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CAVITATION FROM SOLID SURFACES IN THE
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INTRODUCTION

In general, the literature on cavitation and bubble formation presents a very confusing picture. On the one hand, modern theoretical work by Doring (3), Furth (4), Piccard (7), and Harvey *et al.* (5) has indicated that cavitation and bubble formation cannot be accounted for on the basis of random thermal movements in homogeneous solutions unless relatively enormous superheating, supersaturation, or negative tension is established. On the other hand, most experimental work, including that with supersonic vibrations (and everyday laboratory experience), suggests that cavitation and bubble formation require no great driving force. To be sure, Kenrick *et al.* (6) have heated water to 270°C. (54 atm. absolute pressure) before it exploded, and have supersaturated water with oxygen, nitrogen, and carbon dioxide at 100 atm. without producing bubbles when the sample was decompressed. Clare (1) apparently sometimes accomplished supersaturation with oxygen to 250 atm. without bubbles being formed. Dixon (2) achieved negative tensions of up to 150 atm. before a

¹ The work described in this paper was done under a contract, recommended by the Committee on Medical Research, between the Office of Scientific Research and Development and Stanford University.

The work of Harvey and his collaborators progressed simultaneously with our own, and a free exchange of ideas sometimes made the question of priority difficult. One of the authors (D. C. P.) worked with Dr. Harvey's group for the first year of their activity, and the experiments reported here followed naturally upon their work.

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column of water broke (a column of plant sap broke at 207 atm.). Furthermore, laboratory experience does often demand the use of "boiling chips" to prevent considerable superheating.

Much of this confusion has resulted because it has not been generally realized that there are two distinct problems here. One concerns the nature and stability of gas masses which persist in fluids and on surfaces, and can and do act as nuclei for cavitation and bubble formation. When nuclei are present, bubbles can be expected when the driving forces are very low. The other problem, considered in this paper, deals with cavitation and consequent bubble formation *de novo*, in the absence of any preëxisting gas phase.

It has been the considerable recent contribution of Harvey *et al.* (5) to demonstrate experimentally that most commonly observed instances of cavitation and bubbling depend, in fact, upon the presence of gas nuclei. In a dramatic experiment they took a sample of water in a glass tube and subjected it to high hydrostatic pressure in order to force all preëxisting gas masses into solution and thus have a system entirely devoid of gas nuclei. "Water so treated has remarkable properties. It can be heated above 200°C. without bursting into vapor. When intense high frequency sound waves are passed through, no cavitation occurs, and no bubbles arise. Finally, if exhausted to the vapor pressure of water, moderate knocks have no effect and only a very severe blow will cause bubbles to form."

Harvey and coworkers deduce that a bubble nucleus is a gas mass trapped in a crack or depression on a hydrophobic surface. As a consequence, it can have a negative surface curvature (concave) at the fluid interface. Then surface tension will always tend to sustain or enlarge the gas mass, and a true equilibrium state can exist so that the nucleus can persist indefinitely. Thus, dust particles and container walls are a potential source of nuclei which will almost invariably be present unless special precautions are taken. It was only on the basis of the above work that it became possible knowingly to take adequate steps to remove all preëxisting gas nuclei. Thus true cavitation could be studied with this potential source of serious confusion eliminated.

EXPERIMENTAL

1. General method

To produce tension in fluids we adopted the general method of Harvey *et al.* (5), which consisted simply in striking the container wall with an iron hammer. If the fluid column was 4–5 in. high, it was set in motion by the pressure pulse, with a consequent negative component resulting from the inertia. The elastic bounce of the container wall away from the moving column of fluid was an additional component. We have no way of knowing how large a tension is possible with this procedure, but it may be considerable very locally. We did have the empirical knowledge that the force was much more than adequate to produce clouds of bubbles from nuclei which were still stable in air-saturated water exhausted down to its vapor pressure. And we could also observe very large (1 cm.) cavities form and quickly collapse at the vapor pressure of the water

when the system was largely degassed. The tension produced proved completely adequate to make a number of very clear distinctions. The technique was employed throughout because of its great simplicity. In all cases the pressure corresponded to the vapor pressure of the fluid in question, or 2–3 mm. Hg (whichever was greater). Pyrex glassware was employed throughout, and was kept clean and wet by soaking until use with concentrated sulfuric acid saturated with potassium dichromate.

