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Introduction

The variety of disciplines that were accommodated by the 36 Spacelab flights logically group into 3 distinct categories; 1. External Observations in which the Shuttle/Spacelab is used as an observing platform, 2. Microgravity Sciences that make use of the microgravity environment to further the studies of Fluid Physics, Combustion Science, Materials Science, and Biotechnology, and 3. Life Sciences that studies the response and adaptability of living organisms to the microgravity environment. Because of the bulk of the material involved and the diverse interests, the report has been divided into three volumes with the previously mentioned titles. This volume deals with Microgravity Science as defined above.

The purpose of this Spacelab Science Results Study is to document the contributions made in each of the major research areas by giving a brief synopsis of the experiments and an extensive list of the publications that were produced by each Investigator team. We have also endeavored to show how these results impacted the existing body of knowledge, where they have spawned new fields, and, if appropriate, where the knowledge they produced has been applied. Since a new generation of young researchers will make up the cadre of Investigators that utilize the International Space Station (ISS), We feel it is important to leave a legacy of the results, some positive, some negative, of the previous experiments that have been performed. Hopefully, the new generation will build on the successes and learn from the failures of the past.

The material used in study came from many sources including the Mission Summary Reports, Mission and/or Investigator Team WEB sites, the International Distributed Experiments Archives (IDEA, which contains both the NASA Microgravity Research Experiments (MICREX) database and the ESA Microgravity Database), the Compendex*Web, the Science Citation Index, various survey papers, conference proceedings, and the open literature publications of the Investigators. Unfortunately, the MICREX database, which had been an excellent source of information for microgravity flight experiments, has not been maintained since USML-1, so it is only useful up to that point.

The bibliography is rather extensive and includes papers generated by the various investigators during the course of the development of their experiment as well as the results and applications of their results. There is, perhaps, a lack of uniformity in the number of documents listed since some Investigators left a much more extensive

document trail than others. Also, several of the Investigators had spent a good fraction of their carrier in the development of their experiments. Even though this study was restricted to the experiments actually performed on Spacelab missions, in several cases experiments performed on suborbital rockets or on non-Spacelab Shuttle flights went in to the development of the Spacelab experiment. Therefore, the results from these flight were also included in the bibliography.

The number of publications generated by this program is quite impressive as summarized in the table below.

	Total Publications	Journal Articles
Fluids and Combustion	681	378
Materials Science	999	461
Biotechnology	598	360
Total	2278	1199

We regret that time and resources did not permit iteration with the Investigators, as we would have liked to do. So if a result is misinterpreted or if references were missed, we apologize. We tried to include every microgravity experiment that was flown on a Spacelab mission, but invariably, when dealing with this many experiments in a limited time, an important experiment or result is bound to be missed. Again, we apologize to the Investigators I may have slighted.

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Fluids and Combustion in Microgravity

The study of the behavior of fluids in microgravity is fundamental to the understanding of virtually all other microgravity science since the suppression of fluid flows resulting from buoyancy effects is the primary reason for most microgravity experiments. (The exceptions being cases in materials science where the hydrostatic head may cause deformations in extremely weak solids or in the life sciences where there is evidence that the unloading of the cytoskeleton may be responsible for altered cellular behavior.) As a result, many of the fluids experiments were aimed at providing information to support the materials science experiments. One of the striking features in much of the research on the behavior of liquids in space is the importance of capillary or interfacial phenomena after buoyancy effects are essentially removed. Clearly these phenomena are present in normal gravity, but are often neglected because their effects are often masked by buoyancy-driven flows. The ability to uncouple gravity effects from non-gravitational effects, so that the latter can be studied in more detail, has been one of the primary justifications for the study of fluid phenomena in microgravity.

Gravity has a profound effect on the behavior of fluid systems undergoing second-order phase transformations as the compressibility vanishes. Consequently, the microgravity environment has been used to advantage to perform critical tests of fundamental theories dealing with the universality of material behavior near a critical phase transition.

Combustion experiments in microgravity are a special case of fluid experiments in which chemical reaction must be included. However, the motivation for performing this class of experiments in space is basically the same; the need to separate gravity-related from non-gravity related effects and to use the simplifications obtained by effectively eliminating convective transport in order to gain a better understanding of the basic principles involved. It is also important to understand combustion in the virtual absence of gravity to develop design criteria and emergency procedures for dealing with fire safety in the operation of manned laboratories in space.

Capillarity Effects on Liquid Configurations

In dealing with partially filled containers in low gravity, it is important to be able to predict where the liquid will be. Generally this will be determined by the geometry of the container and the contact angle between the liquid and the container wall. The Young-Laplace-Gauss equation can then, in principle, be solved to give the minimum surface. One of the difficulties with the theory is that a friction is involved in moving the contact line. As a result, the contact angle depends on whether the contact line is advancing or receding, giving rise to a phenomena known as contact angle hysteresis. Several experiments were carried out to see how well such systems could be modeled.

For example, on Spacelab 1, Haynes (University of Bristol) recorded the spreading of a tethered drop of silicone oil when it touched another clean aluminum plate. Here, the aim was to understand the dynamics of an advancing contact line.

In another experiment on SL-1, Padday (Eastman Kodak Ltd., UK) established silicone oil floating zones between two axisymmetric plates of unequal sizes. Using the Young-Laplace –Guass equation to calculate the pressure from the configuration of the zone, he was able to measure the disjoining pressure (the pressure that must be applied to remove the film) in the film that spread over the larger plate. Padday likened his directing the Payload Special to do his experiment and having to rely on his surrogate to describe what was happening to the way the pioneering Belgian physicist, Plateau, had to operate more than a hundred years ago when he did similar experiments using neutrally buoyant immiscible fluids. Plateau was blind.

Padday repeated the experiment on D-1 to study the effects of rotation and vibration on the zone shape. Both monorotation (rotation of cone plate only) and isorotation (rotation of both end plates) did not visibly change the zone shape contrary to theoretical calculations based on the Laplace equation. Induced axial vibration did not induce harmonic wave movement and apparently increased the stability of the zone. The rupture of the liquid zones was also analyzed during these experiments. The rupture occurred rapidly at two places in the thin column. The column becomes a satellite drop and the liquid at end plates relaxes to spherical drop shape. The satellite drop rebounded between liquid/air surfaces, but did not penetrating these surfaces.

Vreeburg (National Aerospace Laboratory, Amsterdam) investigated the behavior of silicone oil in a partially filled plastic cylinder as it was spun up and spun down on Spacelab 1. The objective was to test the ability to model the behavior of propellants in a partially filled tanks in low gravity. He conducted a similar experiment on the D-1 flight using doubly distilled water in a plastic cylinder to investigate the effects of vibration and the movement of the contact line. He was able to predict the resonant frequencies with reasonable accuracy, but the behavior of the contact line presented some difficulty. At first glance, it appeared that the contact line had stuck. However, closer analysis revealed that the contact line did move a small amount and that the oscillating contact angle exhibited some hysteresis.

A tribology experiment was carried out on Spacelab-1 by Pan (Columbia University) with Gause and Whitaker (NASA/MSFC). Drops of oil were deposited on stainless steel surfaces with various surface treatments and finishes and the rate of spreading was recorded. In a second part of the experiment, the configuration of the oil film in a journal bearing was investigated. In the normal function of a journal bearing, the clearance space is only partly filled with lubricant and gravity drainage positions the lubricating film so that shear forces can move the lubricant to the region where it is needed. The investigators wanted to know such a bearing would operate in the absence of gravity drainage with and without a load.

Concus (Lawrence Berkeley Laboratory), Finn (Stanford U.) and Weislogel (NASA Glenn Research Center) came up with a design of a container that admitted a continuum of possible rotationally symmetric configurations for a given fill fraction and contact angle, but none of the configurations were stable. They presented an interesting question, how would nature select an equilibrium configuration? They found the answer

using the glovebox on USML-1. No one told Mother Nature that the configuration had to be rotationally symmetric, so she simply selected a nonsymmetric configuration. Again, the effect of contact line sticking and contact angle hysteresis were noted when the Payload Specialist was trying to coax the fluid into its equilibrium shape. The small residual gravity may also have played a role in determining the shape of the liquid.

It can be shown theoretically that a liquid will penetrate into a wedge if the contact angle $\gamma < \gamma_0 = \pi/2 - \alpha$, where α is the half-angle of the wedge. Langbein (ZARM, U. Bremen) fabricated test cells from quartz plates with rhombic cross sections at different half-angles. These were partially filled with an index matching fluid after the walls were coated with FC-724 to provide the desired range of contact angles. The contact angle was changed by heating the test cells in the bubble, drop, and particle, unit (BDPU) on IML-2. Langbein expected to see the liquid rise in the wedge-shaped corners of the test cells when the contact angle became less than the critical value γ_0 . However, the resulting surfaces did not match the computed surfaces, and even though the contact angle became less than the critical value, wetting was not observed. He attributed this behavior to contact line friction which caused the volume change during heating and cooling to be accommodated by varying the contact angle rather than by moving the contact line.

Concus and his team carried out a variation of Langbein's experiments on USML-2. They machined a shape they called a "canonical proboscis" along diametrical opposite sides of an acrylic cylinder. The special shape has the property that for a given radius of curvature, the contact angle remains constant as the liquid penetrates into the cavity. The right and left shapes were chosen to accommodate different contact angles. Three such vessels were constructed; one in which the right and left contact angles were subcritical, one in which the right and left contact angles included the critical angle, and one in which both contact angles were supercritical. It was anticipated that the liquid would rise slightly higher in the side closer to the critical contact angle for the subcritical cell, that the liquid would rise in the supercritical side at the expense of the subcritical side in the intermediate cell, and the liquid would rise in both sides of the supercritical cell. This is essentially what was observed, except that the liquid did not rise spontaneously in any of the cases because of contact line friction. Only after considerable mechanical tapping and coaxing by the Payload Specialist were these results achieved. Observation of the supercritical cell after 7 days indicated that the liquid had continued to creep along the walls, but at a very slow rate. A wedge-shaped container with a variable wedge angle was also used in this series of experiments. Here the liquid in the wedge rose rapidly as the wedge angle reached the critical value.

Zone shape and stability

Microgravity offers the possibility to conduct experiments with free liquid surfaces on a scale not possible on Earth. One process of interest to materials scientists is the use of a floating zone for crystal growth. A molten zone is created in a rod of feed material and is traversed along the rod. New feed material enters the advancing zone and a single crystal can be grown at the receding interface. Of primary interest is the stability of such zones.

Lord Rayleigh (see Proc. Royal Soc. 29 (1879) 71) showed that a cylindrical liquid column would become unstable and break if the length exceeded the circumference. But what happens if the zone is not cylindrical? Or if it is rotated, which is sometimes done to even out asymmetries in heating? Or vibrated by mechanical disturbances in the spacecraft? Many of these questions had been approached theoretically and experimentally using a Plateau tank. But they had never actually tested in an actual microgravity situation. As was discovered when an unexpected “jump rope” or C-mode instability showed up in a simple rotating liquid zone experiment on Skylab, the presence of a neutral buoyant solution in a Plateau tank is a different boundary condition, which can often change the result of an experiment.

Martinez and Meseguer (Universidad Politecnica de Madrid) compared computational predictions of the stability of extended liquid columns of silicone oil under various mechanical manipulations with observations during the SL-1, D-1, and on D-2 flights. The liquid columns were suspended between two metal discs with a radius of 1.75 cm and a 30-degree receding sharp edge to prevent liquid spreading. Cylindrical columns with length/diameter ratios of 2.86 were established several times. This maximum length is short of the Rayleigh limit of 3.14, but appeared to be bounded by the ambient noise (g-jitter) during the mission. A long cylindrical column was subjected to vibrational frequencies of 0.1, 0.3, 0.7, 1.1, and 1.6 Hz. No movement of the liquid was observed for 0.1 Hz vibration. However, standing waves with 2, 3, 4, and 5 inner nodes were found for the remaining frequencies, respectively. The number of nodes for the respective frequency was successfully predicted by theory. Destabilization of the columns, caused by rotation at increasing rates, occurred near the theoretical limit. When liquid bridges were subjected to perturbations beyond the stability limits, they broke in two separate drops. The relative volumes of these drops were predicted by theory. During one of the runs, when subjected to 10 rpm of isorotation, the column broke in an amphora-shape mode, as predicted.

Langbein (ZARM, Bremen, Germany) also investigated the resonances of vibrating liquid columns using pressure sensors mounted on the endplates. This proved to be an effective method for observing when resonance occurs. His results compared favorably with ground tests in a Plateau tank and with theory he developed. An accidental misalignment of one of the discs on one experiment caused the zone to spill, illustrating the sensitivity of the zone stability to non-axisymmetric configurations.

Microgravity offers a unique opportunity for purifying glass by zone refining and then making cylindrical preforms by a quasi-containerless process. A long zone (near the Rayleigh limit) could be formed and allowed to cool below the working temperature in the middle. This portion could then be clamped and the two molten zones extended to the length of the sample. The critical issue becomes the stability limits of a solid suspended on each end by a liquid zone while it is cooling. Using small lexan rods, Naumann (University of Alabama in Huntsville) and Langbein investigated the stability of this double floating zone configuration. If the two zones have equal volume and are bulging, the float will remain centered. However, if the zone are extended, it switches to an antisymmetric mode with a long, slim zone on one side and a short fat zone on the

other. Theory indicates that the presence of the solid between the two liquid zones actually tend to stabilize the system and, for cylindrical zones of equal volume, it will remain stable up to and slightly beyond the limit in which the total zone length equals the circumference.

Using the glovebox on USML-1, Naumann also investigated the feasibility of pulling optical fibers in low gravity using silicone oil with different viscosities as well as honey as model materials. It turns out that it is much easier to pull long strand of viscous liquids on Earth because gravity drainage stabilizes the strand against the Rayleigh instability. Such strands broke almost immediately in microgravity, as predicted by Rayleigh's theory. (Rayleigh had attempted to test his calculations, without much success, by observing the breakup of strands of treacle laid on waxed paper.)

The Rayleigh limit ($L/D = \pi$) for a cylindrical bridge is a consequence of surface tension forces which tend to restore the bridge below the Rayleigh limit and tend to pinch-off the bridge above the Rayleigh limit. However, these forces can be modified by the presence of an electric field. Charging a liquid bridge produces a radial electric field, which makes the bridge more unstable. Conversely, an axial field should stabilize the bridge. The only present electrohydrodynamic theory governing such effects is the "leaky dielectric theory developed by G. I. Taylor (see Proc. Royal Soc. A291 (1966) 27-64) which has remained largely untested.

Burcham, Sankaran, and Saville (Princeton U.) decided to test Taylor's "leaky dielectric" theory by applying strong axial electric fields to liquid bridges, extending them beyond the Rayleigh limit, and then slowly relaxing the field to find the point where the cylindrical shape transitioned to the amphora (vase-like) mode occurred and the point where the bridge would eventually break. Their interest lay in obtaining a reliable, well-tested theory to guide in the development of miniature fluidics systems that utilize electrodynamic forces for pumping and manipulating fluids to carryout chemical reactions on a microchip.

Two dimensionless parameters control the stability of the electrodynamic stabilized liquid bridge, the L/D ratio, and a Δ parameter which measures the electrodynamic stabilizing force to the surface tension destabilizing force. Runs were made with a neutrally buoyant 2-phase system (castor oil in 12,500 St. silicone oil) for comparison with laboratory experiments in a Plateau tank. A single phase bridge (castor oil doped to 10 times the conductivity of neat oil) was extended to $L/D = 4.32$ and became cylindrical with a $\Delta = 0.95$. An unexpected result was the transition from the cylindrical to the amphora shape occurred at different values of Δ , depending on whether the field is increasing or decreasing. Also, according to theory, it shouldn't matter if the applied field is AC or DC, as long as the frequency is above the free charge relaxation time. They were not able to stabilize the bridge with an AC field. As is often the case, a good experiment asks more questions than it answers, and this experiment seems to be no exception. The Investigators are now sorting out which aspects of Taylor's theory are correct and what parts need improvement.

Marangoni Convection

The atoms or molecule at the surface of any solid or liquid cannot form as many bonds as those in the interior simply because they have fewer nearest neighbors. This give rise to an excess surface energy (i.e., the atoms or molecules on the surface have less negative energy than the more tightly bound atoms or molecules in the interior). If the surface is deformable, as in the case of a liquid, it will take a shape which minimizes the surface area in order to lower its energy. Furthermore, work is required to create new surface. This work is the product of the force that must be applied times the distance it must act, so the surface energy per area is equivalent to the force per distance or surface tension.

The surface tension is a function of temperature as well as composition. Therefore, if there is a variation of either temperature or composition along a free surface of a liquid, there will be an unbalanced force that can drive flows along the surface. These flows are usually called Marangoni flows after the Italian who studied these phenomena. (The “no-slip” boundary conditions at a solid-liquid interface suppress the surface flows. Therefore it is generally accepted that Marangoni convection only occurs in the presence of free surfaces.) Microgravity dramatically reduces buoyancy-driven convection, but microgravity experimenters must still contend with Marangoni convection. On Earth, buoyancy-driven flows compete with or add to Marangoni flows, so space provides an excellent place to study Marangoni flows without this interference.

Microgravity offers the possibility to conduct experiments with free liquid surfaces on a scale not possible on Earth. For example, floating zone crystal growth is possible in space for systems whose surface tension is not able to support the zone in a gravity field. Also the zone can be extended in space which allows better control of the thermal gradient and the interface shape. However, temperature gradients along molten zone can cause convective flows in the melt. This prompted a number of fluid experiments to quantify the effect of these convective flows.

From a fluids point of view, it is more convenient to study the flows in the floating zone process in a half-zone. The process is simulated by deploying the liquid column between two metal discs that are maintained at different temperatures. On SL-1 Napolitano, Monti, and Russo (University of Naples) applied temperature differences between columns of silicone oil and measured the flows and heat transport induced by Marangoni convection for comparison against numerical computations. A second experiment on D-1 used a concave cold disc and a radial temperature distribution on the hot to simulate the interface shape in a floating zone crystal growth experiment. The results were similar to those obtained on SL-1. Experiments were also carried out with a two liquid zone by adding dioctyl-phthalate to the silicone oil. Upon heating, the one of the liquids went into the center of the zone, forming a drop.

When growing crystals by the floating zone process, it is often desirable to have the melt in the zone well mixed. Therefore, some convection can be helpful. What needs to be avoided is unsteady or time-dependent convection which can result as the Marangoni flows get stronger. When this occurs, thermal and compositional fluctuations at the

growth interface produce unwanted growth defects called striations in the growing crystal.

Chun (Pohang University, Korea) and Siekmann Universitat Essen, Germany) investigated the transition from steady to unsteady flows in the half-zone configuration on the D-2 mission. They found a critical Marangoni number (ratio of driving force to viscous drag) that produced the lowest oscillating mode; one in which the flow pattern becomes non-axisymmetric and rotates around the axis of the zone. At a higher Marangoni numbers, the flow becomes turbulent or chaotic with no defined structure.

On D-2 Monti (University of Naples) with Carotenuto, Albanese, Castagnolo, and Ceglia (MARS Center, Naples) noted that small scale half-zone experiments conducted in the laboratory went into the unsteady oscillatory mode at lower Marangoni numbers than some of the earlier flight experiments. They investigated the onset of unsteady flow as a function of aspect ratio and diameter of the zone. They concluded that for a given diameter, the critical Marangoni number increased with aspect ratio (length/diameter), and for a given aspect ratio, it also increases with diameter.

One method that has been considered for controlling Marangoni convection in floating zone crystal growth would coat the molten zone with an viscous immiscible liquid-phase encapsulant such as B_2O_3 . Some flow would still result but since the surface of the low viscosity melt would have to drag the viscous encapsulant with it, the flow would be damped to the point that unsteady convection would not result. Several attempts have been made to model such a multi-layer configuration and Legros and Georis (Universite Libre de Bruxells, Belgium) developed a 2-dimensional experiment that was flown on IML-2 and on the LMS mission to test such models. They deployed a three layer fluid system that consisted of a layer of 10 cSt silicone oil sandwiched between two layers of higher viscosity Fluornet FC-70 oil which was contained on the top and bottom by sapphire windows. A lateral thermal gradient was established and the flow was visualized using marker particles and a laser light cut. The observed flows were qualitatively similar to the expected behavior; the interfaces moved from hot to cold with the return flow through the middle of each layer. However, the measured flows turned out to be considerably larger than the computed flows. The reason for the discrepancy is still being investigated. One possible reason is that the computations assumed constant material properties, whereas the viscosities of the flows do change considerably with temperature.

There is also considerable interest in Marangoni convection along horizontal surfaces. Such flows are prevalent in combustion processes such as pool burning and may be seen around the wick of a burning candle. Strong surface tension gradients occur in the growth of silicon and other crystals by the Czochralski process in which the crystal is pulled from a large heated pot of molten silicon. Such flows are usually unsteady and may be turbulent. The resulting thermal fluctuations are the primary cause of the striations seen in Czochralski-grown silicon.

During the D-1 mission, Schwabe, Lamprecht, and Scharmann (Universitat Giessen, Germany) investigated Marangoni convection in a 20 x 20 x 20 mm cell with an open surface sandwiched between two heating blocks. To avoid the problem of having to fill the cell in space, they melted a block of tetracosane (paraffin) which served as their working fluid. With one heater set at 60°C, they raised the temperature of the other block. To their surprise, no flow was observed even after a ΔT of 55°C was established. Finally, at a ΔT of 60°C, a strong flow developed. They concluded that the surface of the tetracosane must have been contaminated with a substance that either lowered the surface tension or resisted the surface stress until it finally broke through at a ΔT of 60°C.

The experiment was repeated using silicone oil on D-2, by Cramer, Metzger, Schwabe, and Scharmann (Universitat Giessen). Care was taken to maintain a flat upper free fluid interface at the beginning of the experiment. Flow was measured by observing tracer particles illuminated by a vertical light cut. The temperature field was measured using holography interferometry. A lower than expected temperature in the cooling loop caused unexpected cooling at the top surface, which resulted in a more complicated three-dimensional flow pattern. The formation of "tracer rings" was observed in which the tracer particles tended to accumulate along streamlines that passed close to a free surface.

Enya (Ishikawajima-Harima Heavy Industries Ltd., Japan) was interested in Marangoni convection in Bridgman crystal growth that might occur if the melt is not in contact with the ampoule walls. He also chose paraffin as a model and saw no evidence of Marangoni flows.

The surface tension of most fluids decreases with increasing temperature, but Limbourg-Fontaine, and Petre (Universite Libre de Bruxells, Belgium) determined that an aqueous solution of n-heptanol had a surface temperature minimum at 40°C. During the D-1 mission, they differentially heated this fluid in a 1 x 1 x 3 cm test cell so that surface tension increased more-or-less symmetrically on either side of the center of the cell. A small convective roll first developed near the hot wall, flowing from cool to hot, or from lower to higher surface tension, as would be expected. However, instead of seeing a counter-rotating flow on the cold side, the flow near the hot end expanded to fill the test cell and eventually formed a second co-rotating cell near the cold end. The reason for this unexpected behavior is still being investigated.

Ostrach, Kamotani, (Case Western Reserve University) and Pline (Glenn Research Center, NASA) carried out an elaborate set of experiments on USML-1 and USML-2 aimed at determining the factors involved in the transition from steady to unsteady surface tension-driven flows. Of particular interest was the role of surface deformation in this transition. If surface deformation is unimportant, as some theories suggest, then it should be possible to predict the onset of unsteady flows with a single parameter, the critical Marangoni number. On the other hand if surface deformation does play a key role in the transition, a surface deformation parameter will be required to completely specify the conditions for the onset of unsteady flows. Thus it became necessary to explore a wide range of parameters in order to establish the transition conditions.

Silicone oil was contained in a cylindrical test cell. A sharp pinning edge confined the height of the oil in the test cylinders so that different surface shapes could be obtained by adjusting the filling. The oil could be spot heated at the center with a CO₂ laser, or heated by an immersed heater. This feature allowed experiments to be conducted in the constant temperature or the constant flux mode. Surface temperature was measured with an imaging infrared radiometer. Marker particles assisted flow visualization.

The test cell on USML-1 was 10 cm in diameter and 5 cm deep. The fluid was 10cSt silicon oil. Very nice surface tension driven flows were observed, but no transition to oscillating flows was observed within the operating range of the instrument. A series of test cells with diameters 1.2, 2, to 3 cm were used for USML-2. The 10cSt oil was replaced with 2cSt oil and a Ronchi interferometer was added for the USML-2 experiment to measure surface deformations.

A total of 55 tests were made with the 6 different size and heating configurations. Flows in the smallest cells with the cartridge heater began oscillation at the same temperature difference as their 1-g counterparts, indicating that buoyancy drive flows are not the dominating factor for this size and smaller. The time-dependent flow exhibited a small azimuthal oscillation superimposed on a slowly rotating flow about the thermal axis. The thermal image indicated first a pulsating or rotating 2-lobe or 3-lobe pattern, depending on the temperature difference and cell geometry. It was found that the Marangoni number alone is not sufficient to characterize the onset of oscillatory flows, but a critical value of a surface deformation parameter, which they defined, describes the onset of oscillation in microgravity.

The previously described Marangoni convection experiments had variations in surface tension along the fluid surface. In such experiments, convection should begin as soon as there is an unbalanced force. In other words, there should be no threshold thermal gradient required to start the flow, just as in the case of buoyancy-driven free convection when the thermal gradient has a component perpendicular to the gravity vector. However, in the famous Rayleigh-Benard problem, the g-vector is aligned with the thermal gradient (cold over hot). Even though this is an unstable configuration, flows will not develop until a critical value of the Rayleigh number is reached. The Rayleigh number is a measure of the rate heat is being convected to the rate it is being conducted. If the Rayleigh number is small, a displaced parcel of fluid can accommodate thermally before it can rise very far, hence will settle back into place. If the Rayleigh number is large, the fluid cannot be accommodated thermally and it will continue to rise, forming circulating Benard cells. Rayleigh was able to predict the critical value of the Rayleigh number corresponding to the onset of convective flows for different boundary conditions at the top and bottom of the cell.

If the top surface is a free liquid boundary, the system is also subject to unstable Marangoni convection (actually this problem was first studied by Pearson. (See J. R. A. Pearson, J. Fluid Mech. 4 (1958) 489-500). The system can lower its energy by replacing the cooler fluid with higher interfacial energy at the top surface with warmer fluid from

the interior that has lower interfacial energy. However, for this to happen, the Marangoni number must exceed a critical value.

One can see immediately that the two types of convection will be in competition in a gravity field. Therefore, it is necessary to eliminate gravity if one is to get an accurate test of the surface tension effect. This experiment was first performed on Apollo missions 14 and 17 during the return from the moon (see P. G. Grodzka and T. C. Bannister, *Science* 176 (1972) 506-508, also *Science*, 187 (1975) 165-167) who measured a somewhat higher value than the theoretical Marangoni number for the onset of convection. It should be appreciated that this is not a trivial experiment to perform accurately. The theory requires a flat interface and that the temperature gradient in the sample be uniform. This latter condition requires a very carefully controlled heating program.

Legros, Dupont, Queeckers, Petre (Universite Libre de Bruxells, Belgium) and Schwabe (Universitat Giessen, Germany) essentially duplicated the Grodzka-Bannister experiment on D-2 with better controls than were available on the Apollo spacecraft. They modified the theory to account for non-equilibrium heating and varied the heating rate to investigate the effect of non-equilibrium temperature profiles on the critical Marangoni number. For a fast heat-up (14 times the heating rate to approach equilibrium heating), they measured a critical Marangoni number of 95 against their calculated value of 101. For a slower heat up (7 times the equilibrium heating rate) they measured a critical value of 77 compared with their theoretical value of 82.4. Unfortunately, due to a technical problem with the heater, they were unable to obtain an experimental value for the equilibrium case.

Lichtenbelt, Drinkenburg, and Dijkstra (University of Groningen, the Netherlands) investigated solutally-driven unstable Marangoni convection in a mixture of acetone and water with a free surface on the D-1 mission. As the acetone evaporated from the surface, the surface tension increases. Since the system can lower its energy by replacing its higher interfacial energy surface layer with fluid richer in acetone from the interior, the system is subject to a convective instability. At a critical Marangoni number, an overturning flow will develop. This is a common situation in many industrial applications such as distillation, adsorption, and desorption and is also an important factor in the drying of paint, especially lacquers with a volatile solvent. A similar process is responsible for "wine tears", the tendency for drops to form above the surface of a fortified wine or brandy. Lichtenbelt, et al. wanted to investigate the effects of the surface tension without the gravitational interference. Quite unexpectedly, no convection was seen in space as long as the fluid interface was kept flat. (This was done by filling the cuvette to the anti-spread barrier.) Convective rolls did appear as some fluid was drained out and the interface became more curved. It was speculated that either the surface became contaminated or that the critical Marangoni number had not been attained. A compositional gradient may have been established when the surface became curved which drove a thresholdless flow.

When a liquid contacts a solid, fluid dynamists usually assume a “no-slip” boundary condition. It is commonly believed that contact of the fluid with the wall resists any imbalance of interfacial forces, so that Marangoni convection need be considered only in experiments that have free surfaces. Consequently, experimenter using closed fluid systems such as the Bridgman configuration for directional solidification, generally ignore the possibility of unwanted flows from Marangoni convection. There has been some speculation about a second order Marangoni effect in which these unbalanced forces can still drive very small flow in spite of the “no-slip” condition, but there has been no direct experimental confirmation of such flows. However, it is well known that Marangoni flows around bubbles in a liquid will drive bubbles toward decreasing interfacial energy (usually toward the hotter regions of the liquid). What is not generally appreciated is that these flows also stir the melt.

Using the glovebox on USML-1, Naumann (University of Alabama in Huntsville) differentially heated a cylindrical cell containing Krytox 143AZ, a low viscosity fluoro-carbon fluid. A 1 cm³ void had been intentionally left when filling the chamber to simulate the head space needed for thermal expansion. Since the fluid wet the container, the void became a bubble, which migrated to the heated end of the test cell. There it lodged between the plug heater and one wall. Marker particles in the fluid revealed a strong flow around the bubble which penetrated the entire test cell. The resulting flows near the cold end, which would represent the forming solid in a directional solidification experiment, were several orders of magnitude higher than the flows expected from spacecraft residual accelerations. Flows such as this may explain some of the unexpected mixing that was observed in the early Skylab and ASTP experiments.

A similar observation was made by Azuma (National Aerospace Laboratory, Japan) on SL-J. In this case, secondary flows associated with a large bubble that had become attached to the hot wall caused smaller bubbles to be brought into its vicinity and formed a line along the thermal gradient.

Drop and Bubble Migration

Young, Goldstein, and Bloch (YGB) solved the Navier-Stokes equations for a spherical drop or bubble in an infinite liquid with an imposed temperature gradient. Taking into account the flows from the unbalanced interfacial forces, they showed that the droplet would be propelled in the direction of decreasing interfacial tension (see J. Fluid Mech. 6 (1959) 350). Since they did not have access to a microgravity environment, they tested their theory by balancing the surface tension forces against buoyancy forces.

