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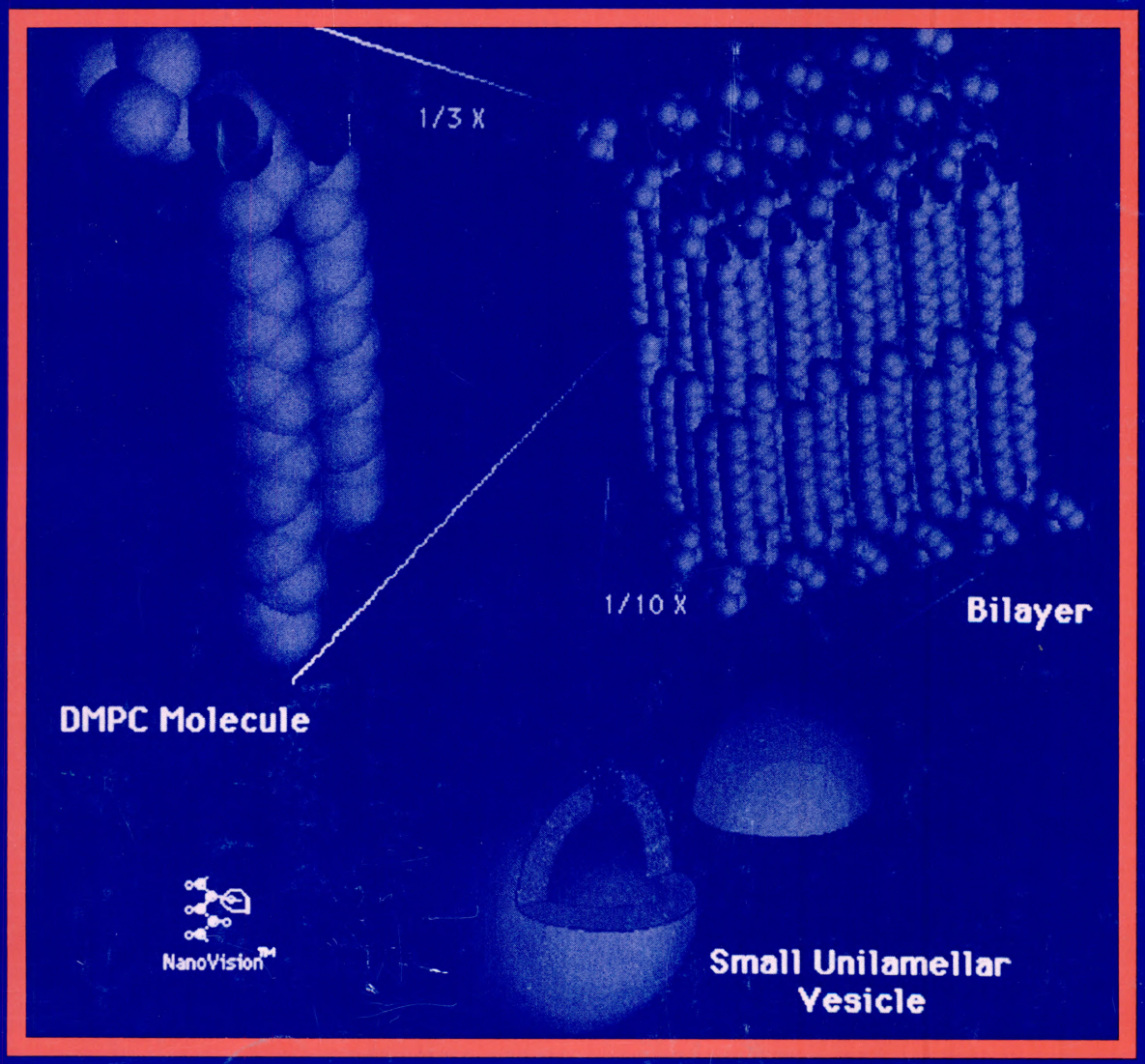

TRIESTE (DSV-1)

The bathyscaphe TRIESTE being loaded aboard the USS POINT DEFIANCE (LSD-31) by a crane in San Diego on April 15, 1963 for transport to Boston via the Panama Canal. The TRIESTE was transferred to the East Coast to investigate the sinking of the USS THRESHER (SSN 593), which she located on the second attempt.

The TRIESTE, designed and constructed by Professor Auguste Piccard, was launched near Naples, Italy, in 1953 and for four years operated in Mediterranean waters. In 1957, the Office of Naval Research (ONR) contracted with Professor Piccard for a series of dives to evaluate the craft. At the completion of all the tests, the craft was purchased by ONR as a research vehicle for the U.S. scientific community. When the Chief of Naval Research, RADM Rawson Bennett, purchased the TRIESTE, he paved the way for the beginning of U.S. involvement in deep submergence research. On January 23, 1960, after a complete overhaul the depth goal for the TRIESTE was reached when the vessel piloted by Lieutenant Don Walsh, USN, and Dr. Jacques Piccard, son of the designer, penetrated nearly seven miles straight down into the Challenger Deep. The verified depth was 35,800 feet, an established world's record.

In 1969, the TRIESTE with her support ship, WHITE SANDS (ARD-20), and tug, USS APACHE (AFT-67), investigated and photographed the wreckage of the USS SCORPION. Over the years, TRIESTE has been used for location and recovery operations, testing new electronic systems, and training dives. In 1977, TRIESTE was deployed for the Seafloor Geophysical Research Program sponsored by ONR and carried scientists to the ocean floor in the Cayman Trough, the Puerto Rico Trench, and the Blake-Bahama Outer Ridge. In 1980, the TRIESTE was retired to the Navy Museum at the Washington Navy Yard, Washington, D.C., where she is today.

As her title, (DSV-1), indicates, TRIESTE is the ancestor of hundreds of manned submersibles and remote operated vehicles currently exploring the oceans. In the last three decades since ONR purchased TRIESTE, the U.S. has become a leader in the designing, building and using of deep submergence systems.

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Computer-generated depiction of the levels of assembly of a phospholipid microstructure. Individual phospholipid molecules assemble into a bilayer which then folds to form a closed sphere called a liposome. See article on page 2.

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Design and Application of Lipid Microstructures

by Bruce Paul Gaber
Naval Research Laboratory

Applications of Lipid Microstructures

One of biotechnology's most exciting and rapidly growing research areas is *Lipid Microstructures*.* It is now possible to control – on a micron-scale – the assembly of certain natural biomaterials to form structures such as hollow spheres and long thin tubules (Figure 1). These microstructures are used in an increasing number of important technological applications[12], including:

- Red blood cell surrogates for casualty care[4,5,13,6,7,21]
- Targeted delivery of drugs in the treatment of cancer[14]
- Controlled release of antifouling agents[19]
- Active elements for biosensors[17]
- Composite materials[23]
- Electronic components[23]

The Center for Bio/Molecular Science and Engineering (CBMSE) at the Naval Research Laboratory (NRL) has been a leader in lipid microstructure research. For example, CBMSE pioneered the development of a red blood cell surrogate. Designed for combat casualty care, the material is prepared by encapsulation of the oxygen–carrying protein hemoglobin into spherical lipid microstructures called *liposomes*. Large volumes of sterile liposome encapsulated hemoglobin can now be prepared routinely and is being used for animal evaluations of efficacy and safety. [21]

A remarkable new class of lipid microstructures was discovered by Drs. Paul Yager and Paul Schoen of CBMSE[23]. Called lipid *"tubules"* (Figure 1), these microstructures can be hundreds of microns long and half a micron in diameter. They are thin-walled and hollow. A major technological breakthrough in the applications of tubules occurred when Mr. Ronald Price, Mr. Jacques Georger and Dr. Jeffrey Calvert discovered that tubules could be plated with thin films of metal[23]. This discovery permits the basic tubule architecture to be preserved, while rendering the microstructures extremely rugged. Metallized tubules are conductive and may be aligned in electrical and magnetic fields. This opens a range of potential applications in microelectronics (Eg., electromagnetic shielding and cold cathodes) and composite materials. An application of particular importance to the Navy is the use of tubules as the active component for anti-fouling paint. Mr. Price has prepared tubules thinly coated with copper that contain tetracycline in their hollow interior. These tubules have been incorporated into a paint base. Their anti-fouling efficacy currently is being compared with the copper oxide paints now in use. It is hoped that this use of lipid microstructures will yield the dual benefits of a longer duty cycle for the anti-fouling coating and reduced environmental toxicity.

* Terms in italics are defined in the glossary at the end of article.

Molecular Design Of Lipid Microstructures

Our research strategy for lipid microstructures consists of three broad elements: 1) Molecular Design — which employs theory and molecular modeling techniques to understand how lipids form microstructures and to suggest lipids with unique properties; 2) Molecular Fabrication — the application of synthetic organic chemistry for preparation of the lipids proposed by the results of molecular design; 3) Microstructure Fabrication — the actual formation and characterization of lipid microstructures. This strategy demands that we have a clear understanding of the nature of the molecules with which we are working. Thus, with ONR support, CBMSE has developed an active research program to model the molecular structures of lipids and their microstructures[10, 11].

What, then, are *lipids* and why do they form microstructures? We are all familiar with biomolecules such as proteins and DNA: they are the stuff of life, providing the catalysts for biochemical reactions and the genetic materials for all living things. Lipids are another class of biomolecule, whose function, though less glamorous, is no less important. These low molecular weight, water-insoluble compounds form the barrier which we call the *cell membrane* and as such delineate the cell's inside from its outside.

Lipids *self-assemble* to form membranes as a result of a molecular property called *amphiphilicity*. That is one portion of the lipid molecule has the propensity to dissolve in water while another portion prefers a non-polar (hydrocarbon) solvent. An example of an amphiphillic molecule is the *phospholipid* known as *DMPC* (Figure 2). The molecule consists of two regions: 1) A water-soluble *polar head group* and; 2) *acyl chains*, hydrocarbon in nature and naturally water-avoiding. These opposing characteristics are balanced

Figure 1:

Electron micrographs depicting two forms of lipid microstructures. A) Liposomes; B) Lipid tubules. Magnifications: (1a = 16,000x; 1b = 10,000x)

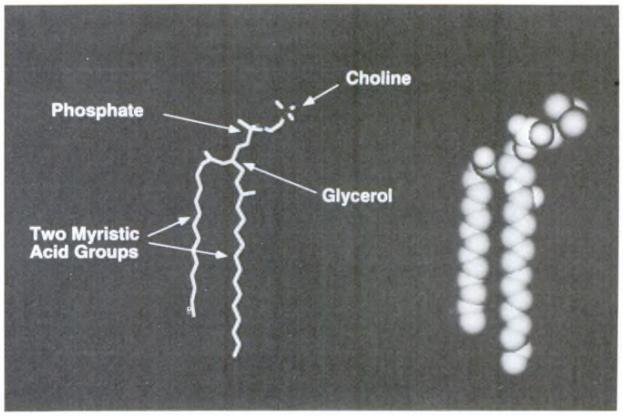


Figure 2:

Computer-generated molecular model of the lipid DMPC. The backbone of the molecule is glycerol to which two myristic acid chains are esterified. A phosphodiester links a choline moiety to glycerol.

by assembly into lipid microstructures[15]. The acyl chains cluster together to avoid contact with water, while the headgroups optimize interaction with water. The resulting lipid bilayer is the fundamental structural element of the cell membrane. The same physicochemical forces which drive lipids to assemble spontaneously to form cell membranes are at work outside of the biological milieu, forming what we have termed lipid microstructures.

Computer-aided molecular graphics permit us to construct models of molecules for which we have detailed structures as well as those for which structural data is incomplete. Some of these models will be proven incorrect. Nonetheless they inevitably provide a stimulus to our thinking and a basis for the design of experiments. While much of our molecular modeling has been done using dedicated graphics computers and software, Dr. William Light of NRL, has developed NanoVision™, a powerful desktop molecular graphics program for the Macintosh personal computer[16]. Using NanoVision we can quickly depict essential aspects of lipid structure. Many of the features of dedicated graphics computers are available with NanoVision. These include several styles of molecular representations such as skeletal, ball-and-stick, van der Waals, and CPK depictions. Multiple windows may be used to display several different structural aspects simultaneously. Images may be rotated and translated with the mouse or by keyboard command. Using the Macintosh II, up to 256 screen colors are available. The essential features of NanoVision are described further in the appendix of this paper.

We have developed a simple system, which we call the *Taxonomy of Lipid Assembly* as an organizational aid to our thinking about lipid microstructure formation. Unlike traditional methods of lipid categorization which rely on relative

solubility in water[26], the Taxonomy emphasize molecular interactions. The preliminary scheme distinguishes three levels of lipid interaction: **alpha, beta and gamma**. Each Level is defined by characteristic molecular interaction: Alpha's interactions are intermolecular, Beta is short-range intramolecular and Gamma is long range. The Taxonomy describes examples of the interaction, the forces governing the interactions, and their structural consequences. For example a characteristic of Alpha interaction is amphiphilicity. Beta represents localized interactions such as those of lipid with lipid, or lipid with protein. Examples of Beta interactions include the packing of lipid chains and the interaction of lipid headgroups with water. Gamma interactions are those which give rise to formation of bilayers and assembly into microstructures

Now, using the concept of taxonomy of lipid assembly as a guide and NanoVision for molecular depiction, we can look more closely at lipid molecules and the microstructures formed from them.

Alpha Interaction

The elements of lipid Alpha interactions for an individual lipid were introduced above in our brief discussion of the amphiphilicity of the DMPC molecule. However, it is the diversity of headgroup and acyl chain chemical functionality which typifies the Alpha level. Several common variations in polar headgroup are shown in Figure 3. The galactose-containing cerebrosides are important constituents of brain tissue; while the ethanolamine lipids are a major constituent of red blood cell membranes. The ethanolamine headgroup is particularly important for biotechnology because it is chemically reactive and provides a convenient point for anchoring proteins to the microstructure surface. Working in collaboration with colleagues at Georgetown University Medical School we have developed procedures for efficiently coupling proteins to the ethanolamine headgroup[1]. These methods permit antibody molecules to be coupled to the surface of a lipid microstructure, providing the basic unit for high-sensitivity immunosensor[9].