2. Water in glass and rubber

As previously mentioned, Harvey *et al.* (5) discovered that a water sample in a clean glass tube could be exposed to high hydrostatic pressure and then evacuated down to its vapor pressure without giving rise to any bubbles. Nor would bubbles appear when the tube was hit sharp blows with a metal hammer. We have repeated this basic experiment many times, deliberately hitting various sorts of glass tubes at the vapor pressure of water with harder and harder blows until the tubes shattered. We go further than Harvey in saying that when additional precautions are taken (which will be obvious later), we never obtained any cavitation or bubble formation in such previously pressurized systems (12,000 lb./in.² applied for 5 min.). The tension developed by the hammer blows was simply inadequate to tear the water away from the glass in the absence of gas nuclei. On three occasions, though, the glass cracked on the inside, but the crack did not extend through the wall. Cavities and bubbles did form in these tubes, suggesting the momentary existence of a much greater tension. It is probable that a very great tension existed momentarily, for the water molecules presumably could not move rapidly enough to fill the crack as it expanded.

We wanted a more rigorous test of the behavior of water when all nuclei were absent. We took a wide-bore tube, and built up a very thick latex rubber plug at one end by repeated dipping. The glass-rubber junction caused trouble until the rubber was run far up within the tube on the first dip. Such a tube, filled with water, was first pressurized and then exposed to a vacuum corresponding to the vapor pressure of the water. Extremely hard hammer blows on the rubber diaphragm did not produce cavitation except in so far as there was surface splashing. Cast latex tubes, filled with water and sealed, and then pressurized, were similarly resistant to the hardest blows that we could deliver to them *in vacuo*. Such pressurized gum rubber appears milky, and is apparently entirely hydrophilic.

The primary conclusion upon which the rest of the work is predicated is that in the absence of a free gas phase (gas nuclei), water itself does not cavitate unless large tensions are produced. Nor does water tear away from a wet glass or gum rubber interface without the application of very considerable force.

Aside from using hydrostatic pressure, it seemed likely that all gas nuclei might be removed by making the system essentially gas-free. A wide-bore tube, 2–3 ft. long and with 4–5 in. of water in it, was clamped upright and kept continuously evacuated with an aspirator pump. At the same time a hammer activated by a solenoid repeatedly hit the bottom of the tube at the rate of one blow per

second. At first, of course, great clouds of bubbles appeared from nuclei. As the gas left the solution, their growth rate became slow and the bubbles remained small, but persisted as centers from one blow to the next. Depending upon the blow intensity and the characteristics of the tube, after perhaps 20–40 min. the water in the tube would stop cavitating entirely. And once stopped, the cavitation could not be started again with any blow that did not shatter the tube! So much gas had been removed from solution that not only were the nuclei dissolved, but also there was insufficient gas to sustain a vapor cavity as a nucleus from one second to the next. In other words, bubbles once formed had a life of less than 1 sec.

Gentle heating to produce boiling *in vacuo* greatly accelerated the removal of dissolved gas. Then a stage could be reached quite rapidly when a continuous vapor column had to be maintained or boiling would stop, cavitation could not be induced, and the water could be superheated at least 60–80°C. without boiling. (Probably much greater superheating could have been attained, but no particular attempts were made in this direction.) This method of removing gas nuclei was in all respects as effective as the hydrostatic pressure procedure. The only important difference was that the system was necessarily degassed, while pressure allowed the use of supersaturated solutions.