Naehle, Neuhaus, Siekmann, Wozniak (DLR, Koln) and Srulijes (U. Essen) tested the YGB model in the absence of buoyancy forces on the D-1 mission by injecting bubbles of air and drops of water into Wacker AK100 silicon oil. They confirmed the fact that the bubbles remained spherical, which eliminated some speculation that the YGB model may be in error because it didn't account for possible distortion of the bubble under the combined influence of surface tension stresses and Stokes drag. They found qualitative agreement with the velocities predicted by the YGB theory for small Marangoni

numbers, but the observed velocities became progressively lower than predicted for $Ma > 1$. The YGB model predicts that the velocity should be directly proportional to the Marangoni number, but does not take into account convective thermal transport. Therefore, it is only valid in the limit of vanishing Marangoni number and corrections are required to the model for this effect. The droplets of water did not move at all. (It is a well-known experimental fact that the Marangoni effect is virtually impossible to observe in water because of trace quantities of surface active contaminants that tend to nullify the driving force.)

Neuhaus and Feuerbacher (DLR, Koln) also tested the YGB model on the D-1 mission. Bubbles were deployed in 3 different silicone oils (Wacker AK100, AS100, and AP100) all of which had the same viscosities and thermal properties, but differed in the number of phenol groups. A temperature gradient was established and the bubbles were monitored holographically. The velocity of the bubbles in the AK100 oil with only 6% phenol groups agreed reasonably with the YGB predictions. Bubbles in the AP100 oil with 28% phenol groups did not move at all. Bubbles in the AS100 oil with an intermediate number of phenol groups moved at 40% of the velocity predicted by the YGB theory. The investigators suggested the additional of a "surface dilatational viscosity" term to the YGB formulation to account for the resistance of the surface to deform.

Subramanian and his team at Clarkson University used the Bubble, Drop, and Particle Unit (BDPU) on IML-2 to measure the velocity of air bubbles and Fluorinet FC-75 drops in 50cSt silicone oil under a thermal gradient. They also found that the scaled velocity decreased with Marangoni number, as would be expected. Since the velocity of a drop or bubble depends directly on the radius, larger drops would be expected to overtake and engulf smaller drops. This effect is believed to be one of the mechanisms in the agglomeration of minority phase droplets during the solidification of monotectic alloys. However, Subramanian et al. observed an interesting effect in that a small drop leading a large drop can slow the motion of the large drop. (Naehle et al. observed that when a large drop leads a small drop, it still moves faster than the smaller drop, but the velocities of both drops are lower than they would be as individual drops.) Subramanian et al. speculated that a thermal wake behind the first drop reduces the driving force on the second drop and designed an experiment on LMS to study this effect further. Here they found that when two or three drops were injected into the chamber, the second and third drops did not always follow a straight path across the chamber, as single drops did. Instead, they followed a sinuous, helical path around their expected trajectory. Sometimes a larger trailing drop would actually move around and pass the leading drop.

Viviani (Seconda Università di Napoli) investigated the motion of bubbles in n-heptynol which has a surface tension minimum at 40°C. Instead of stopping at the 40°C isotherm, as was expected, the bubbles continued toward the cold wall, but did appear to slow down as they approached the 10°C cold wall. On his LMS experiment, Viviani set the cold wall temperature to 5°C, and the bubbles came to rest in the vicinity of the 8-10°C isotherm. Why the statically measured surface tension is a minimum at 40°C, and the apparent dynamic surface tension is a minimum at a lower temperature is still not

understood. (Recall a similar anomaly was observed in Legros' Marangoni convection experiment with n-heptanol on D-1.)

Monti attempted to investigate the interaction of water droplets and air bubbles in tetracosane (paraffin) with an advancing solidification front on IML-2, but encountered technical difficulties. The experiment was completed successfully on the LMS mission. One 0.9mm bubble was pushed by the front which was advancing at the rate of 1 micron/sec. Larger bubbles and water drops were engulfed. No motion of drops or bubbles in the molten tetracosane from Marangoni effect was observed. (Recall that Schwabe et al. observed no Marangoni flow in molten cosane in their Spacelab-1 experiment.)

Bewersdorff (DLR, Koln) attempted to observe bubble transport by chemical waves using the HOLOP facility on D-1. As the chemical reaction spreads, the thermal gradients generated by the heat of reaction can transport gaseous or liquid inclusions by the Marangoni effect. The reaction of Zhabotinski was selected for wave generation and the gas inclusions were to be generated from Zn particles. Unfortunately, problems with the HOLOP prevented detailed recordings from which the migration of the bubbles were to have been recorded.

Straub (LehrstuhlA fur Thermodynamik, Munchen) used the BDPU facility on IML-2 to study evaporation and condensation kinetics by measuring bubble growth (evaporation) and collapse (condensation) respectively in a supersaturated and supercooled liquid (Freon R11) under isothermal conditions. Varying degrees of supersaturation were obtained by varying the pressure in the container. The microgravity conditions permitted the study of the process in a stationary bubble without the buoyancy disturbing the temperature field in the vicinity of the bubble as the latent heat is absorbed or released. This allowed the kinetics of the process to be worked out and the accommodation coefficients to be determined. The results of this experiment were used to design the pool boiling experiment that was developed for the LMS flight.

Heat Transfer in Microgravity

It is generally assumed that heat transport in boiling is largely the result of buoyancy-driven convective flows. The bubbles that nucleate on the hot surface rise, carrying their latent heat with them. Similarly, the hot liquid near the surface, being less dense, will rise, causing overturning flows which carry heat away. The practice of cooling small electronic devices by immersing them in a pool of dielectric liquid with appropriate vapor pressure, such as Freon, was considered by many not to be feasible in space because it was assumed that vapor would form around the device resulting in inefficient heat transfer. However, Straub and co-workers proved otherwise on the LMS flight.

They immersed small heaters in the form of copper discs 1 to 3 mm in diameter in Freon 123 and measured the temperature and power in order to get the heat transfer coefficients over a range of temperatures or heat fluxes. Surprisingly, they found that heat transfer in microgravity was only slightly less efficient than it is in unit gravity. Thermocapillary

jets were observed which appear to be an effective mode of heat transfer. These results may cause the theories of boiling in normal gravity to be revisited and it may be possible to design systems that take advantage of capillarity along with buoyancy to improve the efficiency of boilers on Earth.

The Capillary Pumped Loop (CPL) was developed in the 1960's at the NASA Lewis Research Center (now the NASA Glenn Research Center) as a heat transfer device, similar to a heat pipe. The technique works quite well in normal gravity, but its operation in microgravity has been erratic. A transparent model of the device was fabricated and flown on MSL-1R by Halliman (U. Dayton) and Allen (National Microgravity Research Center, Cleveland) to gain insight into its operation without gravity with the hope of correcting the problem. It was found that in the absence of gravity drainage, liquid films would form and accumulate in the vapor return lines. Eventually, Rayleigh instabilities set in and liquid bridges form which obstruct the lines. In particular, these liquid slugs tend to form in bends in the line. The result is diminished ability to transport heat.

Critical Point Phenomena

A number of peculiar things happen in the vicinity of a second order or critical phase transition, such as takes place at the terminal point of the coexistence region between a liquid and its vapor. As the critical point is approached, the densities of the liquid and vapor become the same and the system fluctuates between the two states as though it can't make up its mind as to whether it wants to be a liquid or a vapor. These fluctuations produce a kind of opalescence when the test cell is viewed. At the critical point, the compressibility becomes infinite so that even the smallest temperature difference can cause very strong convection. Many of the other thermodynamic properties change dramatically near the critical point, e.g., the velocity of sound as well as the thermal diffusivity goes to zero, while the heat capacity becomes infinite.

Other systems, such as a magnetic system near the Curie point (the temperature at which thermal motion becomes sufficient to destroy the magnetization) or the demixing of a homogeneous liquid into two immiscible liquids at the critical consolute temperature, exhibit similar behavior. The divergence of certain parameters near the critical point in each of these systems show the same exponential behavior, thus leading to the theory of universal behavior near a critical phase transition, regardless of the system. Ken Wilson was awarded the Nobel Prize in 1982 for applying group renormalization theory to determine the exponential behavior of these diverse systems near a critical point (see K.G. Wilson, Phys. Rev. B 4 (1971) 3174).

On USMP-2 and -3 Gammon and his group at the University of Maryland used photon-correlation light-scattering spectroscopy to measure the density fluctuations as the critical point of xenon. They were able to record a number of photon correlation functions processed in real time, from which they could measure the decay rate of the fluctuations. The forward scatter intensity from the flight data showed a much sharper peak as the critical temperature was crossed than the ground control. They were able to locate the phase boundary to within ± 20 mK. The limiting factor in the experiment turned out to be

unexpected window heating from the 17 microwatt laser which prevented them from obtaining correlograms closer than 2 milli-K from the critical point.

On IML-1, Beysens (Commissariat a la Energie Atomique, Grenoble, France) was able to show that the phase separation that occurs when a near-critical single component vapor (SF_6) is quenched into the liquid-vapor coexistence region belongs to the same universal class as a two-component immiscible liquid system (methanol-cyclohexane) that is quenched from above its consolute temperature into the two-liquid phase region. Since gravity is also involved in phase separation, this could only be demonstrated in microgravity. He also observed that the growth rate for small volume fractions of the droplet phase in immiscible liquids followed either a $1/2$ power law (diffusive growth) or a $1/3$ power law (Ostwald ripening) (slow growth) but followed a first power growth law (fast growth) for larger volume fractions.

At temperatures below the critical point, a liquid can coexist with its vapor; whereas, at and above the critical isotherm, only a gas can exist. Klein and Wanders (DLR, Koln) sought to observe the homogenization of the two phases as the system is heated to its critical point. Since the compressibility diverges at the critical point, they sought to eliminate any hydrostatic head by performing the experiment on D-1 with near critical sulfur hexafluoride, SF_6 . Surprisingly, they found that it was very difficult to homogenize the sample at the critical point. It was later realized that since the thermal expansion also diverges and the thermal diffusivity goes to zero at the critical point, even the slightest thermal gradient could cause large differences in density distribution and the equilibration time would be much longer than the mission duration.

The divergence of the heat capacity on either side of the critical point is one of the important tests of universality of critical behavior. A characteristic λ -shape of the heat capacity vs. temperature with a singularity at the critical temperature is predicted theoretically. Measurements of the slope in this vicinity are used to determine the exponent governing the rate at which the heat capacity diverges. One of the difficulties encountered in such measurements is caused by the fact that the compressibility of the system also diverges. Thus there is a large density variation in any finite test cell because of the hydrostatic pressure and the actual critical condition is met at only one point in the test cell. Measurement of heat capacity of the cell then integrates over near-critical conditions, but cannot provide accurate data near the peak in the curve.

Nitsche and Straub (LehrstuhlA fur Thermodynamik, Munchen) tried to obtain a more accurate measurement of the heat capacity of sulfur hexafluoride near its critical point on the D-1 flight. Much to their surprise, the data in the vicinity of the critical point was smeared out even more than on Earth. Instead of the expected peak at the critical point, they measured only a broad hump. It was later found that instead of a well-mixed system with the fluid wetting the walls of the test chamber, that a phase separation occurred and persisted because of the very long diffusion time as the critical point is approached.

The test chamber was redesigned by Straub and Haupt for a repeat attempt on D-2. By cooling through the critical temperature, the "real" behavior of C_v could be determined

to within 0.9 mK from T_c , whereas ground measurements became disturbed by gravity at 15-20 mK from T_c . The heat capacity exhibited the sharp peak when cooling through the critical point and the universal coefficients were within experimental error of those obtained from group renormalization theory. Considerable hysteresis was seen in the C_v behavior when heating from the two-phase region, through the critical point, into the single phase region, which is attributed to the “critical slowing down” of phase homogenization as the chemical diffusivity vanishes. The heat capacity is described by the expression $A^{-1} |\tau|^\alpha + B$ the measured critical exponent α was found to be 0.109 ± 0.02 ; theory predicts $\alpha = 0.110 \pm 0.0045$. (See Le Guillou and Zinn-Justin, Phys. Rev. B (1980) 3976.)

The same experiment also confirmed the phenomena of “critical speeding up” or the “piston effect” for rapid heat transport near the critical point despite the fact that thermal diffusivity vanishes in this region. This effect had been seen on the ground, but was attributed to convective mixing as the compressibility diverges. However, the D-2 experiment confirmed the heating was due to an isentropic expansion instead of convective transport. By heating the wall of a container filled with a highly compressible fluid, a thin boundary layer is heated from diffusive heat transfer. The fluid in the boundary layer expands adiabatically, compressing the bulk fluid. Since the bulk fluid becomes heated by the adiabatic compression, heat transfer is virtually instantaneous.

Beysens used the “piston effect” to quench near critical SF_6 from the single phase region into the two-phase region on IML-2. A planned maneuver during one of the runs demonstrated how acceleration disturbs the piston effect thermal transport. He also observed two different growth regimes in the same system; a fast growth regime with a first power time dependence, and a slow growth regime with a $1/3$ power time dependence, depending on the quench depth.

Ferrell (U. Maryland) used the critical point facility on IML-2 to measure electrostriction effects and the time constant for thermal diffusion near the critical point of SF_6 . Electrostriction is the deformation of a fluid from an applied electric field. The effect can be quite pronounced near a critical point because of the divergence in compressibility, however, it is slow to develop because of the long thermal diffusion times. The thermal diffusion measurements agreed with ground based measurements more than 100 mK above the critical temperature, but were lower by a factor of 1.7 at 1.4 mK above T_c .

Precision measurements of the thermal field using high sensitivity (μK) thermistors by Michels (U. Amsterdam) on IML-1 confirmed the theoretical model for isentropic heat transfer from the piston effect.

Klein (DLR, Koln, Germany) used the piston effect to heat and cooled SF_6 through the critical point and observed the effect with laser light scattering. He observed critical opalescence almost immediately after cooling through T_c , but found that hours were required for the system to come to thermal equilibrium. He also determined that the gas-liquid configuration in the two-phase region is determined by interfacial effects.

Homogenization after heating into the single-phase region scales with the correlation length, which goes as $(T-T_c)^{-0.63}$.

Lipa (Stanford U.) sought to circumvent some of the problems associated with attempting to measure critical phenomena at the liquid-vapor critical point. Instead he chose to measure the heat capacity in liquid helium at the lambda-transition, the temperature at which normal He is transformed into superfluid He-II. This transition is known as the lambda transition because of the l-shape of the heat capacity in the vicinity of the transition. Since He remains a liquid on either side of the transition, the divergence in compressibility is avoided. However, the transition temperature is pressure dependent, so that in a gravity field, critical conditions exist at only one plane in the system. However, since the order parameter for the lambda transition is a two-component superfluid wavefunction, as opposed to the scalar density difference in the gas-liquid critical point, these two systems are not in the same universal classes, hence the critical exponents will not be the same.

Lipa and his group at Stanford had developed a thermometry system using superconducting quantum interference devices (SQUID) to detect minute magnetic changes in a paramagnetic salt, which can be directly related to temperature with nanoKelvin resolution. With this device, they were able to measure a sharp peak in the heat capacity curve to within a few 100 nK of the lambda point before the pressure variations in the finite test cell began to smear out the data. They were limited in how small they could make the test cell because of the correlation length over which the atoms act collectively. Therefore, they carried the experiment on USMP-1 to obtain measurements to within a few nK.

One of the unforeseen difficulties was heat pulses from cosmic rays and charged particle radiation in. They were eventually able to calibrate out and work around these events. Lipa found the value for the critical exponent to be -0.01285 ± 0.00038 . This value falls between the theoretical predictions of -0.007 ± 0.006 (Le Guillou and Zinn-Justin, Phys. Rev. B (1980) 3976) and -0.016 ± 0.006 (Albert, Phys. Rev. B (1982) 4912). In a sense, the lambda point is an ultimate test of the theory because of its unique sharpness. The value of such a test can best be described by a direct quote from Lipa,

“...this is at the foundations of condensed matter physics. We need to be sure the foundations are right so we can be confident of the scientific structure which supports our technology base. There is another angle, but maybe even harder [to explain]: RG [renormalization group theory] is used extensively in the Standard Model of elementary particles. There is a well-established relationship between this and critical phenomena. So one might one day get some insight into the 'theory of everything' via an obscure aspect of helium. Bit of a stretch, but that's where Nobel prizes come from!”

A follow-on experiment on USMP-4 extended the heat capacity measurements near the lambda-point in which the He is confined to a spacing of 57 microns by carefully machined Si discs. The objective is to test scaling predictions for the transition to a lower

dimension system. Normally, this transition takes place only when the dimension is on the order of Angstroms, but in semiconductors it can be as large as 0.1 micron, a length being approached by modern electronics. Since the correlation length diverges near a critical point, the distance over which the transition occurs can be greatly magnified. Attempts are now being made to correlate the data from the flight experiment with theory and other measurements.

Drop Dynamics

On Spacelab-1, Rodot and Bisch (CNRS, France) analyzed the deformations of a tethered drop of silicone oil as it was oscillated at various frequencies. They were able to determine the various resonance modes and compare with theory.

Wang (Vanderbilt University) studied the rotation and fissioning of freely suspended liquid drops on Spacelab 3 and again on USML-1 and USML-2 using the 3-axis acoustic levitator. These experiments are tests of a classical astrophysical problem dealing with the formation of double stars (see S. Chandrasekhar, Proc. Royal Soc. London A286 (1965) 1-26). Qualitative agreement with theory was found in the Spacelab 3 experiment, but the drops tended to fission before the theoretical rotation rate was reached but the drop had been flattened by the acoustic radiation pressure. On USML-1, Wang and Trinh measured the bifurcation point as a function of drop shape and were able to show that the bifurcation point agreed with theory in the limit of spherical drop shape. A comprehensive study of the effect of drop flattening on the 2-lobed bifurcation point was carried out on USML-2. The experiments were supported by a series of experiments carried out in the glovebox by Trinh (JPL) to test various droplet injection techniques.

Other experiments conducted with the 3-axis acoustic levitator by Wang and his team at Vanderbilt University investigated core centering in compound drops. It was shown that an induced sloshing mode produced centering forces in drops with a gas core (liquid shells) as well as drops with an immiscible liquid core. Understanding of the centering forces could be important in the manufacturing of perfectly concentric glass shells for inertially confined fusion experiments (ICF).

Weinberg (U. Arizona) attempted to use the three-axis acoustic levitator on USML-1 to measure the interfacial tension between two immiscible liquid phases by oscillating a compound drop, but ran into technical difficulties when attempting to deploy the two droplets. Yamanaka and Kamimura (National Aerospace laboratory, Japan) had similar difficulties when they attempted to measure the surface tension waves on stationary and rotating drops in a tri-axis acoustical chamber on SL-J.

If the induced oscillations in a drop have large amplitudes, various non-linear effects show up. Energy can be fed from one mode of oscillation to another, an effect known as mode coupling was observed. A hysteresis effect in the amplitude response was observed as the exciting frequency was swept back and forth across the resonant frequency, with a

peculiar jump in amplitude. Finally, the onset, transition, and fully developed chaotic oscillations of drops were observed. Understanding the conditions leading to chaotic oscillations are important from a practical as well as an academic point of view because droplet evaporation and combustion increase with increasing oscillation amplitude and frequency. Additional experiments involving the extraction of physical property data from large, non-linear oscillation of acoustically levitated drops were carried out using a single axis interference levitator in the glovebox on MSL-1R by Leal (UCSB), Trinh (JPL), Thomas (JSC), and Crouch (NASA HQ).

Sahdal (USC), with Trinh, Thomas, and Crouch used the same device on MSL-1R to determine if the deformation and rotation of an acoustically levitated drop could be controlled well enough to measure internal flows within the drop. In particular, they wanted to determine if Marangoni flows from spot heating the drop on one side could be measured. By reducing the power level to the minimum required to keep the droplet positioned in microgravity, the shape distortion could essentially be eliminated (at least to their limit of measurement of the ratio of the axes, which was 1%). Drop rotation in a single axis levitator results from any slight misalignment of the acoustic reflector or asymmetric reflections from the container walls and has always been difficult to control. By fine tuning the position of the acoustic reflector, drop rotation could be reduced to 0.1 rps.

Apfel and his team at Yale University used the 3-axis levitator on USML-1 and USML-2 to study the behavior of surfactants by observing the frequency and amplitude of freely suspended oscillating drops. They were able to extract material properties such as dynamic surface tension and shear as well as dilatational surface viscosities. The dramatic difference in diffusion and sorption times between Triton X-100 and bovine serum albumin (BSA) was illustrated. Since BSA is a slow sorber, the Marangoni stresses are significant, leading to much faster damping than for pure water.

Marston (Washington State University) with Trinh and Depew (JPL) used an ultrasonic resonator in the glovebox on USML-1 to investigate the positioning, shaping, and agglomeration of bubbles and oil drops in water. It was possible to coat the inside of a bubble with oil and study the centering mechanism.

Miscellaneous Experiments

Super Fluid Helium Experiment

Superfluid helium possesses several characteristics which make it uniquely suited for cooling space-based instruments. Such instruments include the Infrared Astronomical Satellite (IRAS) and the Space Infrared Telescope Facility. Liquid helium 4 (He 4) and its rare isotope, helium 3, remain liquid at absolute zero. At a temperature of 2.17 K and a vapor pressure of 5.1 kP (38.4 Torr), He 4 undergoes a transformation to a superfluid state. In this state, He 4 can transport large amounts of heat at very small temperature differences. Heat is transported by coherent wave motion rather than by diffusion. Its effective thermal conductivity is several orders of magnitude higher than any other

material. The high thermal conductivity is maintained in thin films and pores so small that a normal liquid would be immobilized. The advantage of this property is that the thin films, held to walls by van der Waals forces are superfluid. Therefore, the entire superfluid mass behaves as a single thermal mass with a temperature difference of a few milli-Kelvins.

Under certain conditions, superfluid helium has zero effective viscosity whereas the viscosity for bulk motions is not zero (about 1/100 of water). Therefore, the system may be extremely sensitive to small surface tension forces and/or vehicle accelerations since the natural damping of these motions is limited.

Another unique characteristic of superfluid helium is known as the fountain effect. In small pores or thin films, the application of a small temperature gradient along the pores sets up a pressure differential that tends to push the liquid to the warmer end. This fountain pressure is used in zero gravity to contain the liquid in the cryostat, while allowing the vapor created by heat flow into the bulk helium to evaporate to space. A porous plug is placed in the vent line. The outer end is cooled by the evaporation of liquid to gas, and the resulting temperature differential generates a pressure which keeps the liquid in the tank.

A Super Fluid Helium Experiment was flown Spacelab 2 by a team from the Jet Propulsion Lab headed by Mason. The technological and scientific objectives were divided into three separate investigations; (1) the Quantized Surface Wave (QSW) experiment to investigate third-sound surface waves in films of superfluid helium, (2) the Bulk Fluid Dynamics (BFD) experiment to determine the response (slosh modes and decay time) of superfluid helium to known acceleration levels, and (3) the Bulk Thermal Dynamics (BTD) experiment to determine temperature fluctuations and variations (to within 10 mK) associated with slosh modes.

Surface waves are one the order of a micron in normal gravity and damp out fairly rapidly. In microgravity, they tend to be thicker and were observed to persist for as long as 60 seconds. The other two objectives were reported met, but details were given.

Geophysical Fluid Flow

Hart (U. Colorado) developed a method of simulating the three-dimensional geophysical fluid flows under the combined influence of rotation, thermal gradients, and a gravity-like central force. The Geophysical Fluid Flow Cell (GFFC) consists of a stainless steel hemisphere surrounded by a sapphire hemisphere with a layer of silicone oil between. An alternating high voltage was applied between the inner and outer so that the induced polarization in the silicone oil interacts with the electric field to give a gravity-like body force on the fluid. By heating and cooling different regions while the system was rotated, convective flows could be produced that are analogous to large scale flows in planetary or stellar atmospheres or interiors. There are 4 dimensional parameters that characterize the flows in the GFFC: the Prandtl number, fixed at 8.4, the aspect ratio (gap width to inner radius), fixed at 2.65, The Taylor number, which measures the ratio of rotational

forces to viscous forces, and the Rayleigh number, which measures the buoyancy-driven thermal convection to conductive heat flow. The convective flow fields in the hemisphere were visualized via Schlieren and shadowgraph photography. An ultraviolet sensitive dye was added to the silicone oil to aid in flow visualization.

The GFFC was flown on Spacelab 3 and again on USML-2. The primary objective of Spacelab 3 experiment was to study the interaction of rotation and convection similar to that which occurs in the atmosphere of a rotating planet like Earth or Jupiter. A variety of interesting flow structures were observed as rotation rates and equator to pole heating was varied. The observed flows were used to check 3-dimensional computational models.

Several classes of experiments were conducted on USML-2: slow rotation, simulating mantle-like flows, fast rotation, simulating solar-like flows; symmetric heating, simulating solar or Earth core; and differential heating, simulating Jupiter's or Earth's atmospheres.

Rotation with spherical heating produced banded patterns not seen before in numerical simulations and may provide an alternative view of the mechanisms responsible for the observed structure of the Jovian atmosphere.

In slow rotation experiments, climatic "states" in the form of two distinct convective patterns were found to exist with the same external conditions, differing only by the initial conditions. These patterns are persistent and are insensitive to small changes in the external conditions. Data was obtained on how these states break down under larger changes in operating conditions. The transition from anisotropic north-south "banana convection" to the more isotropic convection was studied. This information may lead to a scaling argument for classifying different planetary atmospheres.

Other experiments with latitudinal heating show evidence of baroclinic wave instabilities and successfully showed how spiral wave convection breaks down into turbulence.

Order - Disorder Transitions

Chaikin (Princeton U.) used the glovebox on USML-2 to study the assembly of colloidal systems as a function of solid volume fraction. Computer simulations indicated, for volume fractions ranging from 0.545 to 0.74, short range van der Waals-like forces between the spheres would cause them to form into close-packed crystal-like structures, very much like atoms in a metal form close-packed crystalline structures. For volume fractions less than 0.494, the particles should remain in solution, and crystals could coexist with solution in the intermediate range. A metastable, glass-like phase was also predicted to exist for volume fractions greater than 0.58.

These predictions were tested by suspending 0.5 micron PMMA spheres in mixtures of decalin and tetralin for index matching. After homogenization, the suspensions were allowed to relax into their equilibrium configuration. The formation of the crystal structures could be observed and analyzed from diffraction patterns created by shining

laser light through the suspension, similar to the analysis of metallic structures using X-ray diffraction. Particle motion was studied using dynamic light scattering. By “pinging” the system and observing the response of the structure, the elastic properties could also be inferred.

In normal gravity the configurations were not in equilibrium because sedimentation was much stronger than Brownian motion. Crystals were formed which tended to be mixtures of face centered cubic (FCC) and random hexagonal close-packed (RHCP) structures. In microgravity, the FCC phase was not observed and the structure was entirely RHCP. (By random HCP, we mean that the probability of every third layer being different is 0.5, or in other words, the chance of seeing ABC is the same as ABA.) Also, wing-like dendrites were observed in the microgravity structures that were never seen in the ground controls. It is not clear if dendrites actually start to form and are sheared off by sedimentation, or if the conditions favorable to their formation are absent.

A glassy phase was formed on Earth with a volume fraction of 0.619 that remained in this metastable state for more than a year without crystallizing. The same system crystallized in microgravity in 3.6 days. By the end of the mission it had grown to 1 cm and filled the container. Further, it survived re-entry and remained in the lab for 6 months, after which it was “remelted” by stirring. It then re-grew into the disordered glassy phase .

These studies were extended on MSL-1R to study nucleation and growth from time-resolved Bragg and low angle light scattering as well as measurement of elastic modulus from dynamic light scattering.

Mixing And Demixing of Transparent Liquids

Langbein (ZARM, U. Bremen) used a floating zone configuration to study the effects of capillarity on the mixing and demixing of two immiscible liquids on D-1. A mixture of benzylbenzoate and 40Vol.% paraffin oil was deployed between two discs. The upper disc was heated above the consolute temperature. Marangoni convection stirred the mixture and the interior counter flow carried bubbles, that had inadvertently been introduced, to the surface where they ruptured, thus demonstrating this as an effective finning technique. As heating progressed, the critical wetting condition temperature was exceeded and the benzylbenzoate spread across the heated disc, in accordance with the critical point wetting theory of Cahn (See J. W. Cahn, J. Chem. Phys. (1977) 667.) The rising inner column of benzylbenzoate thinned and eventually broke into two segments. Eventually, through diffusion and Marangoni convection, the benzylbenzoate at the heated plate exceeded the consolute temperature and homogenized with the paraffin oil. Under passive cooling, a fog developed in the upper region as the temperature fell below the consolute temperature. The droplet in the fog eventually coalesced to form the two liquid phases.

Particle Dispersion Experiment

Aggregation of various small particles was studied by Marshall (NASA Ames Research Center) in the glovebox on USML-1 and -2. The motivation for these studies was to obtain a better understanding the collapse of dust and debris in astrophysical and planetary settings. The dust grains were dispersed by a puff of gas in a transparent 125 cm³ chamber and the aggregation was observed with high magnification video recording.

Aggregation was observed to be very rapid in all cases. Dielectric grains of quartz and volcanic ash particles aggregated into chains or filaments that were many tens of grains in length. Larger (400 micron) particles formed single particle chains up to a centimeter in length. Conductive copper particles formed similar chain-like aggregates. The size and shape of the particles did not seem to affect the type of structure that was formed, however, the chain length did appear to be proportional to the number density of the particles.

Passive Accelerometer

Until STS-50 (USML-1), the quasi-steady acceleration on the Shuttle from gravity gradient and atmospheric drag had never been measured. The conventional accelerometers, used by the NASA Glenn Research Center in their SAMS system, respond to the higher frequency accelerations from the normal vibrational modes of the Shuttle, but the baseline bias is such that the extraction of a quasi-steady acceleration of less than one micro-g from the milli-g oscillatory accelerations cannot be done accurately. Alexander prepared a simple 2 cm diameter tube filled with water that also contained a 2 mm steel ball. The ball was positioned near one end of the tube with a magnet and then was simply allowed to fall in the residual gravity field. From the observed motion of the ball, the direction and magnitude of the quasi-steady acceleration could be determined from the Stokes formula for a falling sphere (after corrections for wall effects). Accelerations measured at the middeck were typically 4 – 5 micro-g with the direction essentially along the X-axis (along the fuselage - the Shuttle was flying in the tail-down attitude). Accelerations measured near the Crystal Growth Furnace (CGF) were typically 0.5 micro-g and it was evident that the residual gravity vector was not along the furnace axis as had been planned.

Combustion Experiments

There are two compelling reasons for the study of combustion in microgravity. One is the issue of fire safety in the design and operation procedures of orbiting laboratories; the other is take advantage of the weightless state to study certain combustion phenomena in more detail and to test various models in which convection has been ignored in order to be mathematically tractable.

Examples of the first category of experiments are the Solid Surface Combustion Experiment, the Smoldering Combustion Experiment, and Wire Insulation Flammability Experiment were carried out on USML-1.

