

842000

**DEPARTMENT OF THE NAVY
NAVAL SHIP RESEARCH AND DEVELOPMENT CENTER
WASHINGTON, D. C. 20007**

CAVITATION ORIGINATING AT LIQUID-SOLID INTERFACES

by

Frank B. Peterson

This document is subject to special export controls and each transmittal to foreign governments or foreign nationals may be made only with prior approval of Naval Ship Research and Development Center, Code 500.

September 1968

Report 2799

TABLE OF CONTENTS

	Page
ABSTRACT	1
ADMINISTRATIVE INFORMATION	1
INTRODUCTION	1
INTERFACE PHENOMENA	2
THERMODYNAMICS OF AN INTERFACE	5
INTERMOLECULAR FORCES	9
INTERFACIAL FORCES OF ATTRACTION	11
REVIEW OF RELATED PAST RESEARCH	16
INVESTIGATIONS BY HARVEY AND COWORKERS	16
INVESTIGATION BY PEASE AND BLINKS	17
INVESTIGATION BY KNAPP	18
INVESTIGATION BY HOLL AND TREASTER	19
INVESTIGATION BY ACOSTA AND HAMAGUCHI	19
INVESTIGATION BY VAN DER WALLE	21
INVESTIGATION BY RIPKIN	22
INVESTIGATIONS BY BERND	23
NSRDC INVESTIGATION	23
SUMMARY	25
CONCLUSION	25
APPENDIX - STRUCTURE OF WATER	27
REFERENCES	29

LIST OF FIGURES

	Page
Figure 1 – Mechanical Analogy of Surface Tension	3
Figure 2 – Possible Surface Orientations of Ethanol	4
Figure 3 – Equilibrium Contact Angle	7
Figure 4 – Cavitation Inception on Modified Ellipsoidal Head Form	24
Figure 5 – Arrangement of Oxygen and Hydrogen Atoms in Water	27

LIST OF TABLES

Table 1 – Calculated Spreading Pressure for Various Vapors and Solids	6
Table 2 – Work of Adhesion between Various Solids and Water	8
Table 3 – Relative Magnitudes of Intermolecular Interactions	10
Table 4 – Theoretical Bonding Forces	10
Table 5 – Polar Interfacial Interactions on Solid Surfaces	14
Table 6 – Compounds Requiring Only a Few Crystals for Cavitation	17
Table 7 – ITTC Head Form Results at CIT	20
Table 8 – Time for Bubble Volume to Double due to Gas Diffusion	21

NOTATION

E	Total surface free energy (enthalpy)
N	Surface density of chemical specie
P	Pressure
R	Universal gas constant
S	Surface entropy or spreading coefficient
T	Temperature
V	Velocity
W_A	Work necessary to produce a unit area of liquid and a unit area of a solid from a unit area of the liquid-solid interface
W'_A	Work necessary to produce a solid surface in equilibrium with the vapor of the bulk liquid
W_C	Work of cohesion
θ_E	Equilibrium contact angle
ξ	Negative of the spreading pressure
μ	Chemical potential
π	Spreading pressure
γ	Surface free energy (ergs/cm ²) or surface tension (dynes/cm)
σ_i	Cavitation inception coefficient
ρ	Liquid density

Superscripts

o	Two substances in contact, each saturated with the other at the point of contact
d	Dispersion force
m	Metallic bond force
h	Hydrogen bond force

Subscripts

i	i th component
s	Solid phase
f	Fluid phase
v	Vapor phase
L	Liquid phase

ABSTRACT

Cavitation occurring at the interface between a liquid and a solid is considered from the viewpoint of surface chemistry. The thermodynamics of the interface and the interfacial forces of attraction are reviewed. Emphasis is placed on those aspects that tend to suppress cavitation inception. Related past research is reviewed and evaluated using knowledge of the surface chemistry of the interface. It is concluded that cavitation inception can be suppressed by increasing the adhesion between the liquid and the solid and by reducing the amount of undissolved gas trapped on the solid surface.

ADMINISTRATIVE INFORMATION

This work was carried out under the General Hydromechanics Research Program of the Naval Ship Research and Development Center. Funding was under Subproject S-R009 01 01, Task 0101, Problem Number 526-814.

INTRODUCTION

Model and prototype tests have shown that the operating characteristics of flow stream protuberances and hydraulic machines will be affected by the occurrence of cavitation. Typical external and internal flow devices are propellers, hydrofoils, sonar domes, pumps, turbines, and valves. The application of the device determines whether the use of the unit will be limited by acoustic problems, structural problems, or a decrease in hydrodynamic performance.

The inception of cavitation in a region of the flow field depends on the presence of a suitably low pressure or, as is often necessary, a tension. When the proper value is reached for the existing physical and chemical properties of the liquid, a cavity is formed. For the cavities considered in this report, the process of cavity growth and collapse is the result of a highly nonequilibrium force distribution across the cavity wall.

Prototype performance data indicate that cavitation inception generally occurs at different values of the flow parameters from those found on geometrically and kinematically similar models. These differences are referred to as scale effects. Attempts to predict the scaling laws have often shown unaccountable differences between design prediction and model performance. The magnitude of these discrepancies frequently differs between various test facilities. For example, a wide variation was found in the results of cavitation inception tests performed recently throughout the world on an International Towing Tank Conference (ITTC) head form. When the results were compared,¹ the discrepancies could not be explained

¹References are listed on page 29.

using the information available. With such difficulties, it is understandable that many recent papers and reports on cavitation inception have been of little value in helping the engineer and naval architect to theoretically predict the occurrence of cavitation inception. Many theories have been presented to account for this anomaly. Variations in the free-stream nuclei from which the cavities are thought to originate and variations in the turbulence level are typical of the current theories. It is the thesis of this report that the chemistry of the liquid-solid interface can influence the occurrence of cavitation inception.

Very little research has been performed to determine the relationship between the physical chemistry of a liquid-solid interface and the onset of cavitation. It is the intent of this report to demonstrate the importance of surface chemistry in the inception of cavitation. A new dimension is added to cavitation research with the introduction of variables that affect cavitation inception but have no direct relationship to hydrodynamics. For example, recent water-tunnel research has shown that cavitation characteristics are significantly different for metal and teflon head forms.² It has also been shown that when a head form is coated with silicone oil, the character of the cavitation differs considerably from the uncoated condition.³ Although these were not part of a study on the surface chemistry of a cavitating body, the results are not surprising. The water pressurization experiments by Harvey et al.,⁴⁻⁶ and later by Knapp⁷ showed that high tensions could be sustained when the free gas in a flowing water system was dissolved. Equally illuminating is the finding of Pease and Blinks⁸ that cavitation occurred in a previously noncavitating system upon precipitation of crystals from the solution. The effect was reversible—when the crystals were redissolved, the solution again became noncavitating.

If the properties of a liquid-solid interface prove to influence the onset of cavitation, then a knowledge and control of these properties could lead to immediate application in prototype systems. Thus there is the potential for delaying the onset of cavitation and for controlling its inception location. In nearly all of the applicable material, the individual topics could be extended almost indefinitely. In this report, however, treatment will be limited to only the essential background, theory, and experimental results required to present the thesis. Included are observations of pressurization experiments and the variations between cavitation from metallic, organic, and inorganic surfaces. As an integral part, the role of the physical properties of the liquid is described. Finally, new directions for research are considered that should lead to immediate prototype application.

INTERFACE PHENOMENA

Molecules on the surface of liquids are subjected to a one-sided force field. This force field tends to pull the surface molecules into the bulk of the liquid depleting the surface layers and thereby increasing their intermolecular distance.

The physical significance may be seen more clearly by considering the following example of a box filled with a liquid. The box has a sliding cover of a material such that the forces at the interface are the same as those existing in the bulk of the liquid, i.e., the interfacial tension is zero. Now, if the cover is slid back to produce a free surface of area dA , the work required to do this is γdA . The force per unit length of the edge of the cover producing the surface γ is called the surface tension. This increase in free energy of the system is the result of reversible work performed at constant temperature and pressure. The surface free energy can be regarded as the work of bringing a molecule from the liquid interior to the surface against the force unbalance at the surface.

The mechanical analogy of Figure 1 is used to demonstrate how a force directed into the liquid bulk can appear as a surface "tension." For a liquid, an extension of the surface causes molecules to be brought from the interior to the surface region.

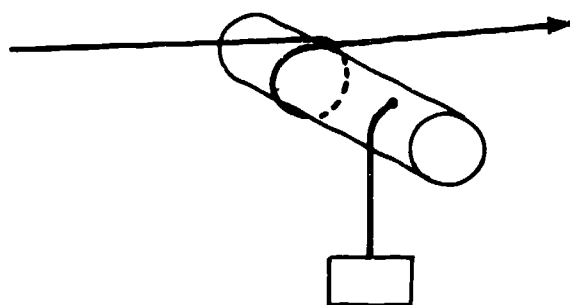


Figure 1 – Mechanical Analogy of Surface Tension

It can be seen that the terms "free energy per unit area" and "surface tension" are equivalent for a liquid and therefore that the units may be either ergs/cm² or dynes/cm. (The units are identical dimensionally.)

In the case of a solid, however, the surface tension is not necessarily equal to the surface stress. The former involves the work spent in forming a unit area of surface, and the latter involves the work spent in stretching the surface. An example by Adamson is helpful in understanding this difference; see Reference 9, page 268. Let the process of forming a fresh surface of a monatomic substance be divided into two steps. First, the solid or liquid is cleaned to expose a new surface, keeping the atoms fixed in the same position they occupied when in the bulk phase. Then, the atoms in the surface region are allowed to rearrange to their final equilibrium positions.