3. Organic liquids in glass

Even though glassware be cleaned with hot concentrated sulfuric acid-dichromate mixture and kept continuously wet until use, it will inevitably carry micronuclei when water is the fluid phase used. This is not the case with several organic fluids which we have tested in contact with glass. One can take a dry glass tube and fill it with paraffin oil, a melted fatty acid (capric or caprylic), or ether, and nuclei will not be retained in the system. The pouring may trap a few nuclei or discrete bubbles, but if the system is evacuated the bubbles will rise to the surface. A few judicious taps will then enlarge all existing nuclei and remove them from the system as bubbles. From then on no cavitation or bubbles can be produced by any amount of striking (except possibly in ether, where unduly high vapor pressures can be produced).

Thus we had a third method of working with systems free of nuclei. This is thought to depend upon the different physical relations at the air-liquid-glass interface when the liquid is not water. The contact angle was small or zero with these organic fluids, so that the negative curvatures necessary to sustain nuclei were not possible. The surface tension at the convex surface then promptly drove any gas mass into solution. Solvent action may have added to their effectiveness in removing any adherent oil or grease films. Presumably any three-phase system with a sufficiently great spreading coefficient of fluid on solid would behave in the same manner.

We have, now, the important conclusion that these organic compounds, like water, will not cavitate or bubble without large driving forces when gas nuclei are absent. We have also found that ether, at least, can be greatly superheated under these conditions.

4. Solid surfaces; various crystals

Having several experimental means of removing gas nuclei, we were now in a position to study the properties of other solid-liquid interfaces. We could work with systems that were either supersaturated or essentially gas-free. We found that the presence of a variety of different solid surfaces allowed very easy cavitation without preëxisting gas nuclei being present.

First of all, it was found that when different crystals were precipitated from their own nucleus-free melt or solution, cavitation frequently could be obtained without the slightest difficulty. The crystallization was accomplished by a slight change in temperature. The effect was completely reversible, and upon remelting or redissolving the crystals, the sample invariably returned to its original condition, lacking nuclei. This work is summarized in table 1.

A glance at table 1 will show that no matter how formed, and irrespective of the fluid medium, the organic crystals always allowed easy cavity formation, even in the absence of dissolved air and in the presence of only a *very few, very* small crystals. The ionic salt crystals behaved differently, in that large numbers of crystals ordinarily had to be formed before cavitation could be induced. Rochelle salt gave an intermediate effect, as might be expected from its structure.

In the above experiments crystals were always formed in a medium known to be free of nuclei, but the results were extended by taking preformed crystals and applying procedures presumably capable of removing all nuclei. Thus, water suspensions of crystalline cholesterol, iodoform, and calcium carbonate, and very thin cast sheets of paraffin, were exposed to 12,000 lb./in.² hydrostatic pressures overnight, or for 2-3 days, to remove existing nuclei. The pressurized samples of cholesterol, iodoform, and paraffin cavitated as soon as they could be tested at reduced pressures. The calcium carbonate cavitated with some difficulty. Exactly the same effects were observed when the nuclei were presumably destroyed by removing the dissolved air, for cavitation continued indefinitely with the first group of substances, and erratically and occasionally with calcium carbonate.

A more conclusive experiment was performed by actually cooling and solidifying melted paraffin under water while it was continuously exposed to 12,000 lb./in.² pressure. This treatment, even when followed by subsequent repressurization, did not prevent easy cavitation from the solid paraffin surface.

The nature of the solid surface was obviously of great importance in these experiments. Experiments were performed which gave considerably deeper insight into the essential requirement of easy cavitation. It was observed early that actively melting or dissolving crystals would no longer allow cavitation by our methods. This phenomenon was specifically observed and studied with crystals of capric and caprylic acids and of ethyl cinnamate in their own melts, and with crystals of succinic acid and potassium dichromate in saturated solution. The results suggested that unstable surfaces were not favorable for cavitation, and this thought was confirmed by a much more precise study of the capric acid crystal-melt system.