Smoldering combustion can be extremely dangerous in a space station since it can remain virtually undetected for some time, but the increased temperature, due to the absence of convection to carry the heat away, can greatly increase the amount of toxic fumes generated. Stocker and Olson (NASA Glenn Research Center) along with Fernando-Pello (U. California, Berkeley) found dramatic increases in CO and light organic compounds when a porous urethane foam smoldered in microgravity as compared to normal gravity, even though there was little difference in temperature and char patterns.

The wire flammability studies were carried out by Greenberg and Sacksteder (NASA Glenn Research Center) and Kashiwagi (NIST) to simulate the behavior of possible electrical fire in space without convection and with forced convection. The wires were nichrome covered with 1.5 mm dia polyethylene insulation. An ignition of a wire without forced convection resulted in quiescent cloud of vaporized which ignited but failed to propagate. Under forced convection, the spreading flame stabilized around a bead of molten insulation. Flame spread in concurrent flow was twice as fast as in counter current flow and soot production was greater under counter current flow. The flames quenched rapidly when the air flow was shut off.

The Solid Surface Combustion Experiment on USML-1 conducted by Altenkirch (Mississippi State University) was the fourth of a series in which thin sheets of combustible materials were ignited in a controlled oxygen environment. Other Spacelab missions that carried this experiment included SLS-1, IML-1, and SL-J. The objective of the series of experiment was to obtain the flame spreading and soot formation as a function of pressure and oxygen content for comparison with theoretical models. These data and the resulting models go into flammability requirements for materials usage requirements in spacecraft and space experiment design. Unfortunately, the experiment design permitted only one test per Shuttle flight.

A capability for running multiple solid surface combustion tests was introduced in a glovebox experiments carried out on IML-3 in the Forced Flow Flame Spread Test (FFFT) which is a forerunner of a facility for use on the International Space Station. Fuel in the form of a tape or cylinder is fed into a small wind tunnel at the same rate as the flame spread so that the flame front remains in the instrumented region for diagnostic measurements. These measurements are used for comparison with theory. A team from the NASA Glenn Research Center led by Sacksteder carried out 15 experiments using sheets and cast cylinders of cellulose with concurrent airflows ranging from 2 to 8 cm/sec.

Kashiwagi and Olson (NASA Glenn Research Center) also used the glovebox on USML-3 to investigate ignition and the transition to flame spread or smoldering combustion in 25 samples. Air flow was varied from 0 to 6.5 cm/sec. Ignition was initiated by a hot wire across the middle of thin (2-D) samples and by the focused beam of a halogen lamp

for thicker (3-D) samples. In the 2-D samples, ignition occurred more readily under microgravity conditions and the flame spread was always in the upstream direction. In the 3-D sample ignition was from a spot in the middle of the sample and char pattern was fan shaped, the internal angle of the fan increasing with air flow velocity.

Griffin (NASA Glenn Research Center) and Gard (NASA Marshall Space Flight Center) compared the ability of the smoke detectors used on the Shuttle and those proposed for the International Space Station to detect fires. A near field module, installed in the USMP-3 glovebox, contained the sample to be burned and the near field diagnostics which included collector grids for TEM analysis of the smoke particles. Combustion products were blown through teflon hoses to the far field module which contained the two smoke detectors, then returned to the glove box to be removed by the glove box filters. Samples tested included a candle, paper, teflon and kapton coated wires, and silicone rubber. It was found that sensitivity to various combustion products in space is different than on Earth because the size distribution of the products is altered by the combustion process in microgravity.

A number of experiments were conducted to take advantage of the quiescent microgravity environment to study a variety of combustion processes. One topic of significant practical interest is soot production. Soot is usually an undesirable product of combustion for several reasons. One reason is that soot is a visible pollutant; one sees soot in the black fumes emitted by diesel trucks, processing plants, and chimneys. (It should be noted that recent changes in Environmental Protection Agency (EPA) regulations call for significant reductions in amounts of such particulate materials in the atmosphere.) In addition, soot production is tied to the emission of carbon monoxide -- a toxic material -- and PAHs (polyaromatic hydrocarbons), many of which are carcinogenic. Another of soot's undesirable qualities is that the thermal radiation, or heat emission, of soot particles is often responsible for the spreading of fires. Soot also hampers efforts to fight fires because its presence can obscure their sources, making it more difficult to extinguish them. However, soot production is useful to the carbon black industry, which is a large industry that uses soot in such products as tires, black plastic, and dry-cell batteries. In addition, many furnace applications rely heavily on heat radiation from soot to transfer heat from flames to boiler tubes in order to produce steam from water. For all of these reasons, understanding the production of soot is a goal that is important to researchers. Once understood, the process could be manipulated to control both visible and invisible pollution from combustion technologies like diesel engines and aircraft gas turbines, to enhance fire-fighting abilities, and to produce soot with qualities that are beneficial to industry.

The geometry and behavior of a candle flame was investigated by Ross (NASA Glenn Research Center) using the glovebox on USML-1. This was the first evidence that diffusive transport was rapid enough to sustain a candle flame. After an initial transient in which the flame is spherical and yellow, indicating soot is being formed, a steady state is reached in which the flame is hemispherical and burns with a blue color, indication little or no soot formation. Minor transient acceleration disturbances caused increased luminosity and soot production.

Fiber supported droplet combustion experiments were carried out on USML-2 and on MSL-1R by Williams (UCSD). By tethering the droplets on a silicon fiber, they could be kept in the field of view of the video recorder so that the burning rate and other parameters could be recorded. The objective is to test theories of droplet combustion and soot formation that are of importance to improving the efficiency of internal combustion engines, gas turbine engines as well as home and industrial oil burning heating systems. Microgravity allows droplet size to be increased to as much as 5 mm so that the combustion process can be studied in detail. Once the theory is developed, its predictions can then be scaled back to the droplet sizes used in the actual combustion processes.

Williams carried out a similar experiment with free floating droplets on MSL-1R to determine if the tether he had used previously had any effect on the combustion process. The droplet is formed by injecting heptane through two injectors on opposite sides of the test platform within the chamber. The injectors are retracted after the drop is formed. The drop is then ignited by two hot-wire igniters that are brought near the droplet from opposite sides to begin combustion with minimum disturbance to the droplet. The burning droplet is observed and recorded using video cameras and high-resolution photographs.

The "Structure of Flame Balls at Low Lewis Numbers" (SOFBALL) experiment of Paul Ronney, (University of Southern California) was performed on MSL-1R. In this experiment, a container was filled with various combustible mixtures near their lean limit of combustion. A flame ball was created by an electrical spark. A stationary spherical flame front develops as fuel and oxygen diffuse into and heat and combustion products diffuse out of the flame ball. This is the simplest possible geometry in which to study the chemical reactions and the heat and mass transport of lean combustion processes. Over 50 years ago, Zeldovich found that the equations for steady heat and mass conservation had a solution corresponding to a stationary flame front, but he also showed that the solution was unstable. He did, however, consider the possibility that heat loss might be a stabilizing factor, which is apparently the case since some of the flame balls lasted the full 500 seconds until the experiment timed-out. It is expected that these experiments will provide new insight on combustion processes in the lean burning limit, which are important in improving the efficiency of engines and heating systems.

Soot formation in laminar flames was also studied on the MSL-1 and MSL-1R mission by Faeth (U. Michigan). Soot formation in turbulent diffusion flames is of greater practical interest, but their direct study is difficult because of their time and spatial dependence. Therefore, laminar flames are studied to obtain the basic relations needed to develop a tractable theory, the justification being that there are known similarities of gas-phase processes between laminar and turbulent flames. Laminar flames are still affected by buoyancy effects that complicate the analysis, thus the need to study them in microgravity. The flames to be studied are hydrocarbon fuelled and burn in still air. Measurements include flame shape, soot volume fraction, soot temperature distribution, gas temperature distributions, and flame radiation. The flames in low gravity were much longer than in 1 g due to the absence of buoyancy-driven convection. It was also found

that the simplified theoretical analysis of non-buoyant laminar flame developed in 1979 by Spalding gave excellent predictions of flame shape after making an empirical flame length parameter to account for the soot luminosity.

Enclosed laminar flames are commonly found in practical combustor systems such as gas turbine combustors, jet engine afterburners, and in power plant combustors. The enclosure is in the form of a duct with either co-flow or cross flow. The diffusion flame is located where the fuel jet and oxygen meet. Typically, the flame is anchored at the burner, but as the fuel velocity is increased, the flame front moves away from the burner jet. Eventually, the flame jumps ahead of the jet and is said to be lifted. Too high a fuel velocity will cause the flame to blow out. The stability of such flames in low gravity were investigated by Brooker, Jia, Stocker, and Chen of the NASA Glenn Research Center on USMP-4. The fuel was a 50V% mixture of methane and nitrogen. A free-jet theory of Chung and Lee predicted that lifted flames would not be stable for Schmidt numbers (ratio of kinematic viscosity to chemical diffusivity) less than 1, which is the case for the dilute fuel mixture used in these tests. However, it was shown that the co-flow in the duct did tend to stabilize the lifted flame, both in normal gravity as well as in microgravity, although higher co-flow velocities were required to lift the flame and to cause blow-out in microgravity.

Assessment of the Science

A number of the early microgravity fluids experiments investigated the shape and stability of liquid zones to support anticipated materials science experiments that might use extended floating zones for crystals growth. Perhaps the most important contribution from most of this work was the demonstration that the behavior of such zones could indeed be computationally modeled. However, one experiment used the zone shape to measure the disjoining pressure of a film and another experiment stabilized an extended zone beyond the Rayleigh limit in a test of Taylor's "leaky dielectric theory). The latter has applications in the design of fluidic systems

Many of the microgravity fluids experiments were directed to the study of Marangoni convection. Since this type of convection is independent of gravity, it clearly acts in terrestrial processes along with buoyancy-drive convection, and therefore must be considered. These space experiments clearly demonstrated the existence of such flows (which may have been debated in some quarters since they cannot be demonstrated independently in normal gravity), as well as the ability to quantify and model their effects, although it was also found that such flows can be unexpectedly quenched by contaminants.. Considerable work went into determining under which conditions the steady Marangoni flows become time-dependent and new criteria for this transition have been developed. This knowledge is important for the design of floating zone crystal growth experiments in which time-dependent flows produce growth defects.

The classical theory of Young, Goldstein, and Bloch, that describes the motion of droplets or bubbles in a fluid driven by the Marangoni effect was found to apply only in

the limit of vanishing Marangoni number and corrections to the theory have been developed. It was also shown that multiple drops or bubbles can interact through the thermal wakes left as they move through the fluid. Finally, it was found that fluid properties such as dilatational viscosity, which are not accounted for in the Marangoni number, can significantly affect the motion. These findings are significant in the design of many materials and chemical processes used on Earth as well as in microgravity.

Several experiments involving pool boiling and heat transfer in microgravity produced some surprising results in that the ability to dissipate heat from a submerged heater was only slightly diminished. Instead of an insulating vapor film forming around the heated, as was expected, strong thermocapillary jets formed which proved to provide an efficient heat transfer mechanism. Not only is this significant for the design of systems that have to work in a microgravity environment, but it may be possible to take advantage of such jets to improve the efficiency of terrestrial boilers.

The behavior of several systems near critical phase transitions were studied. Unanticipated difficulties were encountered in approaching the critical point because of the "critical slowing down" phenomena. These difficulties were overcome and the critical exponents that govern the divergence of thermophysical properties as the critical point is approached were determined with improved accuracy. These appear to be consistent with the predictions of the coefficients obtained from Wilson's group renormalization calculations.

A number of experiments were carried out on levitated drops to test and refine theories of droplet oscillation, shape and fissioning under rotation, core centering, and nonlinear effects. Techniques for extracting property measurements from oscillating droplets were demonstrated. Some of these measurement techniques were utilized in obtaining thermophysical data from undercooled melts in the electromagnetic levitator on MSL-1R.

Other investigations included a three dimensional simulation of geophysical flows under the influence of a central gravity-like force together with rotation and differential heating, particle aggregation, order-disorder transitions in the assembly of an ensemble of hard spheres, mixing and demixing of immiscible systems, the management of superfluid helium in low gravity, and the demonstration of a simple falling sphere method for measuring the quasi-steady residual acceleration on the Shuttle. All told, these fluid experiments produced a total of 563 papers of which 323 were published in peer reviewed journals. The bibliography also includes another 43 references from the various fluid science Principal Investigators, that were of general interest to the behavior of fluids in microgravity, but were not directly related to the experiment they flew on Spacelab missions.

The dozen or so combustion experiments have produced a wealth of information that is not only applicable to fire safety in space vehicles, but also fundamental to understanding the combustion process in droplets, combustion near the lean-burn limit, the formation of soot in various combustion processes. These experiments produced another 118 papers, including 55 in journals.

New Technology and Technical Spin-offs

Heat and mass transport from fluid flow is so fundamental to all of materials processing that it is difficult to single out specific applications where such research has made direct contributions. Marangoni convection, which is often ignored in terrestrial processing, can be significant, even in the presence of buoyancy convection, if there are free surfaces, bubbles, or immiscible droplets present. These space experiments have provided a much better understanding of the effects of these types of flows that are not only needed for the design of future microgravity experiments, but apply to many terrestrial processes as well. Hopefully, the publications resulting from the microgravity research will make the terrestrial process engineers aware of the importance of including the effects of such flows in their process design.

The fundamental work that was done on drop oscillations and the development of techniques for extracting materials properties from their observation, can be considered enabling technology for being able to extend the measurements of thermophysical properties into undercooled molten state using electromagnetically suspended droplets. Such measurements are key to the development of new metallic glass systems and other metastable alloys.

The combustion research has the potential of leading to more efficient combustion processes with a reduction of unwanted combustion products such as soot and other noxious contaminants. Furthermore, the flammability testing and developments in spacecraft fire safety also have direct applications to home and industrial fire safety.

Materials Science Experiments

Normally one categorizes materials as metals, ceramics, semiconductors, and polymers, which reflects the nature of their chemical bonding. Microgravity experiments have primarily focused on metals and semiconductors, although the distinction get blurred which ceramics are added to metals to form composites.. The primary emphasis in the study of metals has been to understand the evolution of their microstructure and to develop techniques for controlling it during processing. The primary emphasis in the study of semiconductors can be the growth of single crystals with controlled composition and defect formation. Key to the success of both of these endeavors is knowledge of the thermophysical properties of the constituents in the liquid phase. As it turns out there is a compelling reason for certain of these measurements to be made in a low gravity environment. Levitation techniques for certain thermophysical properties measurements permit the measurement of certain properties in the deeply undercooled, which are of value for predicting the cooling rate required for glass formation, which leads to the final section of glass formation experiments in microgravity.

Metals, Alloys, and Composites

Introduction

Metals tend to be ductile because their crystal structure contains slip systems which allow planes of atoms to slide over one another through the dislocation mechanism . A dislocation is a missing line of atoms in the otherwise regular spacing in a small crystalline grain of the metal. Under stress, the dislocation can move through the grain, resulting in the net displacement of a whole plane of atoms, much like moving a rug by forming a small kink and then moving the kink across the rug. Pure or elemental metals are generally too weak to be used for most structural applications because of their ductility. However, they can be strengthened dramatically by blocking the motion of the dislocations. There are several methods for accomplishing this. They may be alloyed with other metals whose atoms are larger or smaller than the host metal (solid solution hardening). The resulting irregularity in the lattice tends to block the motion of the dislocations. Since dislocations cannot propagate from one grain to another, promoting a fine grain structure will strengthen a metal. Dispersing very small particles or fibers throughout the metal is also effective means of strengthening a metal . These particles can either be precipitated from a dissolved component as the metal is cooled (precipitation hardening), or a second phase, often a refractory ceramic, can be added to form a composite.

When one attempts to solidify a multicomponent system from the melt, difficulties arise. The foreign atoms don't fit into the lattice as easily as the host atoms forming the matrix, and segregation results. The melt containing the rejected atoms will have a different density from the bulk solution resulting in solutally-driven convection which cause the final solid to have a non-uniform composition on a macroscopic scale

(macrosegregation). Dispersed particles will have a different density and will tend to either sink or float. Particle behavior is also affected by the interfacial energy between their surface and the melt, which determines if they are wetted by the melt.

Much of what goes on in a multi-component melt is affected by gravity, but some of the more subtle interfacial effects are not. Yet these interfacial effects may play important roles in many terrestrial processes, but are poorly understood because they are masked by gravitational effects. Using microgravity as a tool to sort out the non-gravitational from the gravitational effects may add to our understanding of how these processes operate, which can lead to advanced materials with enhanced properties.

With the large computational capability that now exists, much use is being made of computer modeling of solidification processes, particularly in the case of large expensive castings. In principle, it is now possible to compute the temperature and compositional fields as the casting solidifies and use these to predict the resulting microstructure, provided we know all of the processes taking place, and also have accurate knowledge of the thermophysical properties of the materials of interest. Unfortunately, many of the thermophysical properties, such as diffusion coefficients and thermal conductivities are not known for the molten state and are difficult to measure because convective transport can easily influence the measurement. Therefore, there is great interest in using the microgravity environment to make this type of measurements.

Normal freezing generally produces equilibrium phases, i.e., atomic configurations that are the most ordered or have the minimum free energy. Recently, there has been much interest in trapping non-equilibrium or metastable phases by various rapid solidification techniques because of their interesting properties. For example, metallic superconductors with the highest transition temperature (for metallic systems) such as Nb_3Sn and Nb_3Ge have the so-called A15 structure, which is a nonequilibrium phase. Metallic glasses are another example which are useful because their lack of grain structure makes them more resistant to corrosion. Iron-based metallic glasses have found useful applications as high efficiency transformer cores because the absence of grain structure makes it easier for magnetic domains to move resulting in much smaller hysteresis losses.

It is possible to magnetically levitate metallic samples in microgravity so that they can be melted and solidified without physical contact. Without a foreign surface to initiate nucleation, a melt may be cooled several hundred degrees below its normal freezing point. This provides an opportunity to measure properties of a melt in an undercooled state. Knowing the viscosity and surface tension of materials in this state may provide clues for more effective means for trapping metastable phases.

The alloy solidification experiments that have been performed of Spacelab generally fall into three general categories: (1) experiments designed to understand how the microstructure evolves during solidification, (2) studies of interfacial effects that control the distribution of second phase particles, and (3) measurements of thermal physical properties.

Part of the interest in solidifying eutectics in microgravity arose from an experiment performed by Larson, then at Grumman in Bethpage, NY during the Apollo-Soyuz flight. Larson directionally solidified the MnBi-Bi eutectic system, which is a low volume-fraction system in which the MnBi phase forms an aligned rod-like structure instead of lamellae in the Bi matrix. The intermetallic compound, MnBi is an interesting permanent magnet material and Larson was trying to improve its strength by using microgravity to get better alignment in the MnBi rods. To his surprise, he found that the rods were finer and more closely spaced than his ground control sample. Interestingly, the samples he processed on Earth followed the Jackson-Hunt theory very nicely while his space samples departed significantly from the theory. Subsequent tests using magnetic fields on the ground to help suppress convection, gave results similar to his flight samples. This seemed very strange because the Jackson-Hunt theory considers only diffusive transport; no convection. Yet there are apparent departures from the theory when convection is suppressed. Larson attempted to repeat his experiment on the MSL-2 flight using Co-Sm, another important magnetic system. Unfortunately, equipment problems prevented him from obtaining useful data.

Mueller and Kyr (Universitat Erlangen-Nuremberg) performed an experiment similar to Larson's on SL-1 and on D-1 using the InSb-NiSb pseudo-binary eutectic system. They also performed the experiment in higher g-levels using a centrifuge. Their results were similar to Larson's; agreement with Jackson-Hunt theory when convection is present, finer structure and spacing in the absence of convection. They found that the volume fraction of the NiSb phase in their final solid was lower than their starting eutectic composition and suggested that thermal diffusion (Soret effect) may have caused this composition shift away from the eutectic and that this was responsible for the apparent departure from the Jackson-Hunt law. The convective stirring in the 1-g sample apparently does not affect the spacing between the phases, but does keep the bulk fluid at more or less constant composition by simply overwhelming the Soret effect.

However, Favier and de Goer (CEA-CENG, Grenoble) directionally solidified Ag-Ge, Al₃Ni-Al, and Al₂Cu-Al on TEXUS suborbital rockets and on SL-1. They found no change in the lamella spacing or volume fraction for the Ag-Ge and the Al₂Cu-Al systems, but found coarser spacing and increased volume fraction of the minority phase in the microgravity sample of Al₃Ni-Al, just the opposite result of Mueller and Kyr. The change in volume fraction again argues for the possibility that Soret diffusion may have shifted the starting composition away from the eutectic composition, which could explain the change in spacing.

Wallrafen and Dupré (U. of Bonn) attempted to directionally solidify LiF - LiBaF₃ eutectic on D-2. In 1-g experiments, the component LiBaF₃ tended to accumulate in the lower regions of the melt. The accumulation of the LiBaF₃ component was eliminated in the D-2 samples, indicating the separation of this component must have been gravity related rather than a result of Soret diffusion. No difference in volume fraction or lamella spacing was observed between the space and ground samples.

Tensi (Technical Universitat, Munchen) reported a reduction in interdendritic spacing under microgravity conditions in hypoeutectic AlSi11 on D-2 and in AlSi7 on D-1 and found no change in the volume fraction of the Si. These experiments were run with a gradient of 15K/cm at growth velocities of 0.5, 1, and 2 mm/min. The 0.5 mm/min produced a plane front solidification, while the others resulted in dendritic solidification. The material between the primary dendrites had eutectic composition and the spacing of the lamella in this interdendritic material was substantially less in the microgravity samples. Since there was no change in the volume fraction, Soret diffusion was apparently not effective in this system. Tensi argues that the increased spacing in the 1-g sample is a result of micro-convection which increases the transport of material between lamella, thus increasing the effective diffusion length which results in the increased spacing.

Ohno and Motegi (Chiba Institute of Technology) investigated a different aspect of eutectic microstructure. Instead of directionally solidifying, they melted and cooled hypo- and hypereutectic compositions of the Al_2Cu system using the Continuous Heating Furnace on SL-J so that they could compare the resulting microstructures in the presence and absence of gravity. When the hypoeutectic Al_2Cu system is quenched in normal gravity, the first-to-freeze primary Al dendrites, being less dense than the bulk melt, will detach from the wall and float to the top. When the excess Al has been removed in this manner, columnar grains of eutectic composition grow along the direction of heat flow. In space, the primary Al dendrites simply remained on the wall and the remaining eutectic formed columnar structures around them. Grains of primary Al_2Cu are the first to freeze in the hypereutectic composition. Being more dense, these primary Al_2Cu grains settle to the bottom. When the excess Cu is removed in this manner, the remaining melt solidifies as columnar eutectic grains. In space, however, the primary Al_2Cu appeared along then walls, but no free Al_2Cu crystals were observed. Small gas bubbles were also found near the walls and larger ones in the middle of the final ingot. It was speculated that these originated from adsorbed gas in the graphite crucible.

Interfacial Stability

As solidification progresses in a binary or multi-component system, the rejected solute builds up in front of the solidification interface which has the effect of lowering the freezing temperature at the interface since some of the component with the higher freezing temperature has already been removed. However, the bulk melt away from the solidification interface has the original composition, which has a higher freezing point. Therefore, the freezing point of the melt rises from the lower value at the growth front to the higher value of the bulk melt. Unless the imposed thermal field in front of the solidification interface is everywhere higher than the local freezing point of this melt, the melt is said to be constitutionally undercooled, which leads to an interfacial instability. If a small portion of the growth interface is somehow displaced ahead and it finds the local freezing point to be higher than the local temperature, it will continue to advance. Thus the interface will break down, first into a cellular pattern if the constitutional undercooling is small, or into long finger-like projections if the undercooling is larger.

The sides of these projections will also break down to form secondary arms, which in turn can break down to form tertiary arms. The resulting structure resembles a fir tree, hence the term "dendrite".

A simple constitutional supercooling criterion (known as the CS criterion) was developed by Rutter and Chalmers in 1953 (Can. J. Phys. 31 (1953) 15) that predicts the ratio of the gradient required to stabilize the interface to the growth velocity for a given solidification system. In 1964, Mullins and Sekerka (J. Appl. Phys. 34 (1964) 323) developed a more rigorous theory based on a stability analysis that included the liquid-solid interfacial energy which can provide a stabilizing effect on the interface. Like most theories concerning solidification phenomena, it was necessary to assume no convection in order to simplify these analyses.

Carlberg (Mid Sweden University, Sundsvall, Sweden) used a multi zone furnace in a Getaway Special (GAS can) on SL-J to solidify Ga-doped Ge using the gradient freeze technique with Peltier pulsing for interface demarcation. In this process, the solidification rate increases as the specimen is solidified. Carlberg was able to show that the flight as well as ground based results were consistent with the predictions of Mullins and Sekerka so long as the experiment was configured with little convection (vertical with stabilizing thermal gradient). However, he was able to show significant departure from the M-S theory as convection was increased.

Potard, Duffar, and Dusserre (CENG, Grenoble) devised a method for monitoring conditions at the interface based on the heat being supplied and/or extracted from the growth process. The latent heat of fusion being liberated as the crystal grows is proportional to the growth rate as well as the area. Thus, if this heat can be measured, it should be possible to determine the conditions at the growth interface. Three samples were prepared for the Gradient Heating Furnace; one with pure InSb, one with pure InSb but with a step area change, and one with doped InSb to produce an interfacial breakdown due to constitutional undercooling. The ampoules were covered with super insulation to provide an adiabatic radial boundary condition. Heat was introduced and extracted through graphite plugs at each end of the ampoule. The heat flux meters consist of adjacent fine wire thermocouples in the graphite plugs. The technique was demonstrated in a semi-qualitative manner on the D-1 flight in that seeding and growth transients could be identified and the measured heat fluxes were in reasonable agreement with the mathematical models of the process.

A unique and highly sophisticated apparatus for studying details of the solidification process was developed by Favier and coworkers at the CENG, Grenoble under a cooperative program between NASA and the French Space Agency (CNES) and the French Atomic Energy Commission (CEA). The official name is Materials for the Study of Interesting Phenomena of Solidification on Earth and in Orbit or. Three 6 mm diameter, 900 mm long samples are processed in parallel. Resistance and thermal measurements are made on one sample while Seebeck voltage measurements are made on another. Peltier pulsing is applied to the third sample to mark the solidification interface for post flight analysis. The middle 500 mm of the samples are melted using two

furnaces. One solidification front is kept stationary while the other is moved back and forth to create a solidification front that can be move at different velocities. By measuring the differential Seebeck voltage between the stationary and moving interface, the kinetic undercooling can be determined as a function of growth velocity. At the freezing point, a solid will remain in equilibrium with its melt indefinitely. This kinetic undercooling is the driving force for continued solidification. The kinetic undercooling will be small for plane front solidification, but since additional interfacial energy must be provided as the plane front begins to break down, the kinetic undercooling must get larger. Thus, the transition from plane front solidification to cellular growth can be observed as a change in the Seebeck voltage and the critical growth velocity where the plane front interface begins to break down can be determined accurately. Many applications ranging from bulk growth of semiconductors to single crystalline turbine blades require plane front solidification and it is important to know how fast they can be solidified before this breakdown occurs. The MEPHISTO instrument, flown on USMP-1,2,3, and 4 provided the first opportunities to perform a critical test of the Mullins-Sekerka theory as well as to explore other important phenomena involved in the solidification process.

Favier used the USMP-1 opportunity to explore the interfacial breakdown in Bi-doped Sn and the USMP-3 opportunity to quantify the disturbance and recovery of growth interface as a result of thruster firings. Abbaschian (U. Florida) used the USMP-2 and 4 flight s to investigate interfacial stability on the other side of the phase diagram; i.e. Sn-doped Bi. Unlike most metals that solidify in an atomically rough interface, which allows the interface to form nearly along the local freezing line, Bi solidifies along crystalline planes, which are seen as facets. The properties of a faceted crystal depend on the direction relative to the crystal axis and are said to be anisotropic. The primary motivation for the study of the solidification of a Bi-rich alloy was to test the extension of the Mullins-Sekerka stability criterion to include the effects of anisotropy, which acts to stabilize the interface against breakdown into cellular and dendritic growth.

Where single crystals of uniform composition are required, the interface can be stabilized by applying a sufficient thermal gradient at the growth interface to prevent interfacial breakdown. However, in most alloy solidification processes, the first-to-freeze dendrites, surrounded by the last-to-freeze interdendritic fluid, determine the microstructure of the resulting solid. Therefore, it becomes important to know how dendrite growth depends on processing parameters so that one can engineer the desired mircostructure.

Nguyen Thi, and Li (University of Aix-Marseille) with Billia, Camel, Drevet, and Favier (CEA-CENG, Grenoble) investigated the transition from deep cellular to dendritic microstructure. Three aluminum-lithium alloys with the same composition were directionally solidified in the same temperature gradient but at three different velocities in the GFQ. The microstructure of the solid-liquid interface was quenched in. The cellular or dendritic pattern is then revealed by grinding followed by chemical etching on longitudinal and/or transverse sections. Macrosegregation is determined by chemical analysis and microsegregation by SIMS.

A similar experiment was performed using the AGHF on the LMS mission. The samples were Al-1.5wt%Ni. In this system, which can be stabilized both thermally and solutally on the ground, influence of strong convective flows are seen in the 1-g sample.

Billia and Jamgotchian (University Of Marseille) along with Favier and Camel (Centre D'etudes Nucleaires De Grenoble) investigated the effect of convection on cellular growth on D-1. Samples of lead with varying amount of thalium were directionally solidified above the morphological stability limit in order to cause the interface to break down into a cellular structure. The microgravity sample exhibited very regular cellular structures, whereas less regular structures are seen in the ground based control samples. The more complex structures in the 1-g samples was attributed to the effects of thermo-solutal convection. Because of thermal fluctuations in the flight furnace, the actual growth rate is not known, thus relating the cellular spacing to growth velocity was not possible.

Dendrite Formation

Whenever solidification takes place in a medium where the surrounding temperature is lower than the local freezing temperature, the growth front can become unstable and dendrites can form. This situation can occur either by constitutional undercooling in the case of alloy solidification, or by the fact that a certain amount of undercooling is required to nucleate the solid from either the melt or the vapor. A classic example of the latter is the formation of ice dendrites (snow flakes). Their intricate shapes have fascinated scientists and philosophers alike, and the study of their formation is the confluence of pure physics from the point of view of pattern formation and material science whose interest is in the evolution of microstructure in alloys.

Camel, Favier, Dupuy, and Le Maguet (CENG, Grenoble) studied the formation of dendrites in hypo- and hypereutectic compositions of the Al-Cu systems at very low solidification velocities (1 micron/sec with a gradient of 30°C/cm) on the D-1 mission. In the ground control experiment in which Al-24Wt%Cu hypoeutectic composition was directionally solidified in the vertical stabilizing configuration (stable with respect to both thermal and solutal gradients), considerable radial segregation was observed and the interdendritic spacing ranged from 350 – 450 microns. This is much less than the 1400 microns expected from scaling laws based on higher solidification rates. The flight sample showed no radial or longitudinal segregation and the dendrite spacings were very close to the expected scaled value. Apparently, in normal gravity considerable solutal convection occurs in the extended mushy zone resulting from the low solidification velocity. Multiple cross sections taken from the large dendrites in the flight sample allowed, for the first time, the reconstruction of an actual dendrite formed in an opaque system. The resulting reconstruction provided valuable information on the secondary and tertiary arm spacing and on the ripening of the dendrite arms.