In a liquid, the two steps normally occur simultaneously. A solid surface, however, is usually not in an equilibrium position because of the immobility of the surface region. Thus with a solid, it may be possible to stretch or compress the surface region without changing the number of atoms in it, only their distances apart. This is in contrast to a liquid where the surface free energy, which is synonymous with the surface tension, is a direct measure of intermolecular forces. Because of the relative immobility of a solid surface, its surface energy and other physical properties depend on the immediate history of the material. It is known, for example, that the cold-working of metals affects the nature of the surface region; see Reference 9, page 267. Studies of the surface region using low-energy, electron-diffraction

techniques have shown that mechanical polishing gives a nearly amorphous surface layer in iron, copper, and aluminum. When grinding is performed, the molecular crystallinity of the surface is changed very little.

Before we discuss the thermodynamics of an interface and the forces acting there, let us consider the molecular orientation at the interface. The idea of an orientation at an interface for unsymmetric molecules is now very well accepted; see Reference 9, page 270. The Langmuir principle of independent surface action¹⁰ is widely used today in one form or another. Langmuir proposed that, qualitatively, one could suppose each part of a molecule to possess a local surface tension. As an example, we should be able to determine which orientation for an ethanol surface molecule in Figure 2 is correct.

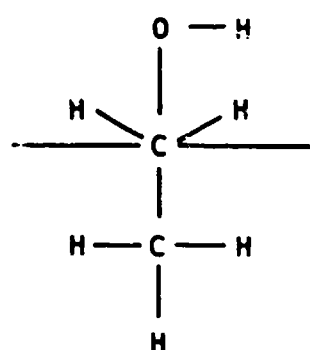


Figure 2a

LIQUID
PHASE

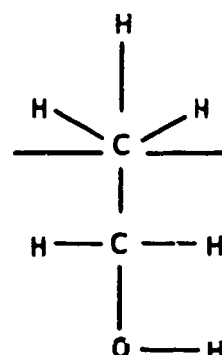


Figure 2b

Figure 2 - Possible Surface Orientations of Ethanol

In (a) the surface tension should be similar to water and in (b) it should be similar to a hydrocarbon. Now it is known that the surface energy of water is greater than that of a hydrocarbon so we would expect (b) to be correct. This conclusion is supported by a measured value of 22 dynes/cm for the surface tension--very similar to hydrocarbons.

Many examples of molecular orientation are apparent in the study of monolayers on liquid and solid surfaces; more will be said about monolayers later. Particularly demonstrative of orientation is a study by Blodgett¹¹ in which a glass plate was raised up through a barium stearate monolayer spread on water. The film that became attached to the plate was oriented with the hydrocarbon side outward and was thus hydrophobic. When the plate was then passed into the water, a second stearate layer was deposited. The second layer was now hydrophilic. It is clear that both the stearate monolayer on the water and the successive layers on the plate were oriented.

THERMODYNAMICS OF AN INTERFACE

The use of thermodynamics allows one to consider interfacial phenomena without specifying the field of intermolecular force between phases. In the material presented here, the approach is basically that of Gibbs¹² and the notation that of Boyd and Livingston.¹³

Gibbs describes the interface as follows:

$$\xi = E_{S0} - TS_{S0} - \mu_1 N_1 - \mu_2 N_2 \quad [1]$$

The quantity ξ evidently represents the tendency to contraction in that portion of the surface of a fluid which is in contact with the solid. It may be called the superficial tension of a fluid in contact with a solid. Its value may be either positive or negative. It will be observed for the same solid surface and for the same temperature but for different liquids the value of γ_{sf} (in all cases to which the definition of this quantity is applicable) will differ from those of ξ by a constant, size, the value of γ_{S0} for the solid surface in a vacuum."

We see that

$$\xi = \gamma_{sf} - \gamma_{S0} = -\pi$$

where π is called the spreading pressure, i.e., the difference between the free surface energy of the clean solid in a vacuum and the free surface energy when in equilibrium with a chemically dissimilar fluid (gas or liquid)—referred to by the subscript f . The superscript zero is a reminder that, at least in principle, when two substances are in contact, each is saturated with the other at the point of contact.

Substituting the relation for the total surface free energy

$$dE_{S0} = TdS_{S0} + \mu_1 dN_1 + \mu_2 dN_2$$

into the total derivative of [1], we have

$$d\pi = S_{S0}dT + N_1d\mu_1 + N_2d\mu_2 = -d\xi \quad [2]$$

If the temperature is constant and the Gibbs plane (from which adsorption is determined) is chosen so that the surface density of the solid is zero, then $N_1 = 0$. This means, of course, that all surfaces and the interface must be in thermodynamic equilibrium.

Equation [2] becomes

$$d\pi = N_2 d\mu_2 = \left(\frac{\partial \pi}{\partial \mu_2} \right)_{T, P_1, \mu_1} d\mu_2 \quad [3]$$

When the fluid contiguous with the solid is a gas or vapor at low pressure, then

$$d\mu_2 = RT d \ln P_2$$

where P_2 is the equilibrium pressure of the gas or vapor and $d\pi = RTN_2 d \ln P_2$.

$$d\pi = RTN_2 d \ln P_2$$

If the solid is immersed in a saturated vapor,

$$\int_0^{\pi^0} d\pi = \gamma_{S0} - \gamma_{SV0} = RT \int_0^{P_2^0} N_2 d \ln P_2 \quad [4]$$

where γ_{SV0} is the surface free energy of the solid in equilibrium with the vapor at pressure P_2^0 and $(\gamma_{S0} - \gamma_{SV0})$ can be considered as a two-dimensional spreading pressure (or as the free energy of immersion at $T = \text{constant}$) of unit surface of a clean solid in an infinite amount of saturated vapor at P_2^0 .

The right-hand side of Equation [4] can be integrated using experimental adsorption data. Typical results are shown in Table 1.

TABLE 1
Calculated Spreading Pressure for
Various Vapors and Solids¹³

$\pi = \gamma_{S0} - \gamma_{SV0}$ (dynes/cm @ 25°C)				
Solid Vapor	TiO ₂ VI	SiO ₂	BaSO ₄	SnO ₂
Water	228	244	246	220
Acetone		85		
n-propyl alcohol	90	110	77	80

The problem now is to relate $(\gamma_{S0} - \gamma_{SV0})$ to the free energy of immersion $(\gamma_{S0} - \gamma_{SL})$ of a clean solid surface in a large amount of bulk liquid. γ_{SL} is the free surface energy for the solid bulk-liquid interface.

Again, following Gibbs

$$\xi_{SV0} - \xi_{SL} = \gamma_{LV0} \cos \theta_E \quad [5]$$

where

$$\pi_{SV0} = \gamma_{S0} - \gamma_{SV0} = -\xi_{SV0}$$

$$\pi_{SL} = \gamma_{S0} - \gamma_{SL} = -\xi_{SL}$$

θ_E = equilibrium contact angle as shown in Figure 2.

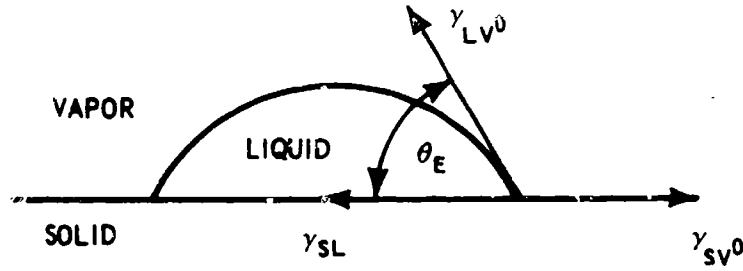


Figure 3 - Equilibrium Contact Angle

Equation [5] leads to

$$(\gamma_{S0} - \gamma_{SL}) - (\gamma_{S0} - \gamma_{SV0}) = \gamma_{LV0} \cos \theta_E \quad [6]$$

or

$$\gamma_{SV0} - \gamma_{SL} = \gamma_{LV0} \cos \theta_E \quad [7]$$

Equation [7] was initially derived by Young¹⁴ to describe mechanical equilibrium for the three phases as shown in Figure 3. Equation [7] can be derived as a thermodynamic relationship if the surface is microscopically smooth and if the solid surface is truly an equilibrium surface.¹⁵

The work of adhesion W_A (originally derived by Dupre¹⁶ in a slightly different form) can be expressed in the following way:

$$W_A = \gamma_{S0} + \gamma_{LV0} - \gamma_{SL} \quad [8]$$

where W_A is the work necessary to produce a unit area of a liquid and a unit area of a solid from a unit area of the liquid-solid interface.

W_A is impossible to obtain in practice because one cannot separate a liquid and a solid without leaving a solid with at least a monolayer in equilibrium with the vapor of the bulk liquid.

A more reasonable form of Equation [8] is

$$W'_A = \gamma_{SV0} + \gamma_{LV0} - \gamma_{SL} \quad [9]$$

where W'_A is the work necessary to produce a solid surface in equilibrium with the vapor of the bulk liquid.

From Equations [7], [8], and [9], we can obtain

$$W'_A = \gamma_{LV0} (1 + \cos \theta_E) \quad [10]$$

$$W'_A - W_C = \gamma_{SV^0} - \gamma_{SL} - \gamma_{LV^0} = S_{LV^0/SV^0} \quad [11]$$

The work of cohesion $W_C = 2\gamma_{LV^0}$ is a natural result of Equation [9]. S_{LV^0/SV^0} , the spreading coefficient of Equation [11], is suggestive of the physical cause of spreading. When S_{LV^0/SV^0} is positive, the liquid would be expected to spread spontaneously on the solid and thereby reduce the free energy of the system.