Like the headgroups, there is considerable Alpha level diversity for acyl chains. They may be composed entirely of single carbon-carbon bonds *(saturated)* or contain one or more double or triple bonds *(unsaturated)*. Lipids containing chains with multiple unsaturation are called *polyunsaturated* and are thought to play a role in reducing serum cholesterol levels. Other aspects of Alpha level chain diversity include branched chains and those containing cyclopropyl groups.

An interesting, and very useful, example of chain unsaturation is the lipid we call $DC_{8,9}PC$ (Figure 4). Alpha assembly of $DC_{8,9}PC$ is distinguished by a pair of acetylenic (triple) bonds midway along the 23 carbon chain. This diacetylenic lipid has the important property of being polymerizable. Thus microstructures formed from $DC_{8,9}PC$ and similar lipids may be useful for applications in harsh environments. It is the diacetylenic lipids which, at the Gamma level, form tubule microstructures. Since the crystal

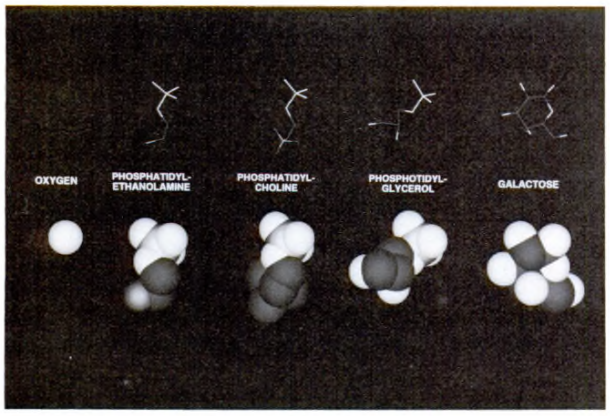


Figure 3:

Common headgroups found in phospholipids. Skeletal and van der Waals representations as well as side and top views are shown

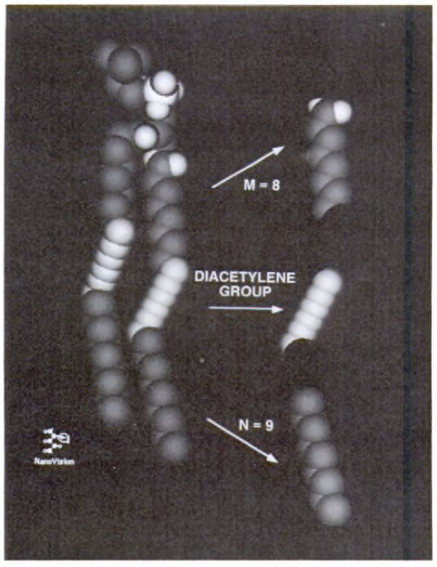


Figure 4:

The polymerizable lipid $DC_{8,9}PC$. A pair of conjugated triple bonds are located approximately midway along each of the 23 carbon chains.

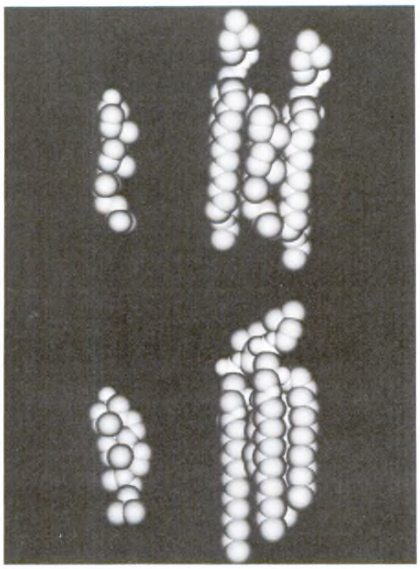


Figure 5:

Cholesterol (left) and cholesterol-DMPC complex (right). Side and front views shown.

structure of $DC_{8,9}PC$ has not been determined yet, our molecular graphics depiction[16] is based upon our knowledge of the structures of lipids with roughly similar Alpha characteristics such as DMPC. Here molecular graphics has been used to suggest a plausible structure and to provide a guide to the chemical intuition of the investigator.

It would be remiss to leave the impression that all lipids are phospholipids. An immensely important family of lipids is formed from *cholesterol* (Figure 5). The family includes the sex hormones (androgens and estrogens) and the corticosteroids such as cortisone. Cholesterol actually constitutes about half of the lipid in a cell membrane. Cholesterol's alpha interaction is characterized by four fused carbon rings and a short aliphatic tail. Because a hydroxyl group resides on the first ring, cholesterol, like phospholipids, is amphiphillic. The amphiphillic character determines the nature of the Beta interaction (see below) of cholesterol (Figure 5) with phospholipids. Neutron and X-ray diffraction data[8] suggest that the hydrophobic portion of cholesterol is immersed in the acyl chains of the phospholipids, while the hydroxyl group forms a hydrogen bond with a carbonyl oxygen of the phospholipid. These data have been used to construct the model in Figure 5.

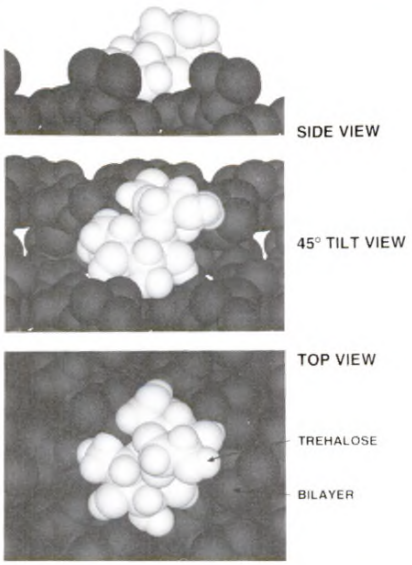


Figure 6:

Model of a possible mode of interaction of trehalose with the DMPC bilayer.

Beta Interaction

Earlier Beta interactions were defined as those which involve short-range intramolecular effects such as the interaction of lipid with lipid, or lipid with other molecules. An example of the lipid-lipid Beta interaction is the interaction of cholesterol with phospholipids described above. Equally important are the interactions of lipids with other molecules such as drugs, peptides and proteins.

One of the most important of these Beta interactions is that of water with phospholipid headgroups. Water

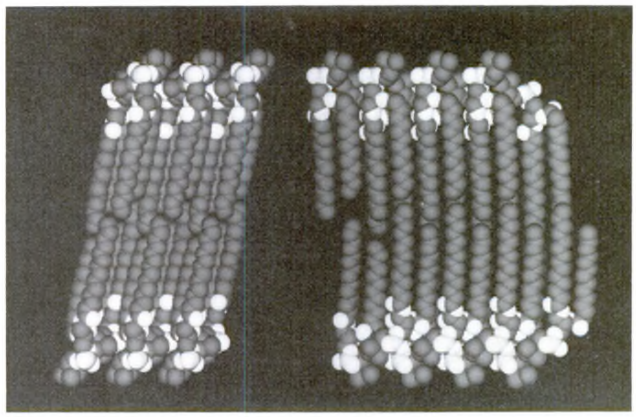


Figure 7:

Molecular graphics representation of the structure of the DMPC bilayer. The model is derived from x-ray crystallographic data[18].

molecules form strong hydrogen bonds with oxygen atoms attached to headgroup phosphorus. An extensive network of such hydrogen bonds serves as a major stabilizer of bilayer structure. In the absence of water biological membranes become unstable. Yet many living organisms (eg. plant seeds, brine shrimp, and yeast) undergo periods of extreme dehydration and enter an *anhydrobiotic* state, from which they regain full function upon rehydration.

What protects an organism during dehydration? One postulated molecular mechanism[3] involves membrane stabilization and may be regarded as an aspect of Beta interaction. Several organisms (yeast among them) synthesize copious amounts of the disaccharide *trehalose* when they begin to dehydrate. Experimental evidence[3] indicates that trehalose substitutes for water as a stabilizer of the bilayer. Molecular modeling done by Dr Indiria Chandrasekhar, a visitor to our laboratory from the Indian Institute of Science, offers a possible explanation as to why disaccharides (and not monosaccharides such as glucose) can stabilize a lipid bilayer[2]. Dr. Chandrasekhar's model (Figure 6) suggests that hydrogen bonds form from both rings of the disaccharide. The hydrogen bonds from one ring form with two lipids along a single row of lipid molecules. Hydrogen bonds from the second ring link to a molecule in the next row over. Thus trehalose forms a bridge crossing three rows of the bilayer. Glucose, which has only one ring, can form hydrogen bonds, but cannot form the stabilizing bridge.

The trehalose-lipid model was the first to use molecular modeling for an exploration of the interaction of small molecules with lipid bilayers. However interactive molecular graphics is only a starting point for further studies. Dr. Barbara Rudolph (Georgetown University) and Dr. Mark Nagumo (NRL) have taken the basic sugar-lipid complex, and subjected it to energy minimization refinement on the Cray supercomputer[22]. They also extended the study to include sucrose and glucose. The task required that development of many new atomic parameters for the lipids and sugars. Since the original interactive models were already at a local energy minimum, the energy minimization did not produce drastical changes in the complexes, but had the effect of shortening most of the hydrogen bonds. The significance of the work resides in the knowledge we have gained about applying molecular mechanics techniques to lipid systems.

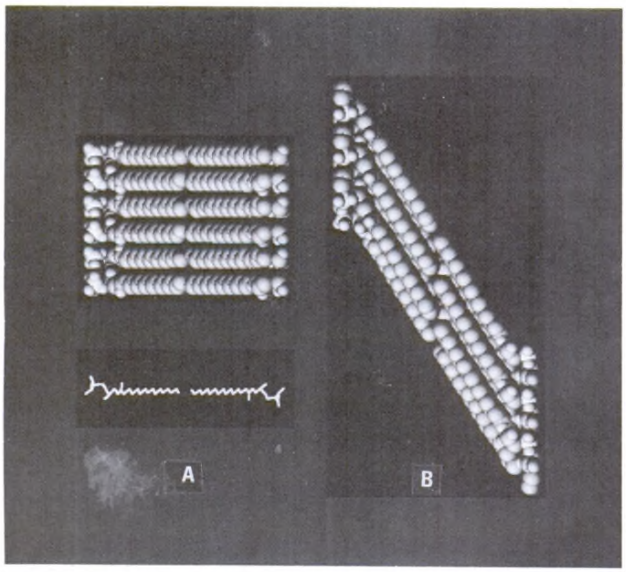


Figure 8:

Bilayer formed by LPPE.

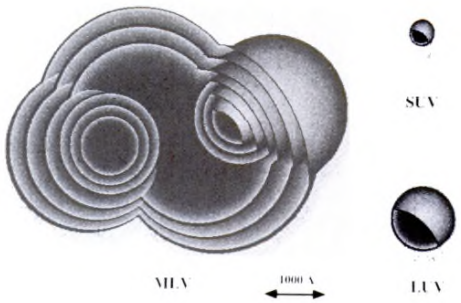


Figure 9:

Computer-derived model of a large multilamellar liposome and of a liposome containing a single bilayer.

Molecular modeling studies of sugar-lipid interactions has its practical significance in developing methods for protecting lipid microstructures in the absence of water. For example Dr. Alan Rudolph of CBMSE has done pioneering work on the use of trehalose to preserve liposome encapsulated hemoglobin during freeze-drying[20]. If routine freeze-drying can be accomplished, it may be possible to store the NRL developed red blood cell surrogate almost indefinitely.

Gamma Interaction

The lipid bilayer itself is a common example of Gamma interaction. Again, DMPC provides our initial example (Figure 7). Note the close van der Waals contact of each headgroup and each acyl chain with its neighbor. The end of an acyl chain from one monolayer abuts with a chain from the opposing monolayer. Viewed along one direction (Figure 8-a), the chains are parallel to the bilayer normal, but when we rotate the view by 90 degrees (Figure 8-b) we see that the

chains are not perpendicular to bilayer plane, but are actually tilted by about 12 degrees to the bilayer normal. Chain tilt results when the cross sectional area of the headgroup exceeds that of chains themselves. The tilt increases the effective chain area projected normal to the bilayer surface, thus permitting a close-packed Gamma interaction.

While the DMPC bilayer may be typical, bilayers of different lipids are by no means identical. For example examination of the structure of lysophsophatidylethanolamine (LPPE) (Figure 8) reveals a different aspect of Gamma interaction. LPPE is a *lysolecithin*, a phospholipid whose alpha assembly is characterized by one acyl chain rather than two. There now exists a considerable disparity in headgroup area versus chain cross sectional area. As a consequence the single chains pack with a net tilt of 60 degrees. Furthermore the chains do not abut; rather they are actually fully interdigited. Because of the interdigitation in the LPPE structure, this lipid might be an ideal starting point for the design of a very sturdy bilayer. It is just these factors which we seek, as we develop a knowledge base of lipid structures for molecular design.

The balancing of molecular forces which begins with the packing of individual lipids to form bilayers continues until the exposed hydrocarbon edges of the bilayer are removed from contact with water by folding into an actual microstructure. Among the most important and thoroughly studied of these microstructures are the *liposomes*. Large multilamellar liposomes (Figure 9) form spontaneously upon hydration of most phospholipids. These liposomes are characterized by an onion skin-like multiplicity of closed bilayers. Ultrasonication or high pressure extrusion of a suspension of multilamellar liposomes results in liposomes with a single bilayer. The diameter of these liposomes is determined by the preparative method and may range from 100-500 nm. Liposomes' large internal volume make them extremely useful "molecular bags" for applications such as the red blood cell surrogate and immunosensor developed at NRL.

Under certain conditions of temperature and solvent, lipids such as $DC_{8,9}PC$ form tubule microstructures (Figure 1) rather than spherical liposomes. We have only recently begun the molecular modeling required to understand this process. However Dr. Alok Singh, an organic chemist in BME, has learned[24] that the specific morphology of the tubules is a critical function of the lipid headgroup chosen. For example, substitution of a choline headgroup with a smaller hydroxy ethanol headgroup results in "licorice sticks"; tight tubules with a pronounced helical spiral (Figure 10). Here we see clearly the interplay of Alpha interaction (headgroup) with Gamma (microstructure morphology).