The McCays (University of Tennessee Space Institute) and coworkers team used the ammonia chloride-water system as a transparent metal analog to study the effect of convection on the dendritic structure of castings on IML-1. The mixture was cooled from

the bottom, representative of a mold placed on a chill block. The growing columnar dendrites were observed holographically as heat was extracted from the system. The dendrites in the ground control experiment grew only half as fast as those in the flight experiment and the mushy zone (the region where the dendrites are growing, which consist of solid dendrites and interdendritic fluid) was much more dense in the ground control. Even though the system is thermally stable (hot over cold), the convective flows along the stalks of the dendrites greatly influence the concentration field in the growth region and must be considered in any attempt to model such a system.

When liquid metal is poured into a mold, columnar dendrites grow from the chilled surface, into the melt. In most cases, it is desirable to have small equiaxed dendrites throughout the final casting to form a fine-grained structure. In practice, this is accomplished by adding inoculants to the melt in order to promote the nucleation of small grains ahead of the solidification front. These grains will grow dendritically in all directions, thus forming equiaxed dendrites. Dupouy, Camel, Botalla, Abadie, and Favier (CEA, CEREM, Grenoble) investigated the transition from columnar to equiaxed growth in by directionally solidifying Al-4Wt% Cu alloy with an Al-Ti-B grain refiner on the LMS mission. A simple theory proposed by Hunt (Mater. Sci. Engr. 65 (1984) 75) relates the transition to the undercooling, the thermal gradient, and the number of nuclei, but ignores the effects of convection and the buildup of the solute boundary layer in front of the advancing solidification front. The purpose of the space experiment is to decouple the convection effects from the solute build up in order to develop corrections to the theory. The experiments showed a continuous transition from a purely equiaxed to an anisotropic microstructure and the transition departed significantly from the Hunt model.

Similarly, Sato (National Research Institute for Metals, Japan) used TiB_2 particles as a grain refiner in a TiAl – based alloy on IML-2. The TiB_2 particles all settled to the bottom of the 1-g when it melted and the resulting structure consisted of columnar dendrites. A uniformly distributed equiaxed grains resulted in the flight sample.

Glicksman and co workers at RPI carried out a series of precisely controlled dendritic growth experiments on USMP-2,3, and 4 to investigate the fundamental theories of dendrite growth. Instead of investigating dendritic growth in constitutionally undercooled systems, these experiments observed the growth of dendrites in pure transparent organic systems at undercoolings ranging from 0.05 to 2.0 K. This choice of systems, succinonitrile for the first two experiments and pivalic acid for the third experiment, allowed real time observations of the actual growth of the dendrites so that precise measurements could be made of the growth rate and tip geometry in systems that were analogs of metal solidification. Succinonitrile crystallizes in a body-centered cubic structure and pivalic acid crystallizes in a face centered cubic structure. Both systems have unusually low entropies of fusion, more typical of metals than of organics.

One of the governing factors in the growth of these thermal dendrites is the heat flow from the dendrite to the surrounding melt. An exact solution the conductive heat flow problem had been obtained by Ivantsov for a parabolic shaped dendrite which relates the product of growth rate and tip radius to the undercooling. However, there seems to be no

fundamental relationship between the tip radius R and the growth velocity V . The question becomes, how does nature select a unique operating state? Experimental observations of pure systems suggest that $V R^2$ is either a constant for a specific material, or a weakly varying function of the undercooling. A large body of terrestrial data has been taken on several systems, but convection effects, especially in the crucial region of low undercoolings where the growth rate is comparable to the convective flow velocities, has not been able to provide an adequate test of the selection rules governing this process. This was the motivation behind this set of flight experiments.

The microgravity experiments show that convection increases the growth rate by a factor of 2 for undercoolings less than 0.5 K, and are still significant for undercoolings up to 1.7 K. The measured product of tip radius and growth velocity in microgravity falls much closer to the Ivantsov solution than the terrestrial data. The slight deviations maybe attributed to the formation of side branches on the dendrites, possible wall effects from the growth chamber, and the fact the observed shape of the dendrite tip is a slightly different shape from the parabola assumed in the Ivantsov solution. Now that the heat transfer away from the growing dendrite is properly accounted for, the physics of shape selection can be approached with reliable data.

In addition to establishing the data required to under the fundamentals of dendritic growth, the large number of highly detailed photographs of dendrites growing under carefully controlled and well documented conditions are being shared with researchers at other universities interested in studying other aspects of dendrite growth such as the side arm growth rates and spacing.

Herlach, Barth and Holland-Moritz (DLR, Koln) with Flemings and Matson (MIT) used the TEMPUS facility on MSL-1R to study dendrite formation in undercooled Ni and Ni-0.6At% Cu. Discrepancies between observed dendrite growth velocity and predictions using the Boettinger, Coriell, and Trivedi (BCT) model (*in Rapid Solidification Processing, Principles and Technologies IV* Ed. Mehrabian and Parrish, Claiborne's, Baton Rouge 1988) were believe to be due to convection, especially at low undercoolings where the growth velocity is on the order of the flow velocities. Surprisingly, the flight results did not show any significant difference .

Coarsening

Coarsening is of major importance in the evolution of microstructure of alloys, particularly dispersion hardened alloys in which the added strength provided by the dispersed phase declines rapidly if the particles grow past a critical size. Coarsening is driven by the excess interfacial energy in a finely dispersed second phase, which could be lowered if fewer larger particles were present. The melting point of a small particle is lower than a larger particle of the same composition (Gibbs-Thompson effect) so the smaller particles dissolve to feed the growth of larger particles (the rich get richer at the expense of the poor). The process was first recognized by Ostwald and is known as Ostwald ripening. The mathematical details were worked out independently by Landau

and Slyozov and by Wagner and is known as the LSW theory. One key result of the LSW theory is that the cube of the average particle radius varies directly with time according to

$$R(t)^3 - R(0)^3 = K_{LSW} t$$

Where $R(0)^3$ is the initial average radius and is a constant which contains the relevant material properties such as the interfacial energy and diffusion coefficient. However, the classical LSW analysis is based on a mean field theory that ignores the finite volume of the dispersed phase. Various attempts have been made to formulate a correction for finite volume, which give widely varying results. However, all of the corrections retain the R^3 relationship and differ only in how the $K(\phi) / K_{LSW}$ varies with volume fraction, ϕ . Furthermore, there has not yet been a definitive test to differentiate between these various theories.

On SI-1, Kneissl (Montanuniversitat Leoben, Austria) and Fischmeister (Max Planck Institut für Metallforschung, Stuttgart) took a different approach to the study of monotectic systems. Instead of cooling from above the consolute temperature into the immiscible region in microgravity, they prepared samples of Zn with small volume fractions of Pb on Earth by rapid quenching. These were heated into the two-liquid phase region in space, thus avoiding the nucleation and possibly the critical wetting that occurs when cooling through the immiscible region. The massive phase separation seen by most of the other experiments with hypermonotectic systems was avoided and they were able to study the coarsening of the dispersed particles. Kneissl and Fischmeister observed considerable coarsening of the dispersed phase. The distribution of the smaller particles resembled the classical LSW theory, but there were more larger particles than the theory predicted. The mechanism for producing these larger particles was not clear. A substantial increase in coarsening rate with increasing volume fraction was observed, but scatter was too large to make a definitive conclusion. A similar experiment was conducted on D-1 by Ratke, Theiringer, and Fischmeister (Max Planck Institut für Metallforschung, Stuttgart) using the Al-In system. However, technical problems prevented useful data return.

Alkemper, Snyder and Voorhees (Northwestern University) attempted such a definitive experiment on the MSL-1R flight. They dispersed 10 micron Sn particles in a Pd-Sn eutectic alloy and heated the samples at 2°C above the eutectic temperature for a predetermined period of time and then quench to room temperature. The samples were later cut into sections and the particle size distribution measured with a digital scanning camera with a microscope objective. The lighter Sn particles all floated to the top in the ground control sample, as would be expected. The flight sample yielded K-values of 2.47, 3.3, and 6.9 micron³/s respectively for volume fractions of 10%, 20%, and 70%. Difficulty was encountered, however, in determining the K_{LSW} , corresponding to 0 volume fraction. Voorhees used the grain-groove technique developed by Hardy at NITS to determine the interfacial energy between the solid and the melt and obtains $K_{LSW} = 1.01$ microns³/sec. The resulting values for $K(\phi) / K_{LSW}$ exceed the predictions of all of

the theories by a factor of 2. The measurements of the physical constants used to obtain K_{LSW} are being reviewed.

Liquid Phase Sintering

Liquid phase sintering (LPS) is a widely used process for forming composites containing refractory particles such as tungsten, Re, or various carbides in a metal matrix. Sintered products include cutting tools, bearings, contact points, and other irregularly shaped parts where it is desirable to combine extreme hardness with the toughness and thermal or electrical conduction of the metal matrix. The refractory particles are combined with the metal matrix powder and isostatically pressed and heated to above the melting point of the host phase. If proper attention is paid to the wettability of the refractory particles, the molten host metal will infiltrate between the grains of the solid particles and envelop them. There are some obvious gravity effects because of the large difference in densities often encountered between particle and host phase. Consequently, this restricts the process to large volume fractions of the solid phase since the solid particles will essentially have to support themselves during the process. Even under these circumstances, there are differences in the particle size and morphology between the top and bottom of the specimen due to the gravity-imposed hydrostatic pressure.

Kohara (Science Institute of Tokyo) conducted liquid phase sintering experiments on SL-J using W in 3.5 – 30 Wt% Ni. The powders were compressed into cylinders, placed in BN crucibles and heated to 1500°C for 60-300 minutes. The samples with low volume fractions on the matrix material retained their shapes during the process, but those samples in which the matrix material could form a continuous liquid layer over the outer surface changed to a spherical shape in microgravity.

German, Upadhyaya, and Iacocca at Penn. State University conducted liquid phase sintering experiments on SL-J, IML-2 and on the MSL-1R missions using W particles in a Fe-Ni matrix. On IML-2, the samples contained from 78 – 98 Wt% W in 5 Wt% increments. Liquid-solid segregation did not occur in the flight sample, but the lack of hydrostatic pressure prevented the sample from achieving 100% densification, as it would have in normal gravity. Instead, gas pores formed which were stable and became a discrete phase within the microstructure. Many of the pores had large distorted shapes as they interconnected W particles. Systems that distort in 1-g also distort in micro-g, except instead of attaining the characteristic elephant foot shape, the micro-g samples tend to reshape into spheres. This would indicate that viscous flows driven by surface tension can be significant. The major results from this series of experiments are universal models for coarsening, slumping and distortion, and grain agglomeration.

Thermosolutal Convection

In dilute systems (systems in which the alloying component is small enough so that its presence does not significantly affect the density of the melt), it is possible to eliminate solute redistribution on a global scale in normal gravity by directionally solidifying the sample in a vertical stabilizing configuration (hot over cold). Since heat must be applied

through the walls, there will still be some convection from the horizontal thermal gradients, but these flows will primarily affect the radial distribution of solute in the solid. Non-dilute systems can be stabilized even more if the rejected component is denser than the bulk melt. However, if the rejected component is less dense, it will tend to rise and upset the stabilizing thermal gradient. Coriell showed that such a system would be unstable even if the thermal gradient were high enough to provide a monotonic decrease in density along the vertical direction. This comes about because solute diffusion is much slower than thermal diffusion so if a parcel of fluid is displaced vertically, it will equilibrate thermally with its surroundings faster than compositionally, find itself still lighter than its surroundings, and will continue to rise. This is known as the double-diffusive problem and received much attention from oceanographers because of the phenomena of salt-fingering. The surface is warmed by the sun which tend to thermally stabilize the system, but evaporation increases the salt concentration at the surface, which tends to destabilize the system and produce overturning convection.

Coriell's analysis also showed that such systems could even be unstable under microgravity conditions if the concentration of solute more than a few percent. This theory was tested by Rex and Sahm (Gietzrei Institut der RWTH, Aachen). On the D-1 mission, they directionally solidified an Al -3 wt%Mg alloy at a growth rate of ~4mm/min under a thermal gradient of 13K/mm. This should place the sample well within the region of stability predicted by Coriell. Indeed, the space sample solidified with a plane front and had a longitudinal compositional profile consistent with purely diffusion-controlled transport. The experiment was repeated on D-2 by Stehle and Rex with Cu-30.1Wt%Mn. The growth rate was varied from ~1.2 microns/sec, which corresponds to the stability limit estimated by Coriell for 10-4 g, to 16 microns/sec. The composition of the flight samples was consistent with diffusion controlled growth throughout.

Unfortunately, the above experiments lie well within the stability regime, so they don't really test the limits of stability. Leonartz (Ingenieurbuero, Aachen) directionally solidified the transparent . succinonitrile-0.45Wt% acetone and succinonitrile-0.33 Wt% ethanol systems on a rotating centrifuge (NIZEMI) facility on the IML-2 flight. In this manner, the g-level could be varied from 0.001 to 1 g by changing the rotation speed of the centrifuge. The observed thermo-solutal convective velocities were well under the solidification velocity for g-levels up to 0.01 g, thus no effect on interface shape could be observed. Coriell's predictions indicated the thermosolutal stability should occur at 0.001g for the succinonitrile-0.45Wt% acetone system for a thermal gradient of 1 K/mm and solidification velocities less than 2 microns/s. Instead, the instability was observed at 0.1g. Coriell's theory considered the most unstable wavelengths in an infinite surface. If this wavelength happens to be longer than the width of the chamber, wall effects will limit the instability, which appears to be the case in this experiment.

Monotectic Systems

As discussed previously, some metallic systems tend to be immiscible in the solid phase and form eutectic structures when they solidify. Other systems also have regions of

immiscibility in the melt. Atoms of one component generally prefer to be next to like atoms, just as molecules of water in an oil and water mixture prefer to be next to water molecules and oil molecules prefer to be next to oil molecules. Such systems are said to have positive heat of mixing, meaning that the internal energy of the system is higher in the mixed state than it would be if the components were separated. If this were the complete story, such systems would always separate, just as oil and water tend to do.

The other factor is the entropy of mixing. Entropy is related to the number of possible states available to the system. If a deck of cards is cut in half, there are only a few ways the deck could be arranged so that all the black cards were in one stack and all the red cards in the other. On the contrary, there are many more ways the deck could be arranged to find the black and red cards mixed. Thus we say the mixed state is more probable, and if we were playing with a randomly shuffled deck, we would almost always expect to find some degree of mixing of the cards.

It was the genius of J. Willard Gibbs to recognize that a system reaches equilibrium, not when the configurational energy (enthalpy) is a minimum, but when enthalpy minus the product of entropy and temperature is a minimum. This combination is called the Gibbs free energy, of sometimes just the free energy and it is this function that determines when an equilibrium phase transformation takes place. For example, atoms are more tightly bound together in a solid than in a liquid, so the solid has a lower (more negative) internal energy than the melt. However, since atoms are free to move around in a melt, the melt has higher entropy. When the temperature is raised to the point where the product of entropy and temperature overcomes the difference in internal energy between the solid and liquid, the liquid phase will have the lowest free energy and the system melts.

Similarly, in a mixture of atoms with a positive heat of mixing, there will be a temperature above which, the entropy of mixing term overcomes the positive heat of mixing and a homogeneous solution will result. The lowest temperature at which this condition is met for all compositions in the immiscible region is called the critical consolute temperature. (Theoretically, there should be a temperature above which oil and water should completely mix, but this is above the boiling point of water.) If this critical consolute temperature happens to fall below the equilibrium freezing point, there will be no liquid phase immiscibility.

The critical consolute temperature corresponds to an inflection point in the free energy vs. composition curve. At temperatures below the critical consolute temperature, the free energy curves will have two minima and two inflection points. The binodal or two-liquid phase region is mapped out by the locus of points where a mutual tangent exists between these two regions of the free energy curve. The inflection points in the free energy curves define a region called the spinodal. Between the binodal curve and the spinodal curve there exists a region of metastability, meaning an energy barrier must be overcome in order to form the second liquid phase, just as an energy barrier must be overcome in order to form a solid from a liquid. Just as in solidification, this energy may be overcome heterogeneously by forming a nucleus at a low energy site such as the container wall, or homogeneously by forming a nucleus from an undercooled melt. However, in the

spinodal region there is no barrier to forming the second liquid phase. If the melt is undercooled into this region before nucleation occurs, it will spontaneously decompose into the two liquid phases. This process is known as spinodal decomposition.

When a region of liquid phase immiscibility exists, it does so only over a limited range of compositions. There will be composition at which the melt will remain homogeneous until it forms a solid rich in the component with the highest freezing point and a liquid rich in the component with the lower freezing point. The temperature and composition at which these three phases can coexist is an invariant point, similar to the eutectic reaction in which a melt of homogeneous composition decomposes into two solids of different composition ($L \leftrightarrow S1 + S2$) except, in this case, $L1 \leftrightarrow S + L2$. This is called a monotectic reaction and systems in which this reaction occurs are called monotectics. Compositions richer than the monotectic composition in the higher melting point component are called hypomonotectics and can be solidified from the melt in the same manner as hypoeutectics. It is also possible to solidify the monotectic composition if care is taken to prevent convective flows from sweeping the second liquid phase away from the solidification front. But any attempt to solidify a hypermonotectic composition by cooling the melt through the two-liquid phase region will result in a highly segregated solid because the two liquid phases will always have different densities and will separate by sedimentation before the solid can be formed by equilibrium solidification. (It is possible to form a fairly homogeneous solid of hypermonotectic composition by various rapid quenching processes in which solidification takes place before the two liquid phases can separate, but this would generally require that the sample be thin so that heat can be removed rapidly.)

There are a large number of binary metallic systems that exhibit monotectic behavior and attempts to form alloys of these systems was one of the first quests of the microgravity program. A mixture of krytox oil and water was shown to remain mixed for several hours in a simple demonstration experiment on Skylab, so it was known that in the absence of sedimentation such a mixture could be held in a metastable state more-or-less indefinitely. But, much to the surprise of these early experimenters, almost complete phase separation was observed in every attempt to solidify a monotectic system by cooling a melt through the two-liquid phase region, even when the process was carried out in a virtually weightless environment. Generally, one of the phases was found to be enveloped by the other phase, much like the yolk of an egg. This was quite different from the ground based results in which the denser phase was always found at the bottom of the crucible. Clearly, some interfacial effects are operating to cause phase separation that had obscured by gravity-driven sedimentation.

As the melt is cooled into the metastable two-liquid phase region, drops of the minority phase may nucleate homogeneously within majority or host phase. As heat is extracted from the system, these droplets will be subjected to a thermal gradient. Since the interfacial energy between the two fluids is temperature dependent, the difference in temperature across the droplet will result in an unbalanced force along its surface. The resulting convective flows, sometimes called Marangoni convection, will drive the droplet toward the region of higher temperature. According to a theory developed by

Young, Goldstein, and Bloch, the velocity of a droplet propelled by this mechanism is directly related to the droplet size. Thus as droplets overtake one another and become larger, they move faster and are able to overtake smaller droplets and become larger still. This mechanism could certainly explain how the minority phase could coalesce in the last region to solidify.

In the meantime, Cahn developed a theory of critical wetting quite independently of the microgravity experiments on monotectic systems. According to Cahn's theory, there will be a region of temperature below and extending to the critical consolute temperature over which one of the two liquid phases will perfectly wet the container wall. When this occurs, there will be no barrier to this phase nucleating and spreading over the container wall, thereby forcing the other phase away from the wall.

A TEXUS rocket experiment by Ahlborn (Universitat Hamburg) and Lohberg (TU Berlin), using Al 10Wt% In in an Al_2O_3 crucible which is preferentially wet by the In-rich phase, found most of the indium-rich minority phase in contact with the crucible and surrounding the aluminum-rich majority phase. Some small amount of In-rich phase was also found near the center of the Al-rich region, presumably driven there by Marangoni convection. Potard (CEA-CENG, Grenoble), in a separate rocket experiment used the same components in a SiC crucible, which is wet by the Al-rich phase. He found the In-rich minority phase was completely surrounded by the Al-rich phase. Gelles and Markworth (Gelles Associates, Columbus, Ohio) flew Al-90Wt% In in an alumina crucible on OSTA-2 and found a few relatively large LI droplets with many smaller ones distributed through the In-rich matrix. These smaller droplets were adjacent to, but generally not touching, the crucible wall. These experiments demonstrate the critical wetting and spreading that occurs according to Cahn's theory if the minority phase wets the crucible walls in preference to the majority phase.

On Spacelab 1 and D-1, Ahlborn and Lohberg (Lehrstuhl Fur Ingenieurwissenschaften Der Universitat Hamburg, demonstrated, with a variety of systems including Zn-Bi, Zn-Pb, Zn-Bi-Pb, and Al-Pb, that the minority phase was always transported to the hottest portion of the sample during the solidification process, presumably by Marangoni-induced droplet motion.

Kamio (Tokyo Institute of Technology) directionally solidified Cu-Pb at the monotectic composition. The resulting microstructure consisted of irregularly shaped Pb rods in a Cu matrix; however, a layer of Pb above the quenched growth front suggest that growth may not have taken place exactly at the monotectic composition. The ground control sample showed similar microstructure. A hypermonotectic Al-In sample was also flown, but a leak in the ampoule prevented any results from being obtained.

Togano et al. (National Research Inst. For Metals, Tokyo) succeeded in casting a ternary monotectic system on SL-J. Compositions of 1, 2, and 3 At% each of Pb and Bi was contained in an Al matrix. The starting material was prepared by chill casting ingots with the specified compositions. These were heated to 1580K in ten minutes, held for 34 minutes, and quenched to 873K in 70 seconds. The flight samples had a reasonably well

dispersed array of (Pb,Bi) particles with 90% under 50 microns, although some voids were also present. Ground control samples had almost complete phase separation, as would be expected. The flight samples were then sheathed in Cu and drawn into wires of 0.35 mm diameter. This resulted in a Type 2 superconductor in the form of a dispersion of (Pb,Bi) fibers in an Al matrix. The superconducting transition was 8.7K, the critical field was 1.9 T, and the critical current density was 5000A/cm².

On the D-2 mission, Sangriorgi, Muolo, Ferrari, Passerone, (Insstituto di Chimica Fisica Applicata dei Materiali, Genoa) and Rossitto (ESA Astronaut Center, Koln) investigated the influence of crucible wetting on the phase distribution when the Cu-Pb monotectic system solidified. Cu-rich and Pb-rich melts were solidified in graphite, sapphire (Al₂O₃), and boron nitride (BN) crucibles. Care was taken to reduce the gradients in the system during cooling to less than 0.4K/cm to reduce Marangoni flows. When the Pb-rich phase was the majority phase, it preferentially wet the sapphire crucible and surrounded the Cu-rich phase, which is consistent with Potard's results. However, when the Cu-rich phase was the majority phase, no preferential wetting of the graphite or the BN crucible was observed and a fairly regular structure resulted. This seems inconsistent with Cahn's prediction that one of the two phases should have become perfectly wetting and spread over the wall of the crucible. However, the temperature at which the Cu-rich composition enters the two-liquid phase region may have been sufficiently lower than the critical consolute temperature so that critical wetting may have been avoided.

An attempt was made to directionally solidify hypomonotectic Al-In by Andrews (U. Alabama, Birmingham) and Coriell (NIST) on the LMS mission. The flight sample contained a number of large voids, apparently from gas trapped or generated during the process. Care was taken to analyze the trapped gas in the ampoule and it was determined that the gas was mostly N₂ with some H₂ and CO₂.

On a follow-on experiment on USMP-4, Andrews elected to work with a transparent monotectic system, succinonitrile-glycerol, to elucidate the wetting and spreading characteristics of the minority phase. Test cells consisted of a sandwich of microscope slides with a thin, 0.13 mm, teflon gasket between them. The cells were heated to 90°C to homogenize the melt (critical consolute temperature is 83°C). They are then placed on a back lighted table for viewing with a video equipped stereo microscope. It was anticipated that succinonitrile-rich droplets would preferentially wet the teflon gasket, so that if succinonitrile happens to be the minority phase, the system would be unstable against critical wetting. If succinonitrile is the majority phase, the system should be stable and a uniform dispersion of glycerol droplets in the succinonitrile host phase should occur. For compositions from 70 to 55Wt% glycerol, droplets of glycerol formed on or near the teflon gasket, but did not spread along it. Contact angles ranged 30 to 80°. However, at 45-50Wt% glycerol, a film of glycerol was observed to have formed along the teflon gasket, indicating perfect wetting. Below 45 Wt% glycerol (succinonitrile is the majority phase), stable dispersions of glycerol droplets were seen as expected. At 15Wt% glycerol, no glycerol droplets were seen near the interface as if they had somehow been repelled by the interface.

One of the applications of the research on monotectic systems is a strip casting technique developed by Metallgesellschaft, Frankfurt that balances the sedimentation of the droplets with Marangoni convection. This process can produce endless strips of finely dispersed Pb or Bi in an Al or Al +5Wt%Si alloy. Aluminum alloys with uniformly dispersed phases of Pb or Bi are presently being investigated as candidates for advanced bearing for automobile engines. The present strip casting process can provide a dispersed phase up to 7 Wt% Bi, but a higher percentage would be desirable. The process has been extensively modeled, but more information is needed on the Marangoni flows and on the resulting coalescence of the droplets. Ratke, Prinz, and Ahlborn designed an experiment for the D-2 mission to obtain the data needed to improve the model. A molten zone is passed through a strip-cast sample freeing the Bi droplets when the monotectic temperature is reached. The droplets are propelled toward the higher temperature region by thermal Marangoni convection where they begin to dissolve, creating a solutal gradient, which also influences the Marangoni convection. As the droplets move forward, a backstreaming flow is produced in the host material, which also changes the local composition. As the temperature is reduced at the cold end of the zone, the droplets the Marangoni-induced flow is reversed and the droplets tend to coalesce before they are incorporated into the dendritically solidifying Al-Si host material.

This highly complex process has been modeled computationally, but present computational capability can only track some 5000 droplets, whereas millions of droplets are involved in the actual process. Measurement of the droplet distribution in the final solid enables the extraction of important physical parameters such as the interfacial energy as a function of composition, and provides information on the importance of droplet coalescence from the Marangoni-induced droplet motion.

One problem with the solidification experiment had always been the fact that the experimenters could only see the final result and had to theorize what sequence of events must have occurred to reach the final state. For example, they had no way of knowing if the melt decomposed spontaneously, or if droplets formed and then coalesced, or if coalescence occurred during the solidification by particle pushing by the solidification front.

Otto (DLR, Koln) tried to resolve this problem using the MAUS facility on the orbital platform SPAS-01 on the OSTA-2 mission (STS-7). Using a small X-ray source, he took shadowgraphs of the decomposition of a Ga-Hg mixture as it was cooled into the two-liquid phase region at different cooling rates. He was able to observe individual droplets after they grew to 0.2 mm in diameter. The droplets did not appear to be homogeneously distributed, but may have nucleated heterogeneously on low energy sites. No particle motion was observed, either from Marangoni convection, or from the residual acceleration. This is a fairly good indication that the droplets either nucleated on or stuck to the teflon container walls.

On D-1 same mission, Ecker attempted to observe the directional solidification of the transparent succinonitrile-ethanol system using holography. Unfortunately, the film transport on the Hasselblad camera failed and the data was lost.

Similarly Braun, Ikier, Klein, Schmitz, Wanders (DLR < Koln) and Woermann (U. Koln) investigated phase separation in immiscible liquid systems using transparent analogs to metallic systems on the D-2 mission. A mixture of butoxyethanol and water has a region of immiscibility that is a function of pressure. The sample is stabilized at 18 bars at a temperature just below the two-liquid phase region and then the pressure is released to 1 bar. Thus the region of immiscibility is entered isothermally with no mechanical mixing. The decomposition and droplet growth was monitored holographically. Initially the droplets grew to an equilibrium diameter of approximately 3 microns by diffusion. They remained at this diameter for 1 hour with a slight increase in diameter due to Ostwald ripening, and then showed a rapid increase in diameter due to Marangoni convection when the thermostat was turned off and thermal gradients developed.

Particle/Solidification Front Interactions

Small ceramic particles are sometimes added to metals to block the motion of dislocations (dispersion hardening) or for flux pinning in type II superconductors. In the preparation of composite materials, it is important to know how such particles interact with the solidification front. If the particle is not wetted by the melt, intermolecular forces will tend to repel the particle. These forces are pitted against inertia and a drag force that tend to engulf the particle. There have been a number of theoretical attempts to model this process and it is generally accepted that, for a particular system, there is a critical velocity, below which the particle will be pushed ahead of the solidification front, and above which, it will be engulfed by the advancing solid. Buoyancy and convective flows complicate the picture in normal gravity and it is important to be able to separate these effects from the more fundamental interactions that take place at the solidification front.

Klein (DLR, Koln) attempted to measure pushing of 40 micron Pb spheres and air bubble in a transparent CsCl melt during the OSTA -2 mission. A gradient of 65 k/cm was established in special furnace with sapphire windows which allowed the advancing solidification front to be photographed. Initially the Pb drops were pushed by a solidification front moving at 4 microns/sec. Interestingly, the bubbles did not move in the direction of the thermal gradient, as would be expected from Marangoni convection, but were overtaken by the solidification front (they may have been stuck on the walls). When the bubbles were overtaken by the solidification front, they were not engulfed, but instead formed channels into the solid. Eventually, the front was disturbed by the bubbles to the point that meaningful data could no longer be extracted.

Potard and Morgand (CEA-CENG, Grenoble) attempted to use a vapor-emulsion technique on SL-1 to obtain a uniform dispersion of bubbles in a directionally solidified Al-Zn ingot. The concentration of Zn ranged from 1-5At%. It was expected that the high vapor pressure of Zn would form a uniform distribution of gas bubbles in the final solid. For reasons that are not clear, the Al failed to wet the SiC crucible and the expected results were not achieved.

Langbein and Roth (then at Battelle Institute Frankfurt, Germany) investigated the interaction of solid particles with an advancing solidification interface on D-1. A copper sample containing 1 vol.% molybdenum particles (2 to 4 microns in diameter) was placed in an alumina container. The sample was directionally solidified with a decreasing rate. Bubbles also formed as the sample was directionally solidified. In the lower region (highest solidification speed) the Mo particles were aligned along boundaries of cellular growth. Some of the Mo particles were captured and transported by the bubbles. In some cases, Mo crystals as large as 20 microns had grown inside the bubbles. Other bubbles had filled with Cu, while others had remained as voids. Some of these voids remained spherical, while others were pear-shaped with their tails pointing toward the hot end.