The work of adhesion W_A for the hydrophilic high energy surfaces (i.e., $\theta_E = 0$) of Table 1 is given in Table 2 using Equations [6] and [8].

TABLE 2
Work of Adhesion between Various
Solids and Water

Solid-Liquid (at 25°C)	$\gamma_{S^0} - \gamma_{SL}$ (ergs/cm)	W_A (ergs/cm ²)
TiO ₂ -H ₂ O	300	370
SiO ₂ -H ₂ O	316	388
BeSO ₄ -H ₂ O	318	390
SnO ₂ -H ₂ O	292	364

If we assume that the range of action of the forces involved at the interface is 10 angstrom (1 Angstrom = 1×10^{-8} cm)—a subject to be discussed in more detail later—then the pressure necessary to rupture the interface can be determined. For the SiO₂-H₂O interface, equilibrium thermodynamics predicts that 8880 atm tension is required to rupture the SiO₂-H₂O bond and leave a water-free solid surface. The tension required to break the cohesive bond of the water is only 1440 atm. Thus, if $\theta_E = 0$, the system will cohesively fail. If $\theta_E \neq 0$, then $W'_A < W_C$ and the bond between the solid and the liquid will be broken.

As is well known, a rupture within a system containing a water-solid interface occurs at orders of magnitude lower applied tensions. These purely thermodynamic equations cannot be expected to be adequate when the solid surface is not in equilibrium and when complete molecular contact between the two phases is not present.

Thus, other aspects of the nature of the interface must be considered. The next section, therefore, concerns the nature of molecular forces present at an interface.

INTERMOLECULAR FORCES

Under normal conditions, a broken object cannot be put together without some intermediary material. This is because the microscopic surface roughness can never be matched and because adsorbed layers of air and water molecules keep the components of the object separated. The usual circumstances are such that an adhesive is necessary to flow into the crevices, displace some of the more loosely adsorbed material, and get near enough to the molecules to make an effective bond. This example of the relationship between an adhesive and an adherend brings up a very important point. The strength of any union between two materials depends upon the forces of molecular attraction between the two sets of molecules. A primary loss of strength is due to the failure of the molecules to approach their proper bonding distances. When the objects are moved to within their bonding distance and adsorbed layers have been removed, then no adhesive is necessary. A typical example of this was recently reported¹⁷ where two beryllium surfaces were cleaned in an ultrahigh vacuum system. Then they were held together at 400 C and 14,000 psi for 1 hr. This bond was shown to be metallographically perfect. From a metallurgical standpoint, these conditions of temperature and pressure are considered very low and not in themselves the reason for the perfect bond.

The forces of molecular attraction can be divided into two main classes—chemical (primary) and physical (secondary) bonds. The secondary forces are known as the van der Waal forces and can be separated into three types:

1. Keesom: dipole – dipole force
2. Debye: dipole – molecule force
3. London: molecule – molecule force

The Keesom force is an orientation effect. Molecules which have permanent dipoles will have a mutual attraction and a mutual alignment.

The Debye force is an induction effect. A molecule with a permanent dipole moment will induce a dipole in a neighboring molecule by polarization.

The London force, normally referred to as the dispersion force, is a completely general interaction occurring between *any* two molecules in close proximity—regardless of their dipoles.

For two isolated molecules, the potential energy for the Keesom, Debye, and London interactions vary inversely as the sixth power of the separation. It may be noted, of course, that the force is found by differentiating the potential energy.

The relative magnitudes of these forces for intermolecular interactions is shown in Table 3.

In a review of the interaction forces, Allen¹⁸ gives some of the theoretical bonding forces between dipole materials and metal surfaces. Some of these results are shown in Table 4. These theoretical bonding forces are very large and of the same order of magnitude as those from equilibrium thermodynamics.

TABLE 8
Relative Magnitudes of Intermolecular Interactions
 (From Reference 9, p. 321)

Molecule	Induction Effect (Debye)	Orientation Effect (Keesom)	Dispersion Effect (London)
H ₂			11
A			57
N ₂			62
CL ₂			61
CO	0.12	0.003	67
HCL	1.03	19	105
NH ₃	1.5	84	93
H ₂ O	1.8	190	47

TABLE 4
Theoretical Bonding Forces (Atmospheres)

Solid-Liquid	London Dispersion Force	Dipole Force Classical	Total Force Classical	Dipole Force Q.M.*	Total Q.M.*
Fe-H ₂ O	2,810	10,240	13,050	3,960	6,770
Pb-H ₂ O	1,630	5,780	7,410	2,440	4,070
(*Q.M. = Quantum Mechanical Treatment)					

For these van der Waal forces, the interactions are all short range, i.e., they normally contribute appreciably to the energy of a system only through interactions over a distance of a few Angstroms. This indicates that the usual chemical and physical properties of matter are explainable in terms of short range forces. Furthermore, the implication is that the region of change across an interface should be only a few molecules thick. Beyond this thin layer, the properties of the bulk phases should prevail. This conclusion is supported by many tests (see page 15) involving materials that may be present at a cavitating interface. If colloidal or macromolecular particles are present, then electrostatic and van der Waals forces may act over a considerable distance; see Reference 9, page 323.

It is apparent that the theoretical methods used to predict bonding strengths have very limited applicability when applied to practical problems involving finite areas. In the following section, the previous equilibrium thermodynamics and theoretical bonding force considerations are combined in a semiempirical approach to predict interfacial phenomena.

INTERFACIAL FORCES OF ATTRACTION

The intermolecular attractions that cause surface tension can result from various intermolecular forces. The secondary forces which include the London dispersion force and the Keesom and Debye forces have already been considered in the section on interfacial forces. Two forces that are a function of a specific chemical nature and particularly influence the water-metal interfacial tension are the metallic and hydrogen bonds (see Appendix).

With significant success in predicting experimental results, Fowkes considers that the total surface tension of a material can be written as the sum of the surface tensions due to each of the forces acting.^{19,20} For example, the total surface tension of mercury can be written as

$$\gamma_{\text{Hg}} = \gamma_{\text{Hg}}^d + \gamma_{\text{Hg}}^m$$

and that of water as

$$\gamma_{\text{H}_2\text{O}} = \gamma_{\text{H}_2\text{O}}^h + \gamma_{\text{H}_2\text{O}}^d$$

Here, mercury is considered to have two main interatomic forces acting, namely, the dispersion force and the metallic bond. The surface tension of water also has the component due to the universal dispersion force plus the contribution due to hydrogen bonding and dipole-interaction effects. Although the London dispersion force is universal and gives an attractive force between adjacent atoms or molecules regardless of their chemical nature, it does not always yield the largest contribution to the surface tension. The implications of this can be seen when one considers the interfacial tension between two materials.

The interface between water and a pure hydrocarbon serves as a good example of interfacial attractions. The region can be considered as composed of two monolayers. If there was no attraction between the monolayers, then the respective surface tensions would remain unchanged. On the other hand, if the attraction between the monolayers was equal, then there would be no interfacial tension. When the attractions are unequal and due only to dispersion forces, Fowkes has shown that they can be estimated by the geometric mean relationship $(\gamma_2^d \gamma_1^d)^{1/2}$. This has been shown to be an accurate estimate if the interacting unit volumes (e.g., a water molecule, a mercury atom, a hydrocarbon CH_2 group, or an aromatic CH group) are nearly equal. The larger than normal CF_2 group in a fluorocarbon may account for the overestimation of the interaction when the geometric mean relation is used. Now,

when only a dispersion force interaction occurs, the surface tension is $\gamma_2 - (\gamma_2^d \gamma_1^d)^{1/2}$ in the hydrocarbon layer and $\gamma_1 - (\gamma_1^d \gamma_2^d)^{1/2}$ in the water layer. The sum is the interfacial tension γ_{12} :

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2(\gamma_1^d \gamma_2^d)^{1/2} \quad [12]$$

This equation can be applied when only dispersion forces are interacting. In the above example, the intermolecular forces of a pure hydrocarbon are entirely dispersion forces. Thus, one is able to calculate the dispersion force contribution in water as 21.8 dynes/cm ($\gamma_1 = 72.8$ dynes/cm at 20 C). In this case, γ_{12} is found experimentally by one of many available methods (e.g., the hanging drop technique).

Similar calculations can be made for a mercury-hydrocarbon interface where γ_{Hg}^d is found to be 200 dynes/cm ($\gamma_{Hg} = 484$ dynes/cm at 20 C). With these calculated values of $\gamma_{H_2O}^d$ and γ_{Hg}^d , Equation [12] can then be used to estimate the interfacial tension between water and mercury assuming that their interaction is due entirely to dispersion forces. The calculated value is 424.8 dynes/cm whereas the direct experimental value is 426.7 dynes/cm.

Equation [6] can be written as

$$\gamma_{LV0} \cos \theta_E = (\gamma_{S0} - \pi_{SV0}) - \gamma_{SL} \quad [13]$$

Recalling that π_{SV0} is the reduction in surface energy of the solid resulting from adsorption of vapor from a liquid, Fowkes assumes that a film of solid material can also spread on the liquid with reduction of surface energy π_{LV0} . Then

$$(\gamma_{LV0} - \pi_{LV0}) \cos \theta_E = (\gamma_{S0} - \pi_{SV0}) - \gamma_{SL} \quad [14]$$

is a more general form of Equation [13].