A heavy sludge of cavitating capric acid crystals was prepared in its own melt. The system, at 3 mm. Hg pressure, and while being continuously struck, was gently warmed to start melting the crystals. Cavitation stopped, and the

TABLE 1
Cavitation brought about by the formation of crystals

COMPOUND	CRYSTALS FORMED IN	MEDIUM		CAVITATION ORDINARILY REQUIRING	
		Air-saturated	Gas-free	Few crystals	Many crystals
Capric acid.....	Melt	+	+	+	
	Water suspension	+	+	+	
Caprylic acid.....	Melt	+		+	
	Water suspension	+		+	
Paraffin.....	Saturated paraffin oil	+		+	•
Ethyl cinnamate.....	Melt		+	+	
	Small drop under water		+	+	
Bromoform.....	Small drop under water		+	+	
Succinic acid.....	Saturated solution	+	+	+	
Rochelle salt.....	Saturated solution		+	Intermediate	
Potassium nitrate.....	Saturated solution		+		+
Potassium dichromate.....	Saturated solution		+		+
Potassium sulfate.....	Saturated solution		+		+

Cavitation was possible when crystals of the above compounds were formed in glass-fluid systems which were known to be previously free of all gas nuclei, and which did not allow cavitation. The ionic mineral salts, however, did not ordinarily allow cavitation until heavy sludges of crystals were present. The other compounds allowed cavitation in the presence of a *very* few, *very* minute crystals, except in the case of Rochelle salt. The latter compound more nearly resembled the other organic compounds than the inorganic, but the effect was intermediate and not entirely definitive. When heavy sludges were required, it is possible that enormous supersaturations produced bubbles as trapped fluid cores proceeded to solidify. This possible source of error could hardly have been involved in the results with the organic compounds.

temperature was lowered slightly so that the crystals were in equilibrium with their own melt. This equilibrium was maintained for 45 min. without the production of a cavity, in spite of the many crystals present. The temperature was then dropped only 0.2°C., and a slow growth phase started which was

barely visible. But cavities appeared at once as soon as the tube was gently tapped.

We conclude that in this sort of an equilibrium system there are no stable surfaces at all, any more than there are when crystals are rapidly melting or dissolving. It appears that a stable surface with "fixed" molecules is an essential requirement for easy cavitation.

5. Stearate monolayer surfaces and the effects of added substances

The above experiments were all of a qualitative nature. It was desirable to develop a semiquantitative technique so that different surfaces could be more precisely compared. These ends were accomplished by using stearate monolayers³ as the basic surface, which could then be modified by the addition of other substances soluble in water.

It was first of all determined that water in stearate-coated tubes cavitared very easily even after treatment with 12,000 lb./in.² hydrostatic pressure applied for days. Also, similarly coated tubes of water continued to cavitate indefinitely after the removal of dissolved gas at the vapor pressure of the water. These were the standard treatments which removed all nuclei and prevented cavitation in similar systems lacking the stearate.

The hammer blow striking the tube was activated by a solenoid. By simply altering the current flow through the solenoid, the intensity of the blow could be varied at will. The frequency of cavitation resulting from striking could be correspondingly altered from 0-100 per cent (of course each tube had its own absolute characteristics).

In making an experiment, the stearate-coated tube with 4-5 in. of water in it would be exhausted with an aspirator pump and repeatedly struck with the hammer for a half-hour or more until we were sure the system was essentially gas-free. The blow intensity would then be adjusted so that the cavitation frequency was known to be within the range from 70-90 per cent. It was then possible to test the effect which various added substances had upon this frequency of cavitation. These were added in solution, and the system once more exhausted and struck until gas-free before determining the new frequency.

³ A saturated solution of ferric stearate in benzene was the source of the stearate monolayers (Langmuir method). The same solution was used throughout, so that any impurities were constant. In applying these layers the history of the glass was very important. Best results were obtained when the glass was either freshly fused and kept hot until application, or was soaked overnight with 0.1 *M* barium hydroxide and then washed and completely dried by evacuation and heat. Even repeated washings with pure benzene would not remove the stearate monolayers applied thus from solution. But simply to remove the excess ferric stearate, the tubes were given two washings with pure benzene, dried, and then washed with a good lather of Ivory soap. Tubes prepared in this manner were "hydrophobic", and the water contact angle would be about 40°. It should be noted, however, that the monolayers applied from solution were presumably open-work structures, for the contact angle never approached the high values of a complete monolayer or a crystalline surface. From our point of view the important fact was that we were able to put monolayer patches of stearate on the glass to give hydrophobic loci where the stearate "tails" were in contact with water and the polar "heads" were in turn fixed to the glass.