Poetschke and Rogge (Krupp Research Institute/Krupp Pulvermetall GmbH, Essen) conducted a similar experiment on D-1. They used 1-20 micron alumina particles as well as 1-4 micron Cu particles in a Cu matrix. The alumina particles formed aggregates they were pushed by the planar solidification front. The Mo particles were strung along cellular boundaries as was the case reported by Langbein and Roth

On the LMS mission, Stefanescu and co-workers at the University of Alabama sought to examine particle engulfment and pushing in the case of a planar solidification front intersecting spherical, non-wetting particles. He chose pure Al for the host metal and zirconia particles, which were found to non-wetting at the melting point of Al. The starting material was prepared by casting ingots of Al with a small volume fraction of 500 micron zirconia particles. He used the AGHF to directionally solidify these ingots at different rates. Preliminary results indicate that the pushing-to-engulfment transition occurs between 1.9 and 2.4 microns/sec in the ground based experiments and between 0.5 to 1.0 microns/sec for the flight samples. Analysis is still in progress to ascertain whether wetting actually occurred in these samples. Stefanescu attributes the difference between the ground and flight results to convective flows near the solidification interface, which can impart a roll to the particles giving them a slight lift. This effect was seen in a transparent analog experiment using succinonitrile as a metal model.

Stefanescu repeated his experiment on USMP-4 using transparent systems so that the actual pushing and engulfment process could be observed. The choice of host materials was succinonitrile, a non-faceting material, and biphenyl, a faceting material. Polystyrene beads of varying diameters were used with the succinonitrile and glass beads were used with the biphenyl. The polystyrene beads had much lower thermal conductivity than the succinonitrile host, whereas the glass beads had much higher conductivity than their host. Several unexpected phenomena were observed. The glass beads tended to move along the surface of the biphenyl in the flight experiment, which was thought to be a result of the anisotropy of the faceted interface. Also the interface began to show signs of a cellular structure toward the end of the experiment and beads that had previously been pushed were engulfed. It was not clear if this was the result of a build-up of solute (even though extreme care had been taken to purify the material

beforehand) or if the thermal gradient was somewhat lower at the end of the cuvette. As a result, only the data taken in the first 5 mm were considered.

Again the critical velocity was found to be higher on the ground than in space. This was attributed to the Saffman force resulting from convective flows that tends to lift the particle away from the interface. A theory developed by Shanguan, Ahuja, and Stefanescu predicts the critical velocity to be given by

$$v_{cr} = \left(\frac{\Delta\gamma a^2}{3\eta KR} \right)^{1/2}$$

where $\Delta\gamma$ is the difference between the particle-liquid and the particle-solid interfacial energies, a is the atomic spacing, η is the kinematic viscosity, K is the ratio of particle to liquid thermal conductivity, and R is the particle radius. This model was validated for the case of zirconia particles being pushed by Al in the LMS experiment and is within the experimental error of the lower bound for the succinonitrile-polystyrene particles on UMP-4. However, the model predictions are much lower than the experimental data for the biphenyl – glass system. The anisotropy of the interface as well as the motion of the particles along the interface may contribute to this discrepancy.

On the LMS mission, Hecht and Rex (ACCESS, Aachen) investigated the pushing and entrapment of 13 micron Al_2O_3 particles on a commercial 2014 Al alloy. They observed pushing during the plane front transient which was consistent with the model predictions of Potschke and Rogge. However, at the higher solidification velocity when the front became dendritic, they found particles trapped in the interdendritic fluid between the secondary dendrite arms and acknowledged their difficulty of extending theories based on idealized conditions to “real-world” problems.

Froyen and Deruyttere (Katholieke Universitat Leuven) formed a number of metal matrix composites on the SL-1 mission. Micron sized SiC and Al_2O_3 particles were mechanically mixed with Al powder and hot extruded into bars. The samples were then coated with an Al_2O_3 skin and melted and solidified in the isothermal furnace. A more uniform distribution of particles was obtained in the flight samples and the microhardness was more uniform, a result the Investigators attribute to the reduced convection and sedimentation. Additional experiments were conducted on D-2 using a Cu matrix in a graphite crucible. Again the Al_2O_3 particles were uniformly dispersed and the flight sample had improved hardness. The SiC particles decomposed, the Si forming a solid solution with the Cu while the graphite was expelled. The W and Mo particles oxidized near the presence of gas bubbles and were not uniformly distributed.

Muramatsu and Dan (National Research Institute for Metals, Japan) reported that they obtained uniform dispersions of TiC in Ni by heating specimens prepared by powder techniques in the Large Isothermal Furnace during the SL-J mission. No further details were given.

Also on SL-J, Suzuki (Hokkaido University) with Miura and Mishima (Tokyo Institute of Technology) coated short carbon fibers with Al-1 At% In and heated the aggregate to 700°C for 10 minutes to form an ultra-low density (10% that of Al) composite material with high stiffness, suitable for on-orbit fabrication of structural components. They did find some unexpected local coagulations of Al in regions where the coatings on the fibers was drawn away. This led to a somewhat lower compressional strength of the composite than had been expected.

One of the more important “real world” problems has to do with attempts to dispersion harden superalloy single crystal gas turbine blades by incorporating very small (submicron) oxide particles during the growth process in order to increase their creep resistance. A uniform dispersion can be achieved by powder metallurgical techniques, which can then be densified by hot isostatic pressing (HIP). But when the blade is melted so that it can be directionally solidified into a single crystal, the particles tend to agglomerate and are not uniformly incorporated into the superalloy matrix. The solidification velocities required to achieve plane front solidification are generally below the critical velocity for engulfment of such small particles. At higher solidification, the particles tend to be pushed laterally by the dendrites and wind up being clumped together, trapped in the last-to-freeze interdendritic fluid. This problem prompted several flight experiments by industrial firms trying to sort out gravitational effects from non-gravitational effects that remain as barriers to developing this process.

One group of experiments focused on the use of a thin oxide skin to replace the ceramic moulds used to form the turbine blades. It was hoped that in the absence of hydrostatic pressure, a thin skin could retain the shape of the blade during the directional solidification process. Eliminating the heat transfer through the mould would allow a much sharper thermal gradient to be applied during the directional process, which helps stabilize the growth front at higher solidification velocities. One of the major difficulties had to do with keeping the skin intact during the volume changes involved during the melting and solidification process.

The use of “skin technology” was first demonstrated on Spacelab-1 by Luyendijk, Nieswaag, and Alsem (Delft University) who directionally solidified a gray cast iron ingot with a 50 micron Al_2O_3 skin. Gray cast iron actually shrinks on melting so the alumina skin did not have to withstand a volume expansion from melting. In fact the melt separated into two parts during the process. The skin remained intact during the process, although some micro-cracks were observed. Small iron droplets were found along the outer surface of the skin. It was speculated that they formed by condensation from the vapor. A similar experiment was flown on D-1 by Nieswaag and Sprenger (MAN Technologie AG) with the objective of determining the diffusion of sulfur in the cast iron. Again the skin kept its shape with only a few drop that squeezed through the pores, but it was not clear if free surface existed near the thermocouple grooves. Unfortunately, problems with the translation mechanism prevented an accurate assessment of the diffusion of the sulfur.

On the D-2 mission Amende (MAN Technologie AG, Munchen) solidified a cast iron rod in which portions were alloyed with different compositions of Cr and Si. The rod was coated with a thin skin of MgO-stabilized zirconia. The thermal expansions of the alloys were twice that of the zirconia skin. The objectives were to see in the ceramic skin could accommodate the alloys during melting

and resolidification and to see if any of the alloys reacted with the skin. The skin did successfully contain the melt, although the portion containing the Cr alloy detached from the remainder of the rod. It was speculated that the skin was preferentially wetted by the Cr alloy and that the interfacial tension was responsible for the separation of this portion.

Barbieri and Patnelli (Universita di Bologna) with Gondi and Montanari (Universita di Roma) investigated a variety of composites, some using powder Ag-Cu as the eutectic composition and others using powder Al as the matrix, some with Al_2O_3 film coating, some with Ni coating, and others with no coating. Some samples contained micron-sized Al_2O_3 particles, while others were compacted to 85% fractional density so that bubbles would serve as the dispersed phase. Generally, the Al_2O_3 coatings retained their shape during solidification, although some leakage was observed. The lamella spacing in the micro-g eutectic samples were twice as large as the 1-g counterparts, which was attributed to a slower cooling rate resulting from less thermal contact in the low-g case. Most the most part, the bubbles were swept by the solidification front to phase and grain boundaries. The oxide particles tended to aggregate in both space and ground control samples, although the aggregates appeared to be more uniformly distributed in the space samples.

Confinement of the melt and shape retention in a superalloy was successfully demonstrated on the D-1 mission by Sprenger (MAN Technologie AG), using a gamma/gamma prime-alpha, Ni/Ni₃Al-Moalloy coated with an 80 micron thick yttria-stabilized zirconia skins that had been applied by plasma spraying. (A similar experiment was attempted on SL-1, but could not be run because of technical difficulties.) Volume expansion was successfully compensated for by a small hole drilled into the end of the sample. Shape was maintained through the cylindrical sample and into the flattened region near the end. There were no holes or pores in the sample and no evidence of Marangoni convection, which indicated that the melt had remained in contact with the skin. Directional solidification of this alloy produces a regular arrangement of Mo fibers contained within a Ni/Ni₃Al (gamma/gamma prime) matrix. The flight sample exhibited a carbide phase not seen in earth-processed samples. It was suggested that convective flows may transport the carbon away from the solidification front, thus preventing this phase from forming during processing in normal gravity.

On D-2, Amende and Holl (MAN Technologie AG) attempted to melt and resolidify actual gas turbine blades that had been formed by powder techniques and coated with a 150 micron yttria-stabilized zirconia skin. The blade material was the Ni-base CMSX6 superalloy with 0.5Wt% 50nm Al_2O_3 particles. The coating remained intact, but the evolution of the gas trapped in the pores of the pressed powder sample caused swelling of the oxide skin and the loss of shape.

Busse (ACCECC e.V.) along with Deuerler and Poetschke (Krupp) investigated the gravitational influence on the aggregation of submicron Al_2O_3 powders on the D-2 mission. It had originally been speculated that such powders tend to agglomerate because they were not wet by their metallic host. If the metal melt did not penetrate the region between two touching particles, London-van der Waals forces would cause the particles to clump together. However, preflight ground based tests revealed that the particles tended to clump whether or not they were wet by the molten . Further, it was found that the particles tended to clump into micron-sized spherical clusters by Brownian motion as soon as the CMSX-6 superalloy matrix melted. These clusters they tended to form chains on the order o 10 microns long during the solidification process . The chains of clustered

particles became trapped in the interdendritic fluid where they tended to be aligned by the dendrites. The only significant difference between the flight and ground samples were a slight increase in the size of the clusters and length of the chains in the ground control experiments, indicating that gravity had little influence on the agglomeration process.

Crystal Growth Experiments

Semiconductors as a class of materials can include semi-metals, ceramics, and polymers. They are characterized by the fact that they have a small energy gap (less than a few electron volts) between their valence band and their conduction band. Because of this small energy gap, they can be easily manipulated to either conduct or not conduct electricity, a property that provides the means for modern electronics. Unlike most metals, in which the current is carried by electrons, conduction in semiconductors take place through the action of both electrons in the conduction band and holes left by the electrons in the valence band. These materials can also absorb photons to promote electrons from the valence band to the conduction band to act as detectors of radiation or solar energy converters. Finally, certain of these materials can be configured so that current flowing through them reunites electrons in the conduction band with holes in the valence band to produce photons, giving rise to light emitting diodes and solid state lasers.

The ability to grow large, extremely pure, single crystals of silicon was key to the vast electronics industry that has been developed over the last several decades and silicon will continue to dominated this industry for the foreseeable future. It is plentiful, cheap to produce, and has all of the desired properties needed for most applications. It does have a few drawbacks, however. The charge carrier mobility is relatively low, so it is not suitable for very high frequency applications or high speed switching applications. Also, it is not a direct band gap material, meaning that electrons cannot directly go from the conduction band to the valence band, emitting light in the process. Therefore, it is not suitable for making the solid state lasers that are finding wide use in the optical communications industry.

For these reasons, there has been considerable attention compound semiconductors such as gallium arsenide (GaAs) because of the high charge carrier mobility which allows much higher switching speeds than Si. Unlike silicon, GaAs is a direct bandgap material, meaning that an electron can fall directly from the conduction band to the valence band and emit a photon of light with an energy equal to the bandgap energy. Thus such a material can be used to fabricate light emitting diodes (LED) or solid state lasers. Thus it can be used as both a transmitter and a receiver on the same chip in fiber optical systems. Its unique band structure allows it to be used as a Gunn-effect oscillator for low cost radar devices. Its higher bandgap allows it to operate at higher temperatures and makes it less susceptible to radiation effects. This feature makes it a more desirable material for use in extreme environments such as in geocentric or deep space missions.

It is also possible to combine elemental or compound semiconductor systems to form solid solution alloys with a band gap somewhere between the band gap of the initial components. Thus it becomes possible to engineer materials to obtain a particular band gap for a specific application. For example, cadmium atoms may be substituted for 20% of the mercury atoms in mercury telluride (HgTe) to form $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te}$ which has a band gap equivalent to 10.6 microns, the wavelength of a CO_2 laser. This class of materials has found extensive use as infrared detectors and thermal imaging devices.

Most electronic or opto-electronic applications require compositionally homogeneous, high quality single crystals. However, materials of interest are not necessarily restricted to the more traditional semiconducting materials (those found in groups II through VI in the periodic table.) Many organic and even some polymers have interesting optical and opto-electronic properties. Studies of single crystals are important to other field as well; e.g., the study of zeolite crystals as catalysts. To include this broader spectrum of activities involving crystal growth, this section will cover all of the microgravity experiments where crystal growth is the primary emphasis (except for protein or other biological macromolecules – here the number of experiments is so large that they require a separate section.)

Melt Growth of Electronic and Photonic Materials

The conductivity of semiconducting materials is extremely sensitive to the presence of trace quantities of certain impurities called dopants, which are often added to bulk semiconductors in order to tailor their electrical properties for a specific task. It is important that the concentration of these dopants be uniform throughout the material so that the electrical properties will be the same. Generally, these impurity atoms are not incorporated into the lattice as readily as the host atoms, which leads to a phenomenon known as segregation. When solidifying from the melt, the rate at which the impurity or dopant atoms are incorporated into the growing crystal is directly proportional to their concentration at the growth interface. Ideally, the concentration of rejected atoms will build up in front of the growth interface as growth proceeds to form a diffusion layer. Eventually, an equilibrium is reached wherein the rate at which dopant atoms from the feed are entering the diffusion layer equals the rate at which the dopant atoms enter the growing crystal. Growth under these conditions is said to be diffusion controlled and once this equilibrium condition is reached, the remainder of the material will have uniform composition.

Convective flows can cause the dopants to be distributed non-uniformly, both on a microscopic scale (microns) as well as macroscopically. Global flows in the melt will tend to stir the diffusion layer containing rejected component back into the bulk liquid, thus preventing the diffusion controlled equilibrium to be reached. The result is a continuously varying composition as growth proceeds. Microscopic nonuniformities, usually in the form of striations, were believed to be a result of growth rate fluctuations caused by unsteady or turbulent convective flows in the melt. If the unsteady flows caused the temperature at the growth interface to fluctuate, even slightly, the interface will jump ahead and fall back as growth proceeds. More dopant atoms are incorporated

when the growth front is accelerated, thus forming what are known as Type I growth rate striations. The early Skylab experiments demonstrated that growth striations in dilute systems such as doped elemental or simple compound semiconductors, could be eliminated in microgravity and that diffusion controlled growth conditions could be established. This prompted a number of attempts to grow bulk multi-component alloy-type systems with the objective of obtaining better compositional homogeneity necessary to achieve uniform electronic and optical properties.

Bridgman Growth

In the Bridgman growth technique, developed by Percy Bridgman at Harvard University, the entire sample is melted (except for the seed if a seed crystal is used) and then the sample is slowly lowered from the furnace to allow the material to solidify so that the successive rows of atoms build up in an ordered fashion to form a single crystal. Stockbarger later added a second heater at the cold end of the furnace to provide better control of the growth interface and to reduce the sample cooling rate in order to reduce thermal stresses in the newly formed crystal. Technically, this should be called the Bridgman-Stockbarger technique, although Bridgman growth is a more-or-less generic term for any directional growth method.

By placing the hotter melt above the cooler growth region, the system is thermally stable and convection can be minimized. However, it is necessary to add heat to the melt through the sides of the growth ampoule and extract it through the growing crystal. This produces small radial thermal gradients in the melt causing the warmer fluid near the walls to rise while the cooler melt near the center falls. This circulation distorts the buildup of the diffusion layer at the growth interface resulting in radial segregation. This effect was first quantified by Brown (1985) using computational fluid dynamical computations.

Macroseggregation becomes a major problem in Bridgman growth of non-dilute or alloy-type systems when the rejected component is less dense than the bulk melt. When the diffusion layer builds up to a critical point, characterized by a dimensionless parameter called the Rayleigh number, its lighter fluid will rise and remix with the bulk fluid. If the growth system is turned upside down to prevent this from happening, the system becomes thermally unstable. Thus it becomes impossible to stabilize such a system against overturning convective flows in the presence of gravity. In fact, Coriell (1980) has shown that such double-diffusive systems may be unstable even in microgravity if the lower density component is more than a few percent of the total composition.

Rodot (CNRS, Meudon, France) grew 3 Ag-doped PdTe crystals that were 17 mm in diameter by the Bridgman method on SL-1. She reported better homogeneity and somewhat lower dislocation densities on the flight samples as compared to the ground control which exhibited growth striations.

Crouch and Fripp from the NASA Langley Research Center attempted to grow homogeneous lead-tin-telluride ($\text{Pb}_{0.8}\text{Sn}_{0.2}\text{Te}$) in the General Purpose Rocket furnace (a

relic left over from the SPAR suborbital program on the D-1 mission and observed almost complete mixing. This material is similar to mercury-cadmium-telluride (MCT) and is of interest for infrared detector and laser applications. The rejected component in this system (SnTe) is less dense than the host material; therefore, is subject to the double diffusive instability predicted by Coriell. Whether or not this experiment met Coriell's stability criterion was not established, nor were there any accelerometers on the mission that could record the direction and magnitude of the quasi-steady residual acceleration.

The experiment was repeated on USMP-3 using the Advanced Automated Crystal Growth Furnace (AADS F). Computational analysis indicated the minimal mixing should occur if the g-vector was nearly along the furnace axis with hot over cold. Three identical ampoules were loaded into a single cartridge for sequential processing. The first ampoule was to be processed with the g-vector nearly along the furnace axis with hot over cold, the second with the g-vector nearly along the furnace axis with cold over hot, and the third with the g-vector nearly perpendicular to the furnace axis. The plan was to compare the solute redistribution with the orientation during growth. For reasons that are not clear, large voids appeared in each of the samples and they were essentially completely mixed. This experiment was repeated on USMP-4. Unfortunately, a growth ampoule ruptured during the growth process and no results have been obtained.

Yamada and Kinoshita (Nippon Telegraph and Telephone Research Labs) also grew PbSnTe by the Bridgman method using the Gradient Heating Furnace on SL-J. Their ampoule contained a plunger to keep the melt in contact with the ampoule walls. Even so, they found voids in the flight sample. However, the fraction of Sn remained about 0.16 after the initial transient, indicating little or no convective mixing. The etch pit density ranged from 1×10^5 to 9×10^5 cm², or about 1/10 the typical value for Earth grown crystals. The intrinsic carrier density is also lower in the space grown crystal and the mobilities are 1580 cm²/Vs at 77K and 2620 cm²/Vs at 4.2K, about 3 times higher than typical Earth grown values. A small amount of melt leaked past the plunger and formed small spherical crystals. The etch pit density in these crystals that formed without wall contact was O(10⁴ cm².)

Tatsumi, Shirakawa, Murai, Araki, and Fujiwara (Sumitomo Electric Industries Ltd.) grew the ternary In_{0.97}Ga_{0.03}As by the Bridgman method on SL-J with the purpose of determining the solute redistribution in the grown ingot. A plunger was used to eliminate free surfaces in the melt. They report an effective distribution coefficient of 2.6 vs. a value of 3.2 for their ground control, indicating that considerable convective mixing had taken place.

Matthiesen (Case Western Reserve University) grew two Se-doped GaAs crystals in the Crystal Growth Furnace on USML-1. The objective was to obtain a uniform dopant distribution, both axially as well as radially. A second objective was to examine the effects of transients on dopant distribution. Two translation periods were executed, the first at 2.5 microns/sec and after a specified time, which was different between the two experiments, the translation rate was doubled to 5.0 microns/sec. The translation was then stopped and the remaining sample melt was solidified using a gradient freeze

technique in the first sample and rapid solidification in the second sample. Post-flight using quantitative infrared transmission imaging, indicated that the first sample initially achieved diffusion controlled growth as desired. However, after about 1 cm of growth, the segregation behavior was driven from a diffusion controlled growth regime to a complete mixing regime. Measurements in the second flight sample indicated that the growth was always in a complete mixing regime. In both experiments, voids in the center line of the crystal, indicative of bubble entrapment, were found to correlate with the position in the crystal when the translation rates were doubled.

The experiment was repeated on USML-2 using a new method for preparing the sample which eliminated the voids seen in the USML-1 flight sample. The first sample went polycrystalline at the meltback interface. The furnace temperature was adjusted to move the predicted growth interface for the second sample toward the hotter part of the furnace. It grew as a single crystal for 5 mm before the onset of polycrystalline growth. Both samples had an initial growth rate of 0.5 microns/second. The interface shapes through the growth have been marked by Peltier pulsing. The dopant distribution has not yet been published.

On D-2, Duffar and Abadie(CENG, Grenoble) grew crystals of Te doped GaSb and $\text{Ga}_{0.9}\text{In}_{0.1}\text{Sb}$ using ampoules whose sides were covered with super insulation to provide an axial heat flow through the sample. Heat was conducted into and out of the ampoule through graphite plugs at either end. The objective was to measure solute redistribution during the Bridgman growth process and to investigate the dewetting effect that had been observed in many previous microgravity directional solidification experiments. For this purpose, the silica ampoules were roughened to reduce the wetting by the melt. One of the seeds for the growth of $\text{Ga}_{0.9}\text{In}_{0.1}\text{Sb}$ contained only 2% In in order to eliminate the growth transient. Two of the ampoules broke, but the liquid was trapped and did not escape. The liquid did not appear to have wet the roughened ampoules, but the roughness apparently caused parasitic nucleation. The dilute sample had an axial solute distribution indicative of diffusion controlled transport, but the non-dilute samples showed extensive mixing. No information was reported on the radial segregation.

Duffar also investigated the effects of interface curvature in a non-dilute pseudo-binary system, $\text{In}_{0.20}\text{Ga}_{0.80}\text{Sb}$ using the Advanced Gradient Heating Furnace (AGHF) on the LMS flight. It was also hoped to obtain more information on the ampoule dewetting phenomenon seen in many microgravity directional solidification experiments. The rejected InSb is more dense than GaSb, so the system can be both thermally and solutally stable. However, since the freezing point is compositionally dependent, the interface will generally not be an isotherm. Two different crucibles were used: a quartz crucible, which has a low conductivity and should minimize the interfacial curvature; and a BN crucible, which is a better conductor and should produce a more curved interface. Since the macrosegregation was the object of interest in the experiment, no attempt was made to grow a single crystal. The flight samples exhibited the classic profile for complete mixing as described by the Scheil equation. This surprising result is still not understood.

Alloy systems that are stable against double-diffusive convection (rejected component more dense than the bulk melt) are subject to another source of radial segregation. This comes about because the thermal conductivity of many semiconductor systems is greater in the melt than in the solid. The heat flow from the melt into the solid is complicated by the presence of the wall of the growth ampoule, which often has a thermal conductivity between that of the solid and the melt of the sample material. This causes some heat to flow from the melt into the wall at the growth interface causing the interface to become concave. If the rejected component is more dense than the bulk melt, it will tend to flow toward the lowest point on the solidification interface and, since the rejected component will generally lower the freezing point, the interface will become even more distorted. Radial segregation produced by this mechanism prompted attempts to grow alloy systems such as HgZnTe and HgCdTe in microgravity.

Before the USML-1 flight, it was recognized that, if good macroscopic homogeneity was to be obtained in the more demanding Bridgman growth systems, it would be necessary to minimize transverse accelerations by keeping the Crystal Growth Furnace (CGF) axis more-or-less aligned with the quasi-steady residual acceleration. A major portion of this mission was flown with the orbiter's attitude calculated to do just that. Lehoczky from the NASA Marshall Space Flight Center prepared a $\text{Hg}_{0.84}\text{Zn}_{0.16}\text{Te}$ experiment, which was considered to have the most stringent requirement for this condition. However, unanticipated venting forces imparted a very slight, ~ 0.5 micro-g, transverse acceleration throughout most of the flight. Lehoczky's experiment was terminated prematurely which prevented a detailed analysis of his sample, but dopant inhomogeneities consistent with this unanticipated acceleration could clearly be seen in the portion that could be analyzed.

For technical reasons, USML-2 could not meet Lehoczky's stringent attitude requirements, but he was able to fly $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te}$ sample in the Advanced Automated Crystal Growth Furnace (AADSF) on USMP-2. During the USMP-2 mission, the Orbiter was maneuvered into several different attitudes so that the residual g-vector made varying angles relative to the growth direction. Lehoczky reports, "Significant differences were observed during three long, but uninterrupted, periods at constant attitude. Compositional variations along the crystal circumference indicate residual fluid flows for the least favorable vector orientations. Identifiable regions exist in which a transverse vector has pushed the material against the ampoule wall and allowed it to readily contract away from the opposite wall. Such surfaces showed etch pits produced by preferential evaporation at defect sites. X-Ray scattering showed that the regions pulled away from the wall tended to be less strained or of higher quality material than the opposite surface, and considerably better than the Earth-grown material. Composition determination on the surface of the material demonstrated significant difference dependent on the direction of the residual acceleration vector. These are clear indications of three-dimensional fluid flow. A significant portion of the boule was grown with a component of the vector aligned in a direction from liquid to solid. Synchrotron X-ray studies of this material showed it to be single crystal and of much lower defect density."

An attempt to re-fly Lehoczky's experiment on USMP-4 was thwarted when a ruptured ampoule from another experiment shut down the furnace before his sample could be processed.

Since Lehoczky's requirements could not be met on USML-2, a substitute experiment was flown to explore the important question of the effect of furnace orientation relative to the residual g-vector on solute redistribution during directional solidification experiments. Lichtensteiger (University Space Research Associates, MSFC) prepared a Ga-doped Ge sample. This model system was chosen because its characteristics are well-understood. Two analytical techniques were used to characterize the material, Peltier pulsing to mark the interface periodically, and high resolution spreading resistance measurements to map out the dopant distribution. The first crystal growth was started with the Shuttle in the most favorable attitude for crystal growth. Later, the attitude was changed to a gravity gradient attitude. The average dopant profile appears to be purely diffusive throughout the entire growth. No change was seen as a result of the maneuver. However, there is a consistent difference in dopant concentration across the sample which is indicative of flows that would produce radial segregation. (Unfortunately, acceleration data at the furnace is not given.) A second crystal was grown during a period when the Shuttle was in the solar inertial attitude. Since this attitude is unstable with respect to the gravity gradient, frequent thruster firings are required. Significant disturbances were seen in the dopant profile for the growth that took place during this attitude.

These results clearly demonstrate the extreme sensitivity of this type of growth system to very small accelerations and verify the predictions based on computational fluid dynamical modeling. They also provide additional evidence that wall effects play a significant role in defect formation.

In many of the earlier US and Russian Bridgman growth experiments in reduced gravity, the solidified ingot was found to be smaller than the growth ampoule and the melt appears to have pulled away from the ampoules during the solidification process. The effect was noticed on the first directional solidification experiments flown on Skylab and several of the investigators reported fewer growth defects in the portions of the sample that apparently solidified without wall contact. Several theories have been suggested to explain why the growing crystal might avoid wall contact in microgravity, but the exact mechanisms have not yet been tested or verified. Clearly, partial wall contact would affect the heat transfer; something that is not considered in setting up the experiment, which could place the growth front in a non-optimum position in the furnace. The existence of free surfaces also opens the possibility for Marangoni convection which can produce unwanted mixing of the diffusion layer with the bulk melt. (More will be said about Marangoni convection in the next sections.)

Single crystalline CdTe is widely used as a substrate for focal plane arrays as well as for nuclear detector applications. Because of its high bandgap, it is transparent to infrared radiation, so it can serve as a window for the HgCdTe detectors, which can be grown epitaxially directly onto the CdTe window. However, it is difficult to grow CdTe with

low dislocation densities and it has a tendency to form twins. Often small quantities of Zn are added to strengthen the lattice. O (then at Grumman Aerospace Corp., Bethpage, New York) wanted to investigate how gravity might influence the formation of these defects in $\text{Cd}_{0.95}\text{Zn}_{0.05}\text{Te}$. Because of the small mole fraction of Zn and because its distribution coefficient is close to 1, macrosegregation is not a serious problem when growing this material in normal gravity. Since the melt in Larson's experiment had some void space in the growth ampoule to allow for thermal expansion, the unanticipated 0.5 micro-g lateral acceleration from the venting on USML-1 had the fortuitous effect of nudging the melt against one wall of the growth ampoule and leaving the opposite side of the melt free of wall contact.

For his USML-1 flight results, Larson reports, "Macro-segregation was predicted, using scaling analysis, to be low even in one-g crystals and this was confirmed experimentally, with nearly diffusion controlled growth achieved even in the partial mixing regime on the ground. Radial segregation was monitored in the flight samples and was found to vary with fraction solidified, but was disturbed due to the asymmetric gravitational and thermal fields experienced by the flight samples. The flight samples, however, were found to be much higher in structural perfection than the ground samples produced in the same furnace under identical growth conditions except for the gravitational level. Rocking curve widths were found to be substantially reduced, from 20/35 arc seconds (in one-g) to 9/20 arc seconds (in μ -g) for the best regions of the crystals. The FWHM of 9 arc seconds is as good as the best reported terrestrially for this material. The ground samples were found to have a fully developed mosaic structure consisting of subgrains, whereas the flight sample dislocations were discrete and no mosaic substructure was evident. The defect density was reduced from 50,000-100,000 (in one-g) to 500-2500 EPD (in μ -g). These results were confirmed using rocking curve analysis, synchrotron topography, and etch pit analysis. The low dislocation density is thought to have resulted from the near-absence of hydrostatic pressure which allowed the melt to solidify with minimum or no wall contact, resulting in very low stress being exerted on the crystal during growth or during post-solidification cooling."

Larson repeated this experiment on USML-2 using a novel ampoule design that would minimize wall contact with the sample. He was able to grow 20 mm of sample without any wall contact and 21mm with only partial wall contact. A second sample had a spring-plunger system that forced the sample to fill the ampoule, thereby assuring wall contact. Preliminary analysis showed that twin formation was virtually zero in the region grown without wall contact; whereas, the sample in the spring-loaded ampoule was highly strained at the exterior and heavily twinned.

These results clearly demonstrate that wall effects are a major source of defect formation on the ground as well as in space grown crystals.