Assuming that only dispersion forces are acting at a liquid-solid interface,

$$\cos \theta_E = \frac{-\gamma_{LV0} + 2(\gamma_{LV0}^d \gamma_{S0}^d)^{1/2} - \pi_{SV0}}{\gamma_{LV0} - \pi_{LV0}} \quad [15]$$

When low energy solids such as waxes, hydrocarbon polymers, and metals or oxides with hydrophobic films are in contact with higher energy liquids, then $\pi_{SV0} = 0$ and $\pi_{LV0} = 0$. As an example, Equation [15] predicts that the contact angle between the hydrocarbon paraffin ($\gamma_{S0}^d = 25.5$ dynes/cm)* and water ($\gamma_{LV0}^d = 21.8$, $\gamma_{LV0} = 72.8$) will be 110.6 deg. The measured value is 109 to 111 deg.²⁰ Equation [15] can also be used to determine γ_L^d . Results of this type emphasize the importance of knowing exactly what forces are involved in an interfacial region. The following are typical of the variations one can expect between liquids:

*In the case of pure hydrocarbons, $\gamma_{S0} = \gamma_{S0}^d = \gamma_c$, where γ_c is defined by Zisman²¹ as the critical surface tension of a solid. The γ_c is the extrapolated value of γ_{LV0} necessary to just produce $\theta_E = 0$ on a solid.

Liquid	$\gamma_{LV}^d / \gamma_{LV}^0$
Hydrocarbon	1.0
Silicone	0.89
Glycerol	0.59
Mercury	0.41
Water	0.30

When a high energy surface is in contact with a lower energy liquid, $\pi_{LV} = 0$ and $\pi_{SV} > 0$. A good example to consider is the contact angle of water on a noble metal surface.²²⁻²⁴ Erb²² studied the wettability of a number of metals under continuously condensing conditions in pure steam for extended periods of time. The metals tested were gold, silver, rhodium, chromium, 316 stainless steel, and a copper-nickel 10-percent alloy. Initially, the surfaces were hydrophobic due to exposure to laboratory air with its organic components; 60- to 100-percent dropwise condensation occurred on all the metals. With the steam essentially oxygen free, the gold and silver quickly had 100-percent dropwise condensation, i.e., the organic materials were washed away and the silver oxide quickly dissolved. The water can interact with these two pure metal surfaces only through the dispersion force and this is insufficient to overcome the cohesive forces of the water. The metals adsorbed the water vapor and developed a finite spreading pressure π_{SV} . This can also be seen by considering the spreading coefficient of Equation [11]:

$$S_{LV/SV} = \gamma_{SV} - \gamma_{SL} - \gamma_{LV}$$

For these pure metals with only dispersion forces acting,

$$[\gamma_{S0}^d(\text{gold}) = 137 \text{ ergs/cm}^2 ; \gamma_{S0}^d(\text{silver}) = 74 \text{ ergs/cm}^2]$$

$$S_{LV/SV} = 2 (\gamma_{S0}^d \gamma_{LV}^d)^{1/2} - 2 \gamma_{LV}^0 \quad [16]$$

it is seen that water will spread $S > 0$ only when $\gamma_{S0}^d > 243 \text{ dynes/cm}$. This also explains why water will not spread on mercury where $\gamma_{S0}^d = 200 \text{ dynes/cm}$.

For the sake of completeness, it should be mentioned that the conditions for $\pi_{S0} = 0$ and $\pi_{LV} > 0$ also exist. This case would typically involve the spreading of a solid low-energy material (e.g., wax) on a liquid such as mercury, decreasing γ_{LV}^0 by spreading pressure π_{LV} . However, it does not appear that this situation occurs with water as a liquid and thus it will not be pursued further here.

A long period of exposure under the oxygen-free condensing steam conditions for the other metals studied by Erb showed that interactions other than dispersion forces were occurring. These are the polar interactions due to the polar nature of a solid such as an

oxide-covered metal. Within 1 day, the stainless steel and chromium surfaces became hydrophilic, i.e., the oxide remained but the organic materials no longer had an effect. After 3 days, the Cu-Ni 10-percent alloy had filmwise condensation except where some of the dark oxide had washed away. When oxygen was introduced into the steam, the surface of the copper alloy quickly reverted to 100-percent filmwise condensation, indicating that the whole surface was again covered with an oxide. Within a week, the rhodium surface was free of organic and oxide material and 100-percent dropwise condensation occurred.

Most metals interact strongly with water chemically or by more than just dispersion forces. These polar effects can be calculated by subtracting the calculated spreading pressure π_{LV}^d from that obtained experimentally using adsorption data. Thus

$$\pi_{LV}^d = \gamma_{S^0} - \gamma_{LV^0} - \gamma_{SL}$$

$$\pi_{LV}^d = 2(\gamma_{S^0}^d \gamma_{LV^0}^d)^{1/2} - 2\gamma_{LV^0}$$

when only dispersion forces are assumed to be acting.

Equation [4] is used to calculate $\pi_{LV^0}^{d(\text{exp})}$. The difference $\pi_{LV^0}^{d(\text{exp})} - \pi_{LV^0}^d$ is the polar effect and is calculated in Table 5 for graphite and several oxides.

TABLE 5
Polar Interfacial Interactions on Solid Surfaces²⁰

Solid	Liquid (ergs/cm ²)	π_{LV}^d	$\pi_{LV^0}^{d(\text{exp})}$	$\pi_{LV^0}^{d(\text{exp})} - \pi_{LV^0}^d$
Graphite ($\gamma_S^d = 115$)	n-Heptane	56	56	0
	n-Propanol	67	73	6
Anatase ($\gamma_S^d = 76$) TiO_2 VI	n-Heptane	38	38	0
	Benzene	36.2	56	19.8
	n-Propanol	37.4	90	52.6
	Water	-64.0	228	292
Silica ($\gamma_S^d = 76$)	n-Heptane	38	38	0
	Benzene	36.2	52	15.8
	Acetone	36.6	85	48.4
	n-Propanol	37.4	110	72.6
	Water	-64.0	244	308
BaSO_4 ($\gamma_S^d = 76$)	n-Heptane	38	38	0
	n-Propanol	37.4	77	39.6
	Water	-64.0	246	310

The hydrocarbon *n*-heptane was used as the reference liquid to measure the dispersion force of the solid. These results show the effect of polar bonds very clearly. For the case of water on silica, the 308 ergs/cm² of polar interaction is nearly four times the dispersion force interaction. This indicates a much stronger bonding of water to oxides than the water-water bond. Herein lies an important consideration with regard to cavitation from an interface. If the metal is covered by one or more monolayers of a material and the polar bonding of the oxide with the water is thus prevented, then spreading will not occur and a significant contact angle will be present. Irving Langmuir noted (1) that the short-range force fields were responsible for nearly all adsorption and (2) that a solid or liquid surface should have its adsorbing properties completely altered when covered by one layer of foreign atoms or molecules. For example, a layer of paraffin wax on a metal oxide gives a contact angle of 110 deg with water. Zisman and coworkers^{25,26} have found that a low-energy organic surface, or a high-energy surface coated with an organic film, is determined essentially by the nature and packing of the exposed surface atoms. This surface is independent of the nature and arrangement of the underlying atoms and molecules. They state further that because of the highly localized nature of the forces between the solid and the liquid, a monolayer of adsorbed molecules is always sufficient to convert a high-energy surface to a low-energy surface. This then justifies the use of the 3 to 10 Angstroms (1 Angstrom = 1×10^{-8} cm) on page 8 as the distance necessary to have separation of the two phases.

This discussion can apply equally well to the interaction of a surfactant in water. These polar molecules are oriented on the water surface in such a way as to reduce the surface free energy. In water, the hydrogen bonding and dipole interactions account for 70 percent of the intermolecular attraction (51.0 ergs/cm² at 20 C). This energy is available to promote adsorption and spreading of polar substances. In fact, it is for this reason that the maximum spreading pressure of surface-active compounds on water is 51 dynes/cm. Studies by Zisman and coworkers²⁶ confirm this. They have found that it is highly improbable that a nonpolar group of the surface-active agent will adsorb on a low-energy surface and thereby convert it to a high energy surface. In other words γ_{SL} will become small at high surfactant concentrations because the interface is between a hydrocarbon liquid and the solid.

These results indicate that if a metal oxide surface is available for polar bonding with water, the addition of a surfactant may be detrimental. However, if the surface is covered with at least a hydrocarbon monolayer, then a surfactant may promote spreading.

It seems clear from the considerations presented in the previous sections that good adhesion requires intimate molecular contact. If this requirement can be satisfied over all of an interface where tensions may be present, then cavitation from the interface should be nonexistent in practical applications. Results from the field of surface chemistry indicate that it should be possible to significantly increase the tension required to produce interfacial cavitation.

In some cavitation experiments, intentional modifications have been made to the interfacial characteristics but, in general, the motivation was not that advocated here. It is particularly enlightening to review these investigations from the point of view of surface chemistry. This will promote a better understanding of the previous results and give an insight into the inherent difficulties of this approach in reducing cavitation.

REVIEW OF RELATED PAST RESEARCH

INVESTIGATIONS BY HARVEY AND COWORKERS

The pioneering work of Harvey and his coworkers on the effect of free air in water has been the foundation and inspiration for many experiments.⁴⁻⁶ Basically, their idea was that free air trapped in hydrophobic crevices of bodies and particles can act as nuclei for cavitation. They theorized that when the water and its containing surfaces are pressurized, the water is driven into these crevices, thereby reducing or eliminating the available nuclei.

