelatin. The data for pore radii of 0.18, 0.27, 0.36, and 0.45 \( \mu \) lie significantly lower than the no-filter and 1.35-\( \mu \) filter results, and their thresholds are systematically displaced to higher values of the supersaturation pressure $p_m$. The solid curves were obtained from the respective radial distributions in Eqs. (8a–12), using radii calculated with Eq. (7b).
A more precise statement can be made by first parameterizing the 1.35 μ and no-filter data with the empirical expression

\[ N(\text{no-filter}) = N(1.35-\mu \text{ filter}) = 380 \exp(-r_0^{\text{al}}/0.120 \mu), \]  

which is the equation of the straight line in Fig. 5. The usefulness of Eq. (8b) is limited to values of \( r_0^{\text{al}} \) above the model breakdown limit of 0.07 μ.

As noted earlier, agreement with the data from the smaller filters (0.18, 0.27, 0.36, and 0.45 μ) cannot be obtained simply by subtracting constant numbers from the 1.35 μ and no-filter results. If, however, we allow the intercept at \( r_0^{\text{al}} = 0 \) to vary, then we can use the same value, 0.120 μ, for the exponential slope parameter and also require that \( N = 0 \) at each of the respective filter-pore radii \( r_\phi \). This procedure gives:

\[ N(0.45 \mu) = \begin{cases} 0 & \text{for } r_0^{\text{al}} > 0.45 \mu, \\ 195 \exp(-r_0^{\text{al}}/0.120 \mu) - 4.6 & \text{for } r_0^{\text{al}} < 0.45 \mu, \end{cases} \]  

where

\[ r_0^{\text{al}} = 2y/p_{ss} \] (for \( p_{ss} = \rho_{\text{crush}} < \rho^* - \rho_0 \)), 

\[ \rho_{\text{crush}} = \rho_{\text{crush}}^0 = \rho_{\text{crush}}^0 (1.01 \pm 0.10) \text{ atm} - \mu/p_{ss} \] (for \( p_{ss} = \rho_{\text{crush}} < \rho^* - \rho_0 \)),

which implies that \( r_0^{\text{al}} \) is equal to \( r_0^{\text{al}} \) and that the increase in nuclear radius that occurs during decompression is exactly equal to the decrease that occurs during compression. It is also worth noting that Eq. (7a) involves only one of the original three "model parameters," namely \( r_0^{\text{al}} \), and that this parameter is measured by the filter experiments reported here.

Substituting into Eq. (7a) the value of \( y \) given in Eq. (1a), we find

\[ r_0^{\text{al}} = (1.01 \pm 0.10) \text{ atm} - \mu/p_{ss} \] (for \( p_{ss} = \rho_{\text{crush}} < \rho^* - \rho_0 \)).

By applying Eq. (7b) to all of the data points in Fig. 3, we obtain the family of integral radial distributions shown in Fig. 5. Without any further analysis, it can be seen that the distributions for the 0.18, 0.27, 0.36, and 0.45-μ filters are cut off with respect to the 1.35 μ and no-filter results and that the cutoff radii calculated via Eq. (7b) are in good agreement with the respective filter-pore radii.
FIG. 5. Number of bubbles per sample versus minimum initial radius for bubble formation in filtered and unfiltered gelatin. The data points were obtained by applying Eq. (7b) to the results plotted in Fig. 3. The solid curves are the radial distributions given in Eqs. (8a–12). The results for the 0.18, 0.27, 0.36, and 0.45-μ filters appear to be suppressed by a constant factor, relative to the no-filter and 1.35-μ values, and to be cut off sharply above the respective filter-pore radii.

These equations for \( N(r_0 > r_0^{\text{min}}) \) are also plotted in Fig. 5. The corresponding curves for \( N(p_{\text{crash}}) \), obtained with the help of Eq. (7b), are compared with the original data in Fig. 3. The equations agree well with the small-filter results for \( r_0^{\text{min}} > 0.07 \) μ. Two minor exceptions are the point at \( (r_0^{\text{min}}, N) = (0.42 \) μ, 0.20 ± 0.20 bubbles) for the 0.36-μ filter and the point at \( (r_0^{\text{min}}, N) = (0.49 \) μ, 0.30 ± 0.30 bubbles) for the 0.45-μ filter. The observation of a single bubble in the five samples run at 0.42 μ, and another in the three samples run at 0.49 μ, may be due to the 20% range of the filter-pore radii, which has not been taken into account.