It was found that various substances, upon addition to the fluid phase, greatly reduced the cavitation frequency. The data are summarized in table 2.

It can be seen in table 2 that the cavitation frequency was reduced much as the expected van der Waals association between stearate and added substance was increased. Substances such as *n*-butyl alcohol, leucine, or gelatin offered a large degree of "protection." All of these substances have polar groups included in the molecule, which would not take part in the association and would

TABLE 2

Effectiveness of various agents in reducing the cavitation frequency from stearate monolayers

CHAIN LENGTH	ALCOHOL	EFFECT	COMPOUND	EFFECT
1	Methyl	0	Gelatin (dilute)	+++
			Egg albumin (dilute)	++
2	Ethyl	0	Potassium butyrate	0
	Isopropyl	+	Sodium benzoate	0
	Tert.-Butyl	++	Sodium stearate	+++
			Sulfonated soap	+++
3	Propyl	+	<i>l</i> -Leucine	+++
	Isobutyl	++	Alkaline leucine	+
	<i>sec</i> -Butyl	++	Glycine	++
4	<i>n</i> -Butyl	+++	Glycerol	+(+)
			Ethylene glycol	0(+)
			Phenol	++
			2 per cent ammonia	0
			Potassium chloride	0

This table indicates the effectiveness of various agents in reducing the cavitation frequency from stearate monolayers when they were added to the water phase. The strength of the hammer blow was adjusted to give a known cavitation frequency from 70-90 per cent before the addition was made. The symbol 0 means that there was no significant effect of the added agent. The other symbols refer to orders of magnitude, with + indicating a small, but significant, effect, a cavitation frequency reduced to about 10-20 per cent. ++ indicates a very decided effect with the frequency reduced about a hundredfold to 1 per cent, and +++ indicates about a thousandfold reduction in frequency.

No specific concentrations were used, the attempt being simply to add a great excess for sorption on the stearate. Whenever solubilities allowed it, 5-10 per cent by volume was added; in other cases solutions were very nearly saturated unless specifically designated.

be presented to the water phase. But they all also have substantial non-polar chains for association with the non-polar fraction of the stearate molecules.

Stearate-coated tubes were tested after the addition of each of the lower alcohols with informative results. Methyl and ethyl alcohols offered no protection, *n*-butyl alcohol excellent protection, with *n*-propyl alcohol intermediate. Here we have serial differences depending upon chain length. But the mass of the non-polar fraction is also important, as can be seen by comparing the

series with two-carbon chains, for ethyl alcohol was ineffective, while isopropyl and tertiary butyl alcohols gave increasing protection in that order.

All of these effects were entirely reversible. Invariably, when the added substance was washed off and removed, the stearate-coated tube returned to its original cavitation frequency. But it was not always easy to remove an added substance. For instance, a tube that had had leucine or *n*-butyl alcohol in it could be flushed with running water overnight and would still not show its original characteristics. This was fortunately not true of a simple soap, which apparently would replace these added substances on the stearate, and then be quickly washed off itself. Application of a good lather of Ivory soap, followed by a few rinses, always returned the tube to its original condition, except possibly after the use of proteins. Thus a tube could be used many times. (Sulfonated soaps offered good protection in themselves, but did not rinse off easily.)

It must be noted and emphasized, however, that we have not been able to add any substance to the aqueous phase which offered complete protection against cavitation from the stearate monolayer. The cavitation frequency could be reduced more than a thousandfold, but it none the less occurred at a finite rate. We must assume that we were dealing with equilibrium conditions; that not all of the stearate chains would be associated with the added substance at any given moment, and thus there was no complete coverage and protection.