These investigators produced cavities at the blunt downstream end of a 5-mm pyrex glass rod by rapidly moving it in a 16-mm-diameter tube filled with water. The rod was pulled with a steel crossbow arrangement. Dust was removed from the water in a centrifuge with 800g. The rod, the container, and the water were all pressurized to 16,000 psi for 15-20 min. The water itself was saturated with air at atmospheric pressure. When the glass rod was cleaned in hot trisodium phosphate and then hot concentrated sulphuric acid-bichromate prior to pressurization, no cavitation was produced for the maximum attainable velocity of 37 meters/sec. When a cleaned rod was coated with a thin layer of paraffin ($\gamma_{SO}^d = 25.5$ ergs/cm²), cavitation occurred at a velocity of less than 3 meters/sec. This same situation occurred when the rod was not cleaned or was coated with a water-repellent varnish. When a varnish-covered rod was moved rapidly in water containing the surfactant aerosol OT (dioctyl sodium succinate), cavitation occurred practically at the start of rod movement. On occasion, dust particles from the air were allowed to fall into the already pressurized water; isolated bubbles then formed at a distance from the moving rod (i.e., in the body of the pressurized water). There did not appear to be any relationship between the rod velocity and the occurrence of the isolated bubbles.

Although this work is only qualitative, it demonstrates an important point. If essentially no free gas is present in the water, then the physical nature of the interface is very important. When good molecular contact was made between the oxide (pyrex) and the water, very high tensions were produced. When hydrocarbons were on the surface, complete molecular contact and polar bonds were not possible and cavitation was readily produced.

The use of the surfactant to lower the surface tension of the water did not increase the interfacial bonds and thus cavitation still readily developed.

INVESTIGATION BY PEASE AND BLINKS

The fact that the mere elimination of gas nuclei on a surface is insufficient to eliminate surface cavitation was well demonstrated by Pease and Blinks.⁸ They found that when crystals were precipitated from their nucleus-free melt, or solution, cavitation could frequently be obtained without the slightest difficulty. Crystallization was produced by a slight change in temperature. The effect was reversible; when the crystals were redissolved, the solution again became free of cavitation. Initially, the solutions were freed of nuclei either by pressurizing to 12,000 psi or by cavitating the fluid for a long period by repeatedly striking the container. When water was put into hot acid-cleaned glass, nuclei were inevitably present. This was not the case when paraffin oil, a melted fatty acid (capric or caprylic), or ether were used instead of water. The authors state that "... organic crystals always allowed easy cavity formation, even in the absence of dissolved air and with very few, very small crystals."

The cavitation was generated by striking the container with a repeatable impulse. Some of their results are shown in Table 6.

TABLE 6
Compounds Requiring Only a Few Crystals for Cavitation
(From Reference 8)

Compound	Crystals Formed In	Medium	
		Air Saturated	Air Free
1. Capric acid Capric acid	Melt Water suspension	+	+
2. Caprylic acid Caprylic acid	Melt Water suspension	+	
3. Paraffin	Saturated paraffin oil	+	
4. Ethyl Cinnamate	Melt Small drop under water		+
5. Bromoform	Small drop under water		+
6. Succinic acid	Saturated solution	+	+

Pease and Blinks also found that water in glass tubes coated with a stearate acid monolayer cavitated easily even after treatment at 12,000 psi for days. After removal of the dissolved gas in the water these coated tubes continued to cavitate indefinitely. When various substances such as *n*-butyl alcohol, L-leucine, and gelatine were added to the aqueous phase, the cavitation was reduced 1000 fold. These compounds were added to make 5 to 10 percent by volume or to make a very nearly saturated solution. However, at no time were the authors able to reduce the cavitation entirely on a stearate monolayer surface.

The authors concluded that when gross crystals were used in their own melt, there was no possibility of supporting the negative gas curvatures which are the prerequisite for the stable nuclei of Harvey.⁴⁻⁶ Also, they feel that the ionic crystals should be grouped with glass as noncavitating surfaces.

These results are not surprising in the light of the previous considerations of the interfacial bonds. For example, the fatty acid monolayers of stearic acid will present its methyl groups CH_3 toward the water. The surface tension is approximately 24 dynes/cm and the contact angle with water is 106 deg.²⁶ It is entirely possible that the water molecules were not uniformly close enough to the stearate surface and thus that the short range (4×10^{-8} cm) dispersion force was not acting over the whole surface.

INVESTIGATION BY KNAPP

In an attempt to learn more about the gas nuclei that Harvey postulated, Knapp⁷ performed some experiments in which a water-filled glass venturi and an upstream reservoir were pressurized to diminish gas nuclei on the surface and in the water. He found that when the glass was cleaned in hot chromic acid and the whole system pressurized as a unit to 2000-3000 psi, single cavities formed in the freestream of the water. The reported absolute pressure in the working section varied from -4 to -41 psia. This is reasonable since the glass was never exposed to the atmosphere after cleaning and one would expect a very good bond between the glass and the water. If dust particles were initially present in the water, then even after pressurization, they would have been expected to be "weak spots."

It appears that Knapp was not aware of the work of Pease and Blinks, but some of his findings confirm their work. In addition to the venturi results just cited, this is also shown by his boiling point experiments. Closed-top test tubes were cleaned, filled with water, and pressurized. After pressurization, the water was flushed out with unpressurized water. The bubbles first appeared 1 or 2 deg from the saturation temperature and were observed to originate in the body of the liquid. When uncleaned and unpressurized glass tubes were used with unpressurized water, the bubbles usually occurred first at the glass-water interface.

From the diverse experiments just considered, one can see that it is not sufficient to simply pressurize a solid-water interface and thereby drastically reduce or eliminate cavitation originating at the interface. The nature of the molecular bonding should be considered.

Various other workers have investigated the effect of modifying the solid surface with treatments and coatings. Unfortunately their tests do not appear to have been organized to evaluate the ability to reduce or eliminate cavitation from the interface.

INVESTIGATION BY HOLL AND TREASTER

Holl and Treaster² found, for example, that 1/4-in. teflon coated and solid teflon hemispherical head forms had significantly different cavitation inception characteristics when compared to those of a standard stainless steel model. They felt that the ease with which cavitation occurred on these teflon headforms indicated that "surface nuclei" played an important role. It was apparent that the presence of teflon promoted cavitation, but the cause was not known. Was it a matter of increasing the number of gaseous surface nuclei, a molecular bonding problem, or a combination of both? Could the same effect have been produced with a stearate monolayer over smooth clean glass?

Work is currently being pursued to obtain better information on the nature of a teflon surface. For example, Schonhorn and Hansen²⁷ have found that a short exposure of teflon to ionic and metastable species of inert gases leads to the formation of a cross-linked surface layer. This treatment did not change the wettability or surface tension of the surface but substantially increased the joint strength with an adhesive. It is theorized that the initial weak boundary layer present before treatment is due to the presence of low molecular weight polymer molecules at the surface. These molecules were forced to the surface during solvent evaporation or recrystallization of the melt. The authors feel that although a good molecular contact could be made, the presence of the weak boundary layer allows cohesive failure at very low applied stresses.

INVESTIGATION BY ACOSTA AND HAMAGUCHI

A recent study by Acosta and Hamaguchi³ may have touched on all of the above questions. In the process of testing a stainless steel ITTC head form* for a comparative cavitation inception test, they concluded that it was "... reasonably likely that the source of nuclei which contributed to the inception of cavitation probably originated on the body."

The acetone-cleaned surface of the head form regularly had inception occur in the form of a band around the periphery, 0.45 diameters downstream from the nose. At speeds of 20 meters/sec, spot cavitation occurred at 0.28 diameters downstream. The band cavitation had a clear cavity with a smooth leading edge that attached to the surface and extended a finite distance around the circumference of the head form. The spot cavitation originated at a point on the surface and spread in the form of a V.

In an attempt to modify the surface, the head form was coated with Dow-Corning 703 silicone oil. This oil has the ability to dissolve a large amount of gas, and it was hoped

*Hoy²⁸ computed that the minimum surface pressure position on this body was located 0.28 diameters downstream of the nose.

that its application would increase the number of surface nuclei. Initially, free bubbles located at the minimum pressure point of the silicone-coated surface were observed to grow from the body surface at reduced pressure. After the coating became "aged somewhat" (quotation marks added), the results were similar to those obtained with the uncoated surface. Further deaeration and aging of the surface produced band cavitation inception indices less than those obtained with the silicone oil free surface. The tests also showed that the silicone oil coating increased the occurrence of spot cavitation. Cavitation inception for these two surfaces is summarized in Table 7.

TABLE 7
ITTC Head Form Results at CIT

Surface	Type Cavitation Inception	Location (Axial Dimension) (Diameters)	Inception Index* $\sigma_1 = \frac{p - p_v}{\frac{1}{2} \rho V^2}$
303 Stainless steel, Acetone cleaned	Band (Spot)	0.45 (0.28)	0.41
303 Stainless steel, Silicone oil coated	Bubble	0.28	0.47
	Band (Spot)	0.45 (0.28)	0.41
	Band	0.45	0.37
*At a water speed of 12 meters per second.			

One further difference noted was that the desinent cavitation numbers were typically higher for the treated surface than for the untreated surface.

The band type of cavitation was previously described by Kermeen et al.²⁹ From photographs of the boundary layer on a hemispherical head form, they observed that at a slightly higher cavitation index "microscopic" cavitation bubbles existed in the boundary layer. These bubbles were significantly downstream of the minimum pressure point and apparently originated at or downstream of the calculated boundary layer transition zone. Eventually these bubbles produced irregular patches of cavitation called "macroscopic" cavitation. When the pressure was slightly lowered, the microscopic cavitation disappeared and the attached band cavitation was formed.