Travelling Heater Method

A variation of the Bridgman growth technique, is the traveling heater method (THM). Instead of melting the entire charge, only a small portion of the charge is melted and the

molten zone is moved through the sample by the traveling heater. Usually the dopant atoms of interest have a small distribution coefficient meaning that only a small fraction of the dopants in the melt will be incorporated into the solid. Thus a specific quantity of dopant can be added to the initial zone to be melted and this quantity will remain almost the same as the zone is moved through the sample. This process, known as "zone leveling", produces a reasonably uniform distribution of dopant on a macroscopic scale. However, turbulent flows in the molten zone can still result in microscopic inhomogeneities or striations.

For compound systems, such as gallium arsenide (GaAs) or cadmium telluride (CdTe), the material is often grown by the traveling solvent zone, a variation of the traveling heater method in which the melt that contains an excess of the metal. The excess metal lowers the melting point of the solution, which allows the growth to take place at lower temperatures and also lowers the vapor pressure of the volatile component. The lower growth temperature reduces the number of inherent point defects that will always be present in crystals, and also reduced the thermal stress on the lattice, which generally reduces the dislocation density.

Schoenholtz, Dian, and Nitsche (Kristallographisches Institut Universitat Freiburg Germany) grew Cl-doped CdTe crystals by the travelling heater method using a Te solvent zone on SL-1 and on D-1. The SL-1 experiment was terminated prematurely which caused the crystal to crack, but the experiment was repeated on D-1. There were some problems with heating lamp in the Mirror Heating Facility (MFT) and the rotation mechanism failed. As a result, the travelling zone was asymmetric and the desired temperature was not reached. The etch pit density (a measure of dislocations) was 5 to 10 times lower than the seed on the hot side of the grown material, but was many times higher on the cooler side.

Benz and Danilewsky at the Institute of Physics, University of Stuttgart, together with Nagel, Wacker-Chemitronics, also carried out a series of growth experiments with doped compound semiconductor using the traveling heater method (THM). The mono-ellipsoid ELLI furnace was used to process a 15 mm diameter S-doped InP and a 10mm diameter Te-doped GaSb during the SL-1 and D-1 missions. Benz reported reduced striations in the InP sample and "space-grown Te doped GaSb crystal was found to be nearly striation free with only residual dopant inhomogeneities, while ground-processed crystals showed pronounced structures of rotational and non-rotational periodic striations over the whole cross section of the crystal" (the sample is rotated to smooth out axial thermal inhomogeneities which causes the rotational inhomogeneities). On the D-2 mission, a 20 mm diameter GaAs crystal was grown from a traveling Ga solvent zone. The heater lamp was dimmed periodically to mark the growth interface. The results were very much like those obtained on the D1 flight in that the Type I striations due to convection driven growth rate fluctuations were eliminated.

Harr, Dornhaus, and Brotz (Battelle Institute, Frankfort) grew the solid solution ternary, lead-tin-telluride ($\text{Pb}_{0.8}\text{Sn}_{0.2}\text{Te}$) from a Pb-Sn rich solution during the D-1 mission. As mentioned previously, this material is subject to double-diffusive convection and is

impossible to stabilize using the Bridgman growth technique in normal gravity. The traveling solvent zone technique has the advantage that complete convective mixing in the solvent zone is not undesirable because the source material is continually feeding new nutrient into the traveling solvent zone, thus keeping the composition more-or-less constant. However, it is essential to control the solvent zone temperature very precisely in order to obtain the desired composition of the growing solid. Harr found improved compositional homogeneity in the flight sample whereas "a tin content segregation was found in THM part of the earth-grown sample, but not in the microgravity sample. Additional oscillation of tin content were found along the entire ground sample." It was noted that the diameter of the flight crystal was slightly smaller than the ampoule and that growth facets and etch pits could be seen on the surface. In the absence of hydrostatic pressure, the melt did not press against the wall, allowing the solid to form without direct wall contact. Selective evaporation from the free surface apparently formed the etch pits. The material was p-type and the hole mobility was found to be $5500\text{cm}^2/\text{Vs}$ in the microgravity sample, compared to $1900\text{cm}^2/\text{Vs}$ found in the ground-based reference sample. Harr attributes this improvement to a reduction of scattering centers induced by a reduction of stresses produced by contact with ampoule wall.

Iwai and Segawa (Institute of Physical and Chemical Research, RIKEN) grew single crystal PbSnTe by the travelling zone method using the mirror furnace on SL-J. The starting material was a 10 mm diameter Bridgman-grown rod of PbSnTe. A zone was melted and translated at 2 mm/hr for 4 hours. Te bubbles were observed on the surface of the molten zone. On the ground control, these bubbles rose, creating a void, which eventually caused the zone to become unstable and break. The bubbles in the flight sample remained distributed in the molten zone, but no void was found in the grown crystal. The Sn content in the grown crystal increased with distance from the seed but eventually leveled off as equilibrium in the zone was reached. Again it was found that intrinsic carrier concentration was lower and mobilities were higher in the micro-g sample.

Floating Zone Growth

In the traveling heater method described above, the samples were enclosed in quartz ampoules. However, short molten zones can be supported by their surface tension even in normal gravity and much larger zones can be deployed in microgravity. Removing contact with the ampoule wall offers many potential advantages such as elimination of contamination from the wall material (a serious problem at high temperatures), elimination of wall-induced stress which cause dislocations, and elimination of heat transfer through the wall in the vicinity of the growth interface which warps the isotherms in this critical region causing growth defects. However, thermal gradients along the freely suspended melt can drive strong and even turbulent convective flows (Marangoni convection). Steady flows in the molten zone may even be desirable since they tend to homogenize the composition of the melt, but turbulent flows can produce unwanted growth rate striations. Because of this, Marangoni convection has been the subject of intense study, both from the fluid dynamists as well as from the crystal growers.

Eyer and Nitsche from the Kristallographisches Institut Universität, Freiburg grew P-doped Si using the Mirror Heating Facility on the SL-1 mission. They found that the striations in the flight sample were similar to those seen in the ground control sample and concluded that turbulent Marangoni convection, rather than buoyancy-driven convection was indeed responsible for the striations. Croell and Nitsche repeated this experiment on D-1 in which the Si rods were coated with a 5 micron thick, coherent, amorphous silica film. Two sources of boron were also deposited on the surface to serve as the dopant. Despite some technical difficulties with sample overheating, they were able to show that the thin Si coating was effective in suppressing Marangoni flows.

Koelker (Wacker-Chemitronic, GmbH, Munich) used a pedestal melt technique to solidify a Si sample with free surfaces (similar to the method used by Walter to solidify an InSb drop on Skylab). The end of a Czochralsky-grown Si rod was melted in the mirror furnace to form a spherical drop approximately 1 cm³. On SL -1 the sample was rotated at 10 rpm as it was pulled out of the furnace at 1 mm/min. The initial molten silicon drop was spherical, but the growing crystal very strongly deviated from the spherical shape and assumed more or less the shape of a rocket nose once solidified. Post-flight examination of the sample revealed that a thin, dark surface layer had formed on the surface of the specimen, probably due to a carbon-based impurity of unknown origin. Initially, only widely spaced striations were observed which appeared to be associated with the rotation and translation of the sample (due to the heating asymmetry of the double ellipsoid furnace). Toward the end of growth, more closely spaced striations were seen, which were attributed to non-steady Marangoni flows. On D-1, the sample was not rotated and remained uncontaminated. In this case, a dense pattern of randomly fluctuating striations were seen which are clearly due to non-steady Marangoni flows.

Nishinaga, Sugano, Saitoh, and Katoda (University of Tokyo) wanted to see if Koelker's result may have been due to thermal non-uniformities in the image heating furnace, so they used a more stable resistance heated furnace on their SL-J experiments. In one of their experiments, they heated a single crystalline Si rod to form a spherical drop, similar to that of Koelker, except for the use of a resistance heated furnace. Unfortunately, instead of the drop remaining at the tip of the rod, it moved to the side where it contacted the quartz ampoule and broke into pieces as it cooled. In the second experiment, they heated a single crystal of Si in the form of a sphere which was contained in a quartz crucible. The plan was to melt the outer layers of the sphere and allow it to recrystallize using the unmelted center as the seed. However, the molten Si got through the quartz ampoule and touched the Ta cartridge, which resulted in a eutectic reaction causing a loss of Si. Consequently, the regrown region was a hemisphere with several facets on the outer surface. This portion, when cut and polished, revealed no striations.

Carlberg (Mid Sweden University), Camel, and Tison (Centre d'Etudes Nucleaires, Grenoble, France) grew two 10 mm diameter gallium-doped germanium crystals using the float zone process during the D-2 mission. The evacuated growth ampoules had getters to remove any traces of oxygen and other impurities that might contaminate the melt surface. Seebeck voltage measurements were made to detect growth rate fluctuations that might occur from unsteady Marangoni convection. No fluctuations were

observed, although an asymmetrical dopant distribution in the sample was attributed to steady Marangoni convection.

Building on the findings from SL-1 and D-1, several investigators attempted to grow gallium arsenide on D-2. As mentioned previously, gallium arsenide (GaAs) is a material of great technological importance. Being a compound rather than an elemental system, the growth problems with GaAs are multiplied. Not only is it necessary to be able to control dopant homogeneity and structural defects, but stoichiometry must also be controlled, which means an overpressure of arsenic vapor must be maintained to prevent loss of this volatile component. Unlike silicon which has a strong covalent bond and can be grown dislocation-free in large diameters by the float zone process on Earth, the surface tension to density ratio of GaAs limits the diameter that can be grown by the float zone technique on Earth to about 7 to 8 mm in diameter, too small for device applications. The mixed ionic-covalent bonds in GaAs are weaker and dislocations and other defects form more readily. As a result, dislocation densities tend to be fairly high, typically on the order of $10^5/\text{cm}^2$.

Hermann and Muller from the Institut fuer Werkstoffwissenschaften, Universitat Erlangen, grew four single crystals of silicon doped-gallium arsenide by the float zone process that were 20 mm in diameter, more than twice the diameter than can be grown by float zone in normal gravity. A special heater controls an arsenic source to provide the necessary arsenic overpressure. As a result, stoichiometry was maintained with no evidence of either gallium or arsenic precipitates. They were able to control the shape of the growth interface by controlling the height of the molten zone. When the interface was nearly flat, the dislocation density dropped to $5 \times 10^3 \text{ cm}^{-2}$. Rocking curve width, which measures the internal order of the crystal, was as low as 11.6 seconds of arc, comparable to best quality crystals grown on Earth. Dopant striations were observed, which were attributed to unsteady Marangoni convection. A cobalt-samarium magnet was inserted near the end of several samples to help suppress the Marangoni convection, but the field was too weak to prevent unsteady Marangoni flows. Similar results were obtained by Croell, Tegetmeier, Nagel, and Benz (Kristallographisches Institute der Universitat Freiburg) with Te-doped gallium arsenide.

Nakatani, Takahashi, Ozawa, and Nishida (National Research Institute for Metals, Japan) grew a single crystal of InSb by the float zone process using the mirror furnace on SL-J. The seed was a 20 mm diameter rod of single crystal and the feed was polycrystalline InSb. A zone 45 mm long was melted and propagated at the rate of 0.33 mm/minute, resulting in a single crystal 20-30 mm in diameter and 100 mm long. An oxide skin formed on the crystal which apparently prevented Marangoni convection since the grown crystal was free of striations, as was determined by X-ray topography. Dislocation densities were also low and the electrical resistivity doubled over the length of the zone.

Samaraskite is a naturally occurring mineral that is composed of 5 phases containing Ca, Fe, Y, U, Th, Nb, Ta, and O. Alpha particles from the decay of U and Th have destroyed its native structure, so it is difficult to determine how this mineral was formed. Takekawa (National Institute for Research in Organic Materials, Japan), Shindo (ASGAL Co. Ltd.)

and Sugitani (Kanagawa University) set out to crystallize this material using the traveling solvent floating zone in the Image furnace on SL-J. Several peritectic reactions are apparently involved in which solid 1 plus a liquid reacts to form solid 2. This means that solid 1 must diffuse through the liquid to reach the forming solid 2. Because of the various density differences, this scenario is difficult to arrange in normal gravity. The material was successfully melted, but large bubbles in the melt interfered with the growth process and the results are inconclusive.

Liquid Phase Epitaxial Growth

As discussed previously, there are advantages to growing systems with high melting temperatures from a solution in which one of the metal components acts as a solvent. Suzuki, Kodama, and Ueda (Space Technology Corporation, Tokyo) developed a unique method for growing GaAs from Ga which they demonstrated on SL-J. The Ga doped with Sn was enclosed in a cube whose sides were single crystal wafers of intrinsic GaAs with different orientations. When the system was heated, some of the GaAs dissolved in the molten Ga and then redeposited as Sn-doped GaAs when the system was cooled back to ambient. Since there were no free surfaces, Marangoni convection was eliminated and the liquid phase epitaxial growth could be studied in the absence of convective flows.

The growth on the top wafers was thicker than on the bottom wafers in 1-g and was uniform and thicker in microgravity. The surface morphology of the upper wafers was much rougher than the bottom wafers in the ground control while the flight samples were generally smoother, an effect that must be due solely to convective flows. In general, growth on (111) surfaces was somewhat thicker than on (100) faces. There was no difference in the normalized depth distribution of the dopant atoms. Type II striations, which arise from macrostep propagation, are seen in both flight and ground control sample, but are distinctly different. In the flight samples, the striations are thin and run parallel to the growth surface; whereas, the striations pass through the growth layer.

Crystal Growth from the Vapor

For materials that lend themselves to physical or chemical vapor transport, growth from the vapor offers some attractive alternatives to growth from the melt. Growth can take place at temperatures considerably lower than the melting point, thus avoiding some of the higher temperature problems associated with melt growth. Gravity-driven convection will definitely influence the growth process, perhaps in ways that are not yet completely understood or appreciated. For example, Rosenberger has shown that compositional gradients arising from the interaction of multicomponent systems with any vertical wall will always result in horizontal density gradients which produce buoyancy-driven convective flows. Convective transport is governed by the product of the Grashof and the Schmidt number. The Grashof number is directly proportional to gravity and measures the convective flow. The Schmidt number, which is the ratio of kinematic viscosity to chemical diffusivity, can be as high as several thousand for melt growth systems, but is ~ 1 for a typical vapor growth process. Therefore, diffusion limited growth conditions

can be obtained under far less stringent acceleration conditions than those required for melt growth .

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Several vapor crystal growth experiments on the Shuttle have produced provocative results that are not at all understood. For example, on OSTA-2, Wiedemeier (Rensselaer Polytechnic Institute) grew unseeded GeSe crystals by closed tube physical vapor transport using the General Purpose Rocket Furnace that was developed for the SPAR suborbital program. The two growth ampoules contained different pressures of Xe which served as a buffer in the transport since the primary purpose of the experiment was to understand the vapor transport process without the effects of gravity. In the ground control experiment, many small crystallites formed a crust inside the growth ampoule at the cold end. The flight experiment produced dramatically different results; the crystals apparently nucleated away from the walls and grew as thin platelets which eventually became entwined with one another, forming a web that was loosely contained by the ampoule. Even more striking was the appearance of the surfaces of the space-grown crystals. These were mirror-like and almost featureless, exhibiting only a few widely spaced growth terraces. By contrast, the crystallites in the ground control experiments conducted under identical thermal conditions had many pits and irregular, closely spaced growth terraces. The experiment was repeated during the D-1 mission using two additional pressures of Xe in order to add additional points to the transport vs. pressure curve. The unusual morphology of the space grown crystal was also seen on this flight.

Additional vapor growth experiments was carried out by Wiedemeier on USML-1 and on USML-2 in which $\text{Hg}_{0.4}\text{Cd}_{0.6}\text{Te}$ was grown epitaxially on (100) CdTe substrates by closed-tube chemical vapor deposition using HgI_2 as the transport agent. Considerable improvements in the USML-1 flight samples were observed in terms of surface morphology, chemical microhomogeneity, and crystalline perfection. The surfaces of the ground control samples had a wavy step-terrace structure, whereas the flight samples were mirror smooth such that growth steps could not be resolved at 500x. Compositional differences were 2 – 3 times smaller in the flight sample. Rocking curve widths of the space-grown epitaxial layers were 90-120 arc seconds, less than half the ground control and equal or less than the best epitaxial layers grown on the ground by the MOCVD technique. These improvements were attributed to the sensitivity of the $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ -

HgI₂ vapor transport system to minute fluid dynamic disturbances that are unavoidable in normal gravity.

The primary objective of the USML-2 experiment was to measure the effect of microgravity on the initial epitaxial growth process; effects that had been annealed out during the growth in the USML-1 experiment. Consequently, the growth times were much shorter on USML-2 so that the transition from the initial growth islands to epitaxial layers could be observed along with the propagation of birth defects from the interface to the epitaxial layer. Inspection of the growth islands on the flight sample revealed well-developed faces and facets indicating a higher degree of order than the ground control which was confirmed by their measured etch pit densities that were 50 times lower.

Mercuric iodide (HgI₂) forms a layered structure, similar to graphite, in which the A-B planes are bonded by van der Waals forces. Consequently, the crystalline structure is very weak, especially at the growth temperature, and it was thought that the performance of the material as a room temperature nuclear spectrometer might be limited by defects caused by self-deformation during the growth process. Schnepple and van den Berg (EG&G Corporation) grew mercuric iodide crystals by physical vapor transport on Spacelab 3. Their growth technique was similar to the method used by EG&G to grow this material commercially. A seed was placed on a temperature controlled pedestal and was surrounded by a container whose walls had been coated with the source material. A small temperature difference was maintained between the walls and the seed to drive the growth process.

It was possible to increase the growth rate on Spacelab 3 to more than twice the rate on the ground without spurious nucleation. The space-grown crystal was 1.2 x 1.2 x 0.8 cm and weighed 7.2 grams. It exhibited sharp, well-formed facets indicating good internal order. This was confirmed by γ -ray rocking curves which showed a single peak and were approximately one third the width of the multi-peaked curves from the ground control crystals; however there was still evidence of lattice strain in the flight sample. Measurements just after the flight showed that both electron and hole mobility were significantly enhanced in the flight crystal, although, for reasons that are not clear, these values decreased after some time. It was speculated that this degradation may be a result of handling this extremely soft material.

The experiment was repeated on IML-1 with similar results. This time the rocking curves on the flight crystal were sharper and more symmetric, although, in one area, a second peak was observed which indicated two domains misoriented by 0.1 degree. Again the electron mobility and $\mu \tau$ product (product of mobility and carrier lifetime) showed slight improvement over the ground, while a dramatic improvement was seen for the hole mobility and hole $\mu \tau$ product. It is still not understood whether the improved quality of the flight crystals was due to the elimination of the weight of the crystal during its growth, or to the diffusion-controlled transport conditions that produced a more uniform growth environment.

Cadoret (Universite Blaise Pascal, Aubiere, France) also grew HgI_2 on SL-1 and on IML-1. On SL-1, he used an unseeded closed tube physical vapor transport technique. Three growth ampoules were prepared, one was under high vacuum, one contained 0.1 Torr Ar as a buffer gas, and the third contained styrene to poison one of the growth faces in order to promote growth of flat platelets. Larger single crystals were obtained in space as opposed to smaller polycrystals in the ground control. A seeded technique was used on the IML-1 experiment with highly purified material supplied by EG&G. The space-grown crystal exhibited flat, well-defined faces and produces a rocking curve with a FWHM 0.04° . The ground control crystal was quite irregular in shape and was of such poor quality that a rocking curve could not be obtained.

On the D-1 mission, Bruder, Dian, and Nitsche (University of Freiburg) grew a CdTe crystal from the vapor phase by closed tube sublimation/condensation by placing the source material in the focus of the monoellipsoidal mirror furnace and heated it to about 880 degrees Celsius. The heat flow in the ampoule was modified by a tight fitting Ni net on the outside to give a slightly convex shape to the growth interface to prevent parasitic nucleation. Unfortunately, the seed quality in the flight sample turned out to be much poorer than the ground control so that a meaningful comparison could not be made. The large etch pit density in the material near the seed did diminish somewhat as the growth of the flight sample progressed, but did not reach the lower value of the ground control.

Using the 3-zone Gradient Heating Facility on D-1, Launay (Universite Bordeaux) grew Ge by closed tube chemical vapor transport with GeI_4 as the transport agent. Polycrystalline Ge was located at the hot and cold zones and a single crystal substrate was attached to a wall at an intermediate temperature. Three ampoules with different transport gas pressures were processed simultaneously to obtain the mass flux as a function of transport gas. These results were in good agreement with a one-dimensional model assuming purely diffusive transport. The quality of the epitaxial layers grown in space is much higher than those made on earth. On earth the layers exhibit a multitude of little holes on the surface, whereas the flight layers were smooth.

Kimura, Nishimura, and Ono (Space Technology Corporation, Tokyo) with Takayami (Mitsubishi Corporation, Tokyo) grew InP during the D-2 mission using a closed tube chemical vapor transport using InCl_3 as the transport agent. The grown layer is doped with S while the substrate is doped with Fe so that the layers will be distinguishable. Rocking curves for the both the space and ground control epi-layers showed single peaks, signifying that they were single crystalline, although the FWHM of the space sample was slightly wider than the ground control, which was also slightly wider than the substrate. This would indicate slightly more lattice strain in the layer grown in microgravity. The transport rate increased linearly with pressure of the transport gas in the ground control experiments, but started to fall off to a constant value for the flight experiments, which would be expected for diffusion controlled transport. The thickness of the epilayers varied considerably in the ground control samples which were much thicker in the center and thinned rapidly near the periphery of the substrate. The flight samples, on the other hand, were uniformly coated.

Crystal Growth from Solution

Co-deposition Growth

Galster and Nielson used a three chamber method to grow calcium tartrate and calcium carbonate crystals from solution on SL-1. Solutions in the outer chambers are allowed to interdiffuse through a buffer in the middle chamber where they react to form the crystal as a coprecipitate. An attempt was also made to grow TTF-TCNQ, an organic conductor, but the growth solution deteriorated before the experiment was activated. No information on the quality of the crystals was given.

Authier, Lefaucheu, and Robert (Universite P and M Curie, Paris) grew brushite ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$) and lead monite (PbHPO_4) crystals on SL-1 using a similar method. The space grown crystals were analyzed by X-ray topography and were found to be of comparable quality to those grown on the ground using gels to control convection.

On IML-1, Kanbayashi (NASDA) and Anzai (Himeji Institute of Technology) grew an organic charge transfer complex by diffusing donor and acceptor starting materials into a central chamber containing a suitable solvent, similar to the method used in the above experiments. One growth apparatus was mounted to a passive vibration damper to see if g-jitter affected the growth of the system. By shortening the distance over which diffusion must occur and using more concentrated solutions, they reported that they were able to grow a crystal in space in one week that would take three months on the ground. Their space and ground control crystals were comparable, although the space crystal grown with the vibration damper was somewhat fatter. Electron spin resonance showed that the space and ground crystal had the same electronic structure in which free electrons existed in a narrow conduction band. Both space and ground crystals had a superconductivity transition at 1.2K under 7 kilobars applied pressure.

Anzi also attempted to grow TTF-TCNQ by the same technique on SL-J, but no crystals formed because of technical difficulties.

Controlled Nucleation

Controlling nucleation in microgravity experiments presents several difficulties. Cooling a solution into saturation usually results in nucleation at the walls. Inserting a seed generally caused the propagation of defects into the growing crystal (ghost of the seed). Using the glovebox on USML-1, Kroes, Lehoczy, and Reiss (NASA MSFC) demonstrated a novel method for initiating and controlling nucleation in solution crystal growth. A hot concentrated solution of L-Arginine Phosphate Monohydrate ($\text{C}_6\text{H}_{14}\text{N}_4\text{O}_2\text{H}_3\text{PO}_4 \cdot \text{H}_2\text{O}$) or LAP was injected into a cooler lightly saturated solution of the same. Copious nucleation resulted as the warmer solution cooled. Most of the crystals drifted to the walls under the influence of residual gravity. A few of the crystals remained suspended and grew to as large as 3 x 5 x 0.5 mm.

Cooled Sting Growth

Triglycene sulfate TGS is a long wavelength pyroelectric infrared detector material. Lal (Alabama A&M University) grew TGS crystals on Spacelab 3 and on IML-1 using a novel cooled-sting approach. The seed crystal is mounted on a small pedestal through which a heat pipe can extract heat from the crystal using a thermoelectric device. Thus the bulk growth solution can be held at near saturation while the fluid at the growth interface is driven to supersaturation required for growth by extracting heat through the crystal. This technique eliminated the spurious nucleation within the growth cell which had plagued many of the earlier attempts to grow crystals from aqueous solution in microgravity. By growing under diffusion controlled transport conditions, it was hoped to avoid liquid/vapor inclusions. These are the most common types of defects in crystals grown from solution and are believed to be caused by the nonuniform growth conditions resulting from convective flows.

On SL-3, an oriented seed was cut from an Earth-grown TGS crystal. Irregular growth occurred primarily around the perimeter of the seed, which made it difficult to analyze. An improved seeding technique was used on IML-1 which produced a much more uniform region of new growth. In normal gravity, good crystal can be grown on the (100) face, but growth on the (010) tends to be non-uniform and multi-faceted. However, uniform growth was achieved on the (010) seed used in the IML-1 flight. In order to grow sufficient material to analyze during the mission, an undercooling of 4°C was used to promote faster growth (~1.6 mm/day). Despite this accelerated growth, the quality of the crystal was exceptionally good. There was a smooth transition from seed to new growth without the veil of dislocations surrounding the seed crystal ("ghost of the seed"), which is normally seen when crystals are seeded on the ground. The TGS crystal grown on the IML-1 mission was examined with high resolution monochromatic synchrotron X-radiation diffraction imaging using the National Synchrotron Light source at Brookhaven National Laboratory. The X-ray topographic images indicate an extraordinary crystal quality. The only inclusions are due to the incorporation of polystyrene particles intentionally inserted in the growth solution to study the fluid motion in low-g. The detectivity (D^*) of the space grown crystal was found to be significantly higher than the seed crystal and the loss tangent was reduced from 0.12-0.18 for the seed to 0.007 for the space grown material.

The growth of these crystals was monitored by periodically taking shadowgrams, Schlieren photographs, and holograms of the growing crystal and its surrounding medium. The concentration profiles could be visualized from the shadowgraphs and Schlieren images, and determined quantitatively from the reconstructed holograms. These graphic images confirmed that the concentration field was purely diffusion-limited and inspired some of the protein crystallographers to try growing their protein systems in space. Small polystyrene marker particles were added to the growth solution on the IML-1 flight to visualize whatever flows might exist as a result of residual accelerations.

Growth of Zeolites

Zeolites are a class of crystalline aluminosilicate materials that form the backbone of the chemical process industry worldwide. They are used primarily as adsorbents and catalysts. One of their most important roles is that of a “cracking” catalyst in the petroleum industry. New applications for zeolites include selective membranes, chemical sensors, polymer-zeolite composites, and molecular electronics. For these reasons, this is an intensive interest in obtaining a better understanding of how they nucleate and grow with the aim of being able to tailor their structure for specific applications.

Various forms of zeolite crystals, including zeolite-A, X, Beta, and Silicalite were grown by Sacco (Worcester Polytechnic Institute) on USML-1 and -2 with the aim of getting larger and more uniform crystals. In general, the crystals grown in space with nucleation control grew 10 to 25% larger in linear dimension than their ground controls. The zeolite-X crystals grown on USML-2 were 25 to 50% larger than their ground controls and twice as large as grown on USML-1. For the most part, the flight samples had higher Si/Al ratios than did their control samples and one of the A crystals exhibited the theoretical Si/Al ratio of 1.00, which not been seen before. Space-grown Beta crystals were free of line defects that are common in those grown on the ground. X-ray diffraction studies indicated slightly smaller unit cell volumes, which indicates fewer defects. A comparison of the catalytic activity of the space and ground-grown crystals has not yet been published in the open literature.

Thermophysical Properties Measurements

Anyone attempting to model solidification processes will soon find that reliable thermophysical property data, especially data on transport properties such as diffusion coefficients and thermal diffusivity for molten systems, are difficult to come by. Generally such measurements are made in thin capillary tubes to minimize the effects of convective transport, but any attempt to measure such transport properties on Earth will always be contaminated to some degree by buoyancy driven convective flows. Furthermore, a simple demonstration experiment by the crew on Skylab, in which they layered strong tea and clear water into a plastic toothbrush holder, showed a bullet-like diffusion region between the tea and water instead of the expected planar diffusion front. This observation suggested that wall effects may influence to diffusion of one component into another and raised the specter that much of the diffusion data that had been taken in capillary tubes may also be in error.

Measurement of Diffusion Coefficients

On Spacelab-1, Froberg, Kraatz, and Wever (Institut Fur Metallforschung Technische Universität Berlin) measured the interdiffusion coefficient of Sn¹¹² and Sn¹²⁴ over a temperature range of 240°C to 1250°C. The diffusion coefficients measured on the ground were 30-50% higher than those measured in space, which they attribute to convective transport. Results in a 3 mm dia. cell were indistinguishable from those in a 1

mm dia. cell, indicating that wall effects were not significant. The precision with which the interdiffusion coefficient could be determined from the space data was 50 times better than the ground-based data. With this higher precision, the isotope effect could easily be measured. An unexpected result was the fact that the space data seemed to follow a T^2 law rather than an Arrhenius law, typical of diffusion in solids. This departure from the classical vacancy diffusion law for solids may shed new light on the structure of liquid metals. They followed this experiment with measurement of interdiffusion of In¹¹³ and Sn at different temperatures on D-1. Again they found that the diffusion coefficient followed a T^2 dependence.

The finding that the diffusion coefficient seems to follow a T^2 law in the liquid metallic systems investigated on Spacelab-1 and D-1 raised a number of interesting issues. Does this law apply to all liquid metals? What happens in the undercooled or glassy state? Where does transition to the solid Arrhenius-like behavior occur? Does the T^2 law also apply to diffusion in aqueous solutions? A group of diffusion experiments were planned for the D-2 mission to address these questions.

Frohberg et al. looked for possible deviations from the T^2 law in systems that had low coordination numbers or those that tended to form associates. The argument was that if the glass forming metals followed an Arrhenius behavior in the glassy state, there might be some deviation from the T^2 law at the lower temperatures. Consequently, they chose to measure self-diffusion in Pb, Sb, and In and for impurity diffusion for In in Sn and for Sn in In. They found no significant deviation from the T^2 law for any of these systems.

Richter and Merckens (RWTH, Aachen) developed a flowing junction cell for the measurement of diffusion coefficients using a Savart Interferometer which they had tested on TEXUS 8. They attempted to use this cell on the D-1 mission to measure the interdiffusion of NaNO₃-AgNO₃, but technical difficulties prevented them from being able to locate the phase boundary of the molten system.

Merckens, Richter, Golbach, Jurek, Klessascheck (RWTH, Aachen) next attempted to measure the ionic diffusion in the molten KNO₃-AgNO₃ eutectic salt system at 5 different temperatures ranging from 150°C to 330°C using real time holography. The molten salts were injected into a flow cell for each run. Unfortunately, bubble in the melt made it difficult to extract the holographic data and, consequently, diffusion coefficients at only two temperatures were obtained. These values were substantially lower than ground based measurements, again demonstrating the necessity of making this type of measurement in space, but it was not possible to test the T^2 law for salt systems with only two datum points.