Since \( p_{\text{crash}} = 2\gamma/\rho_\ell \) is the condition for bubble formation at the final pressure \( p_\ell \), the transformation \( r_0^{\text{min}} = 2\gamma/p_{\text{crash}} \) used in generating Fig. 5 from Fig. 3 can be derived from any model for which \( r_0^{\text{min}} = r_f \). It is important, therefore, to point out that most of the data in Fig. 1 do not satisfy the condition \( p_{\text{crash}} = p_{\text{eq}} \) which led to this transformation. In particular, all of Eqs. (5)–(6c) were required to generate the theoretical curves in Figs. 1 and 2, and hence the model is tested by these data in both the permeable and the impermeable region. Furthermore, the radial distributions obtained from filtered samples with \( p_{\text{crash}} = 8.2, 13.6, \) and 20.4 atm, like those shown in Figs. 3 and 5 for \( p_{\text{crash}} = p_{\text{eq}} \) are cut off at the filter-pore radii and can be accurately summarized by Eqs. (9)–(12) with the same parameter values.

Equations (9)–(12) suggest that the smaller filters have two independent effects. First, each filtered distribution is suppressed by a constant normalization.
factor, e.g., $135/380 = 0.351$ in the 0.45-μ case. Second, because of the subtracted constant, e.g., $-4.6$ in the 0.45-μ case, the suppressed distribution is cut off sharply at the filter-pore radius $r_p$. The sharpness of this cutoff is not obvious in the integral distributions of Fig. 5 but can easily be seen in the distributions obtained by differentiating Eqs. (9)–(12) with respect to $r_0^{(a)}$. The result of this operation, $n(r_0)$, where

$$N(r_0 > r_0^{(a)}) = \int_{r_0^{(a)}}^{r_0} n(r_0) dr_0, \quad (13)$$

is a decaying exponential which drops abruptly to zero at $r_0^{(a)} \approx r_p$.

The observation of a cutoff in the filtered distributions leads to the principal conclusion of this paper: The parameter $r_0^{(a)}$ calculated in the varying-permeability model is the radius of an actual physical structure capable of initiating bubble formation in gelatin. In particular, some bubbles are associated with gas nuclei having physical radii equal to $r_0^{(a)}$, and none are observed in association with physical radii smaller than $r_0^{(a)}$. This statement has been tested and is valid in both the permeable and the impermeable regions of the model. However, the observed suppression of entire filtered distributions suggests that some of the structures which initiate bubble formation in gelatin may have physical radii larger than $r_0^{(a)}$. If so, $r_0^{(a)}$ should be interpreted as the radius of the gas phase or of the surfactant-gas interface. This point of view, which assigns to each nucleus a definite gas radius and a definite physical radius, has some support from the data in Table I, which seem to imply that filtration is a purely geometric question.

Anomalously large physical radii could be due to solid debris, clumps of gel, dust particles, etc. which become attached to preexisting gas nuclei. The composite radius $r_c$ must be less than 1.35 μ because the loss of nuclei in filters of this gauge is negligible. Furthermore, the probability for a nucleus of radius $r_c < r_p$ to form a structure with composite radius $r_c > r_p$ must be independent of $r_c$ since the suppression is uniform. A simple model embodying these conditions is outlined in Appendix B. The model is generally consistent with the observed suppression factors and supports our view that suppression is an artifact that results from the use of commercial gelatin.

Having raised the issue of solid debris, we should reconsider the possibility that some nuclei may be stabilized by crevices in solid particles. Independent of the varying-permeability model, Eq. (7b) and the data in Figs. 3 and 5 establish a one-to-one correspondence between the threshold supersaturation pressure $p_{crush}$ for a filtered sample and the filter-pore radius $r_p$, namely,

$$r_p \approx (1.01 \pm 0.10) \text{atm} - \mu/p_{crush}^{(a)}, \quad (14)$$

Such a correspondence can also be derived from the crevice model and is applicable to the special case when the liquid–gas interface spans the crevice aperture. In this configuration, increases in gas volume cause the radius of the interface to decrease until a hemisphere is formed which has the same radius as the crevice aperture. Further increases in volume then result in bubble formation. Thus the aperture radius becomes the critical radius for bubble formation, and filtration should yield a sharp cutoff since the physical radius of the particle cannot be smaller than the aperture radius of the crevice. The fact that particle radii would usually be larger than aperture radii could provide an explanation for the uniform suppression of the filtered distributions for nuclear gas radii smaller than the filter-pore radii.