If the behavior of a stearate monolayer could be modified by the addition of various substances, so should gross crystal surfaces. Here it was much harder to standardize conditions, but the essential experiments of the stearate series have been performed using suspended cholesterol crystals as the hydrophobic solid surface. The results seemed identical, although obtained with less comparative exactitude. There was no doubt, though, that *n*-butyl alcohol, leucine, and soap gave a very great degree of protection.

DISCUSSION RELATIVE TO GAS NUCLEI

Our most basic finding is that certain types of stable solid surfaces are essential prerequisites for easy cavitation in the absence of gas nuclei. Since Harvey *et al.* (5) have made it amply clear that cavitation will occur without difficulty from gas nuclei, it is important to consider whether or not preëxisting nuclei could have survived our treatments. The most convincing experiments are certainly those with stearate monolayers, for here it seems incredible that preëxisting gas nuclei could have withstood the great hydrostatic pressures that were applied, since every crack necessarily must have been exposed to the fluid phase. As far as gross crystals are concerned, they were often used with their own melts as the fluid phase. Under such circumstances there was no possibility of supporting the negative gas curvatures which are prerequisite for stable nuclei.

The possibility that nuclei formed *de novo* on some types of solid surfaces requires more serious consideration. Harvey *et al.* (5) assume that minute vapor cavities might form as a result of statistical fluctuations of the molecules. They go on to calculate the very limited conditions whereby such a cavity might become a stable nucleus by acquiring gas from solution. To begin with,

most of our systems which have given easy cavitation do not fall within these limited conditions. But a much more serious objection questions their assumption that statistical fluctuations of molecules will produce vapor cavities at all at any finite rate. The experimental evidence denies this, for such cavities would allow tears to start in the body of a fluid, and slight tension should produce cavitation without any difficulty. Yet we now know that water in a clean glass tube will not cavitate when the gas nuclei are removed. And we must remember that Dixon (2) achieved tensions that often exceeded 100 atm. before the water column broke. These tensions were built up relatively slowly, and would not have been possible if minute cavities had been constantly forming. Similarly, Kenrick *et al.* (6) would not have been able to superheat water to 270°C. if there had been spontaneous cavities.

A more difficult suggestion to rule out supposes that first of all a sorption process concentrates gas molecules from the fluid on certain types of solid surfaces. And then, conceivably, statistical fluctuations of the concentrated molecules might form a nucleus *de novo*. However, the work with "gas-free" systems makes this most unlikely, and there do not appear to be any theoretical or experimental reasons for believing that this sort of molecular concentration would be possible. Furthermore, we can fall back on the work of Kenrick *et al.* (6) and Clare (1), who often did not obtain bubbling when water saturated at 100–250 atm. was decompressed. This is indicative of the driving forces that would be required, and thus we do not believe that we can account for our results on any basis which involves gas nuclei.

CONCLUSIONS

We believe that when we have produced cavitation under the described conditions, we have done so by quite literally starting a tear where no gas phase existed before. We presume that the tensions applied as driving forces were small (a few atmospheres at most). Thus any tear must have started at a very "weak" locus where the intermolecular forces momentarily approached zero.

We have found that a solid surface is a prerequisite for easy cavitation. And certainly, "hydrophobic" surfaces with exposed non-polar groups allowed tears to start most easily. Indeed, it is doubtful that any other sort of surface would allow this easy cavitation, for impurities, as well as other explanations, could account for any cavitation which required a heavy sludge of crystals. It is not likely that the ionic crystal surfaces allow easy cavitation *per se*. Rather, they should probably be grouped with glass as non-cavitating surfaces.

We can ask ourselves why it is that fluctuating intermolecular forces only approach zero when non-polar groups are fixed on solid surfaces. A reasonable explanation supposes that a "fixed" molecule is less able to follow the thermal movements of the fluid molecules around it. If the forces of adhesion are low to begin with, such as van der Waals forces, it would seem that there can be a momentary escape of a fluid molecule away from the attractive sphere of the associated fixed molecule. Thus a hole quite literally comes into existence.