An attempt to explain the observations reported for the previous two head form investigations would be pure conjecture. However, it is clear that the silicone oil coating did significantly affect the cavitation characteristics of the head form. Certainly one possibility is that the oil covered or displaced much of the gas trapped on the surface. Although the

silicone oil-water molecular bond would still be small after oil deaeration, one would expect it to present greater resistance to cavitation inception than the original surface.

INVESTIGATION BY VAN DER WALLE

Van der Walle³⁰ feels that the observations of band cavitation by Kermeen, McGraw, and Parkin²⁹ can be explained in the following way. A microscopic bubble is produced at a crevice or pore downstream of the minimum pressure on the head form surface. When the bubble reaches a certain critical size, it is detached from the surface and transported downstream within the boundary layer. During its travel, the bubble will grow by gas diffusion and when the positive pressure gradients and gas diffusion rate are sufficiently great, the bubble will reattach to the surface. This fixed bubble initiates the sheet (band) cavitation. The theoretical calculations of van der Walle indicated that only gaseous cavitation can explain the inception of cavitation downstream of the minimum pressure point where the static pressure is higher than the vapor pressure. He further shows that, as expected, the onset of vaporous cavitation from a stable equilibrium bubble in the absence of gas diffusion is possible only when the liquid pressure falls below the vapor pressure. The time required for a bubble volume to double due to gas diffusion is shown in Table 8.

TABLE 8
Time for Bubble Volume to Double Due
to Gas Diffusion

$R_0 = 1 \text{ mm}$	0.1 mm	0.01 mm	0.001 mm
$t_c = 10^4 \text{ sec}$	10^2 sec	1 sec	0.01 sec

From his results van der Walle concludes that the contribution of the stream nuclei to the inception process will be rather small compared to that of the surface nuclei.

The work of Bindel and Lombardo³¹ with model propellers and fixed profiles appears to support the conclusions of van der Walle. They found that the inception of leading edge sheet cavitation was highly dependent on the dissolved air content.* On the other hand, bubble cavitation inception was found to vary only slightly with dissolved air content. Of course, what is not known is the extent to which the free-stream bubbles (nuclei) will enter into the boundary layer and influence the inception of sheet cavitation. Johnson et al.^{33,34} consider that the dissolved gas is of little importance. They feel that the trajectories of certain size free stream bubbles will be more influential than surface nuclei in the inception of all types of cavitation.

*This is in contrast to earlier work by Edstrand³² who found that sheet cavitation on model propellers in fresh and natural salt water was independent of gas content.

INVESTIGATION BY RIPKIN

Ripkin³⁵ has recently reported studies on the reduction of cavitation damage by surface treatment. His premise is that the gas nuclei on a surface are primarily responsible for the damage due to cavitation. These nuclei were considered to be gas-trapped in surface cracks or gas produced by electrochemical activity (corrosion).

Initial work with supersaturated water showed that oil coatings would reduce the number of gas nuclei on various materials. Further tests with a vibratory apparatus indicated that the surface treatment of specimens did not reduce cavitation damage. This is contrary to the results of Poulter³⁶ who used oil films in a lower intensity test facility. Five "nonmetallic" films were applied by Ripkin to C 1010 mild steel specimens. Four of these were manufactured by Minnesota Mining and Manufacturing Company. The first, FC-75, is similar to the Du Pont product Freon. This liquid has a low surface tension but is not a solvent for many common hydrocarbons found on surfaces exposed to the atmosphere. After Ripkin had air dried the specimen, probably not even a monolayer remained on the surface.* The other 3M products, FX-161, L-1495, and L-1541, all have properties similar to each other. After application, these materials were air dried and/or oven baked. This procedure should produce a low energy monolayer with a critical surface tension (Zisman's γ_c) of 16-18 dynes/cm.* One can see that these chemicals should not produce any significant reduction in gaseous surface nuclei. The production of a low energy surface would make it even harder for the water to thoroughly wet the steel surface and penetrate into the surface cracks. The fifth film, Penton by Northstar Research Institute, performed similarly to the 3M products.

Physical treatments such as shot peening and chemical treatments such as the production of surface films of insoluble and stable oxides and salts did not improve the cavitation damage resistance of mild steel. Since Ripkin does not indicate any attempt to promote wetting in the surface cracks, it appears clear that these treatments would also not reduce the number of available surface gas nuclei. A zinc plating was also tested on the assumption that it contains fewer crevices. The erosion rate for this plating was greater than for an uncoated specimen.

The investigation just reviewed presented results that could have essentially been predicted beforehand using surface chemistry considerations. The motivation for the work is stated to be the suppression of cavitation inception, but it is not clear what considerations were used to select the coatings and to prepare and test the specimens. As the author pointed out, a vibratory apparatus permits "... repetitive pressure cycling on unsealed water-borne particulate near the boundary and the cavitation continues despite any depressive characteristics of the specimen itself." Thus it appears that the real effectiveness in suppressing cavitation inception could not be evaluated.

*Private communication from Mr. Verne Francine of the Minnesota Mining and Manufacturing Company, St. Paul, Minnesota.

INVESTIGATIONS BY BERND

Bernd has shown that the solid-liquid interface can form the weak link in putting acoustic power in water.³⁷⁻³⁹ His results indicated that most solid materials were unable to achieve a high interfacial strength unless gas was first removed from the surface. Many of the tests were performed using pressurized water saturated with CO₂, and some were carried out with acoustic equipment at 18 kHz. Bernd concluded that poor bonding between water and a solid is not a cause of cavitation. He found that diffusion of gas to the surface from the bulk of permeable materials such as rubber was important. He also found that cracks and crevices on the surface of nonpermeable materials were important, but he did not attempt to explain the discrepancy between his results and those of Pease and Blinks. (They found that cavitation was readily produced when crystals were formed in previously nuclei-free solutions.) Bernd further concluded that pores and cracks ceased to be troublesome in causing cavitation after soaking material for a day or, at most, several weeks. The exceptions were permeable materials and ceramic materials with imperfect glazes on the surface. It appears that the author did not mean to imply that all cavitation would cease after soaking but only that trapped surface gas could be substantially reduced. In fact, for many materials, he used 5000-psi pressurization for 24 hr and longer just to reduce the surface gas.

Bernd demonstrated an interesting surface characteristic by abrading and cutting a polyurethane surface underwater.³⁸ The material was placed just below the water surface and then a vacuum applied to reduce the pressure. At a vacuum of 25 in. of mercury, the original cast surface had one bubble form per square centimeter. There were 29 bubbles/cm² when the surface was abraded underwater and more than 50/cm² when it was cut with a knife. These results indicate that it may be impossible to produce a cavitation-free surface by mechanically producing a fresh surface underwater. The minute amounts of gas in a solid may be sufficient to negate any such procedure.

NSRDC INVESTIGATION

Exploratory tests at this Center on a 2-in. head form* have shown that the interface can play an important role in cavitation occurrence. In these tests, the head form (with a 4- to 6- μ in. surface finish) was initially cleaned with reagent A.C.S. acetone, air dried, and tested for cavitation inception at nominal velocities of 20 and 24 ft/sec. The head form was then soaked in acetone for 65 hr, washed in distilled water, quickly pressurized to 19,000 psi, and installed in the filled water tunnel. Each step was performed without exposing the surface to the atmosphere. The qualitative results (Figure 4) indicate that this procedure inhibited cavitation occurrence. After continuous submergence for five days, the latter results were essentially reproduced. When the head form was air dried and retested, the results were comparable with those obtained initially. All of these tests had a total gas

*Modified ellipsoidal head form with $a/b = 3$, $a = d/2$, as described in Reference 40.

content of nominally 200-percent saturation referred to the test section pressure (30-percent saturation referred to atmospheric pressure) and were performed using the same procedures. The results are interpreted as demonstrating that improved molecular contact reduces the number and size of surface gas pockets instrumental in cavitation inception. This improved contact was the result of the pressurization of the wetted surface and the fact that the treated surface was kept free of direct contact with the atmosphere.