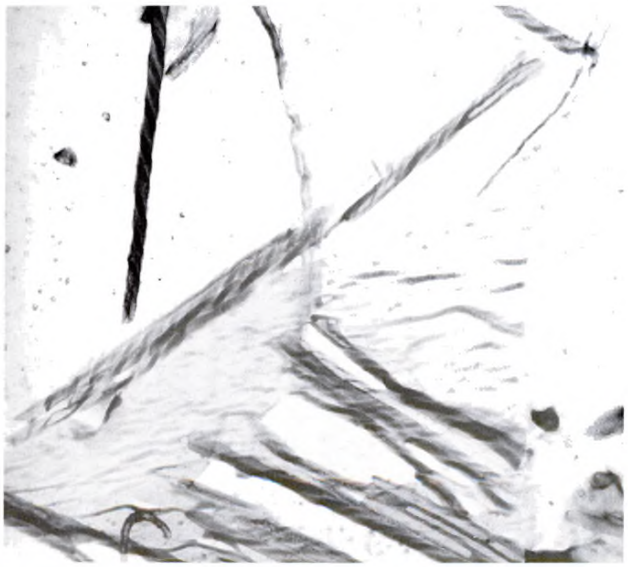


Figure 10:

Electron micrograph of tubules formed from a lipid with hydroxyethanol substituted for the bulkier choline headgroup. The tubules have a diameter of approximately 0.12 microns. Note the pronounced helical ridges which give the structure the appearance of a licorice stick. Magnifications = 16,000x.

Summary

Lipid microstructures are finding an increasingly important role in meeting the technological needs of the Navy and the Nation. We have applied molecular modeling tools to develop a rational approach to the design and fabrication of lipid microstructures.

Acknowledgement

All of the computer images were realized by William R. Light III using NanoVision™. Brian Kahn prepared the electron micrographs.

Much of this work was supported by ONR's Molecular Biology Program within the Division of Biological Sciences. We thank Dr. Michael Marron for his continued support and interest in our effort to extend modern molecular modeling techniques to lipid systems. Additional support has come from the NRL Core Program in Molecular Design of Microstructures.

Biography

Dr. Bruce Paul Gaber is Deputy Head of the Center for Bio/Molecular Science and Engineering at the Naval Research Laboratory. His research interests include the application of molecular modeling techniques to problems of biomembrane structure and function. He is currently writing a book for Academic Press entitled *Lipids – A Structural Atlas*.

Appendix

NanoVision™ — Molecular Graphics for the Rest of Us

Our initial work on the molecular graphics of lipid structures was conducted on dedicated graphics computers such as the Evans & Sutherland PS330 and the Silicon Graphics Iris 3030. These machines, and the software packages which run on them, are unquestionably extremely powerful. However, they have their drawbacks. Computer and software are expensive; out of reach, or at least of limited accessibility for many small laboratories. In part because of their power, dedicated graphics computers are not easy to learn to use or particularly "user-friendly". Finally, dedicated graphics computers do not support the range of desktop publishing applications which are becoming increasingly important in scientific communication. Our goal with NanoVision is the development of a low cost, easy to learn, desktop molecular graphics package for the individual scientist which has very nearly the power of a dedicated system as well as new features not available on large machines.

NanoVision is written specifically for the Apple Macintosh line of computers. The Macintosh was chosen because of its powerful graphics-oriented environment, large amount of addressable memory, and ease of use. Our foremost design criterion has been that the program (written in Pascal) meticulously follow established Macintosh programming rules. This assures compatibility within the complete line of Macintosh hardware and with all other properly-written applications. As a consequence of this approach, NanoVision runs on the Mac Plus or Mac SE (in black and white) and on the Mac II (256 colors). Applications compatibility assures that NanoVision images can be easily transferred (cut and paste) to word processors, presentation graphics packages such as Macdraw or Macpaint and animation programs such as Videoworks. NanoVision is designed to be straightforward and intuitive. We wanted a program with which a novice or casual user could quickly do molecular graphics. Consequently the program maintains an uncluttered screen and makes extensive use of pull-down menus and mouse control of images. NanoVision has the look and feel of a typical Macintosh application.

Many of the display features of dedicated molecular graphics computers are available with NanoVision. These include various molecular representations such as skeletal, ball-and-stick, van der Waals, and CPK depictions. Multiple windows may be used to display several different structural aspects simultaneously. Images may be rotated and translated with the mouse or by keyboard command. Shading with 256 screen colors are available from a palette of 4 million colors using an exclusive pallet manager.

Glossary

Acyl Chains:
Long fatty acid (hydrocarbon) chains of di- and triglycerides.

Amphiphilicity:
From the Greek: literally " both loving". Lipids usually have both a water soluble and an organic-soluble domain; hence they "love both" water and organic phases. We are familiar with this property from the action of soaps and detergents. These materials function because they are water-soluble at one end, and fat soluble at the other. Hence grease can be solubilized and washed away with water.

Anhydrobiosis:
Literally "life without water"

Bilayer:
An aspect of lipid Gamma interaction characterized by a tail-to tail arrangement of the lipids.

Cell membrane:
The barrier defining the inside and outside of a living cell. The major structural component of the cell membrane is the lipid bilayer. About half the actual material comprising the membrane is protein.

Cholesterol:
A highly water-insoluble lipid formed from fused rings and a hydrocarbon tail.

DMPC:
Dimyristoylphosphatidylcholine. A phospholipid whose Alpha interaction is characterized by two fourteen carbon acyl chains (myristic acid) and a choline headgroup.

$DC_{8,9}PC$:
A phospholipid similar to DMPC, in which the acyl chains are 23 carbons long and contain a pair of conjugated triple bonds mid-way along the chain.

Lipids:
Class of water-insoluble biomolecules. Among this large class of compounds are phospholipids (often called lecithins), cholesterol and its derivatives (such as steroids), di-and triglycerides, fats (and their salts, the soaps), and biomodulators such as prostaglandin.

Lipid Microstructures:
Microscopic structures formed from self-assembly of lipid molecules.

Liposomes:
An aspect of lipid gamma interaction characterized by closed bags or spheres made up of one or more lipid bilayers.

LPPE:
Lysopalmitoylphosphatidylethanolamine

Lysolecithin:
A phospholipid which has lost one acyl chain.

phospholipid:
A lipid characterized by one or more acyl chains and a phosphodiester linkage to a polar headgroup.

Polar Headgroup:
The water-soluble, often charged, region of phospholipids.

Polyunsaturated:
Containing multiple double or triple carbon-carbon bonds.

Self-Assembly:
Process of spontaneous aggregation of molecules to form larger macromolecular structures.

Taxonomy of Lipid Assembly:
A hierarchical characterization concerned with the evolution of organization in lipid systems.

Tubules
Long hollow cylindrical lipid microstructures.

Saturated
Containing no double or triple bonds (ie "saturated" with hydrogen).

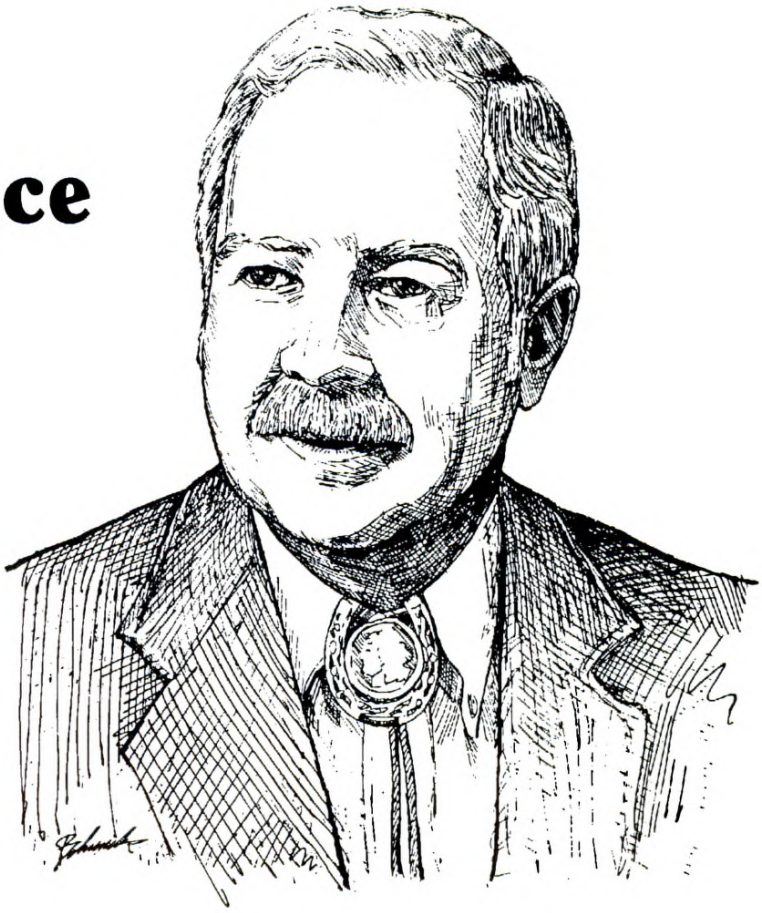
Trehalose:
A disaccharide formed from two glucose molecules. Trehalose stabilizes certain phospholipid bilayers and natural membranes in the absence of water.

Unsaturated:
Containing one or more double or triple bonds.

References

1. Bredehorst, R., F. S. Ligler, A. W. Kusterbeck, E. L. Chang, B. P. Gaber and C.-W. Vogel. Effect of Covalent Attachment of Immunoglobulin Fragments on Liposomal Integrity. Bioch. **25**: 5693-5698, 1986.
2. Chandrasekhar, I. and B. P. Gaber. Stabilization of the Bio-Membrane by Small Molecules: Interaction of Trehalose with the Phospholipid Bilayer. J. Biomol. Struct. Dyn. **5**: 1163-1171, 1988.
3. Crowe, L. M., J. H. Crowe and D. Chapman. Preservation of Membranes in Anhydrobiotic Organisms: the Role of Trehalose. Science. **223**: 701-703, 1984.
4. Farmer, M. C. and R. Beissinger. Scaled-Up Production of Liposome-Encapsulated Hemoglobin. : 1988.
5. Farmer, M. C. and R. Beissinger. Blood Substitute Comprising Liposome-Encapsulated Hemoglobin. : 1989.
6. Farmer, M. C. and B. P. Gaber. "Liposome-Encapsulated Hemoglobin as an Artificial Oxygen Carrying System." Methods in Enzymology. Green and ed. 1987 Academic Press. New York.
7. Farmer, M. C., S. A. Johnson, R. L. Beissinger, A. B. Lynn and K. A. Carter. "Liposome-Encapsulated Hemoglobin: A Synthetic Red Cell." Biotechnological Applications of Lipid Microstructures. Gaber, Schnur and Chapman ed. 1988 Plenum Press. New York.
8. Franks, N. P. Structural Analysis of Hydrated Egg Lecithin and Cholesterol Bilayers. I. X-Ray Diffraction. J. Mol. Biol. **100**: 345, 1976.
9. Gaber, B. P., R. Bredehorst and F. S. Ligler. "Liposome-Based Immunoassays for Detection of Small and Large Molecules." Biotechnological Applications of Lipid Microstructures. Gaber, Schnur and Chapman ed. 1988 Plenum Press. New York.
10. Gaber, B. P., I. Chandrasekhar, M. Nagumo and N. Pattabiraman. "Molecular Modeling of the Phospholipid Bilayer." Biotechnological Applications of Lipid Microstructures. Gaber, Schnur and Chapman ed. 1988 Plenum Press. New York.
11. Gaber, B. P., W. R. Light III and R. M. Brown. Molecular Graphics of Lipid Structure. J. Mol. Graph. **6**: 212-213, 1988.
12. Gaber, B. P., J. M. Schnur and D. Chapman. Biotechnological Applications of Lipid Microstructures. **238**: 397, 1988.
13. Gaber, B. P., P. Yager, J. P. Sheridan and E. L. Chang. Encapsulation of Hemoglobin in Phospholipid Vesicles. FEBS Letters. **153**: 285-90, 1983.
14. Gregoriadis, G. "Targeted Drug Delivery: Optimization Strategies." 1989 Plenum Publishers. New York.
15. Israelichvili, J. N., D. J. Mitchell and B. W. Ninham. Theory of Self-Assembly of Hydrocarbon Amphiphiles into Micelles and Bilayers. Faraday Discuss. Chem Soc. **72**: 1525, 1976.
16. Light, W. R., C. R. Vinayaka and B. P. Gaber. Approaches to Computer Graphics of Lipid Structures. Biophys. J. **55**: 139a, 1989.
17. Ligler, F. S., R. Bredehorst, A. Talebian, L. C. Shriver, C. F. Hammer, J. P. Sheridan, C. W. Vogel and B. P. Gaber. A Homogeneous Immunoassay for the Mycotoxin T-2 Utilizing Liposomes, Monoclonal Antibodies and Complement. Anal. Bioch. **163**: 369-375, 1987.
18. Pearson, R. H. and I. Pascher. The Molecular Structure of Lecithin Dihydrate. Nature. **281**: 449-50, 1979.
19. Price, R. R. and R. F. Brady. Fouling Control Using Tubule Encapsulation of Toxicants. U. S. Patent Appl. Navy Docket # 71-593. : 1989.
20. Rudolph, A. S. and R. O. Cliff. Preservation of the Blood Substitute Liposome Encapsulated Hemoglobin by Freeze-Drying. J. Cryobiol. **submitted**: 1989.
21. Rudolph, A. S., R. Rabinovici and G. Feuerstein. Characterization on Hemodynamic, Hematologic and Biochemical Responses to Administration of Liposome Encapsulated Hemoglobin in the Conscious Freely Moving Rat. J. Circl. Shock. : 1989.
22. Rudolph, B. R., M. Nagumo, I. Chandrasekhar and B. P. Gaber. Molecular Modelling of Saccharide-Lipid Interactions. Chem. Phys. Lipids. **Submitted**: 1989.
23. Schnur, J. M., R. Price, P. Schoen, P. Yager, J. M. Calvert, J. Georger and A. Singh. Lipid-Based Tubule Microstructures. Thin Solid Films. **152**: 181-206, 1987.
24. Singh, A. and S. Marchywka. Synthesis and Characterization of Head Group Modified 1,3 Diacetylenic Phospholipids. Polym. Mat. Sci. Eng. : 1989.
25. Singh, A. and J. M. Schnur. A General Method for the Synthesis of Diacetylenic Acids. Synth. Comm. **16**: 847-852, 1986.
26. Small, D. H. "The Physical Chemistry of Lipids: From Alkanes to Phospholipids." Handbook of Lipid Research. Hanahan ed. 1986 Plenum P.