These conditions were realized when hydrocarbon chains were exposed on solid surfaces. Then the nature of the fluid made little if any difference.

Fluid systems, chemically identical with those allowing cavitation in the presence of a solid surface, did not cavitate. So the corollary of the above conclusions is that holes do not actually develop in the body of a fluid even when the cohesive forces are low. It seems that any particular fluid molecule tends to follow the thermal movements of all others around it. This it must do by moving sufficiently on its own account so that all of the molecules involved stay within one another's spheres of attractive force. There is no "escape," so that the cohesive forces do not approach zero, and a tear cannot be started easily.

Furthermore, there was no cavitation from "solid" surfaces which were presumably unstable enough to allow some molecular displacement. Thus we were not able to start a tear from the surface of dissolving or melting crystals, or unstable crystals in temperature equilibrium with their melt. And the protective action of a layer associated by van der Waals forces presumably also resulted from the mobility of the associated molecules.

From our own experiments we are not able to say how much tension would be required to tear the body of a fluid. We have not been able to do it by our procedures. But we have already referred to experiments in the literature reporting high values of applied tension, superheating, and supersaturation. These allow us to say that the force required cannot be less than 100–200 atm. in the case of water, and that it is of the same order of magnitude for some organic compounds. If one examines the methods employed by these workers, it is obvious that the techniques of all involved some previous pressurization. One can see in retrospect that they were dealing unknowingly with systems free of gas nuclei. Thus their results are a valid indication of the forces necessary to produce true cavitation. But even these values may be much too low for the body of a fluid because of contamination, or because at best there was a glass-fluid interface which seems likely to be "weaker" than the body of the fluid.

The theoretical treatments of the subject mentioned in the introduction are substantiated in principle by our work. What we may designate as true cavitation is not possible without large driving forces being applied, unless certain types of solid surfaces are included in the system. What has usually been encountered experimentally is a false cavitation in which the cavities were derived from preëxisting gas nuclei rather than *de novo*.

SUMMARY

The literature on cavitation has been confused because means have not been available to distinguish experimentally between false cavitation from preëxisting gas nuclei, and true cavitation *de novo* in the absence of any gas phase. Three procedures are described which remove all gas nuclei. Under these circumstances, water-glass systems will not cavitate unless forces of at least 100–200 atm. are applied. On the other hand, we find very easy cavitation when molecules with non-polar hydrocarbon groups are "fixed" on solid surfaces, either

on a crystal face or spread as monolayer patches on glass. The nature of the fluid phase then makes little qualitative difference. Substances which associate with the non-polar surface groups by van der Waals forces, and then present polar groups to the fluid phase, prevent easy cavitation in so far as equilibrium conditions allow a greater or lesser coverage.

Since certain types of solid surfaces are essential prerequisites for easy cavitation, we conclude that fluctuating intermolecular forces can approach zero only under very limited conditions. This happens only in those molecular combinations where the forces are relatively low irrespective of the phase relationships. We believe that when we have produced cavitation in the absence of gas nuclei, we have quite literally torn the fluid away from the solid, the tear beginning at a "weak" locus where non-polar groups were exposed on the solid surface. There, only, fluid molecules momentarily can escape the attraction of fixed molecules which are unable to follow their movements. Conversely, in the body of any fluid, or at such solid-liquid interfaces where the attractive forces greatly exceed van der Waals forces, molecules are unable to separate sufficiently far to get out of one another's attractive spheres even momentarily, and large forces must be applied to initiate a tear.

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AN UNUSUAL LIQUID INTERFACE

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Two well-behaved immiscible liquids usually arrange themselves in the container in two horizontal layers with the denser liquid underneath; consequently a system such as the one depicted in figure 1, where one liquid forms a column inside the other, has been rather startling to most people who have seen it, physical chemists included. (The bottle is shown immersed in a larger vessel of water in order to give a truer picture of its contents.) The original bottle has indeed often served as a final examination question for a course in surface phenomena, and few students have been able to state all of the essential condi-