Robert, Lefauchaux, and Bernard (P&M Curie University, Paris) measured the diffusion coefficients of aqueous solutions of glycine, valine, and lead nitrate at three different concentrations on the D-2 mission using real time optical holography. The experiment was activated by pulling out a thin metal sheet that separated the portion of the cell containing the solute from the pure solvent portion. In all cases the diffusion coefficients became smaller with increasing concentration. For valine and glycine the diffusion

coefficients measured in flight were slightly higher than the ground control, but for lead nitrate, the space value was twice as high as the ground control. This later effect was unexpected and is still being investigated. It is possible that the fluid motion imparted by removing the sheet separating the two chambers produced unwanted mixing in the flight sample. Such mixing would have been suppressed in the ground control experiment because of the large stabilizing density difference between the two liquids.

Urbanek and Hehenkamp investigated the diffusion of Ni in molten Cu, Cu-Al and Cu-Au. A single crystal of Ni was diffusion bonded to the Cu alloys and the melt was held at 1150°C so that the Ni remained solid. This was done to assure a plane diffusion front at the Ni source. The Ni that dissolved into the Cu alloy melt was allowed to diffuse through the sample until it was quenched. The distribution of Ni was determined by electron microprobe tracing. The measured diffusion coefficients again were significantly lower than those measured on the ground. However, the isoconcentration profiles show more Ni in the middle of the Cu and Cu-Ag alloys and the interface between the Ni single crystal and the melt shows a bulge in the middle. This suggests that convective flows must have occurred along the outer surface of the melt toward the Ni interface with a return flow through the core of the sample. This type of behavior would be expected of Marangoni flows, except that, in this case, the sample had been coated with a 200 micron thick layer of alumina skin that had remained intact. The possibility of second order Marangoni flows that can occur without a free surface has been speculated, but no such flows have ever been observed directly.

A follow-on experiment to measure self-diffusion in molten Sn at five temperatures up to 1622K was carried out on MSL-1 by Itami et al. (Hokkaido University). Sn¹²⁴ was used as a tracer and its distribution was determined by SIMS. They found that the diffusion coefficient varied as $T^{1.81}$ for their data and $T^{2.04}$ for all microgravity data.

Using a combination of rocket experiments along with an experiment on MSL-1, Uchida et al. (Ishikawajima Heavy Industry, Inc. Ltd.) measured the diffusion of Pb_{0.8}Sn_{0.2}Te-Pb_{0.7}Sn_{0.3}Te over a temperature range of 1223K (melting) to 1573K. This composition is of interest as an infrared detector material, but it is difficult to grow by directional solidification because it is subject to double diffusive instabilities. Consequently, the diffusion coefficient had not previously been determined. Their combined set of experiments determined an expression $D = 6.7 \times 10^{-9} (T / T_{\text{melt}})^{2.6} \text{ m}^2/\text{s}$.

Yoda, Masaki, and Oda (NASDA) measured the diffusion coefficient of Sn as a function of temperature on SL-J and on MSL-1R. Their results fall right on the same curve as Frohberg's data.

However, on SL-J, Yamamura, Yoda, Ohida, and Masaki (Tohoku University) doped LiCl-KCl eutectic with a trace quantity of AgCl and measured the diffusion of Ag⁺ using an electropotential method over a temperature range of 640K to 860K. Their data seemed to follow an Arrhenius curve.

Dan and Muramatsu (National Research Institute for Metals, Japan) attempted to measure the interdiffusion of Ag and Au on SL-J. However, the sample appeared to have been convectively mixed by Marangoni convection.

On SL-1 Braedt, Braetsch, and Frischat (Technische Universität, Clausthal, Germany) measured the interdiffusion between $\text{Na}_2\text{O}-3\text{SiO}_2$ and $\text{Rb}_2\text{O}-3\text{SiO}_2$ glass melts. The sample consisted of stacked cylinders of glasses having different compositions and were heated to 1180°C with an effective processing time of 1370 seconds. The concentration profiles were obtained using an electron microprobe. The microgravity samples exhibited concentration profiles parallel to the original interface, while the ground control samples had wavy profiles indicative of convective flows. The interdiffusion coefficient at 1180°C fits the Arrhenius plot with the results of TEXUS missions and ground based results at lower temperatures.

The removal of a bubble from a viscous glass is difficult enough on Earth, but becomes a major problem in micro-gravity without the assistance of buoyancy forces. For this reason, it is necessary to measure diffusion coefficients of gases in glass melts. During the D-2 mission Jeschke and Frischat (Technische Universität, Clausthal, Germany) measured the diffusion of He in a model glass system by observing the shrinkage of a preformed He bubble in a cylindrical glass sample as it was heated to 1100°C .

Thermomigration, sometimes called the Soret effect or the Ludwig effect, results from the migration of atoms of different species in a thermal gradient. One of the techniques used for isotope separation is based on this principle. It can also be important in the solidification of multicomponent alloys by shifting the composition at the interface as the solidification proceeds, although in most Earth-based processes, the effect of thermal migration is completely overwhelmed by convection and it is generally ignored. However, the effect may have been responsible for shifting the composition away from the eutectic point in several microgravity eutectic solidification experiments.

Malmejac and Praizey (CENG, Grenoble) demonstrated the effectiveness of microgravity for measuring thermomigration (Soret effect) on Spacelab-1. They loaded Sn with 0.04 Wt% Co into zirconia shear cells and subjected them to a $200\text{K}/\text{cm}$ thermal gradient for six hours. A graphite piston kept the melt in contact with the walls to prevent unwanted Marangoni convection. The cells were then sheared into 6 segments which were analyzed for Co concentration by neutron activation. Similar cells were processed in a thermally stable configuration (hot over cold) on the ground. The flight samples had two times as much Co in the hot end as in the cold end; whereas the ground control samples showed a constant Co concentration throughout. From the flight samples, the investigators were able to determine the heats of transport and the Soret coefficients for both the Co in Sn and for the different isotopes of Sn. A follow-on experiment on D-1 confirmed the isotopic heat of transport for Sn and obtained the heat of transport for Ag^{109} and for Bi^{209} in Sn.

Bert and Dupuy-Philon (Matériaux Université Claude Bernard, Lyon) investigated the thermomigration of the Ag^+ and K^- ions in the molten salt system, $\text{AgI}_x\text{-KI}_{1-x}$ near the

eutectic composition on D-1 and D-2 by potential difference between electrodes at the hot and cold ends of the sample. This measurements is then related to the Soret coefficient. The Soret was much smaller than anticipated so that the D-1 experiment could only determine that the Soret coefficient is positive (the heavier AgI migrated to the cold side of the cell). The longer duration of the D-2 experiment permitted the first accurate measurements of the Soret coefficient for this system.

Undercooling Experiments

The equilibrium melting (freezing) point is the temperature at which there is no difference between the free energy of the melt and solid, thus a solid can remain in equilibrium with its melt at this temperature indefinitely. A solid will began to melt as its temperature is raised to the equilibrium melting point, but a melt will not began to freeze at this temperature. The interfacial energy between the embryonic solid and the liquid must somehow be found. This required energy is proportional to the interfacial area, or the square of the radius of the solid, assuming it is a sphere. However, the tighter binding energy of the solid, which is proportional to the cube of its radius, can lower the free energy. According to this elementary model of nucleation, the free energy of a potential nucleus initially increases with size because of the extra interfacial energy, but eventually decreases with size due to the increased solid bond formation. Therefore, there is a critical size for a viable nucleus and a free energy barrier that must be overcome to form a viable nucleus. Near the equilibrium melting point, atoms or molecules in the liquid start to form clusters, which are broken up by thermal agitation. As the temperature is lowered below the freezing point these clusters can grow larger before they are broken up by thermal agitation. The probability that a sufficient number of particles will come together to form a viable cluster before it is broken up by thermal agitation increases with decreasing temperature. If there are solid surfaces present, especially if they are crystalline in nature, they offer a low energy nucleation site and the solid can form by heterogeneous nucleation at temperatures close to equilibrium melting temperature, or with very little undercooling. If there are no low energy nucleation sites, the melt will continue to undercool until it nucleates homogeneously. Thus, if low energy nucleation sites can be avoided, it is possible to undercool a melt by as much as 20-25% of its absolute melting temperature. When nucleation in a undercooled melt occurs, the heat of fusion is quickly given off heating the melt back to its equilibrium melting point, a phenomenon known as recalescence. However, if the melt is undercooled to the point that the heat of fusion is not sufficient to raise the temperature back to the melting point, the melt is said to be hypercooled.

In recent years, great deal of attention has been given to rapid solidification processing. If the heat can be removed rapidly enough so that the atoms in the melt simply do not have time to arrange themselves into orderly crystalline form, they more-or-less become frozen in place. Such processing has led to amorphous or glassy metals, quasi-crystals with 5-fold symmetry, and a variety of non-equilibrium phases, some with interesting properties such as the niobium based A-15 superconductors. The ability to form metastable phases is greatly enhanced by starting with a deeply undercooled melt.

Therefore, there is a great need to understand the properties of melts in the undercooled state.

There are essentially two ways to eliminate the low energy nucleation sites; eliminate physical contact with the melt, or encase the melt in an amorphous, non-reacting flux. The latter has been demonstrated by Whittmann, Gillessen, Otto, and Roestel (DLD, Koln) on D-2. By suspending melts in B_2O_3 , they were able to undercool eutectic Ag-Ge by 100K below its melting point of 924K and Fe -22Wt% Ni was undercooled by 392K, into the hypercooling regime. When this system is undercooled, the δ -ferrite phase is nucleated first. However, during recalescence, the released heat of fusion brings the undercooled melt back to the melting temperature and the γ -austenitic phases forms. However, when hypercooled, as was the case here, some of the original d-phase is retained.

Free falling droplets in drop tubes have been deeply undercooled, but it is difficult to measure the thermophysical properties of a falling drop. An orbiting spacecraft provides an opportunity to study a free falling drop, but because the drop and the spacecraft do not fall at exactly the same rates, a small non-contacting body force is required to keep the droplet in position. Non-contacting positioning forces can be electrostatic, electromagnetic, acoustic, or aerodynamic.

Electromagnetic position is particularly suited for the study of undercooled metallic melts in space. While it is possible to levitate metallic melts in normal gravity, the sample becomes distorted to the point that it is not possible to obtain surface tension and viscosity data from drop oscillation and measuring volume changes with temperature becomes difficult. Also, the heat input from the induced currents required for levitation interfere with the undercooling of the sample. These difficulties are avoided in a microgravity environment.

An early attempt to use electromagnetic levitation to study undercooling on orbit was made on MSL-2 using a modified version of the EM levitator developed for use on the SPAR suborbital rocket program, prior to the time the Shuttle became operational. Flemings (MIT) provided 6 samples but a coolant loop problem prevent useful data from being attained.

The TEMPUS facility was developed by the Institute for Space Simulation, Cologne, Germany. It uses a quadrapole coil for positioning and a dipole coil for heating. Since very small positioning forces are required in a microgravity environment, electromagnetic-driven flows for positioning can be minimized. The sample chamber can be evacuated, or backfilled with an inert gas to suppress evaporation of samples with high vapor pressure. The system was first flown on the IML-2 mission. Unfortunately, most of the samples had gotten contaminated during their preflight storage and could not yield the desired thermophysical data. Also, some positioning instabilities were discovered. As a result, the facility was reworked and was reflown on the MLS-1 and MLS-1R flights.

Egry, Lohoefer, Seyhan, and Feuerbacher (DLR, Koln) measured the viscosity and surface tension of two alloys, $\text{Co}_{80}\text{Pd}_{20}$ and $\text{Pd}_{78}\text{Cu}_6\text{Si}_{16}$. The first was chosen because it has a low viscosity and deeply undercools; the second is a good glass former and consequently has a high viscosity. Surface tension is obtained by pulsing the positioning coils to cause the drop to oscillate. The frequency of oscillation is related to the mass and surface tension by Rayleigh's formula and the viscosity can be obtained by the rate of decay of the oscillations. (Since Rayleigh's formula only applies to spherical drops, this method cannot be used with the distorted melts levitated in normal gravity.) Egry was able to run 30 heating and cooling cycles on the $\text{Co}_{80}\text{Pd}_{20}$ alloy, undercoolings as much as 350K were obtained, well into the hypercooling regime. The surface tension was found to decrease linearly with temperature while the viscosity follows an Arrhenius behavior.

The eutectic point of the $\text{Pd}_{78}\text{Cu}_6\text{Si}_{16}$ alloy was used to calibrate the pyrometer. The addition of Cu supposedly improves the glass forming ability of this system, but lowers the amount of undercooling that can be achieved to about 70 K, probably to the formation of CuO on the surface. This also may be responsible for the increased scatter in the surface tension and viscosity data. The surface tension again is seen to decline linearly with increasing temperature, but the scatter in the viscosity is such that no distinction can be made between Arrhenius, Vogel-Fulcher, or power law behavior.

The changing resistivity of the sample with temperature changes the inductance of the TEMPUS heating coil, thus by measuring the voltage, current, and phase of the heating current, resistivity could be inferred. Calibration to obtain the coil constants was done with samples of known resistivity. The resistivity of the $\text{Co}_{80}\text{Pd}_{20}$ alloy was found to increase linearly with temperature in both the solid and liquid state, but with a higher value and slightly higher slope in the case of the liquid.

Solid $\text{Co}_{80}\text{Pd}_{20}$ is a good ferromagnet with a Curie temperature of 1250 K. The measured inductance in both solid and undercooled melt exhibited a dramatic change when cooled below 1360 K with a sharp increase at 1250K. This increase was interpreted as magnetic ordering. There had been speculation as to whether a ferromagnet could exist in the liquid state. There appears to be no fundamental reason to believe that it could not; it is just that the Curie temperature of every known magnetic material happens to lie below its melting point. This is the first evidence suggesting that ferromagnetism does indeed exist in the liquid state.

In order to estimate the nucleation probability, and thus the cooling rate required to form a metallic glass, it is necessary to know the difference in the Gibbs free energy between the solid and the liquid state as well as the viscosity and the interfacial energy. The Gibbs free energy is the sum of the enthalpy of the liquid plus the product of the entropy of fusion and temperature. The enthalpy of the liquid can be obtained by integrating over the heat capacity of the liquid.

Fecht (Universitat Ulm) and Johnson (California Institute of Technology.) developed a non-contact method for measuring the heat capacity, thermal conductivity, and total hemisphere emissivity of a small spherical sample using A.C. calorimetry. The heating

field is modulated at frequencies ranging from 0.05 Hz to 0.2 Hz. The heat capacity is related to a correlation function of modulation frequency, the internal (heat up) relaxation time, and the external (heat loss) relaxation time. Also, thermal expansion and volume change on melting can be determined by direct observation of the suspended drop.

This technique was applied by Fecht and Wunderlich (TU Berlin) to two glass-forming alloys, $Zr_{65}Al_{7.5}Cu_{17.5}Ni_{10}$ and $Zr_{60}Al_{10}Cu_{18}Ni_9Co_3$. The $Zr_{65}Al_{7.5}Cu_{17.5}Ni_{10}$ system exhibited an large increase in heat capacity near the glass transition temperature, which was not seen in the other system. This anomalous behavior is thought to be associated with some liquid structure and is still being investigated. Also, the ratio of thermal conductivity to electrical conductivity in the crystalline $Zr_{65}Al_{7.5}Cu_{17.5}Ni_{10}$ system follows the Wiedemann-Franz law, but the measured thermal conductivity in the undercooled state was significantly higher. This departure could be a result of flows from electromagnetic stirring, although the viscosity in this temperature range is so high that it cannot be measured by the drop oscillation method.

Johnson, Lee, and Glade (California Institute of Technology) carried out similar investigations on $Zr_{57}Nb_5Ni_{12.6}Al_{10}Cu_{15.4}$ and $Ti_{34}Zr_{11}Al_{7.5}Cu_{47}Ni_8$. They also find a strong increase in heat capacity with undercooling. The $Ti_{34}Zr_{11}Al_{7.5}Cu_{47}Ni_8$ sample exhibited a large anomaly in heat capacity just above the liquidus temperature. This was thought to be the result of a possible phase separation in the melt.

Frohberg, Roesner-Kuhn, and Kuppermann (TU Berlin) developed a real time method for analyzing surface oscillations of liquid levitated drops based on a FFT analysis of the temperature-time signal and applied this technique to the measurement of the surface tension of pure zirconium, several stainless steel alloys, and glass forming alloys $Zr_{11}Ti_{34}Cu_{47}Ni_8$ and $Zr_{57}Cu_{12.6}Ni_{15.4}Nd_5Al_{10}$. In these glass forming alloys, the viscosity increases so rapidly with decreasing temperature that surface oscillations cannot be detected, thus making surface tension measurements in the undercooled state impossible. However, measurements at higher temperatures can be used to infer surface tension in this region. Unlike other systems in which surface tension increases as temperature is lowered, the $Zr_{57}Cu_{12.6}Ni_{15.4}Nd_5Al_{10}$ system exhibits a strong decrease in surface tension with decreasing temperature. It is speculated that this anomalous behavior may be due to a change in the surface composition as temperature is lowered. Al has a surface tension near the lowest measured value and if it segregated to the surface, it would be the surface active component.

Volume change with temperature is a basic measurement in glass formation. In most materials (except for those that have open diamond-like structures), specific volume decreases as the melt temperature is lowered and a sharp drop in volume is seen as the crystalline solid is formed. As the temperature of the solid is lowered further, the volume continues to decrease, but at a slower rate – reflecting the volumetric coefficient of expansion for the solid. For glass formation, the nucleation of the crystalline phase must be avoided and the melt continues to shrink in volume at the liquid rate past the normal freezing temperature. When the glass transition temperature is reached (the point at which the atoms or molecules no longer have sufficient thermal energy to freely move

about each other) the material becomes a glassy solid rather than an undercooled liquid. This transition is identified, not by an abrupt change in volume, but by a change in the slope of volume versus temperature to reflect a volumetric coefficient of expansion more typical of a crystalline solid.

Samwer and Damaschke (Universitat Augsburg) developed a special camera for measuring volume changes in samples being processed in the TEMPUS. On the MSL-1R mission they measured the volume vs. temperature of the glass forming alloy $Zr_{11}Ti_{34}Cu_{47}Ni_8$. They found two distinct slopes in the liquid phase; a smaller slope well above the normal melting point, and a steeper slope beginning approximately 40°C above melting point that continued past the melting point. The data did not extend to the glass transition temperature because of poor contrast between the sample and the background.

Bayuzick, Hofmeister, Morton (Vanderbilt University) and Robinson (NASA MSFC) used the TEMPUS on MSL-1R to investigate the effect of convective flows on nucleation. The possibility of “dynamic” nucleation, perhaps the result of subcritical embryonic clusters somehow being brought together by shearing flows to form a viable nucleus, has been speculated, but no definitive experimental confirmation of whether or not this is a significant factor in nucleation has been obtained. The electrostatic levitator allows them to conduct repeated undercooling experiment on the same sample, thus eliminating this source of variability. Their choice of materials was pure zirconium because it has a high solubility for contaminants found in the bulk and in the high vacuum environment and oxides, nitrides, and carbides do not form in the melt or on the surface.

They measured the distribution of undercoolings where nucleation occurred with the positioning coils set at the minimum power, and at the highest power. Numerical modeling indicates that the flows are laminar at the lowest power setting with characteristic velocities of 4 cm/s, corresponding to a Reynolds number of ~200. At the higher power setting the flows approach the transition regime. They found no significant difference in the undercooling statistics. However, in experiments in which the heater power had been above 220 V, they found the samples would not undercool. Based on a computation model of Flemings and Trapaga, it believed that the flows associated with the higher heater setting caused cavitation and that the collapse of these cavitation bubbles cause nucleation to occur.

Flemings and Matson (MIT) investigated the phase selection process by which undercooled Fe-Cr-Ni steels solidify. Initially the δ -ferritic phase nucleates with the characteristic recalescence signature and starts to grow; shortly thereafter, a second recalescence is seen as the metastable δ phase transforms into the stable γ or austenitic phase. However, it was observed that in microgravity, the second recalescence was delayed by a considerable amount compared to samples levitated electromagnetically on the ground. The decreased convection in microgravity is believed to be responsible for this delay. This investigation has led to a new growth competition model to account for the role of convection in the phase selection in the final solid.

Herlach, Holland-Moritz, Kelton, Bach, and Feuerbacher attempted to determine the maximum undercooling as well as the thermophysical properties of alloys that form polytetrahedral quasicrystals with short range order. Since this order is similar to what is believed to exist in the melt, there should be a low interfacial energy between the melt and the solid, hence the degree of undercooling should be limited. Samples of $\text{Al}_{60}\text{Cu}_{34}\text{Fe}_6$ and $\text{Al}_{65}\text{Cu}_{25}\text{Co}_{10}$ were processed in the TEMPUS facility. Unfortunately, the samples had become contaminated and no significant undercooling was achieved.

Optical Glass Formation

Single crystals have good optical transmission, but are impractical for many applications. Multiple reflections from grain boundaries of polycrystalline materials make them totally unsuitable for optical applications. Therefore, glasses, which do not have grain boundaries, are used for the vast majority of optical systems. Grain boundaries also represent regions where there are unsatisfied bonds and therefore are more vulnerable to chemical attack. Thus glasses also find many applications as corrosion resistant coatings or containers.

The crystalline state has the lowest configurational energy for most materials, hence is the equilibrium state. The amorphous or glassy state is metastable, but can exist more or less indefinitely if the viscosity of the material is high enough to prevent the atoms from moving into their equilibrium crystalline configuration. Good glass formers are systems that have high viscosities near the melting point so that, if crystallites are nucleated, they cannot grow significantly while the material is being cooled to ambient. Glass formation can always be enhanced by rapid cooling, but there is a limit to the rate at which heat can be removed from a system, especially from larger systems. Also rapid cooling produces large strains in the system which can produce optical distortion and possibly cracks or other defects.

An alternative method for enhancing glass formation is to lower the probability of nucleation. In order for a more ordered phase to form, an ordered cluster of atoms must first form to serve as a substrate for the ordered phase to grow on. This can occur either spontaneously in the melt (homogeneous nucleation) or the ordered phase can heterogeneously nucleate on a foreign solid particle or on the crucible wall. The probability of homogeneous is extremely small near the melting point, and does not become appreciable until the material is cooled to some 20-25% below its absolute melting temperature. Since viscosity increases exponentially with decreasing temperature, eliminating heterogeneous nucleation sites can greatly decrease the cooling rate required for glass formation, and thus the ability to form glasses in systems that do not generally form glasses. There are a number of such systems that are of potential interest because of their extended infrared transmissivity, their electro-optical properties, or hosts for lasers.

Braetsch and Frischat (Technische Universitaet Clausthal, Germany) investigated the nucleation and crystallization of glasses on the D-1 mission. Lithia-silica and $\text{Na}_2\text{O}-\text{B}_2\text{O}_3$ -

SiO₂ glasses were formed in a glassy carbon crucibles at different cooling rates. The glasses formed in space exhibited greater homogeneity than the ground control based on variations in refraction analysis and microprobe analysis. The difference was ascribed to the fact that nuclei that formed at the wall were not transported to the remainder of the melt in microgravity. The crystalline phase Li₂O-2SiO₂ in the lithia-silica system showed a spherulitic growth under normal gravity, whereas a dendritic growth was observed under microgravity. In the Na₂O-B₂O₃-SiO₂ system both micro-g and 1 g samples displayed microstructure which could have been formed by a spinodal type phase separation process, however, the micro-g sample was more fine-grained.

Soga (Kyoto University) heated a glass specimen contain Au particle in the Image Furnace during the SL-J mission with the objective of obtaining the temperature-volume relation and to analyze the flows as it melted. A large unexpected volume increase was encountered near the glass transition temperature, bubbles formed in the specimen, and devitrification occurred at the surface. (No further details were available.)

The ability to position and melt a sample without physical contact offers some unique opportunities to extend the range of glass formation from ceramic systems by eliminating potential nucleation sites that might exist on container walls. Also, many glass forming systems are extremely corrosive in the melt and will easily become contaminated by the crucible. Generally, such systems are not conductive enough in the melt to be levitated and heated electromagnetically. Since they also generally require an atmosphere to prevent loss of volatile components, acoustical levitation is an attractive choice. However, difficulties have been encountered in attempts to use a resonance chamber, such as the 3-axis levitator developed by JPL for the study of drop physics, when it is necessary to operate over a wide temperature range. The single axis levitator technique, which uses a reflector to set up a series of interference node is more tolerant of temperature changes. Its principal disadvantage is the weak radial positioning forces which are provided by the Bernoulli effect; consequently samples are frequently lost.

The Single Axis Acoustic Levitator (SAAL), originally developed as a suborbital facility, was flown on OSTA-2 and on D-1 with samples prepared by Ray and Day (University of Missouri-Rolla). Technical difficulties were encountered on OSTA-2 flight and no useful results were obtained. On the D-1 mission, 2 samples of pressed gallia-calcia powder were successfully melted, cooled into the glassy state, and retrieved. This low viscosity glass was formed at a much slower cooling rate (2 to 3 times slower) in space than is possible in a crucible, which reflects the absence of low energy nucleating sites on the levitated sample. A sample of soda-lime glass containing a large void was also deployed with the objective of producing a concentric shell suitable for use as an inertially confined fusion target. The sample was successfully melted and recovered, but the bubble escaped during the process.

A more sophisticated acoustical levitator furnace was flown on SL-J. Hayakawa (Government Industrial Research Institute, Osaka) and Makihara (Kohei Fukumi) successfully processed a CaO-PbO-B₂O₃ sample and two gallia-calcia-germania samples, although they reported that some bubbles remained in the samples.

Miscellaneous Experiments

Fukuzawa and Furuyama (National Institute for Metals, Japan) set out to analyze the mechanisms by which Al, Si, and Mn act deoxidizing agents for steel. An Iron alloy containing about 1% of each of these elements was rolled into a 0.1 mm sheet which was sandwiched between 5 mm diameter iron rods containing different levels of oxygen content. These samples were then placed in alumina crucibles and sealed under 100 Torr Ar in a Ta cartridge. The cartridges were heated in the Large Isothermal Furnace on SL-J at 1600°C for 54 minutes and then quenched. The results appear to be inconclusive.

Wada et al. (Nagoya University) and Dohi (Shizuoka Institute of Science and Technology) investigated the production of nano-particles in microgravity on SL-J. Four glass bulbs were prepared in which 50 mg of Ag was attached to the W filament. The bulbs were then filled with different pressures of Ar or Xe. The filaments were heated to ~ 1150°C and the brightness and smoke evolution was recorded on video. Particles ranging from 20-50 nm were deposited on the walls of the bulbs containing Ar. Then bulb containing Xe produced a burst of smoke that, according to the investigators, "...indicates a local accumulation of vapor atoms with pressure higher than the surrounding gas, which cannot be interpreted in terms of a conventional diffusion model of a Langmuir sheath".

Assessment of the Science

Metals, Alloys and Composites

Many of the earlier flight experiments in this field were exploratory in nature and yielded results that were difficult to interpret. As a result, their findings were reported in conferences and often were never published in the mainstream literature were they were likely to be read by scientists not involved in the space program. As the investigators became more sophisticated and knew what lines of investigation were more likely to pay off, they the program became more productive scientifically.

The primary advantages of studying solidification of metallic systems in microgravity is the ability isolate gravitational from non-gravitational effects, to make properties measurements that are difficult to make accurately in the presence on gravity, and to test fundamental theories that have help transform metallurgy from an art to a science over the past 40 years.

Most of the theories that guide our laboratory experiments and that we use to design industrial processes contain simplifying assumptions, such as ignoring convection. Such assumptions are necessary in order to be able to establish general laws that extend over a wide range of conditions; whereas the addition of convection would generally be applicable to a specific situation. Of course, since convective flows are a fact of life in most process carried out on Earth, the theories do not always apply directly unless the effects of convection is modeled into the process for a specific task (which is becoming

more common give the computational capabilities now available). Still many of the theories we use have never been rigorously tested because before flight opportunities became available, we had no way to impose the conditions assumed by the theory. Observed discrepancies were generally explained away by convective effects that we not able to control. But this leaves a nagging question; are there subtle errors in the theory because something important was left out? Or were the simplifying assumption that were made too unrealistic? These are important issues that need to be settled.

The importance of microgravity experiments such as Glicksman's work on dendrite growth is to assure that the basic theories used for modeling microstructures in castings are on firm foundations, or at least to understand where their weaknesses lie. Obviously, these theories will have to be modified to account for convection if they are to be used in terrestrial applications, but it is essential to be able to start from a theory that is at least fundamentally correct.

The ability to isolate gravitational from non-gravitational effects has unmasked many subtle, but important effects and provided much new insight into modeling and controlling processes. For example, it was generally not suspected that Soret diffusion could be instrumental in changing the composition of the system during a directional solidification process. The effect did not become apparent until the convective flows were essentially eliminated, but it operates just the same and should be considered in a process model if good accuracy is required. Similarly, the profound influence of interfacial effects that produce phase separation in immiscible systems were not appreciated until the effects of gravity were removed.

The bibliography contains 456 total publications of which 135 are in peer reviewed journals.

Crystal Growth

The quasi-steady acceleration requirements for diffusion-controlled solutal transport have proven to be very stringent, especially for Bridgman growth of materials with high Schmidt numbers (ratio of viscosity to chemical diffusivity) that are characteristic of many semiconductor systems of interest. The Shuttle is not a practical platform for this class of experiments since they require close alignment of the net residual acceleration vector with the furnace axis over a period of days. This was attempted on USML-1, only to be thwarted by an unsuspected acceleration of less than a half micro-g from the venting of the flash evaporators. Hopefully, the environment on the ISS will be more suited to this important crystal growth technique.

Melt growth experiments that used the traveling zone or float zone technique are more tolerant of the residual acceleration because of the much smaller melt region and because some gentle convective mixing in the molten region can actually be beneficial so long as it does become unsteady. The Japanese as well as the Europeans have had outstanding successes in growing various semiconductor systems up to 20 mm in diameter using the float zone process in the mirror furnace. For reasons that are not clear, US Investigators

have not pursued this process in microgravity. Perhaps the most important contribution from the melt growth experiments in microgravity was the clear demonstration of the role of wall effects in the formation of twins and other growth defects. Even in enclosed growth systems the dislocation densities seemed to be generally lower and the mobilities seemed to be higher than in the ground controls. Whether this effect was a result of less convection at the growth interface, partial wall contact, or of lack of hydrostatic pressure is not clear, but the reason begs for an answer.

Similarly, crystals grown by both closed tube physical and chemical vapor transport continue to exhibit better uniformity and lower defects when grown in microgravity for reasons that are not well-understood. Also crystals grown from aqueous solution under diffusion limiting conditions were of outstanding quality, virtually free of the dislocations, inclusions, and other visible defects. All of these results indicate that convective flows in the vicinity of the growth interface are somehow responsible for the generation of growth defects, even the exact mechanism is not understood. This would appear to be a fruitful topic for the theoreticians to consider while waiting for the next experimental results to come from the ISS.