Profile in Science



Dr. James O'Brien is the Secretary of the Navy Professor in Meteorology and Physical Oceanography at the Florida State University, Tallahassee, Florida. The Office of Naval Research recently designated him as an ONR Distinguished Educator. In this new role, he will train Ph.D's in mathematics and physics to be ocean modelers. Many of his M.S. and Ph.D students and postdoctoral research assistants either work for the Navy at the Naval Oceanographic and Atmospheric Laboratory (NOARL), Naval Oceanographic Office (NAVOCEANS), the Supreme Allied Commander Atlantic (SACLANT), or teach at various universities. He has graduated 20 Ph.D's and trained 15 postdoctoral assistants since 1970 when he received his first research contract from ONR. Recently the Navy has sent officers to receive M.S. degrees under O'Brien at FSU. In the mid-70's, he came to Washington to be the Program Director for Physical Oceanography at ONR.

His research has spawned a unique and efficient mathematical type of numerical model for upper ocean currents, now commonly called the FSU ocean modelling technique. These fine horizontally resolved wind-driven models have been used to explain the seasonal and interannual variability of upper ocean currents in each ocean basin by O'Brien and his ex-students. The NOARL Global Circulation Model is based on this model formulation.

In 1987, O'Brien was awarded the Sverdrup Gold Medal by the American Meteorological Society. He has been selected a Fellow the American Meteorological Society, the American Geophysical Union (AGU), the American Association for the Advancement of Science and the Royal Meteorological Society for his research on understanding how intense cyclones effect the ocean, understanding and forecasting the oceanic aspects of El Nino and explaining the interannual variability of the equatorial Pacific and Indian Oceans. He has published over 100 papers and edited several oceanographic technical books and journals. He has been the President of the Oceanographic Section of AGU. He is currently the President of the International Association of the Physical Sciences of the Ocean. He has served on or directed numerous committees of the National Academy of Sciences. He completed a 6 year stint as Chief Editor of the *Journal of Geophysical Research, Oceans*, in 1989.

Transition Issues Associated with the Development of the *Li/SOCl2* Battery Technology

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The period for a typical R&D project, from inception to production is from 5 to 10 years, depending on the maturity of technology at the point of project initiation, the complexity of the system and the specific design requirements; although occasionally longer periods may be required. Present day fiscal constraints, military considerations (*e.g.*, the fear of obsolescence of hardware) and international competition place great demands on scientists and engineers to accelerate and optimize development programs. Since the almost exponential growth of funding of the past decades has leveled off, much greater effort must be exercised to match opportunities presented by scientific inquires with requirements of applications. One way to accomplish this objective is through a smooth and expeditious transition from the concepts of fundamental research to specific technology issues and into the construction of engineering models. To achieve such a transition requires the identification and solution of problems, both technical and procedural, impeding the process. We present here a synopsis of the development of the *Li/SOCl2* battery technology and use this development as an example to emphasize both positive and negative aspects of the transition process.

The *Li/SOCl2* battery development is an excellent example because it illustrates two important points. First, a significant technological advancement was born unexpectedly as a "spin-off" from fundamental research; a result, which in itself confirms the value of a fundamental technology-base research program. Second, it brings into focus consequences of an attempt to parallel research and engineering, *i.e.*, to accelerate the development by producing an engineering model without adequately solving the underlying technical problems and fully utilizing the power of rational transition.

Historically, the *Li/SOCl2* technology originated from a small Office of Naval Research (ONR) contract on new concepts in liquid lasers; a concept quite unrelated to battery technology. The careful analysis of the processes observed led to the discovery and the construction of this powerful battery

system. It possesses the highest energy density of any commercially produced battery and is a leading contender for numerous military applications. Largely as a result of the latter, an intense development effort, both in this country and abroad, has been undertaken to provide the needed power sources. Some of these efforts are nearing completion, whereas others are still on-going. Among the latter is the development of a high discharge rate battery. It is upon this development activity that we focus our attention relative to the transition process.

Concept of a Transition

Transition is defined as a passage or evolution from one stage to another. It is not a one-step process; rather, it consists of a set of events that can be illustrated by a donor-acceptor concept. For the transition to occur, ideas or results generated within the context of activities of one stage must satisfy the constraints imposed by the next stage. The nature of these constraints may vary from case to case, but, in general, they can be reduced to human factors, including management philosophy, and technical considerations. The transition process is completed when a kind of equilibrium is reached whereby conflicting interests are satisfied. But equilibrium conditions cannot be satisfied unless the issues are clearly defined. Using the analogy of a pendulum, an oscillatory behavior of ever decreasing amplitude is sought by identifying and dealing with driving forces as well as the opposing factors. In practice, we are confronted with reaching a compromise between requirements, specifications, and private interests.

Before discussing the factors affecting the transition process, we should consider the scope of each category of activities. Research, broadly defined, includes investigations aimed at discovery and/or interpretation of facts, revision of existing theories in light of new facts and the practical application of such facts. The dominant feature of pure research is in seeking an extension of knowledge for its own sake. Applied research, on the other hand, examines the use of new theories and observations for practical ends. Its prime interest is to identify the technology issues and propose their reduction to practice. The transition process provides the necessary coupling even though the boundary between them is quite nebulous. On the other hand, the boundary between applied research and development is, generally, better defined. In particular, the developmental phase of the transition process is the conversion of the technology into a product which, at a minimum, demonstrates the practicality of the technology.

Factors affecting the transition process are not exclusively of a technical nature. The attitudes of individuals and the infrastructure of the performing or supporting organization may either facilitate or hinder a transition. Individual attitudes can include boredom, zeal and proprietary, as well as genuine, interest in expeditious development. Obviously, the latter is no problem as long as it does not advance overzealousness. Boredom is often encountered: Many researchers lose interest in a problem once a solution has been identified or a feasibility demonstrated. In this case, care must be taken to maintain sufficient interest without excessive zeal which might inhibit the transition process by pursuing technology beyond the point necessary for a smooth transition. The situation may be further aggravated by the proverbial arrogance of which scientists are often accused. Obviously, such perception is counter-productive. There is a natural tendency for individuals and, collectively, organizations to favor technologies discovered or proposed from within. Alternatively, individuals or organizations may seek to pursue the development produced from within, even though others are better equipped to affect the transition. The merits of technological advancement and professional judgement often surrender to misplaced priorities and decisions made long in the past. Proper organizational infrastructure and attitude can prevent these becoming issues.

Mechanism of Transition.

A conceptual representation of the transition process is summarized in Figure 1. A certain observation, often unrelated to the intent of original research, gives rise to a set of

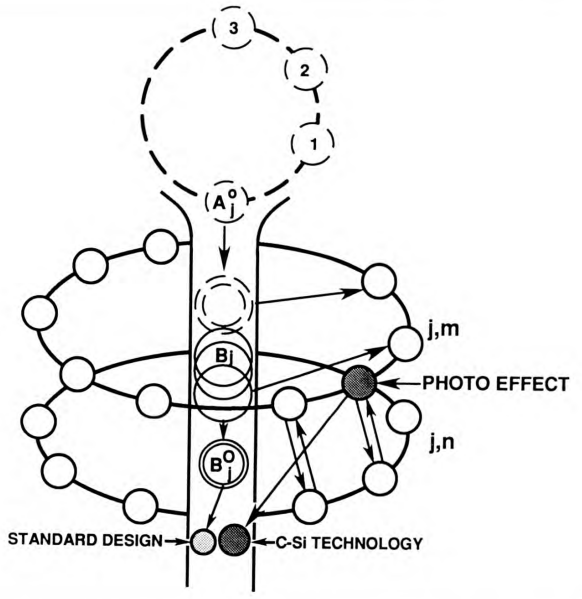

Figure 1

Representation of the transition process.

interesting conclusions, A_j. Among them is the technologically important spin-off situation, A_j^0 . To exploit the potential of A_j^0 and assess its practicability, a transition to B_j^0 must be undertaken. In practice, relevant issues must be clearly defined and solutions outlined. In terms of the donor - acceptor concept, the $A_j^0 \rightarrow B_j^0$ transition is analyzed and, in particular, constraints imposed by B_j^0 are examined. This examination requires a set of consultative interactions to secure additional fundamental information, $B_j^0 \rightarrow B_{j>m}^0$, as well as those needed for design purposes, $B_j^0 \rightarrow B_{j,n}$. The expected net result is a clear definition of issues as well as preferred solutions.

The sequence of activities presented in Figure 1 is over-simplified. We considered an ideal situation, just as the theoretical scientist would choose controlled environment for his work. However, transitions from pure to applied research are diffuse because theorists formulate their problems in the simplest way and try to arrive at a clear conclusion and a well defined physical model. The reality is quite different. Only rarely can the situation be described by mathematical equations that allow solutions in closed form. The interplay occurring between the various participating processes demands highly developed computational skills to sort out the relevant from the irrelevant.

Restating, theoretical scientists deal with individual phenomena/processes which are observed under simple and controlled conditions while developmental-type persons consider the same problem in a real world environment. The process under investigation is not an isolated event but a set of events occurring simultaneously. Consequently, the mathematical treatment involves the interplay between the various processes, with feedback conditions, usually leading to a set of nonlinear equations. Today, because of availability of fast computers, realistic modeling becomes an accessible and powerful tool to guide developmental efforts.

The Development Program: An Early Period

The *Li/SOCl₂* battery development program was running pretty much on the 10 year R&D project life up until about 1980. Realistically, however, the completion time of the project would likely have exceeded the 10 year period, since the high discharge rate battery under development presented technical problems not yet encountered by the battery community.

The *Li/SOCl₂* system was first disclosed in 1973. Following that, considerable research, including applied research and exploratory development were applied to the system leading to a decision to transition the technology to engineering development about 1980 with the subsequent call to develop a high discharge rate battery required for propulsion. Several proposals were reviewed, but upon review, all were rejected and the program was effectively cancelled. The technology reverted back to exploratory development, where it remains today.

A summary of activities in the early period were as follows: Much of the fundamental research was performed under the original ONR contract and subsequently in some industrial laboratories. The initial transition within the Department of Defense occurred through ONR when the Naval Ocean Systems Center (NOSC) was tasked with a small exploratory development project for a sonobouy battery. Shortly thereafter, both the Army and Air Force initiated development programs of their own. As a consequence, the characteristic feature of this period was a proliferation of military development programs and an attempt of rapid transition from applied research to engineering development.

On somewhat closer examination of this period, one negative result emerges: The objectives in each case were different. Consequently, the cross communication as well as the establishment of a common data base were inadequate. A duplication of effort was common-place with solutions of little generic value to other workers investigating this system. On the positive side, however, the technology advanced to the stage where we knew that we could build *Li/SOCl₂* batteries. We had some understanding of the chemistry, cell design and, likely limits of performance. Also during this period, the technology was commercialized with the production of a *Li/SOCl₂* heart pacemaker battery, a very low discharge rate system. More importantly, however, this technology spawned the formation of new companies whose objectives were to produce *Li/SOCl₂* batteries. The expected payoff from this high energy density system for military applications led to numerous development projects. In fact, these activities drove the expansion of the field.

Development of the Power Dense *Li/SOCl₂* System.

Several reasons can be cited as being responsible for the decision to cancel the engineering development transition. In general, these can be collected under the topics of safety and manufacturing. In this, as in any other very high energy density system, an uncontrolled release of the energy produces effects similar to explosives. Moreover, events with other lithium batteries had emphasized the need to ensure safe operation. The safety issue was further compounded by a general lack of understanding of the basic chemical processes responsible for battery operation which, in turn, produced an uneasiness about the ability to control the discharge.

Manufacturing uncertainties took the form of a concern as to whether the battery designs produced in the exploratory development phase could actually be scaled to the appropriate size, subject to the volume/weight specifications of the application. Issues such as thermal management, quality control, shunt current effects, and, here also safety, were involved. An additional factor contributing to cancellation of the development program was a competing technology, the so-called lithium/water system. The exact role that this competition played in the decision to delay the transition cannot be determined. It should be noted, however, that this technology has now been abandoned altogether. Also involved in the decision was the parallel development of a thermally-based system for propulsion which, to date (and at the time of the proposed transition), is the official power source of choice for torpedo propulsion. While the latter has an overall impeding effect on acceptance of a battery power source, the effect is that of reducing time criticality, that is, relieving the pressure to develop.

Re-examination of Issues

In the interim period since the cancellation of the engineering development program, considerable progress has been made in understanding both the technology of the $Li/SOCl_2$ system and the design features of the high discharge rate battery. This progress raises several issues about the transition process, presented here in a form of "Monday morning quarterbacking". It can be argued that the decision to transition was premature because the technology was insufficiently advanced to assure success. Moreover, it could be said that the research and exploratory development phases were improperly pursued either in terms of the issues addressed or in the applicability of the results produced. Alternatively, the developmental community might have failed to exploit the available information and technology base in their project definition. Reality is a combination of these factors. Again, in retrospect, the issues of safety and manufacturing along with the technical components were inadequately treated in the exploratory development phase. This was not for lack of identification, or even effort. Rather, we believe, it was due to a failure to address successfully the technical problems necessary to overcome the issues. The complexity of the system undoubtedly contributed to this shortcomings; definitive experiments were difficult to conceive and perform. As we see it now, there were no shortcuts then nor are there now. Consequently, it was necessary to resort to the slower but surer systematic development of understanding; first, of the basic physical and chemical properties of the individual components and second, of the systems as a whole followed by the construction of a model to demonstrate the behavior of the final product.

Because of the attractive performance parameters for the system, we never considered dropping the technology. Rather, we set out to define a research program which would address both the aspects of the technology which were impeding the development of a high rate system and the most interesting unanswered scientific questions fundamental to *Li/SOCl₂* and other oxyhalide electrolyte systems. What follows is a brief summary of the resultant program which we, the authors, have pursued.