Interpretation of the data via the crevice model breaks down as soon as we require sensitivity to crushing. Generally speaking, crevices small enough to exhibit a radial dependence, such as that described in the previous paragraph, are insensitive to $p_{crush}$, while those large enough to be sensitive to $p_{crush}$ exhibit no radial dependence. In addition, the model has internal inconsistencies that become evident when a quantitative comparison with the gelatin data is attempted.

The main sources of error in the identification of filter-pore radii with the calculated cutoff radii are the ±10% uncertainty in the surface tension $\gamma$, which is propagated into the values of $r_0^{(a)}$ calculated from Eq. (7b), and a typical statistical uncertainty of comparable magnitude in the analysis functions shown in Fig. 5. The 20% range of the pore radii in a given filter contributes very little, assuming the average pore radius is at the center of this range. Combined in quadrature, these errors result in an overall standard deviation of about ±15%. The difference in filter-pore radii and calculated cutoff radii is then (0 ± 15%)..

As indicated in Figs. 1, 2, 3, and 5, the agreement obtained with the varying-permeability model is quite good for supersaturation pressures less than 14 atm. For $N=0.1$, 1.0, 10, 30, and 100 in Figs. 1 and 2, $(p^* - p_o)$ was set equal to 8.2 atm, while for $N=200$, a value of 12.9 atm was used. The calculations are not very sensitive to this parameter, and the results for $(p^* - p_o)$ are similar to those found with gelatin batch A.

From thermodynamic equilibrium considerations, it is predicted in Eq. (31) of Ref. 1 that the crumbling compression $\gamma_c$ should increase linearly with the initial radius $r_0^{(a)}$. Comparison of the varying-permeability model with the data from gelatin batch A then gives [Eq. (39a) of Ref. 1]

$$\gamma_c = \gamma + 1.40 \gamma r_0^{(a)}, \quad (15)$$

where $r_0^{(a)}$ is expressed in microns. It can be shown by direct calculation that for values of $r_0^{(a)}$ of interest here, Eq. (15) restricts the model predictions to a family of curves which cross the line

$$p_{crush} = p_{crush} + p_o \quad (16)$$

at a common intercept in the vicinity of the point

$$p_{crush} \approx (-0.37 \text{ atm}, +0.63 \text{ atm}). \quad (17)$$

Conversely, one can require such an intercept and obtain an excellent description of the data, as illustrated in Figs. 1 and 2. This is similar to assuming that $\gamma_c$ is the same in the two gelatin batches, and it is consis-
tent with the experimental results. However, one should not attempt to extract the initial radius $r_0^{\text{mis}}$ in this manner since the approximate intercept defined by Eq. (17) lies very close to the line $p_{\text{crash}} = 0$, and small deviations from the exact curves in this region can produce significant errors in $r_0^{\text{mis}}$ calculated from Eq. (5) with $p_{\text{crash}} = 0$. The initial radial distribution in gelatin batch D is faithfully represented by the no-filter and 1.35-μ data in Fig. 5, which are summarized by Eq. (8b).

III. DISCUSSION

The principal new finding of this paper is that the parameter $\eta_0^{\text{ml}}$ calculated in the varying-permeability model is the radius of an actual physical structure capable of initiating bubble formation in supersaturated gelatin. We have also confirmed several of the earlier results from Ref. 1. For example, we again observe a model breakdown in the regions of $p_88$ and $r_0^{\text{TM}}$ indicated in Figs. 1, 3, and 5. The fact that the model itself is breaking down can best be appreciated in Fig. 5 where $r_0^{\text{mis}} < 0.07$, the number of nuclei with radii larger than $r_0^{\text{ml}}$ decreases as $\eta_0^{\text{ml}}$ decreases, a mathematical impossibility. Following Ref. 1, we note that a pressure schedule that probes down to $r_0^{\text{ml}} = 0.07$, will have a maximum pressure $p_{\text{as}}$ such that $r_0^{\text{ml}}$ will be of the order of 50 Å. At this level, it is plausible that the skin thickness $\delta$ is an appreciable fraction of the nuclear radius $r_0^{\text{ml}}$, which would violate one of the assumptions upon which the original model equations were based. Observation of a breakdown is then evidence that the skin thickness is of the order of 50 Å or less, and that the 50 Å level is actually reached at high pressures, as predicted by the model.