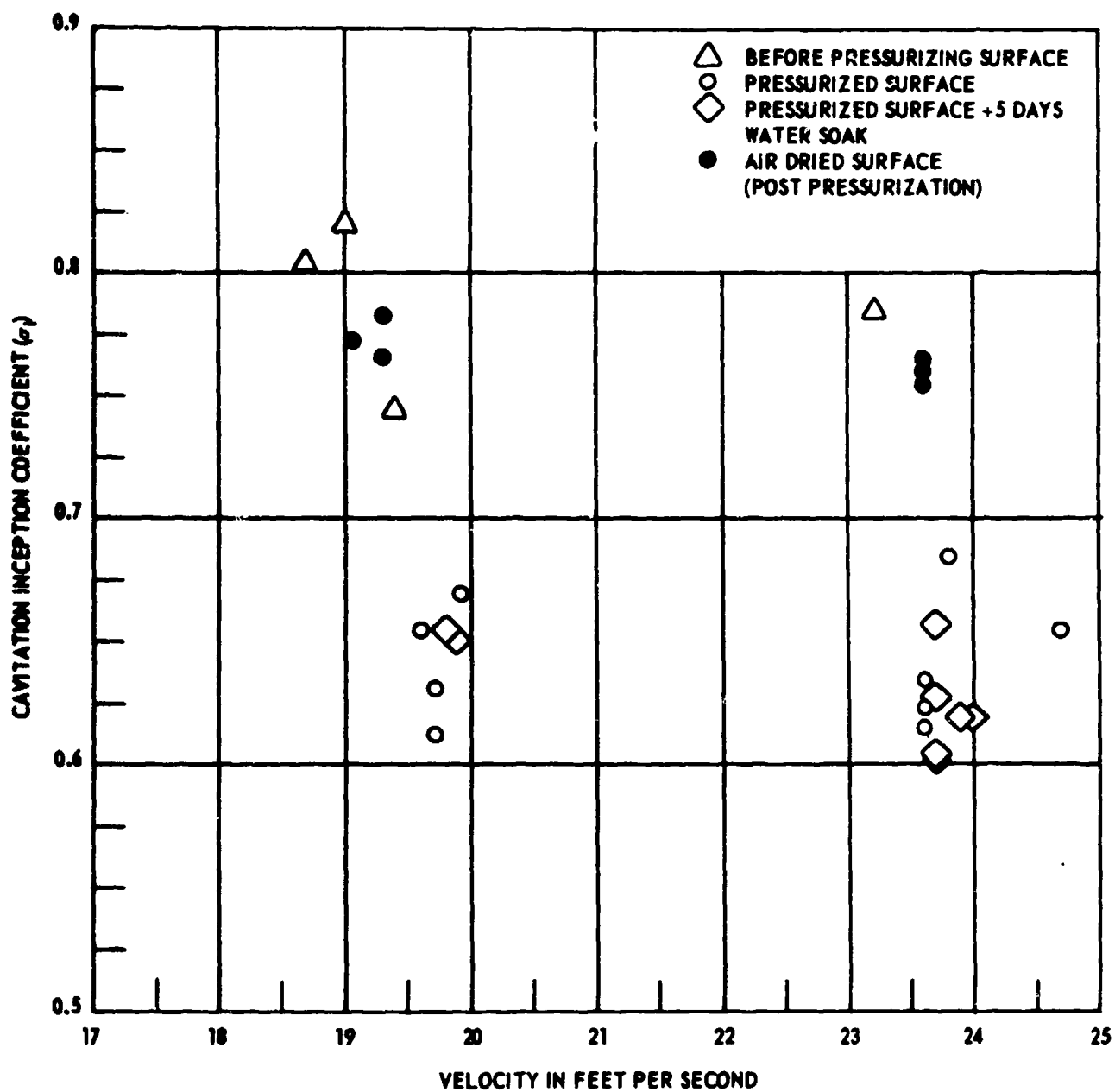


Figure 4 - Cavitation Inception on Modified Ellipsoidal Head Form

SUMMARY

The investigations reviewed here have considered cavitation from diverse points of view. However, they all indicate that the characteristics of the liquid-solid interface can influence cavitation inception. It has been shown that cavitation is suppressed when the free gas in water and on a very clean solid surface is greatly reduced. When the solid, its coating, or an adsorbed layer has a low surface-free energy and is free of undissolved gas, little suppression has been found. Thus it appears that two factors influence the inception of cavitation at the liquid-solid interface. First, if the water is in contact with a solid surface of low surface-free energy, then cavitation is easily initiated regardless of the amount of undissolved gas present. Second, the amount of undissolved gas present at an interface can influence cavitation inception. The extent to which this undissolved gas influences cavitation depends on the chemistry of the interface and the pressurization history.

The investigations show that it is difficult to correlate cavitation in a flowing system and in a vibratory apparatus and also misleading under certain conditions. With a flowing system, the cavity collapse and cavity inception regions are not superimposed but, at most, they overlap. Thus erosion damage of the surface is less likely to affect the surface chemistry of the interface in the inception region.

Research with head forms in the normal untreated water of water tunnels has shown that cavitation inception can be suppressed with surface treatment. This has been accomplished by changing the nature of the liquid-solid interface and by pressurizing the solid to reduce undissolved gas.

CONCLUSION

The theory of adhesion at a liquid-solid interface has been considered from several viewpoints. In the light of the available experimental data on cavitation originating at the interface, one conclusion seems particularly evident. Decreases in cavitation at an interface will result from a transformation of 3-phase equilibrium points to 2-phase equilibrium points. That is, the occurrence of a gas pocket at an interface represents a potentially weaker interfacial region than the liquid-solid interface itself. Any direct control of interfacial cavitation will be possible only when wetting or sealing of the surface pores, interstices, and crevices is accomplished on a microscopic scale.

With no difficulty at all, one can treat a surface and thereby change the magnitude of the flow parameters that produce cavitation. In the past, either intentionally or inadvertently, many of these changes promoted cavitation occurrence. Much of the nonreproducibility of test results, both within a laboratory and between laboratories, may very well be traceable to the conditions existing at the liquid-solid interface.

More complete surface wetting on a microscopic scale should be possible with methods other than those involving high pressures (as in the NSRDC investigation). Typical of methods that appear to offer promise are the following:

1. Increase the work of adhesion by the production of an electrical double layer at the interface using a polyphosphate coating (or other inorganic ionic coating).
2. Seal a surface with a gas-tight coating such as polyvinylalcohol.
3. Enhance the magnitude of the interfacial forces by coating the surface with colloidal silica.
4. Wet the surface with Dupont Freon TF ($\gamma = 19$ dynes/cm) or Dow-Corning 200 silicone fluid ($\gamma = 15.9$ dynes/cm, viscosity = 0.65 centistokes) and selectively remove with solvents soluble in water.

From a pragmatic point of view, the surface chemistry of the liquid-solid interface must be considered in future cavitation research. The unraveling of the unknown causes of the phenomena commonly referred to as "scale effects" may depend at least partially on a knowledge of surface chemistry. Predictability and control of cavitation will require systematic studies of the type advocated in this paper.

APPENDIX

STRUCTURE OF WATER

An investigation into the structure of a water molecule is particularly revealing when one is interested in the interaction at a water-solid interface. The molecules are held together by covalent bonds with the hydrogen atoms arranged on one side of the oxygen atoms as shown in Figure 5.

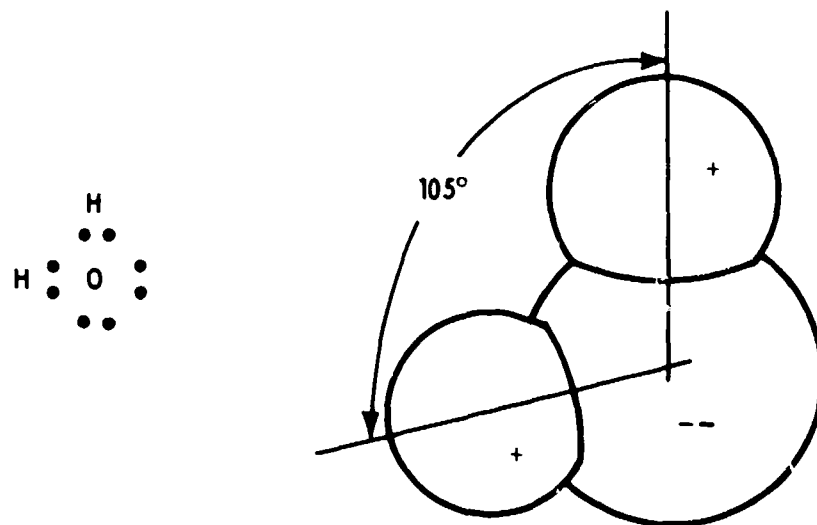
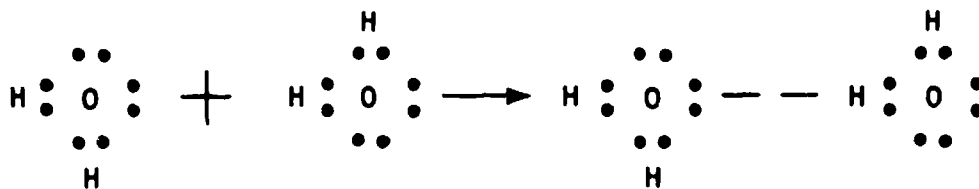


Figure 5 — Arrangement of Oxygen and Hydrogen Atoms in Water

This arrangement produces an unequal distribution of charges in the molecule, i.e., water molecules are polar. X-ray diffraction pattern studies of liquid water indicate that the molecules tend to associate or unite with each other.⁴¹ They form a loosely bound lattice that is pseudocrystalline in nature. This uniting of water molecules is due to the hydrogen bond. The bond is the result of the attraction of a positive hydrogen atom of one water molecule for some of the electrons of the oxygen atom of another water molecule. Although the hydrogen bond is stronger than the van der Waals attraction, it is weaker than the covalent bond. Two water molecules are united with a hydrogen bond as shown diagrammatically below,



with a dashed line indicating the bond. As water is heated, more and more of the hydrogen bonds are broken; finally in the vapor phase, there is essentially no bonding between the molecules. This means of bonding, over and above the normal van der Waals attraction, is in contrast to most other liquids that have no internal molecular arrangement.