Modeling.

An individual cell in a battery may be viewed as an electrochemical reactor operating in response to imposed demands. When at rest, it is a constrained system that reacts spontaneously as the constraints are removed. Thus, the operation of a battery, a single cell, or even a selected functional element, is a dynamic event where the participating processes occur within a well defined reaction space. These processes, inclusive of interactions among them, can be cast into a set of precise mathematical statements. It follows, therefore, that cell modeling is among the first tasks to be undertaken when attempting the transition: $A_j^0 \rightarrow B_j^0$. In practice, difficulties arise in the formulating of an acceptable model, i.e., a model that reflects the physical reality and yet, where the mathematical expressions are simple so that, at least in the preliminary stages, they yield solutions in a closed form. The modeling exercises may be of the 6.1 type, here the $B_{j,m}^0$ series, or the 6.2 type, here the $B_{j,n}^0$ series, depending upon their complexity and our current level of understanding.

In the course of our research effort, we examined a number of issues: thermal management (A.6), initiation of catastrophic events (F.4), magnitude of parasitic (intercell) currents (F.3) and selected scale-up problems (R.5). These problems were treated with simple models which agreed rather well with observation. However, the most important modeling, offering predictive capabilities, is the cell modeling by Tsaur and Pollard under a small ONR contract (F.13 and ref. therein). This relatively modest undertaking yielded information of enormous value – it focused on the fundamental issue of the reaction path and catalytic effects, and clearly showed that the formation and growth of precipitated *LiCl* within the porous structure must be addressed (F.8).

Mechanistic Studies.

Equations that describe the behavior of *Li/SOCl₂* cell include material and energy balances, conservation of volume, Ohm's law and kinetic relationships. Formulation of the conservation and transport equations is straightforward. On the other hand, developing the expressions for the

electrode kinetics requires care and attention. It is here that reliable information is of utmost importance: the input parameters for modeling exercises, as well as proposed models, must reflect the realism of the discharging cell. To this end, we elucidated the structural properties of the electrolyte phase from the transport measurements (F.2), refined them by spectroscopic examination (F.9) and resolved ambiguities by theoretical calculations (F.5, F.9). The charge transfer reactions occurring within the *Li/SOCl₂* cells are very complex, indeed. Although these studies are not yet completed, a somewhat clearer picture has emerged that provides better insight into their nature and complexity (F.1, F.6, F.11, F.12).

Dissemination of Information.

Timely dissemination of information is one of the essential activities aiding a rational development of the technology base. It encourages a free exchange of ideas and promotes discussion. It also prevents accumulation of so-called "proprietary" information, (i.e., information developed, often at public expense, for private exploitation). For convenience, the information developed in the course of this program is divided into three groups, viz. review papers (R.1 -R.6), applied research (A.1-A.7) and fundamental research (F.1-F.13). Review papers, published at more or less equal time intervals, were designed to summarize the progress made and identify the unresolved technology issues. The second group offered solutions to well defined issues and the third was devoted to the discussion of selected fundamental aspects of the *Li/SOCl₂* power source technology.

Another Spin-off.

Scientific development promotes its own acceleration: ideas are converted into factual observations, observations lead to applications and applications create product. One such example is the extension of the *Li/SOCl₂* cell lifetime arising from the study of the properties of the pre-passive and passive films formed on the electrode surface. In an earlier communication, we observed that a cathodically polarized electrode (C, Pt, Au)/electrolyte interphase behaves as a p-type semiconductor (F.7). Extending this investigation to the Si/electrolyte interphase, we noted the absence of passivation (F.6). Consequently, the incorporation of elemental Si into the cathode structure was predicted to substantially increase the cell lifetime (F.13). This has now been confirmed (P.1). This spin-off has led to new design concepts (F.14) and a new category of cells yielding an estimated 30% increase in the extractable energy content.

Obstacles To Effective Transition.

The two most common obstacles to effective transition attributed to human factors are: (i) failure to take the next step, i.e., to authorize the transition effort; and (ii) *scientific chauvinism*, which simply means: if I cannot reproduce somebody's else results in the first (rough) trial, I will simply dismiss them as irrelevant or, at least, questionable.

Two points concerning transition activities in battery development can be made. First, it is customary to select the battery system having the highest Gibbs free energy, which is the measure of the available driving force. This fact alone, however, should not be taken as the central point because it provides no information on losses associated with cell operation. Hence, cell modeling is the prerequisite to any discussion concerning the expected performance, especially at high discharge rates.

The second point concerns the allocation of resources (funding). The construction and testing of special purpose batteries is expensive. In some of the above cited references, we have commented on the value of a systematic approach to the establishment of a sound technology base for *Li/SOCl₂* batteries. A combination of this work with that of others (also cited in the above references) now provides a much more secure base for a high discharge rate *Li/SOCl₂* development project. This enhancement has been achieved at a relatively modest cost, particularly when compared to some of the earlier efforts in which battery and module tests were used to collect data. As an example, the cost to "demonstrate" performance of a *Li/SOCl₂*, 9 kW module was *ca* 30 thousand dollars per module, while the cost of the above outlined activities, summarized in 25 publications in refereed journals, was but a small fraction of the millions of dollars spent via the "demonstration" route.

Biographies

Dr. S. Szpak is a scientist at the Naval Ocean Systems Center, San Diego, where he has been for 20 years. Previously he was with Lockheed , Palo Alto, and the Stanford Research Institute. His research and publications have been primarily in the fields of electro chemistry and battery technology, specifically lithium batteries.

Dr. J. J. Smith is the Program Manager for Solid State Physics in the Division of Materials Sciences of the Office of Basic Energy Science, Department of Energy. His research and publications have been primarily in the fields of electro chemistry, specifically the electro reduction of *Li/SOCl₂*. Dr. Smith was a scientist at the Naval Weapons Center and before that with the Chemistry Division of the Office of Naval Research.

References

(i) Review papers,(R.)

1. S. Szpak and H. V. Venkatasetty, High rate *Li/SOCl₂* power source: approach and progress, **Power Sources 9**, Proc. 13th International Power Sources Symposium, Brighton, UK 1982
2. Driscoll, R. Pollard, J.J. Smith and S. Szpak, Development of high rate *Li/SOCl₂* system: theory and practice, **Power Sources 10**, Proc. 14th International Power Sources Symposium, Brighton, UK 1984
3. J. R. Driscoll, R. Pollard, J. J. Smith and S. Szpak, Selected aspects of high rate *Li/SOCl₂* power sources technology, **Proc. 20th IECEC**, Miami Beach FL, 1985
4. J. J. Smith, S. Szpak and W. A. West, Function of electrocatalysis on the reduction of *SOCl₂* at porous electrodes, in **Power Sources 11**, L. J. Pearce, ed., International Power Sources Symposium, 1987
5. P. A. Mosier-Boss, L. A. Parnell and S. Szpak, Scale-up problems in batteries for propulsion, **AIAA/SAE/ASME/ASEE** 23rd Joint Propulsion Conference, San Diego CA, 1987

(ii) Applied aspects, (A.)

1. J. R. Driscoll and S. Szpak, High discharge rate *Li/SOCl₂* battery: SEM and EDAX examination of cathodes, Proc. **30th Power Sources Symposium**, Atlantic City, NJ 1982
2. J. R. Driscoll and S. Szpak, Investigation of positive electrode characteristics in high rate *Li/SOCl₂* cells, J. Power Sources, **10**, 343 (1983)
3. H. V. Venkatasetty and S. Szpak, Properties of *SOCl₂* – based electrolytes: conductivity, viscosity and density, J. Chem. Eng. Data, **28**, 47 (1983)
4. B. Carter, H. Frank and S. Szpak, Reaction products on current or potential reversal in *Li/SOCl₂* cells, J. Power Sources, **13**, 287 (1984)
5. J. R. Driscoll and S. Szpak, Thermal behavior of electrochemical cells by liquid crystal display, J. Power Sources, **14**, 321 (1985)
6. L. A. Parnell and S. Szpak, Thermal behavior of *Li/SOCl₂* batteries of thin cell design, Electrochim. Acta, **30**, 913 (1985)
7. J. R. Driscoll and S. Szpak, Quality assessment of unactivated cells by AC impedance technique, J. Power Sources, **16**, 285 (1985)

(iii) Fundamental research, (F.)

1. M. Madou and S. Szpak, Investigation of *SOCl₂* reduction by cyclic voltammetry and AC impedance measurements, J. Electrochem. Soc., **131**, 2471 (1984) 2.
   S. Szpak and H. V. Venkatasetty, Transport properties of *AlCl₃ - SOCl₂* - based electrolytes, J. Electrochem. Soc., **131**, 961 (1984)
3. S. Szpak, C. J. Gabriel and J. R. Driscoll, *Li/SOCl₂* battery intercell currents, J. Electrochem. Soc., **131**, 1996 (1984)
4. S. Szpak, C. J. Gabriel and J. R. Driscoll, Catastrophic thermal runaway in Li batteries, Electrochim. Acta, **32**, 239 (1987)
5. C. J. Gabriel, P. A. Mosier - Boss and S. Szpak, Resolution of vibrational bands into Voigt profiles, Spectrochim. Acta, **43A**, 1293 (1987)
6. M. J. Madou, J. J. Smith and S. Szpak, Comments on electroreduction of *SOCl₂*, J. Electrochem. Soc., **134**, 2794 (1987)
7. M. Madou, T. Otagawa, S. Gaisford, J. J. Smith and S. Szpak, Photoeffects on polarized electrodes in the *SOCl₂ - LiAlCl₄* system, J. Electrochem. Soc., **135**, 262 (1988)
8. R. J. Nowak, D. R. Rolison, J. J. Smith and S. Szpak, Role of *Fe - Pc* in a discharging *Li/SOCl₂* cell, Eletrochim. Acta, **33**, 1313 (1988)
9. P. A. Mosier - Boss, R. D. Boss, C. J. Gabriel, S. Szpak, J. J. Smith and R. J. Nowak, Raman and infrared spectroscopy of the *AlCl₃ - SOCl₂* system, J. Chem. Soc., Faraday Trans. **I 85**, 11 (1989)
10. S. Szpak, P. A. Mosier - Boss, J. J. Smith and R. J. Nowak, On the mechanism of *SOCl₂* reduction in lithium cells, Proc. Battery Div., The Electrochemical Society, Oct. 1988
11. P. A. Mosier - Boss, S. Szpak, J. J. Smith and R.J. Nowak, *LiCl - AlCl₃ - SOCl₂* system: structures, species and equilibria, J. Electrochem. Soc., **136**,1282 (1989)
12. P. A. Mosier - Boss, S. Szpak, J. J. Smith and R. J. Nowak, Electroreduction of *SOCl₂*. I: *AlCl₃ - SOCl₂* system. ibid., accepted
13. K. C. Tsaur and R. Pollard, Precipitation of solids in electrochemical cells, ibid., **133**, 2296 (1986)

(iv) Patents, (P.)

1. M. Madou and S. Szpak, Navy Case - 69586 (Patent pending)

Research in Ceramic Composites at NRL*

by David Lewis III
Naval Research Laboratory

Introduction

The U.S. Navy has long supported fundamental and applied research directed toward its present and future needs. In recent years, the perceived need for improved high-temperature structural materials, as well as the need for higher performance materials for specialty applications such as radomes and IRdomes, has led to substantial efforts in ceramic matrix composite materials. These efforts were initially conducted in the Ceramics Branch and now are carried on in the Composites and Ceramics Branch, which consists of approximately 40 professionals and 10 contract employees covering a wide range of disciplines and expertise in ceramics, ceramic composites, and metal matrix composites. Much of the work of this group is directed toward present or perceived future Navy needs, but a substantial portion is also devoted to other Department of Defense (DoD) and government activities, including the Strategic Defense Initiative (SDI), the National Aerospace Plane (NASP), materials for stealth applications, and ceramics for advanced heat engines. Some of these outside research activities relate very directly to the programs in ceramic matrix composites, e.g., the NASP and materials for advanced gas turbine engines.

The research efforts in ceramics at Naval Research Laboratory (NRL), both those internally funded and those supported by outside funding, have historically been divided into three major subject areas: electronic ceramics, structural ceramics, and fundamental studies in the physical behavior of ceramics. Each of these subject areas has typically included some efforts involving ceramic matrix composites. The research efforts have addressed needs for ceramic materials in applications including: advanced heat engines, e.g., adiabatic diesels and advanced gas turbines; armor; bearing and seals; electronic packaging and substrates; IR windows (IRdomes); laser hardening; radar windows (radomes), radar absorbing materials and structures, and sonar. In many of these cases the needs suggested or required the use of composite material approaches and thus a large part of the research in ceramics at NRL has, in fact, been devoted to the development and understanding of the behavior of ceramic matrix composites of various types for a variety of applications.

The efforts at NRL in ceramic matrix composites are currently supported in part by indirect funding from the Office of Naval Research (ONR) through NRL core funds and

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Table I

Research Programs in Ceramic Composites and Related Programs at NRL

Title	Funding Source
Laser Hardening and Effects in Ceramics	DARPA
Processing of Ceramic Turbine Materials	DARPA, ONR
Processing of Particulate Ceramic Composites	NAVAIR, ONR
Mechanical Properties of IR and Radar Ceramics	NAVAIR
Thermal and Corrosion Barrier Coatings for Marine Gas Turbines	NAVSEA[(a)]
Low-Radar Cross Section Materials	NAVAIR
Composite Tranducer Ceramics	ONR (NRL)
Ceramic Fiber Composites	NAVAIR
Rapid Solidification Processing of Ceramics	ONR (NRL)
Self-Propagating Synthesis Processing of Ceramics	DARPA
Oxidation-Resistant Carbon-Carbon Composites	DARPA
Fracture Toughening and Tribology of Ceramics	ONR (NRL)
Evaluation of BN-Producing Polymers	ONR
Ceramics with Ordered Voids	ONR, NAVAIR
Ordered Void Materials for Towed Sonar Arrays	NUSC[(b)]
Substrates for High Speed, High Density Circuitry	ONR
Strengthening of Ceramics with Ordered Voids	NAVAIR
High-Temperature Structural Composites	NASPO[(c)]
Evaluation of Fibers for Ceramic Matrix Composites	NAVAIR

[(a)]Naval Sea Systems Command
[(b)]Naval Undersea Systems Command
[(c)]National Aerospace Plane Office

by funds from the Naval Air Systems Command (NAVAIR). In the past, the ceramic composites program at NRL has been supported extensively by direct funding from ONR, NAVAIR, the Defense Advanced Research Projects Agency (DARPA), and to a lesser extent by monies from the other Navy System Commands and the Department of Energy. Historically, the efforts in ceramic composites at NRL have been funded at the level of $100,000 to $500,000 a year. Table 1 shows a partial listing of past and present NRL ceramic composites research programs and related efforts roughly in chronological order.