Another result, in agreement with Ref. 1, is that the initial radial distribution given by Eq. (8b) and illustrated by the no-filter and 1.35-μ filter data in Fig. 5 is exponential. The slope parameter, $b = 0.120$, is larger than that found in Ref. 1, $b = 0.088$, and it gives a correspondingly smaller value for the area $S$ occupied by individual skin molecules,

$$S = 48 \text{ Å}^2. \quad (18)$$

The limits on the energy stored in the area $S$ when the skin tension increases from its "initial small-scale equilibrium value" $\gamma$ to its "large-scale value" $\gamma_{C}$ are also smaller, $^{1}$

$$0.018 \text{ eV} \leq (\gamma_{C} - \gamma)S \leq 0.14 \text{ eV}. \quad (19)$$

We view the variations in $b$, $S$, and $(\gamma_{C} - \gamma)S$ from gelatin batch A to gelatin batch D as an indication of the experimental errors in the two measurements and not as evidence that the respective gas nuclei differ in any way.

The equality of the filter-pore radii with the calculated cutoff radius can be used to set limits on the effective charge density of nuclear skins. For a constant charge density $\sigma$ in C/cm$^2$, the outward pressure due to the repulsion of like charges is

$$p_C \approx \sigma^2/2\epsilon \kappa, \quad (20)$$

where $\epsilon = 8.85 \times 10^{-21}$ C$^2$/dyn-cm$^2$ is the permittivity of free space, and $\kappa \approx 3$ is the dielectric constant for an air bubble in water. Equation (7a) is then modified by the presence of an additive, constant pressure to give

$$r_0^{\text{mis}} \approx 2\gamma/(p_{\text{as}} + \sigma^2/2\epsilon \kappa). \quad (21)$$

The $(0 \pm 15\%)$ difference between the filter-pore radii and the calculated cutoff radii $r_0^{\text{mis}}$ implies a one-standard-deviation limit of

$$\sigma^2/2\epsilon \kappa < 0.15 \text{ m}. \quad (22a)$$

For example, the filter-pore radius $r_0^{\text{mis}} = 0.45 \mu$ corresponds via Eq. (7b) to $p_{\text{as}} = 2.2 \text{ atm}$ and gives limits of

$$\sigma^2/2\epsilon \kappa < 0.33 \text{ atm} = 0.33 \times 10^6 \text{ dyn/cm}^2, \quad (22b)$$

and

$$\sigma < 1.3 \times 10^{-7} \text{ C/cm}^2.$$

If the area per skin molecule is 48 Å$^2$, as indicated by Eq. (18), then the magnitude of the charge per skin molecule is less than or of the order of 0.4% of the electron charge. For comparison, we note that Alty observed a charge density of $-1.35 \times 10^{18}$ C/cm$^2$ on a gas bubble that collapsed at a diminishing rate to a radius of 12.5 μ.

ACKNOWLEDGMENTS

It is a pleasure to thank our colleagues Ed Beckman, Joe D'Arrigo, Tom Kunkle, Yoshihiro Mano, and Dave Watt for useful discussions and for constructive comments during the preparation of this manuscript. This research was supported by the University of Hawaii Sea Grant College Program under Institutional Grant Numbers 04-6-158-44025, 04-6-158-44114, and 04-7-158-44129 from NOAA Office of Sea Grant, U.S. Department of Commerce.

APPENDIX A. THEORY OF PARTIALLY CLOGGED PORES

Basic assumptions:

1. For gas nuclei having radii smaller than the filter-pore radius, the survival fraction is equal to the fraction of the liquid which passed through the unclogged pores.