REFERENCES

1. Lindgren, H. and Johnsson, C.A., "Cavitation Inception on Head Forms I.T.T.C. Comparative Experiments," Proc. Eleventh International Towing Tank Conference, The Society of Naval Architects of Japan, Tokyo (1966), pp. 219-232.
2. Holl, J.W. and Treaster, A.L., "Cavitation Hysteresis," Trans. American Society of Mechanical Engineers (ASME) Vol. 88, Series D. No. 1 (1936), pp. 199-212.
3. Acosta, A.J. and Hamaguchi, H., "Cavitation Inception on the I.T.T.C. Standard Head Form," California Institute of Technology Hydrodynamics Laboratory Report E-149.1 (Mar 1967).
4. Harvey, E.N. et al., "Bubble Formation in Animals; Physical Factors," J. Cellular and Comparative Physiology, Vol. 24 (1944), pp. 1-22.
5. Harvey, E.N. et al., "Removal of Gas Nuclei from Liquids and Surfaces," J. Am. Chem. Soc., Vol. 67, (1) (1945), pp. 156-157.
6. Harvey, E.N. et al., "On Cavity Formation in Water," J. Appl. Physics, Vol. 18 (1947), pp. 162-172.
7. Knapp, R.T., "Cavitation and Nuclei," Trans. ASME Vol. 80 (1958), pp. 1315-1324.
8. Pease, D.C. and Blinks, L.R., "Cavitation from Solid Surfaces in the Absence of Gas Nuclei," J. Physical and Colloid Chemistry, Vol. 51 (1947), pp. 556-567.
9. Adamson, A.W., "Physical Chemistry of Surfaces," Second Edition, Interscience Publishers, New York (1967).
10. Langmuir, I., "Colloid Symposium Monograph," The Chemical Catalog Company, New York (1925), p. 41.
11. Blodgett, K.B., "Films Built by Depositing Successive Monomolecular Layers on a Solid Surface," J. Am. Chem. Soc., Vol. 57 (1935), p. 1007.
12. Gibbs, J.W., "Collected Works," Longmans, Green, and Co., New York, (1928), p. 314.
13. Boyd, G.E. and Livingston, H.K., "Adsorption and the Energy Changes at Crystalline Solid Surfaces," J. Am. Chem. Soc., Vol. 64, (2) (1942), pp. 2383-2385.
14. Young, T., "An Essay on the Cohesion of Fluids," Philosophical Trans. Royal Society (London), Vol. 95 (1805), p. 65.
15. "Contact Angle, Wettability, and Adhesion," Advances in Chemistry Series, No. 43, edited by R.F. Gould, American Chemical Society, Washington (1964), "The Status of Contact Angle as a Thermodynamic Property," (A.W. Adamson and I. Ling), p. 57.
16. Dupre, A., "Theorie Mechanique de la Chaleur," Gauthier-Villars, Paris (1869), p. 369.
17. Bunshah, R.F., "Vacuum Metallurgy, Past, Present, and Future," Research/Development, Vol. 18, No. 10 (1967), p. 64.
18. "Aspects of Adhesion - 1," Edited by D.J. Alner, University of London Press Ltd. (1965), "Strength and Structure," (Allen, K.W.) p. 11.

19. Fowkes, F.M., "Attractive Forces at Interfaces," *Industrial and Engineering Chemistry*, Vol. 56, No. 12 (1964), pp. 40-52.
20. "Surfaces and Coatings Related to Paper and Wood," Syracuse University Press, Syracuse (1967), "Molecular Forces at Interfaces" (Fowkes, F.M.) pp. 99-125.
21. Zisman, W.A., "Influence of Constitution on Adhesion," *Industrial and Engineering Chemistry*, Vol. 55 (1963), p. 18.
22. Erb, R.A., "Wettability of Metals Under Continuous Condensing Conditions," *J. Physical Chemistry*, Vol. 69, No. 4 (1965), pp. 1306-1309.
23. Bewig, K.W. and Zisman, W.A., "The Wetting of Gold and Platinum by Water," *J. Physical Chemistry*, Vol. 69 (1965), p. 1238.
24. White, M.L. and Drobek, J., "The Effect of Residual Abrasives on the Wettability of Polished Gold Surfaces," *J. Physical Chemistry*, Vol. 70 (1966), pp. 3432-3436.
25. Fox, H.W. et al., "Wetting Properties of Organic Liquids on High Energy Surfaces," *J. Physical Chemistry*, Vol. 59 (1955), p. 1097.
26. "Contact Angle, Wettability, and Adhesion," *Advances in Chemistry Series No. 43*, Edited by R.F. Gould, American Chemical Society, Washington (1964) "Relation of Equilibrium Contact Angle to Liquid and Solid Constitution" (Zisman, W.A.) pp. 1-51.
27. Schonhorn, H. and Hansen, R.H., "Surface Treatment of Polymers for Adhesive Bonding," *J. Appl. Polymer Sci.*, Vol. 11 (1967), pp. 1461-1474.
28. Hoyt, J.W., "Wall Effect on I.T.T.C. Standard Head Shape Pressure Coefficients," *Proc. Eleventh International Towing Tank Conference, The Society of Naval Architects of Japan, Tokyo (1966)*, pp. 257-259.
29. Kerneon, R.W. et al., "Mechanism of Cavitation Inception and the Related Scale Effects Problem," *Trans. ASME*, Vol. 77 (1955), pp. 538-541.
30. van der Walle, F., "On the Growth of Nuclei and the Related Scaling Factors in Cavitation Inception," *Netherlands Ship Model Basin, Laboratory Memorandum No. V2, Wageningen (1963)*. See also *International Shipbuilding Progress*, Vol. 10, No. 106 (1963), pp. 195-204.
31. Bindel, S. and Lombardo, R., "The Effect of Water Speed and Air Content on Model Cavitation Inception," *David Taylor Model Basin Translation 823 (Apr 1966)*.
32. Edstrand, H., "Cavitation Tests with Model Propellers in Natural Sea Water with Regard to the Gas Content of the Water and its Effect Upon Cavitation Point and Propeller Characteristics," *Swedish State Shipbuilding Experimental Tank Publication 15, (1950)*.
33. Johnson, V.E. and Hsieh, T., "The Influence of Entrained Gas Nuclei Trajectories on Cavitation Inception," *Sixth Naval Hydrodynamics Symposium, Washington, D. C. (1966)*, p. 7-1.
34. Johnson, V.E. and Eisenberg, P., "Environmental and Body Conditions Governing the Inception and Development of Natural and Ventilated Cavities," *Proc. Eleventh International Towing Tank Conference, The Society of Naval Architects of Japan, Tokyo, (1966)*, pp. 171-181.

35. Ripkin, J.R., "Reduction of Cavitation Damage by Surface Treatment," University of Minnesota St. Anthony Falls Hydraulic Laboratory Project Report 81 (1966).

36. Poulter, T.C., "The Mechanism of Cavitation Erosion," J. Appl. Mech., Vol. 9, No. 1 (1942), pp. A31-A37.

37. Bernd, L.H., "Cavitation, Tensile Strength and the Surface Films of Gas Nuclei," Sixth Naval Hydrodynamics Symposium, Office of Naval Research, Dept. of the Navy (1966).

38. Bernd, L.H., "Study of the Surface Films of Gas Nuclei (as Related to Cavitation and Tensile Strength in Water), Part I, General Electric TIS Report No. 64GL143 (Sep 1964), Part II - General Electric TIS Report 66-C-164 (Jan 1966), Part III - General Electric Report S-67-1138 (May 1967), ONR Contract No. NONR-4296(00), administered by the Naval Ship Research and Development Center.

39. Bernd, L.H., "Sonar Cavitation Suppression," Vol. I: General Electric Co. (Mar 1963), DDC No. AD-107473; Vol. II: General Electric Co. (Sep 1964), DDC No. AD-108640, Navy Bureau of Ships Contract No. NOBSR-85237.

40. Rouse, H. and McNown, J.S., "Cavitation and Pressure Distribution, Head Forms at Zero Angle of Yaw," State University of Iowa, Studies in Engineering Bulletin 32 (1948).

41. Wood, J.H. and Keenan, C.W., "General Collect Chemistry," Harper and Brothers, New York (1957), p. 155.

UNCLASSIFIED

Security Classification

DOCUMENT CONTROL DATA - R & D		
(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)		
1. ORIGINATING ACTIVITY (Corporate author) Naval Ship Research and Development Center Washington, D. C. 20007		2a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED 2b. GROUP
3. REPORT TITLE CAVITATION ORIGINATING AT LIQUID-SOLID INTERFACES		
4. DESCRIPTIVE NOTES (Type of report and inclusion dates)		
5. AUTHOR(S) (First name, middle initial, last name) Frank B. Peterson		
6. REPORT DATE September 1968	7a. TOTAL NO. OF PAGES 39	7b. NO. OF REFS 41
8a. CONTRACT OR GRANT NO. b. PROJECT NO. S-R009 01 01 c. Task 0101 d.		9a. ORIGINATOR'S REPORT NUMBER(S) 2799 9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)
10. DISTRIBUTION STATEMENT This document is subject to special export controls and each transmittal to foreign governments or foreign nationals may be made only with prior approval of Naval Ship Research and Development Center, Code 500.		
11. SUPPLEMENTARY NOTES		12. SPONSORING MILITARY ACTIVITY Naval Ship Research and Development Center
13. ABSTRACT Cavitation occurring at the interface between a liquid and a solid is considered from the viewpoint of surface chemistry. The thermodynamics of the interface and the interfacial forces of attraction are reviewed. Emphasis is placed on those aspects that tend to suppress cavitation inception. Related past research is reviewed and evaluated using knowledge of the surface chemistry of the interface. It is concluded that cavitation inception can be suppressed by increasing the adhesion between the liquid and the solid and by reducing the amount of undissolved gas trapped on the solid surface.		

DD FORM 1473

1 NOV 65

(PAGE 1)

S/N 0101-807-6801

UNCLASSIFIED

Security Classification

UNCLASSIFIED

Security Classification

14 KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Cavitation - inception - surface properties Bubbles - nuclei Surface chemistry - adhesion						

DD FORM 1473 (BACK)
NOV 68

GPO 862-524

Security Classification