Specific Research Programs

Electronic Ceramics: In research on electronic ceramics, the Ceramics Branch has historically worked in several areas directly related to specific Navy needs. Some programs have addressed the needs of high-speed circuitry for packaging and substrates and various other electronic ceramic applications. The largest of these programs has sought the improvement of existing ceramic piezoelectric materials and the development of new materials. The

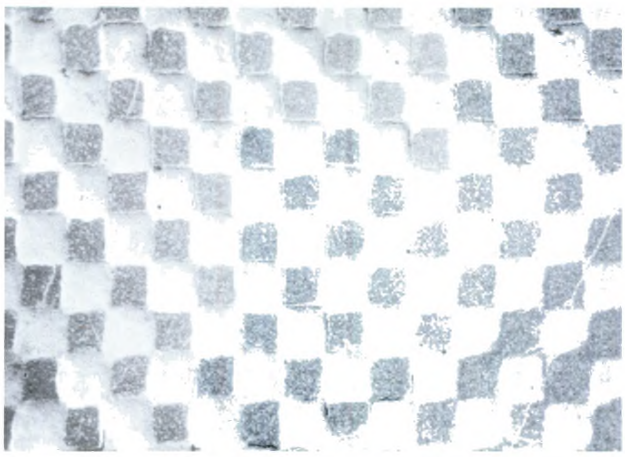

Figure 1

Ordered voids in PZT ceramic produced by silk screen/tape casting process: a) top view of material with lenticular voids, approx. 0.7 mm diameter by 0.06 mm thickness; b) top view of square void array pattern.

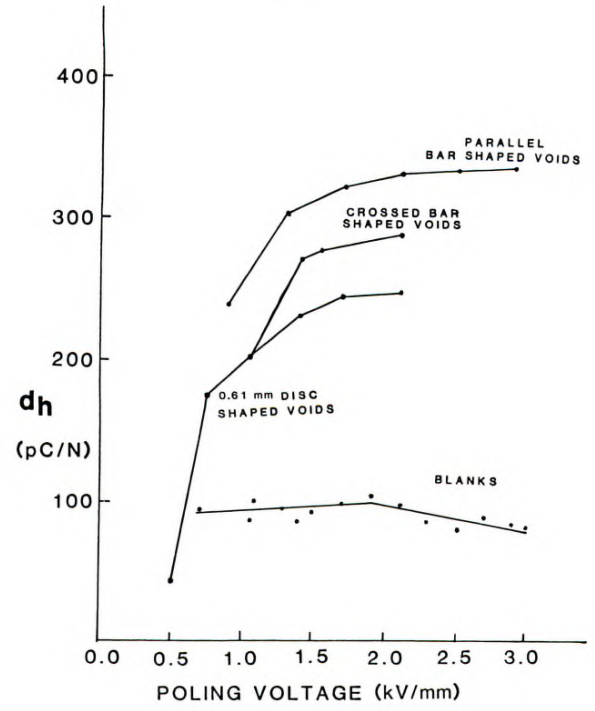

Figure 2

Hydrostatic sensitivity, d_h, versus poling voltage for various ordered void materials and control material (blanks), showing increase of 300-400% in hydrostatic sensitivity.

piezoelectric ceramic materials, barium titanate and lead zirconate titanate (PZT), are incorporated into the many active and passive sonar systems that consume a significant amount of the Navy budget. The Ceramics Branch initially worked primarily in the area of failure analysis and the development of appropriate test procedures, but subsequently has become involved in the development of new sonar transducer materials.

Recently, the group has worked extensively on the design, fabrication, and testing of sonar transducer materials incorporating arrays of ordered voids. These materials are effectively composite materials, in this case an atypical composite consisting of a ceramic material (PZT) and air. These materials, produced by combinations of tape casing and silk screen printing techniques, convert an isotropic polycrystalline (monolithic) material into a highly anisotropic composite body with significantly different piezoelectric properties, see Figures 1 and 2. The most impressive gains have been in the area of hydrostatic sensitivity, but the same technique can be used for precise control of local dielectric properties (e.g., in substrates) to provide cooling passages in packaging and has been shown to increase the strength and

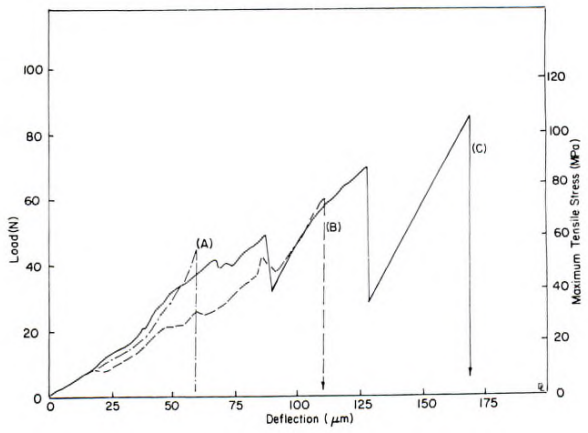

Figure 3

Load-deflection (stress-strain curves) for monolithic PZT, and PZT containing ordered void arrays showing increase in load or stress at failure and increased work-of-fracture (area under curve) associated with introduction of ordered voids.

toughness of the PZT[1-3] (see Figures 3 and 4). The latter effect, where the addition of 10 to 20 volume percent (v/o) porosity increases both the flexural strength and toughness (work-of-fracture) of a material is rather unexpected. However, it may have application to other materials if the scale of the ordered void pattern and the tape thickness can be reduced to dimensions on the order of 10 to 20 μm (this is

Figure 4

Fracture surface in PZT ceramic with array of lenticular voids, showing complex fracture interaction with void arrays associated with increase in strength and work-of-fracture over dense PZT. Fracture direction is left to right, and void plane spacing is approx. 0.12 mm.

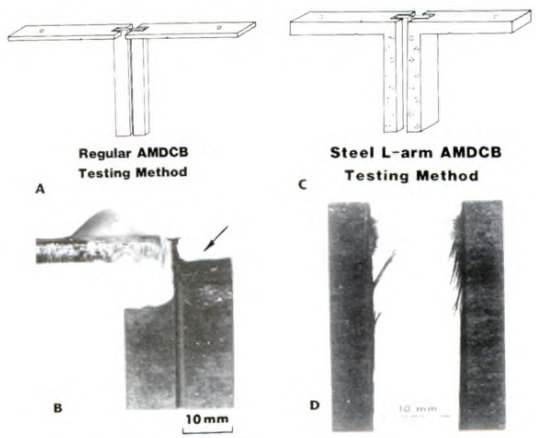

Figure 5

Modification of applied moment double cantilever beam fracture toughness test (L-arm method) permitting successful testing of tough, anisotropic fiber composite (sample on right).

close to the limit of current tape casting and fugitive ink patterning technology).

Current work on these materials stresses the use of combinations of experimental development and 3-D finite difference analyses to optimize the ordered void materials for various piezoelectric properties, to explain the effects on strength and crack propagation, and seeks to explore other possible uses of this unusual type of composite technology.

Basic Fracture Studies: Recent efforts at NRL in the area of basic fracture mechanics have focused on three areas: the details of fracture in ceramic single crystals, improving and measuring the fracture toughness of ceramic matrix-ceramic fiber composites, and tribology and wear in ceramics. As part of the long-term efforts to provide reliable fracture mechanics data for ceramics, the applied moment double cantilever beam (AMDCB) fracture toughness specimen was developed at NRL[4,5], and have been applied since to a great variety of materials, ranging from alkali halides (detector crystals for the Gamma Ray Observatory) with K_{Ic} (fracture toughness) values less than 0.1 MPa-$m^{1/2}$, to highly anisotropic ceramic composites with toughnesses

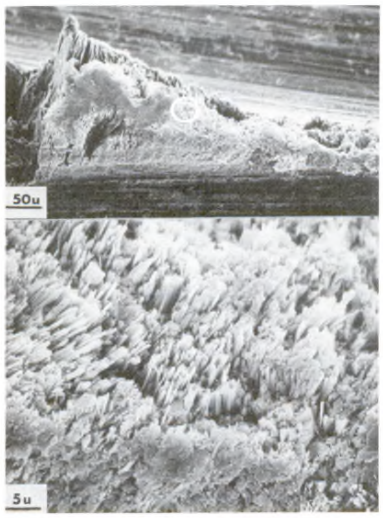

Figure 6.

Fracture surface topography in AMDCB specimen of commercial Lou Bon Hornblende (one of the 'jade' family of minerals, showing fibrous structure associated with high fracture toughness. Fracture surfaces are from fracture toughness test specimen performed with L-arm AMDCB technique.

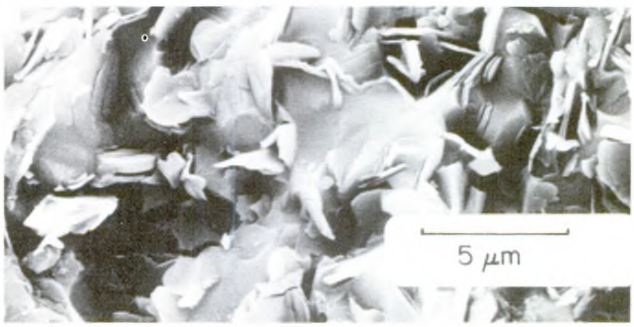

Figure 7

Fracture surface in mullite (alluminum silicate)-30 v/o BN particulate composite showing flaky BN grains embedded in mullite matrix.

in excess of 50 MPa-$m^{1/2}$ and on samples ranging in size from less than 1 cm to greater than 20 cm in length. This test has the great advantage (for opaque materials) of not requiring measurement of crack length during testing, nor for any compliance calibrations, all of which are problems for typical ceramic composite materials.

The modification of this test and its successful adaptation for high toughness, highly anisotropic ceramic matrix-ceramic fiber composites has been a significant accomplishment and permitted, for the first time, an accurate determination of the true toughness of these materials. Recently, this modified AMDCB test has been successfully applied to ceramic fiber composite materials such as UTRC's Compglas™ and to natural fiber composites such as jade[6], see Figures 5 and 6. The difficulty here is in testing highly anisotropic materials, where the fracture toughness may vary by more than an order of magnitude for different directions, e.g., from 2-50 MPa-$m^{1/2}$ for the weak and strong directions in Compglas™ unidirectional ceramic

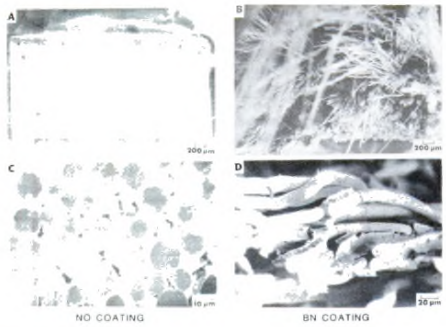

Figure 8

Effects of BN coatings on fracture behavior of $ZrTiO_4$ matrix-Nicalon SiC fiber composites: a) and c) composite without fiber coating exhibits low fracture toughness and relatively planar fracture; b) and d) composite with coated fibers exhibits extensive fiber pullout and fracture toughness approx. 25 times higher.

fiber-ceramic composite materials. The previous design for the AMDCB apparatus was modified to constrain the crack propagation to the desired direction, and this modification, and the necessary corrections to the K_{Ic} calculations have been tested successfully on a wide range of materials.

The wear efforts initially focused on *conventional* ceramics, such as alumina, silicon nitride, and silicon carbide, using the Pin-on-Disc test (POD), and the POD test has now been applied to the study of the wear behavior of some natural fiber composites, jadeite and hornblende[7], with very interesting results in one case. These natural materials are interesting model materials in this regard (wear) and in relation to mechanical properties such as fracture toughness, since they represent a wide range of microstructures, ranging from randomly oriented elongated grains to highly oriented fibrous grains (Figure 6). In the last case, the material consists of essentially 100 percent unidirectional fibers (highly acicular grains), bonded together by a minimal amount of matrix phase. The wear results here suggest that a suitable composite (i.e., one with hard fibers and matrix) with the bulk of the fibers oriented normal to the wear surface should have exceptional resistance to sliding wear.

Structural Ceramics: NRL has long had a strong program in structural ceramics and ceramic composites, initially focusing on such materials as silicon nitride and silicon carbide. This work evolved into a program studying particulate and fiber composites as well, producing significant results on alumina-BN and mullite-BN particulate composites, as shown in Figure 7, which exhibit favorable combinations of erosion resistance, thermal shock resistance, dielectric properties, toughness, and machinability. This work, which was reported extensively in the past [8-10], produced composites with the combination of moderately high strength, 400-500 MPa, high toughness, 8 to 10 MPa-$m^{1/2}$, excellent machinability (similar to Macor™), and good dielectric properties, and was directed toward production of better material for supersonic radomes.

More recently, the focus of the work in structural ceramics and composites has fallen on fiber-reinforced ceramic matrix composites, and, in particular, on interface control in these materials[11-15]. The group at NRL was one of

Figure 9

Bilayer SiC/BN coating on Nicalon SiC fibers in composite; micrograph shows region where two fibers touch.