2. The clogging rate $\lambda$ is proportional to the flow rate $\rho$. Let $M$ be the total number of pores; $N_j(t)$ the number of pores with $j$ clogs at time $t$; $\rho_j$, the flow rate through one pore with $j$ clogs; $\lambda_j = k\rho_j$, the clogging rate for one pore with $j$ previous clogs; $R_0(t) = N_0(t)\rho_0$, the unclogged flow rate at time $t$; $R(t) = \sum_{j=0}^M N_j(t)\rho_j$, the total flow rate at time $t$; $f(t) = R_0(t)/R(t)$, the instantaneous survival fraction at time $t$; $Q_0 = \int_{0}^{t} R_0(\tau) d\tau$, the total quantity passed through
unclogged pores;

\[ Q = \int_0^t R(\tau) \, d\tau, \text{ the total filtrate volume; } \]

\[ F(t) = \frac{Q_o(t)}{Q(t)}, \text{ the integral survival fraction for a sample collected during the interval } 0 \leq \tau \leq t. \]

Then

\[ dN_0(t)/dt = -N_0\lambda_o, \]

\[ dN_1(t)/dt = +N_1\lambda_1 - N_0\lambda_1 - N_2\lambda_1, \]

\[ dN_2(t)/dt = +N_2\lambda_2 - N_1\lambda_2, \]

\[ dN_3(t)/dt = +N_3\lambda_3 - N_2\lambda_3, \]

e tc.

The solutions to the differential equations are

\[ N_0 = M \exp(-\lambda_o t), \]
\[ N_1 = M\lambda_o \lambda_1 \left( \exp(-\lambda_o t) - \exp(-\lambda_1 t) \right), \]
\[ N_2 = M\lambda_o \lambda_1 \lambda_2 \frac{\exp(-\lambda_o t)}{(\lambda_1 - \lambda_0) (\lambda_2 - \lambda_3) + (\lambda_0 - \lambda_3) (\lambda_1 - \lambda_2) + (\lambda_1 - \lambda_3) (\lambda_0 - \lambda_2)} \]
\[ N_3 = M\lambda_o \lambda_1 \lambda_2 \frac{\exp(-\lambda_o t)}{(\lambda_1 - \lambda_0) (\lambda_2 - \lambda_3) + (\lambda_0 - \lambda_3) (\lambda_1 - \lambda_2) + (\lambda_1 - \lambda_3) (\lambda_0 - \lambda_2)} \]

APPENDIX B. ATTACHMENT OF GAS NUCLEI TO SOLID DEBRIS

Basic assumptions:

1. Some gas nuclei are attached to solid particles which yield a composite radius \( r_c \) that is larger than the radius \( r_0 \) of the gas phase per se.

2. The probability for a nucleus with radius \( r_0 < r \) to form a composite structure with radius \( r > r_0 \) is independent of \( r_0 \), where \( r_0 \) is the filter-pore radius.

3. A composite structure is trapped by the filter if and only if \( r_c > r_0 \).

4. The largest value of \( r_0 \) is less than 1.35 \( \mu \).

A simple model incorporating these assumptions can be constructed by attaching a spherical gas phase of radius \( r_0 \) to a spherical particle of radius \( r_4 < 1.35 \mu \), where \( r_0 \) is independent of \( r_4 \). The composite structure passes through a filter pore if and only if both \( r_0 \) and \( r_4 \) are smaller than \( r_0 \). That is, the composite structure aligns itself along the pore axis so that \( r_0 \) is effectively the larger of \( r_0 \) and \( r_4 \).

For example, assume that the radial distribution of particles attached to gas nuclei is constant below 1.35 \( \mu \) and zero above. The probability for a gas phase to attach to a particle with \( r_c > r_0 \) where \( A = 1(A(1.35 \mu - r_0)) \), where \( A \) is a constant. The survival fraction for this mechanism and for \( r_c < r_0 \) is \( [1 - A(1.35 \mu - r_0)] \). Letting \( A = 1/1.79 \mu \), we get 1.000, 0.497, 0.447, 0.397, and 0.346 for the 1.35, 0.45, 0.36, 0.27, and 0.18- \( \mu \) filters, respectively. Multiplying by the corresponding factors 1.000, 0.495, 0.441, 0.387, and 0.320, we obtain net survival fractions of 1.000, 0.495, 0.441, 0.387, and 0.320. The experimental fractions calculated...
from the normalization constants in Eqs. (8b)–(12b) are 1.000, 0.514, 0.435, 0.395, and 0.132. The low experimental value for the 0.18-μ filter suggests that the number of particles with radii in the interval 0.18 μ ≤ r ≤ 0.27 μ is somewhat larger than expected for a constant radial distribution.