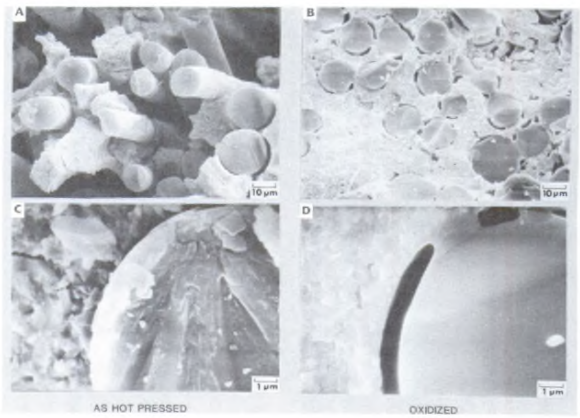

Figure 10

Effect of oxidation at 1000°C on $ZrTiO_4$ matrix-SiC/BN coated Nicalon fiber composite a) and c) as prepared composite shows high toughness, rough fracture surface and extensive fiber pull-out associated with low bonding; b) and d) oxidized composite shows low toughness, smooth fracture surface and strong matrix-fiber bonding.

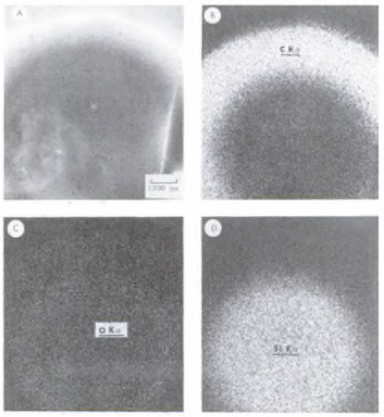

Figure 11

Elemental maps for polymer-derived SiC fiber after heat treatment in CO, showing surface depletion of Si (removed as SiO vapor) leaving a C-rich surface layer.

the pioneers in the use of fiber coatings for interface control in CMC's, obtaining a patent on the use of borazone-derived BN for this purpose. An example of the beneficial effects of the BN coatings is shown in Figure 8. The use of borazine and low pressure CVD allowed the reasonable uniform coating of unspread fiber tows at deposition temperature sufficiently low (900°C) that fiber degradation was minimized. This process also involved the evolution of no aggressive species such as HC1 gas, with similar benefits. Subsequent work explored the use of various multilayer coatings to overcome some of the limitations of the single layer BN coatings. Two layer BN/BN coatings were produced, with the lower layer from borazine, deposited at low temperature to protect the fiber, and the upper layer from $BC1_3$ at higher temperature to obtain a more chemically stable hex-BN coating. Various other materials and combinations of materials were tested as coatings, including carbon, and combinations of BN and SiC, the latter derived from trichlormethylsilane.

The most successful results, for these fiber composites, using two layer, BN/SiC coatings on Nicalon fibers in a $ZrTiO_4$ matrix, as shown in Figure 9, have been tensile strengths of approx. 1000 MPa and fracture toughnesses of ca. 50 MPa-$m^{1/2}$. An example of a fiber-matrix interface, for a BN/SiC-coated Nicalon fiber in a $ZrTiO_4$ matrix is shown in Figure 5. These mechanical properties for ceramic matrix composites are sufficient to make them strong candidates for high temperature structural materials, replacing superalloys, if problems of high temperature oxidative degradation of the interface can be overcome (Figure 10). Research is currently in progress at NRL on several problems related to this oxidative degradation, fiber degradation at high temperature in various environments; the effects of fiber coatings on this problem, and the effects of fiber coatings on the degradation of the mechanical properties of ceramic matrix composites at high temperatures in oxidizing environments[16-17]. This research is also exploring further developments in the coating areas, including the use of three layer coatings designed to minimize the interaction of the fiber and matrix with the BN layer.

The part of this current research program which may have the most significant implications for ceramic matrix composites is the study of the dependence of fiber degradation on environment. While it is well known that fibers such as Nicalon degrade significantly at high temperatures in air, because of oxidation of the free carbon in the fibers and the loss of CO and SiO from the fibers, this is not the environment typical of either processing or service for these fibers. Where composites are prepared by hot-pressing, the processing environment is likely to be reducing, and a high overpressure of CO may be present. The environment within a composite in service at high temperature is more difficult to define, but is certainly not equivalent to free air at 1 atmosphere. The study noted has sought to characterize the changes and degradation in fibers such as Nicalon SiC and other polymer-derived fibers in various atmospheres, such as air, argon, nitrogen, oxygen, carbon monoxide, etc., over a wide range of temperatures and times. Figure 11 shows the changes in the fiber chemistry occurring with heat treatment of a ceramic fiber in CO gas, where the surface chemistry of the fiber is significantly modified.

Recent results[18] on the effects of a CO processing atmosphere and on the effects of heat treatment, in a CO atmos-

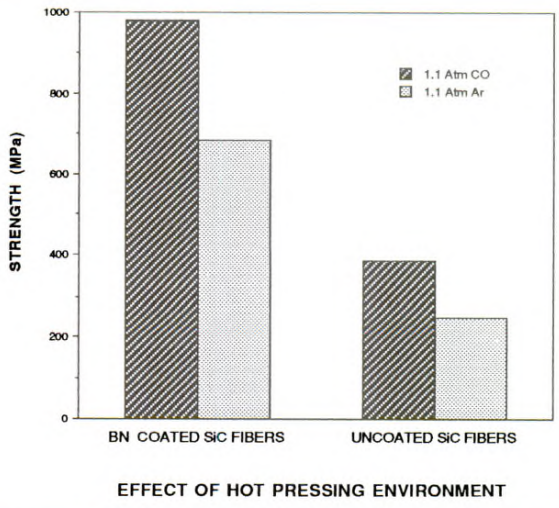

Figure 12

Effect of Processing Atmosphere and Fiber Coating on Tensile Strength of Nicalon™ SiC Fiber/$ZrTiO_4$ Matrix Composites.

phere, of polymer-derived in SiC fibers (Nicalon™ and Tyranno™) have shown that such treatment may increase the strength of such fibers, and certainly permits the use of heat treatments to increase the density and elastic modulus of these fibers without adversely affecting their tensile strength. More recently, studies of the use of a CO atmosphere during composite fabrication, with a 0.1 atm. overpressure of CO, have shown very interesting and significant findings. The CO atmosphere permits the use of higher processing temperatures without degradation of the fibers in the composite; this provides significant increases in the number of matrix materials which can be considered. Of more importance, composites made with the CO atmosphere exhibit mechanical properties which are far superior to those obtained with other, more traditional, hot pressing atmospheres (e.g., argon, nitrogen, and vacuum). An example of the results is shown in Figure 12 where the tensile strength of composites, measured at ambient temperature, is shown as for CO and argon atmospheres, and for both uncoated SiC fibers, and fibers protected by a BN coating. Current composites made with BN-coated Nicalon fibers and a $ZrTiO_4$ matrix, processed in the Co atmosphere, show tensile strengths ranging from 750 to 1250 MPa (110-180 ksi) averaging about 1000 MPa (145 ksi), strength values comparable to the best engineering light alloys, and in a material with a density approx. 80% that of titanium.

One of the results of this study was an indication that there are very large differences in the extent of fiber property degradation for various atmospheres, the degradation here characterized primarily by the tensile strength measured on individual fibers, for various atmospheres. Another result indicated that some atmospheres, e.g., nitrogen with a carbon source result to provide reducing conditions, have very little effect on fiber properties. There are, in addition to the effects on fiber strength, many visible and very interesting changes in the fiber morphology with these heat treatments, as shown in Figure 13. This shows in-situ formation of silicon nitride whiskers on a polymer-derived 'SiC' fiber associated with one particular treatment. While there is significant fiber degradation associated with this whisker growth, there is also potential here, especially with carbon-carbon or metal matrix composites, for providing significantly increased transverse shear and tensile properties in these composites. Currently, these properties, not the greatly higher longitudinal tensile strength, are the design-limiting properties, and a tradeoff of longitudinal tensile strength for increased transverse tensile strength and shear strength may well be worthwhile. Other effects noted here include the formation of a dense SiC layer on these fibers; this coating may serve a useful protective function on these relatively unstable and reactive fibers.

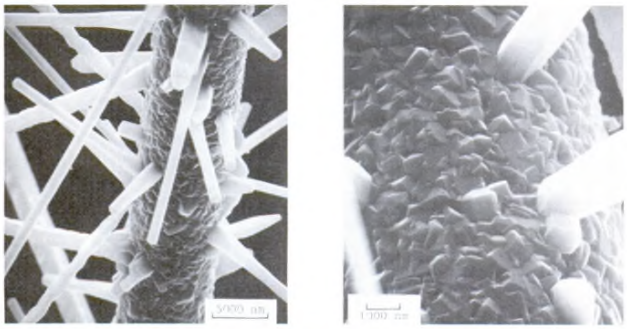

Figure 13

Effect of heat treatment in nitrogen on polymer-derived SiC fibers, resulting in extensive growth of silicon nitride whiskers from surface of fibers.

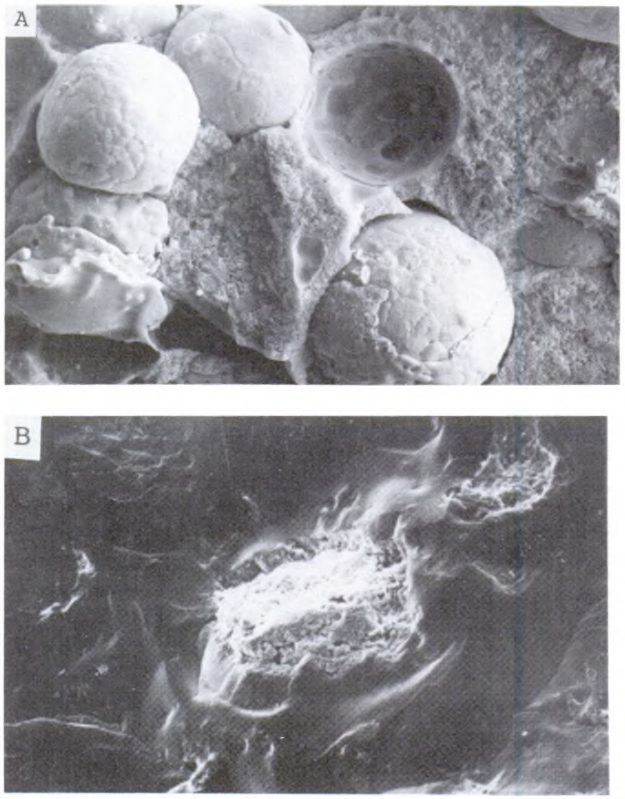

Figure 14

Fracture surfaces in model particulate composites: a) Si_3N_4-coated iron alloy particles in Macor™ glass-ceramic matrix, with minimal particle-matrix bonding and matched thermal expansion coefficients resulting in particle debonding during fracture, and b) oxidized Kovar particles in Corning 7052 glass matrix with matched expansion coefficients but strong particle-matrix bonding, resulting in particle fracture and higher fracture toughness.

Another current project (in the Composites and Ceramics Branch) which is interesting from a basic scientific standpoint is the incorporation of metal particles into a glass or glass-ceramic matrix to form a model particulate composite[19-20]. This type of particulate composite, which has been widely used in the past for various studies regarding composite properties, has the advantage of great flexibility in a number of composite parameters, such as volume fraction, particle size, particle shape and orientation, residual stress state, etc. Figure 14 shows fracture surfaces in such a glass matrix-metal particle composite for unbonded and bonded particles, showing the effect of such differences on the fracture mode. Here the experimental analysis is coupled with a theoretical analysis based on that of Eshelby for arrays of ellipsoidal particles in a matrix. With some processing techniques such as uniaxial hot-pressing, it is possible to produce particle alignment of non-spherical particles, or to distort spherical particles into oblate spheroids. Theoretical calculations of various properties, e.g., strength, modulus, fracture toughness, optical properties, electromagnetic properties, of these materials can here be compared directly with experimental measurements.

Current efforts on these model particulate systems address the details of the interactions of a crack front with the dispersed phase, and the effects of crack size and crack velocity on the effectiveness of the dispersed phase in making

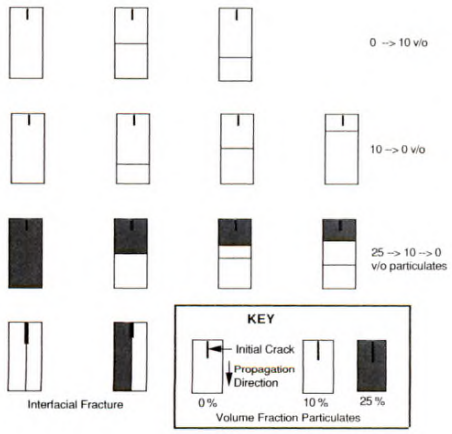

Figure 15

Schematic of various possible graded composite structures to assess effects of crack velocity and other factors on toughening effects of particulate dispersions. Fracture proceeds downward from starter crack at top of specimen.

Figure 16

Hollow, fine grain spherical particles of t'-ZrO_2, intended as plasma spraying feed material, single phase and with chemical homogeneity, obtained by rapid solidification processing of zirconia from a melt.

the composite tougher. One interesting result of this research program is the finding that the major effect of the dispersed metal particles is on the initiation of crack propagation, not on its subsequent propagation. Experimental measurements on composites with graded structures (see Figure 15) have shown that a layer of composite material with high volume fraction of particulate phase, overlying a material with lower or zero volume fraction of particulates, is as tough (resistant to fracture) as a monolithic material with the high volume fraction of particulates. (see Figure 7) This has significant implications in indicating that it is only necessary to toughen the surface or near-surface region of a material, thus achieving large savings in both weight and cost, since the reinforcing particulate phases are typically both more dense and most costly than the matrix materials.

Another interesting area of research at NRL, which includes a significant ceramic composite effort, is that of rapid solidification processing (RSP) of materials. This effort has included work to produce fine Si_3N_4-coated iron particles which have been used as one of the particulate phases in the model particulate system noted earlier. Another effort in this regard has been the production of alumina-zirconia and zirconia alloys of unique phase structure and with extremely good chemical homogeneity[21]. The alumina-zirconia materials can be prepared by several techniques from melts of the utectic composition and have potential as a hard, tough refractory insulating material. The reduction in scale of the eutectic structure associated with the rapid solidification processing should permit fabrication of alumina-zirconia eutectic materials with high values of strength as well. A result with more technological importance has been obtained with yttria-partially stabilized zirconia materials produced by rapid solidification from the melt (at ca. 2800-

3000°C). Here unique phase structures are obtained, e.g., t'-ZrO_2 in a nominally two phase tetragonal-cubic region, and the material shows very great chemical homogeneity. One particular process has been used to produce spherical particles intended as a plasma spray feed powder (see Figure 16). It has already been demonstrated, in a joint project with the Chemistry Division[22], that the RSP zirconia is significantly more resistant to molten salt corrosion than the conventionally prepared zirconia turbine coating materials. This presumably results from the chemical and phase homogeneity and the high purity of the powder. These same features are also expected to result in greater thermal stability as well; thus these materials may also function better as turbine coatings where thermal rather than chemical stability is the issue.

Summary

The preceding is intended as a broad overview of past and present research programs in ceramic composites at the Naval Research Laboratory, and it is hoped that it will give the reader an idea of the breadth of the efforts there as well as some details of some of the more interesting research projects and developments. Those interested in further details should contact the author.

Acknowledgements

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Biography

Dr. Lewis joined NRL as a research ceramic engineer in 1979. He is currently the associate branch head of the Composites Branch and is the head of he Structural Ceramics Section. His areas of expertise include processing and characterization of ceramics and ceramic composites, fracture mechanics, mechanical properties of ceramic and ceramic composites, theoretical modeling of the fracture and toughening processes in ceramics and ceramic composites, and the statistical analyses of mechanical properties of ceramics. He has authored approximately 75 publications and made over 200 technical presentation.

References

1. M. Kahn, R.W. Rice, and D. Shadwell, "Preparation and Piezoelectric Response of PZT Ceramics with Anisotropic Pores," *Adv. Ceram. Mater.* **1** [1] 55-60 (1986).
2. M. Kahn, "Acoustic and Elastic properties of PZT Ceramics with Anisotropic Pores," *J. Am. Ceram. Soc. Soc.* **68** [11] 623-628 (1985).
3. M.S. Duesbery, M. Kahn, B. A. Kovel and D. Lewis, "Fracture in PZT Ceramics Containing Arrays of Flat Voids," subm. to *Am. Ceram. Soc.*, 1988.
4. S.W. Freiman, D. R. Mulville, and P.W. Mast, "Crack Propagation Studies in Brittle Materials," *J. Mater. Sci.* **8** [11] 1527-1533 (1973).
5. C. Cm. Wu, K. R. McKinney and D. Lewis, "Grooving and Off-Center Crack Effects on Applied Moment Double Cantilever Beam Tests," *J. Am. Ceram. Soc.* **67** [8] C166-C168 (1984).
6. C. Cm. Wu, K.R. McKinney and J. Cunniff, "Modified DCB Method for Measurement of High Toughness Ceramic Composites," *Ceram. Eng. Sci. Proc.* **6** [7-8] 550-557 (1985). Also see C. Cm Wu, D. Lewis and K. R. McKinney, "Strength and Toughness Measurements of Ceramic Fiber Composites," 53-60 in *Fracture Mechanics of Ceramics*, ed. R. C. Brandt et al., Plenum Publ. Corp., NY 1986.
7. C. Cm. Wu, "Wear of Ceramic Natural Fiber Composites, 79-84 in *Engineered Materials for Advanced Friction and Wear Applications,*, ed. F. A. Smidt and P. J. Blau, ASM International, 1988.
8. D. Lewis, R. P. Ingel, W. J. McDonough and R. W. Rice, "Microstructure and Thermomechanical Properties in Alumina- and Mullite-Boron Nitride Particulate Ceramic-Ceramic Composites," *Ceram. Eng. Sci. Proc.* **2** [7-8] (1981).
9. R. W. Rice, P. F. Becher, S. W. Freiman and W. J. McDonough, "Thermal-Structural Ceramic Composites," *Ceram. Eng. Sci Proc.* **1** [7-8(A)] 424-443 (1980).
10. D. Lewis and R. W. Rice, "Thermal Shock Fatigue of Monolithic Ceramics and Ceramic-Ceramic Composites," *Ceram. Eng. Sci. Proc.* **2** [7-8] 712-718 (1981).
11. B. Bender, D. Shadwell, C. Bulik, L. Incorvati and D. Lewis III, "Effect of Fiber Coatings and Composite Processing on Properties of Zirconia-Based Matrix SiC Fiber Composites," *Am. Ceram. Soc. Bull.* **65** (2) 363-369 (1986).
12. D. Lewis and R. W. Rice, "Further Assessment of Ceramic Fiber Coatings Effects on Ceramic Fiber Composites," NASA Conf. Publ. 2406, ed. J. D. Buckley, 13-26 (1985).
13. W. S. Coblenz et al., "Progress in Ceramic Refractory Fiber Composites," NASA Conf. Publ. No. 2357, J. D. Buckley, ed., 191-216 (1984).

14. D. Lewis, C. Bulik and D. Shadwell, "Standardized Testing of Refractory Matrix/Ceramic Fiber Composites," *Ceram. Eng. Sci. Proc.* **6** (7-8) 507-523 (1985).
15. D. Lewis III, "Strength and Toughness of Fiber-Reinforced Ceramics and Related Interface Behavior," 265-274 in *Whisker and Fiber Toughened Ceramics*, ASM International, 1988.
16. J. S. Wallace, B. A. Bender, and D. Schrodt, "Thermochemical Treatment of Tyranno Fibers," NASA Conf. Publ. No. 2482, ed. J. D. Buckley, 201-1212 (1987).
17. B. A. Bender, J. S. Wallace and D. J. Schrodt, "Effect of Thermochemical Treatments on the Strength and Microstructure of SiC Fibers," to be publ. in Proc. NASA/DoD Conf. on Metal Matrix, Carbon and Ceramic Matrix Composites, January, 1988, Cocoa Beach, Fl.
18. B. A. Bender and D. Lewis III, "Fiber-Interphase-Matrix Interactions in Ceramic Matrix Composites," 110-114 in *1988 NRL Review*, Naval Research Laboratory, Washington, D.C., July, 1989.
19. T. L. Jessen, Examination of the Slow Fracture Characteristics of a Metal Particulate Glass Composite, M. S. Thesis, The Pennsylvania State University, August 1987.
20. T. L. Jessen, "Fracture Toughness Testing of Graded Particulate Composites," to be publ. in *Ceram. Eng. Sci. Proc.*, 1989.
21. B. A. Bender, R. P. Ingel, W. J. McDonough and J. R. Spann, "Novel Ceramic Microstructures and Nanostructures from Advanced Processing," *Adv. Ceram. Mater.* **2** 137-144 (1986).
22. R. L. Jones and C. E. Williams, "Hot Corrosion Studies of Zirconia Ceramics," *Surf. and Coatings Tech* **32** 349-58 (1987).

Research Notes

NRL-Developed SDIO Satellite To Be Launched

A team of scientists and engineers at the Naval Research Laboratory (NRL) has designed and built a satellite system to support two primary Strategic Defense Initiative Organization (SDIO) experiments. The satellite is scheduled to be launched in early 1990.

One of these experiments, the Low-power Atmospheric Compensation Experiment (LACE), will assess the effectiveness of techniques for compensating for atmospheric effects on ground-based laser beams. The other primary experiment, the Ultraviolet Plume Instrument (UVPI), is designed to form images of the ultraviolet emission produced by rocket plumes.

A third SDIO-sponsored experiment, the Army Background Experiment (ABE), managed by the Army Strategic Defense Command and built by Los Alamos National Laboratory, is designed to measure background neutron activity in space.

Each of these experiments addresses a particular phase of SDIO's planned defense program, and according to NRL researchers, each will obtain useful data that will be used by the scientific community to verify analytical models and confirm scientifically based best estimates.

Low-Power Atmospheric Compensation Experiment (LACE)

The LACE experiment provides an instrumented scoring target for low-powered, ground-based lasers to determine how well the atmospheric distortion of laser beams can be corrected.

The NRL-developed LACE system comprises a satellite whose primary component is the Sensor Array System (SAS), three ground stations, and an operations control facility.

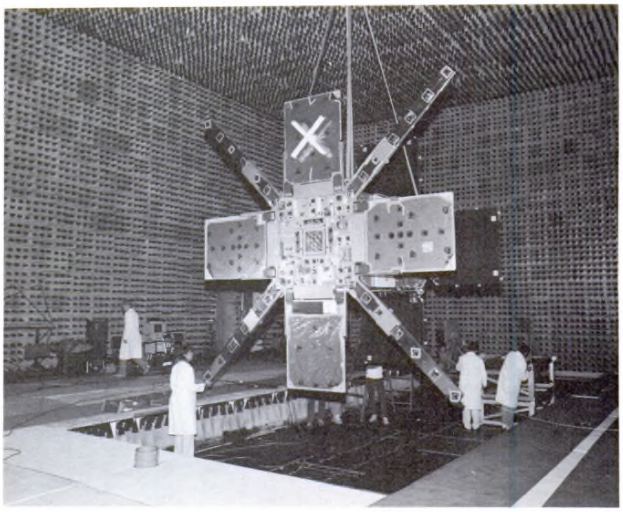
The SAS aboard the satellite contains more than 200 sensors that measure laser beam intensity. Each of three separate sensor arrays will measure a different type of laser emission.

Two of the supporting ground stations are transportable. One of these stations, located in Hawaii at the Air Force Maui Optical Station (AMOS), supports experiments involving adaptive optics developed by MIT/Lincoln Laboratory to study atmospheric compensation for laser beams. The other transportable station will be located in the continental United States and can be easily moved to sites of interest across the country.

The third, permanently sited, NRL ground station will be used for the daily "health" maintenance of the satellite.

The operations control facility, located in the state of Virginia, will be used to plan, coordinate, and control all command and telemetry required for conducting satellite operations. This facility will also manage the acquisition and distribution of telemetered data from the various experiments.

LACE experiments are scheduled to be conducted over a 30-month test period.



LACE Satelite undergoing systems level testing

Ultraviolet Plume Instrument (UVPI)

The UVPI will use two cameras to track and make images of solid- and liquid-fueled rocket plumes to confirm that the ultraviolet component of a rocket's exhaust retains its compact shape and can be used to pinpoint a rocket's location.

UVPI will also help researchers develop a table of ultraviolet signatures of rocket exhaust plumes, enabling them to identify different targets by their plumes' size, shape, intensity, and composition.

On a typical UVPI mission, a test missile will be launched when the spacecraft is within range. Then the UVPI will be activated to initiate tracking and imaging. The instrument is designed to point within a 50-degree half-angle cone to locate

an exhaust missile plume, lock onto and track the missile, record ultraviolet emissions from the missile's plume, and transmit real-time plume information to the controlling ground station. The UVPI has a design lifetime goal of six months.

Research Team

The research team is from NRL's Naval Center for Space Technology (NCST) with the assistance of members of NRL's Optical Sciences and Space Science Divisions and other members of NCST. The principal contractors to NRL that support the satellite program, listed alphabetically, are Bendix Field Engineering Corporation (BFEC), Fairchild Space Company (FSC), Instrumentation Technology and Engineering (ITE), and Loral Electro-Optic Systems (LEOS).

LACE/UVPI Technical Information

Satellite

Launch weight:	1400 kg
Volume:	Main body; 1.4m x 1.4m x 2.4m (plus sensor panels, solar cell panels, booms)
Sensor panels:	Four; 1.0m x 1.3m each
Booms:	Three; 46m, extendable
Stabilization	Gravity gradient
Attitude sensing:	Horizon, solar, magnetometer
Propulsion:	None
Telemetry downlink:	3 Mbps
Command uplink:	2 Kbps

LACE/Sensor Array System (SAS)

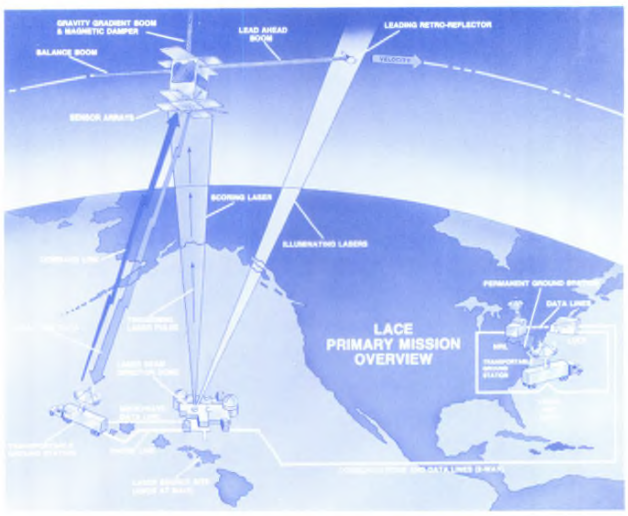
Accuracy:	10% radiometric accuracy
Arrays:	Three distributed: 1. Visible: 85 sensors 2. IR: 40 sensors 3. Pulsed: 85 sensors

Ultraviolet Plume Instrument (UVPI)

Instrumentation:	Two intensified charge coupled device (ICCD) technology based cameras
Operational capabilities:	Automatic pointing, acquisition and tracking Up to 30 plume images per section Stellar and internal light source calibration Data recording within experiment

Launch Vehicle

Delta II launch vehicle.



LACE primary mission overview

Navy Awards Ocean Sciences Educators

Five academicians at four institutes of higher education have been recognized by the Office of Naval Research (ONR) for their distinguished records as researchers and educators in Navy-relevant areas of Oceanography. Each recipient will receive grants of $75,000 per year over the next three years.

Receiving the first ONR Ocean Science Educator Awards are: Dr. James O'Brien, Florida State University; Dr. Douglas Inman, Scripps Institution of Oceanography; Dr. Harry DeFarrari, University of Miami; and Drs. Peter Jumars and Peter Rhines, University of Washington. The selections were made from a field of 24 researchers from 17 institutions.

Goals of this new ONR program are to recognize ocean scientists who are outstanding educators, to identify and support exceptional post-doctorate researchers entering ocean sciences from other scientific disciplines, to expand the pool of high quality ocean science researchers, and to enhance interactions between academia and Navy laboratories. At least $65,000 of the grant funds are intended for direct support of ONR-sponsored Postdoctoral Fellows within the educators' programs. Any remaining funds are available for support of the educator.

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