Crystals grown from aqueous solution under diffusion controlled conditions were also of outstanding quality, especially when the supersaturation could be controlled using the cooled sting technique. The zeolite crystals also showed some encouraging results.

Altogether the crystal growth experiments produced a total of 324 papers including 208 journal articles.

Measurement of Thermophysical Constants

Anyone involved in process modeling will applaud the possibility of obtaining accurate thermophysical data, especially data on the properties of high temperature melts. The most disturbing aspect of the results from diffusion measurements in microgravity is the realization of how inaccurate our present data base on properties of molten systems really must be. The fact that diffusion coefficients of melts measured in space turn out to be typically 30-50% lower indicates that virtually all of diffusion measurements for molten materials are in error and would imply similar errors for thermal conductivities and other transport-related properties. Since it would hardly be practical to try to remeasure all of our liquid phase thermophysical properties in space, we should carefully re-evaluate our laboratory measurement techniques with the aim of either eliminating or accounting for convective transport.

Of equal importance is the new microgravity data on the temperature dependence of the diffusion coefficient. For the first time, these data are sufficiently accurate to establish that liquid phase diffusion, at least in some molten systems does not follow an Arrhenius type behavior, indicating a substantially different mechanism from solid state diffusion. Establishing the temperature behavior of various transport coefficients of a variety of melts will give new insight into the theory of liquids as well as provide benchmarks for such theories to predict.

Finally, the amount of thermophysical data that could be extracted from a levitated melt without contact is truly impressive as well as the insight such data gives to the behavior of materials in the undercooled state.

The bibliography includes 173 papers reporting on the measurement of thermophysical properties of which 76 are journal articles.

Optical Glass Formation

Despite the potential for being able to undercool corrosive melts without physical contact in microgravity in order to form glasses of unique composition, such experiments have been hampered by the lack of a reliable levitator. Several attempts at levitating such melts using acoustic pressure have produced only limited success because of instabilities that occur as the temperature is changed over a wide range. Consequently, this important class of experiments has received little attention in the recent microgravity program. In spite of this limited activity, the Spacelab experiments generated 46 papers including 28 journal articles.

New Technology and Technical Spin-offs

Unless the cost of going to space can be dramatically reduced, most of the technological payoff from the microgravity materials science program will have to come from applying the knowledge gained in space to Earth-based processes. Knowing that the basic principles upon which most of our processing technology is based together with the prospect of obtaining more accurate thermophysical data, will improve process modeling resulting in higher quality, lower cost product. The Europeans are making extensive use of process modeling to substitute lower cost precision casting for machining in automotive frames, engine parts, and in fittings used in the A330 Airbus. They have also used data obtained from microgravity experiments to develop a continuous casting process in which Marangoni convection is used to balance sedimentation in order to get a uniform dispersion of bismuth particles in an aluminum-silicon alloy for use in self-lubricating bearings.

Crystal growers are learning about the effects of convection from the microgravity community and are now making more use of static and rotating magnetic fields in order to control unsteady flows. They too are now making extensive use of computational modeling to design their processes to achieve computational control. Given the deleterious effects of wall contact, new techniques may evolve that use a "soft" wall or other method for avoiding this problem in terrestrial growth processes.

Traditional methods for measuring transport properties of molten systems certainly need to be reexamined and calibrated against measurements made in microgravity.

Biotechnology

The Biotechnology investigation carried out on Spacelab Missions include biomolecular crystal growth, electrokinetic separations, electrofusion, and the applications-oriented biotechnological research being carried out by the NASA-sponsored Centers for Space Commercialization. The vast majority of the experiments have been devoted to the growth of biomolecular crystals such as proteins, nucleic acids, and viruses. The more fundamental experiments dealing with living organisms, such as those carried out in the Biorack will be covered under Life Science.

Biomolecular Crystal Growth

Background

The biological activity of a protein (or other biological macromolecules) depends on its three-dimensional conformation or structure. Knowing this structure not only provides important clues to understanding of the function of living organisms at the molecular level, but also offers the means of directly altering or blocking the action of certain unwanted proteins or viral particles associated with a disease state. This intervention requires finding its active site and then finding or designing a molecule that fits into this site to render it inactive, much like fitting a key into a lock. In fact, many pharmaceutical agents operate in this manner. Until recently, effective drugs had to be sought out by intuition and much trial and error testing. Now it is becoming possible to design a drug for a specific task by knowing the structure of the target molecule. It is much easier to design a key to fit a lock if one knows the structure of the lock. X-ray crystallography remains the most powerful (and, for large macromolecules, the only) method for determining the three-dimensional structure of such molecules.

When a crystal is illuminated by an X-ray beam, the beam is reflected by the various planes of atoms in a particular direction according to Bragg's law, which relates angle between the incident beam and the reflection to the lattice spacing of the planes producing the reflection. The array of Bragg reflections forms a diffraction pattern that can be recorded, either on film or electronically. Mathematically, this diffraction pattern is equivalent to a complex Fourier transform of the three-dimensional electron density map of the atoms in the unit cell of the crystal, which happens to be the protein molecule of interest. In principle, the Fourier transform can be inverted to obtain the electron density map of the protein molecule from which, with a lot of skill and patience, the three dimensional structure of the molecule can be inferred.

Unfortunately, present technology, i.e. the lack of a coherent X-ray source such as an X-ray laser, allows us to record only the intensity of the Bragg reflections which corresponds to the real part of the complex Fourier transform; the imaginary part containing the phase information is lost. One method for recovering the lost phase

information, requires the growth of additional crystals in which a heavy metal, such as mercury, is incorporated into the molecule of interest. Because of the large number of electrons associated with the heavy metal atom, it acts as a reference point of zero phase and, by comparing the diffraction patterns with and without the heavy metal atom, the phase information can be recovered. Pioneers in this field, such as Nobel Laureates Max Perutz and John Kendrew, spent many years developing this technique and were able to solve the structure of some of the simpler biological-macromolecules (hemoglobin and myoglobin), which earned them the 1962 Nobel Prize in Chemistry. Since then, at least 27 Nobel prizes have been awarded for work in this field.

It should be appreciated that before NASA got involved in this field, the structures of only a few hundred unique proteins had been solved. With the advent of powerful new computers, ultra bright synchrotron X-ray sources, and sophisticated data collection methods, the number of unique protein structures that have been determined has risen dramatically. However, the ability to obtain crystals of sufficient size and internal order has now become the limiting barrier in this field of research.

Microgravity's Contribution to Protein Crystallography

The protein crystal growth experiment developed by Walter Littke (University of Freiburg) that was carried out during the first Spacelab mission may prove to be the single most significant experiment in the Spacelab program. Littke reported that his space-grown crystals of beta-galactosidase grew 27 times (by volume) larger than his ground control crystals, and that his lysozyme crystals grew 1000 times larger. Although the crystals of beta-galactosidase were still too small to provide meaningful X-ray diffraction data, this was the first real indication the microgravity could significantly improve an Earth-based process.

When Charlie Bugg, then the Associate Director of the Comprehensive Cancer Center at the University of Alabama in Birmingham, learned of Littke's result, he immediately began preparations for a flight experiment involving proteins of interest to his Center. He also recruited several major pharmaceutical companies to join in a collaborative effort to explore the use of microgravity to obtain better crystals of proteins they were attempting to structure, which resulted in the formation of the Center for Macromolecular Crystallography, supported by the NASA Commercialization program.

A few simple try-and-see protein crystallization experiments were carried out during Shuttle flights prior to the Challenger accident. By the time the Shuttle flights resumed, MSFC, with Teledyne-Brown Engineering had developed a semi-automated Vapor Diffusion Apparatus (VDA) that deployed 20 individual hanging drop protein crystallization experiments. Several of these trays can be inserted into the middeck locker Refrigerator/Incubator Modules (R/IMs) developed by McDonnell Douglas to support their earlier electrophoresis experiments. The individual cells in the VDA are equipped with a double barreled syringe so that the protein could be stored in one barrel and the precipitating agent in the other to prevent premature nucleation and crystallization before the experiment was in orbit. The solutions were mixed by a crew

member repeatedly extruding and withdrawing the two fluids. After mixing, a small drop of the mixture is left hanging in a small chamber surrounded on three sides by a porous medium containing a higher concentration of precipitating agent. The water in the hanging drop diffuses through the vapor space to equilibrate against the higher the concentrated precipitating agent in the porous medium, thus providing the driving force for crystallization. Before de-orbit, the crew member manually retracts the drops containing the crystals back into the syringe and a plunger seals the end of the syringe for the trip back home.

The first Shuttle flight after the Challenger accident (STS-26) yielded crystals of 4 different proteins that were shown to have better diffraction resolution than the best crystals of these proteins that had ever been grown on Earth. This feat is even more remarkable, considering that the crystals produced in only a handful of space experiments are compared with the best crystals of these particular proteins that have been grown in thousands of experiments by the world's most qualified researchers whose professional success depends heavily on obtaining the molecular structure from the X-ray diffraction data from these crystals. These results formed the impetus for the present major effort in protein crystallography sponsored by NASA and ESA. (See DeLucas, et al., *Science*, 246: (1989) 651 - 654.)

It should be understood that one does not solve a protein structure with one or two crystals. Because of the very complex structure of large biological macromolecules, many thousands of data points must be taken in order to obtain the inverse complex Fourier transform of the diffraction pattern. Crystals also tend to degrade in the X-ray beam, so a number of crystals may be required to obtain a complete data set. The process may then have to be repeated with a heavy metal additive to recover the lost phase information. Hydrogen atoms do not have enough electrons to show up in the diffraction pattern, so critical hydrogen bonds must be inferred from complementary structure. Often the available data is not sufficient to accurately describe the critical shape and bond structure in the active area, so there is a constant search for higher resolution data in order to refine the structure. Finally, if a drug is to be designed to block the active site of a particular protein or other biological macromolecule, additional crystals must then be grown in which the candidate drug molecule, called the substrate, is incorporated into the active site of the target protein in order to check the fit. Therefore, it can be appreciated that a more-or-less steady supply of high quality crystals may be required to obtain the structure of a protein molecule.

If space is to play a significant role in obtaining the structure of biological macromolecules, a permanent facility in space, such as the Internal Space Station, will be required. Many of the proteins that did not crystallize, or did not grow large enough crystals to analyze during the times available to the various Shuttle missions, should produce results on the Space Station. Since protein crystals have a limited storage time, they may degrade before they can be taken back to Earth during the planned crew exchanges. Also, bringing them through re-entry g-loading may also degrade them (this is still an open issue). Therefore, serious concern is being given to an on-orbit X-ray analysis facility on the Space Station.

In order to appreciate the advantages offered by space-grown crystals, something needs to be said about the requirements needed to obtain good diffraction data from crystals. The ability of a crystal to diffract X-rays depends on the size and shape of the crystal, on the periodicity or regularity of the lattice points which locate the unit cells (long range order), and how well the individual molecules in each unit cell are positioned and oriented. The intensity of a Bragg reflection is proportional to the square of the number of unit cells illuminated by the X-ray beam. Generally, a crystal must be somewhere around 0.3 – 0.5 millimeters on a side to produce the required number of higher order reflections needed to obtain high resolution data. However, with the very bright X-ray sources now available from synchrotrons, it is becoming possible to work with smaller crystals.

However, larger crystals don't necessarily mean higher resolution or diffraction efficiency. Defects such as dislocations, small angle grain boundaries, twins, or inclusions eliminate large numbers of molecules from producing coherent reflections as well as contribute to the incoherent noise background, thus reducing the signal to noise ratio even at small diffraction angles. Diffraction efficiency is defined as the total number of Bragg reflections at some level (usually 5 standard deviations) above the background noise. Resolution is defined as the spacing of the highest index planes that produce detectable Bragg reflections. Since Bragg's law requires that the sine of half the angle between the incident beam and the reflected beam be inversely proportional to the lattice spacing producing the reflection, the largest angle at which reflections can be seen is a measure of the resolution. Even if the lattice has good long range order, molecules that are misoriented or slightly out of place at each lattice site will degrade the large angle diffraction data needed to obtain the molecular structure to high resolution.

The space-grown crystals tend to show improvements both in terms of long range order as well as better molecular orientation within the unit cells. Interestingly, a number of space-grown crystals seem to last longer in the X-ray beam before degrading. This increased radiation resistance could also be an indication of higher internal order in which more molecular bonds are available to hold the structure together. It should be emphasized that, even apparently incremental improvements of a fraction of an Angstrom in resolution, can be crucial in locating the binding sites in the active region. The increased resolution from the space-grown crystals has allowed the refinement of several important molecular structures and, in some cases, the determination of structure for the first time.

Results from the Protein Crystal Growth Program in the United States

Since the resources for protein crystal growth on orbit are small and since the acceleration requirements needed to improve the growth of protein crystals does not seem to be as stringent as for other fields of microgravity research, NASA-sponsored protein growth experiments have been able to utilize the available space on a number of Shuttle flights that were not dedicated to microgravity research, thus giving them many more flight opportunities than ESA or NASDA experiments. Since many individual growth

experiments can be carried on each mission, the 40 Shuttle flights, including 8 Spacelab flights and 6 MIR deployments, as of August 7, 1997, have produced many hundreds of individual experiments. Some 183 different biomolecular systems had been investigated (some only once, others repeatedly). Many of these individual experiments produced no crystals or crystals that were too small for X-ray diffraction analysis (usually due the limited flight time available on the Space Shuttle). A few experiments yielded crystals that were inferior to those grown terrestrially, but 72 of these experiments produced crystal that definitely had superior qualities. Of these 72 experiments, 34 produced larger crystals of that particular system than had previously been grown on the ground, 14 experiments produced crystals with a new morphology, 40 experiments produced crystals that had 10% or better diffraction efficiency (better signal to noise ratio indicating better long range order, 9 experiments had less thermal motion (indicating better order in the unit cell), 27 experiments had increased resolution up to 0.3 Å, 4 had increased resolution from 0.3- 0.5 Å, and 14 had increased resolution by better than 0.5 Å. A complete summary of these experiments can be found on "Marshall Space Flight Center Protein Crystal Data on the WEB", <http://199.254.187.151/>.

The VDA mounted in a temperature-controlled enclosure, such as the R/IM, the CR/IM, the Thermal Enclosure System (TES), or the Single locker Thermal Enclosure System (STES), was the workhorse in the early part of the US through USML-2 when it was replaced with more efficient hardware. Since the University of Alabama in Birmingham's (UAB) Center for Macromolecular Crystallization (CMC) had become the original focal point in the United States for crystallizing macromolecules in space, they offered Guest Investigator flight opportunities to both domestic and foreign collaborators from industries and other universities. They not only maintained the VDA hardware, but were also able to assist other investigators in preparing their samples for flight and in analyzing the post flight results. Significant results from the various Spacelab missions using the VDA are summarized below.

IML-1 (STS-42)

- Guest Investigator, H. Einspahr, (Bristol-Myers Squibb) reported larger crystals of 2 Domain CD4. No increase in resolution was noted.
- Guest Investigator, K. Ward (NRL), reported larger crystals of Bacterial Luciferase. No increase in resolution was noted.
- Co-Investigator, A. McPherson (U. California), reported Canavalin crystals that were comparable in size to 1g, with uniform high visual quality. Increased reflections over resolution range (higher diffraction efficiency), but no increase in resolution. Canavalin is the major storage protein of leguminous plants and a major source of dietary protein for humans and domestic animals. It is studied in efforts to enhance nutritional value of proteins through protein engineering. It is isolated from Jack Bean because of its potential as a nutritional substance. (In the next section, these crystals will

be compared to those grown by liquid-liquid diffusion in the ESA cryostat on this mission.)

- Guest Investigator, S. Aibara (Kyoto U.), reported a new monoclinic form of Lysozyme crystals with different lattice parameters.
- Co-Investigator, D. Carter (NASA/MSFC, now New Century Pharmaceuticals), reported a dramatic improvement in diffraction efficiency over all Bragg angles for Human Serum Albumin. Crystals diffracted to highest resolution ever obtained, including growth in gels. Human Serum Albumin is the most abundant blood serum protein; it regulates blood pressure and transports ions, metabolites, and therapeutic drugs. It also has multifunctional binding properties that range from various metals, to fatty acids, hormones, and a wide spectrum of therapeutic drugs.
- Co-Investigator, A. McPherson (U. California), found a new hexagonal crystalline form for Satellite Mosaic Tobacco Virus (SMTV) and collected the first X-ray diffraction data on this form. The Satellite Tobacco Mosaic Virus is the Spherical T=1 icosahedral satellite virus of the classical rod virus TMV, and is a plant pathogen. Its importance lies in the study of virus structure, RNA structure and virus assembly. (In the next section, these crystals will be compared to those grown by liquid-liquid diffusion in the ESA cryostat on this mission.)
- Guest Investigator, L. Delbaere (U. Saskatchewan), obtained two diffraction quality crystals of anti-HPr fab fragment crystals. Unfortunately, the crystals began to deteriorate while waiting to get time on the synchrotron. Even so, the data collected was comparable to the crystals grown on STS-31, which had narrower mosaic spread and diffracted to the same resolution as Earth-grown crystals with 10 times the volume.
- Guest Investigator, G. Birnbaum, (NRC, Canada), grew Fab YST9-1 crystals that exhibited slightly higher resolution with much higher diffraction efficiency (higher signal to noise) throughout the resolution range. Fab YST9-1 represents a class of antibodies that have specificity to polysaccharide antigens, those that occur on cell surfaces. Thus, it can be used to recognize a certain type of cell.

Spacelab-J (STS-47)

- Guest Investigator, C. Betzel (European Molecular Biology Lab, Hamburg), obtained the highest resolution ever obtained from a crystal of the receptor of Epidermal Growth Hormone which allowed, for the first time, the evaluation of the real space group by partial data collection. The space crystal diffracted to 6 Å, which is an improvement of 2-4 Å over the best Earth-grown crystals. The receptor for the epidermal growth factor is increasing in its importance as a prognostic factor for a

series of human malignancies since many such malignancies are characterized by its overexpression. Knowledge of the three-dimensional structure of this receptor would open the possibility of tailoring appropriate drugs for the treatment of numerous types of tumors. At the present time, however, the crystal structure of only one hormone receptor (growth hormone) and none of the growth factor receptors have been solved.

- Guest Investigator, S. Aibara (Kyoto U.), repeated his IML-1 experiment with lysozyme and again found the monoclinic form with different unit cell parameters.

USML-1 (STS-50)

- I. Co-Investigator A. McPherson obtained several large crystals of recombinant canavalin. The crystals apparently degraded somewhat before they could be analyzed, but even so, a slight improvement in resolution was seen.
- II. Guest Investigator, E. Arnold (Rutgers U.), obtained several large crystals of HIV Reverse Transcriptase complexed with antibody (Fab) against gp4. Relative Wilson plots showed the space crystals to be better ordered (less thermal noise) as the limiting resolution was approached.
- III. Guest Investigator M. Navia (The Althexis Co.) grew Human Proline Isomerase crystals that were considerably larger than the ground control, large enough that neutron diffraction analysis would be possible. No twinning or clustering was observed in the space-grown crystals which is often a problem with these crystals when grown in normal gravity. The space-grown crystals were optically clearer and had sharper facets than the Earth-grown crystals. Unfortunately, they began to degrade (edges began rounding) before X-ray analysis could be performed. Even so, they exhibited significantly higher diffraction efficiency, but no significant increase in resolution.

USMP-2 (STS-62)

- Guest Investigator, L. Delbaere (U. Saskatchewan), repeated his growth experiment with anti-HPr fab fragment crystals. Again he was able to grow larger crystals with a significant increase in diffraction efficiency, but with no significant increase in resolution. The detailed structure of the Anti-HPr Fab Fragment protein would provide a picture of an antibody binding site that recognizes a bacterial "foreign" protein antigen. By learning what antibody binding sites look like we may better understand how antibodies function in the immune system.
- Co-Investigator D. Carter repeated his Human Serum Albumin growth experiment. Again he got larger crystals with higher diffraction efficiency, but no significant increase in resolution.

ATLAS-3 (STS-66)

- Co-Investigator E-K. Ossama (UAB) obtained crystals of Aldehyde Reductase that exhibited higher diffraction efficiency, but no significant increase in resolution.
- Guest Investigator D. Eggleston (Smith-Kline Beecham) grew crystals of Bovine Parathyroid Hormone that had higher diffraction efficiency, but no significant increase in resolution.

ASTRO-2 (STS-67)

- Guest Investigator L. Delbaere (U. Saskatchewan) obtained larger crystals of PEP Carboxykinase that showed higher diffraction efficiency, but no significant increase in resolution.

USML-2 (STS-73)

- No significant results were obtained from the VDA hardware on this mission because the proteins degraded during the multiple launch delays.

One of the most significant experiments in the US-sponsored program was the set of crystallization experiments performed in the glovebox in which Larry DeLucas, the Payload Specialist on USML-1, was able to mix proteins and set up experiments on orbit, very much as he does in his own terrestrial laboratory. He had developed a special set of hardware that would allow him to monitor the nucleation and early growth and make necessary adjustment when necessary. When the crystal appeared to be growing properly, this glovebox hardware could be transferred to the Commercial Refrigerator/Incubator Module (CR/IM) to provide thermal control during the rest of the growth process. This apparatus was flown in USML-1 and USML-2.

Much was learned from the opportunity for a trained crystallographer to fly as a Payload Specialist on the USML-1 mission. Four proteins that were crystallized with the glovebox hardware had failed to crystallize in previous shuttle missions using the VDA hardware. It was suspected that the mixing of the protein with the precipitant been inadequate in the VDA, especially when the more viscous precipitants such as polyethylene glycol were used. With the glovebox hardware, the Payload Specialist could mix the protein and precipitant solutions thoroughly by stirring or by withdrawing and re-extruding the solution from a Hamilton syringe. It was noted that many of the growth system seemed to take longer to nucleate and grow than they did on the ground and that many experiments had crystals that were growing nicely, but were still too small for diffraction experiments when the mission was over.

For some experiments, a micro-manipulator was used to withdraw small seed crystals grown on previous days with the glovebox hardware and inject them into a more concentrated growth medium. This procedure proved to be straightforward in microgravity. It was shown that a similar technique could be used in microgravity to withdraw grown crystals and mount them in x-ray capillaries for analysis. Since the

crystals are typically suspended within the middle of the protein drop, the most difficult aspect of this procedure (withdrawing the crystal into the capillary) was easily accomplished in microgravity.

It also became clear that high magnification microscopy with video transmission will be extremely useful on future missions. This capability will allow crewmembers to display results to scientists stationed on the ground so that they can aid in the decision making process, thereby optimizing the chance of producing high quality crystals. Hopefully, this demonstration will serve as a model for how such experiments will be performed on the International Space Station in which the growth process can take full advantage of the extended low gravity time.

Significant results using the glovebox hardware are:

USML-1 (STS-50)

- Principal Investigator, L. DeLucas, grew the longest crystal of monoclinic Factor D ever grown, a form that is difficult to grow reproducibly on Earth. Although, the space-grown crystal was only 1/3 as thick as the best Earth-grown crystal, the diffraction intensity was comparable to the best Earth-grown crystal, and it diffracted to 0.1 Å greater resolution. Also, the relative Wilson plot indicated a significant improvement in internal order at the higher resolution range. Using the X-ray data from the space crystal together with previous Earth-grown crystals, the three-dimensional structure of Factor D was worked out. This represents the first structure of a complement protein ever determined at atomic resolution. (See Narayana, Structure of Human Factor D: A Complement System Protein at 2.0 Å Resolution, *Journal of Molecular Biology*, 235 (1994) 695). Factor D is an enzyme necessary for activation of the complement system that plays an important role in host defense against pathogens.
- Malic enzyme is an NAD-dependent enzyme isolated from a parasitic nematode. It is being studied to exploit the differences in the structure from the human form to aid in the development of an antiparasitic drug. Guest Investigator, H. Einspahr (Bristol-Meyers Squibb), obtained crystals of malic enzyme that were much smaller than typical Earth-grown crystals. However, these space-grown crystals proved to be of exceptional quality. A space-grown crystal only 1/5 the volume of an Earth-grown crystal produced 25% more Bragg reflections and diffracted to 2.6 Å resolution, an improvement of 0.6 Å. The relative Wilson plots also show a dramatic improvement in internal order as the resolution limit is approached. The enhanced stability of the space-grown crystals in the x-ray beam was documented with these crystal, which is further evidence of better internal order (more bonds satisfied).

USML-2 (STS-73)

- IV. Guest Investigator, S. Aibara (Kyoto U.), obtained lysozyme crystals that showed slightly higher improved diffraction efficiency and resolution as compared to his ground control, but were inferior to the best lysozyme crystals grown on Earth.
- V. Duck delta II crystallin is a protein that is similar to the key enzyme that causes the disease argininosuccinic aciduria. The three-dimensional structure of this protein will lead to a better understanding of the metabolic processes involved in this disease. The protein supplied by Co-Investigator L. Howell (Hospital for Sick Children, Toronto) produced square pyramidal crystals rather than the usual flat plates seen on the ground. However, the crystals appeared to be striated and diffracted poorly. It is believed the protein was degraded by the launch delays associated with STS-73.

Engineers at the UAB-CMC developed an improved second generation VDA-2, which was flown on MSL-1 and MSL-1R. The primary difference between this new device and the old VDA is the addition of a third barrel to aid in mixing the sample. After the protein and precipitating agent are deployed as before, the drop is repeatedly sucked into and extruded out of this third barrel. The VDA-2 carries 80 individual crystal growth experiments in a CR/IM that provided temperature control.

It was known the crystals grown in the VDA-2 on the shortened MSL-1 flight did not have sufficient time to grow large enough to produce useful data, so the experiments were reactivated after the Shuttle landed in hopes of salvaging the valuable proteins. None of the resulting crystals produced diffraction data that was superior to their ground control. Consequently, the same set of proteins was flown on MSL-1R with spectacular results. Eight of the ten growth systems produced diffraction quality crystals, 5 of that produced the best X-ray quality crystals ever obtained. Some of the results from investigators using the VDA-2 are summarized below.

- The Hyaluronidase crystals grown by M. Jedrzejas (UAB-CMC) diffracted 0.2 Å better than the best data ever collected on earth-grown crystals and these data are being used to refine the structure for a vaccine against bacterial infections.
- Glyceraldehyde 3-phosphate dehydrogenase (GAPDH), a target for drugs to combat Chagas' disease provided by G. Oliva (University of Sao Paulo), produced crystals of a different space group that diffracted to 2.0 Å, an improvement of 0.8 Å over the best ground-based data. From these results, ground-based growth procedures were modified to produce the new space group, which diffracted to 2.2 Å resolution.
- The MSL-1R experiments with 5S rRNA by V. Erdmann (Freie Universitat Berlin) produced the best crystals ever grown of this ribosomal RNA. The space-grown crystals diffracted to 7.5 Å and yielded the first complete data set for this macromolecule from which the space group could be determined. The best ground grown crystals diffracted only to 9.0 Å. 5S rRNA is an essential

component of ribosomes. Structural data will aid in understanding the process of protein biosynthesis.

- NAD synthetase is also a target molecule for anti-bacterial drugs. Crystals of a complex of NAD synthetase with an inhibitor drug provided by Y. Devedjiev (UAB-CMC) yielded diffraction data 0.3 Å better than had ever been obtained before. The data are being used to study how well the proposed drug block the active site for this target molecule.
- Crystals of Proteinase K and Proteinase K with a substrate complex provided by C. Betzel (DESY, Hamburg) showed a 0.3 Å improvement over the best crystals ever produced before. Proteinase K is one of the most aggressive proteases known and can even degrade keratin. It is used in several industrial applications such as soap powder. This investigation is aimed at understanding the binding between the target molecule and the substrate.

The UAB-CMC also developed hardware for batch crystallization that was termed the Protein Crystallization Facility (PCF) to produce large numbers of crystals to meet a commercial requirement. Crystallization was driven by withdrawing heat from one end of a cylinder. The PCF first flew on STS-37 where it was used to produce batch quantities of insulin crystals. Most of these crystals remained suspended in the growth medium, but some were stuck to the walls. It was found that the free-floating crystals were much better ordered than those that grew on the walls, thus confirming one of the hypotheses as to why crystals seem to grow better (at least some of the time) in microgravity. Further, the increased X-ray resolution of these crystals provided the clearest picture yet of the structure of this important molecule. Results from Spacelab flights of the PCF are summarized below.

USMP-1 (STS-52)

- Alpha-Interferon crystals grown by M. Long (UAB-CMC) grew somewhat larger than their ground controls but were still too small for X-ray diffraction analysis.

USML-2 (STS-73)

- The objective of this experiment conducted by G.D. Smith (Hauptman-Woodward Medical Research Institute) and Eli Lilly was to produce large quantities of a new form of recombinant human insulin. Unlike the earlier flights in which both bovine and human insulin produced well-formed free-floating crystals, all of these crystals grew on the container walls. It is not clear whether the slightly different molecular of this form of insulin caused the crystals to nucleate on the walls, or if the optimal crystallization conditions were different for this system.

Eventually, some of the UAB-CMC collaborators developed new hardware more suited to their purposes, and formed additional collaborative teams of Investigators interested in using their new hardware. For example, Carter, while he was at the NASA Marshall Space Flight Center, was selected as a flight Principle Investigator by NASA. He developed the protein crystallization apparatus for microgravity (PCAM) module that was first flown on USMP-2 and the diffusion-controlled crystallization apparatus (DCAM) which was flown together with the PCAM on USML-2.

The PCAM is a simplified vapor diffusion apparatus that utilizes a sitting rather than a hanging drop. A stack of 9 units can be activated and deactivated by turning a single knob. A single locker temperature enclosure system (STES) that fits in a middeck locker can accommodate 378 units, 6 times the capacity of the older VDA. Furthermore, an inexpensive disposable user interface is provided that permits rapid *in situ* evaluation of results and allows users to carry the grown crystals back to their laboratories without having to remove the crystals from the apparatus. The PCAM can also be cryogenically stored.

The DCAM is a liquid diffusion dialysis method for growing crystals designed primarily as a totally passive device to be used on MIR. Since there is limited crew time available, the DCAM was designed to be totally passive, i.e. require no crew interaction. The protein solution and precipitating agent are stored in adjacent chambers connected by a small diameter tube filled with a gel. This gel-filled plug acts as a fuse that controls the activation rate of the experiment. A total of 27 DCAM units can be fitted into a STEC.

Both the PCAM and DCAM have attracted a variety of Guest Investigators who want to use his hardware. Carter later left NASA and founded New Century Pharmaceuticals, Inc. but remains a NASA-sponsored Principle Investigator. In this role he continues to offer Guest Investigator flight opportunities to both domestic and foreign collaborators from other industries and universities whose requirements are suited to his hardware.

Many of the protein and life science experiments were degraded by the delays in the launch of STS-73. Nevertheless, there were some successes with the PCAM hardware as summarized below.

USML-2 (STS-73)

- Guest Investigators C.H. Chang and P.J. Ala (Dupont Merck Pharmaceutical C.) obtained the largest crystal and highest quality data yet obtained for a particular HIV protease/inhibitor complex. The increased resolution allowed a refinement of the data so that a better understanding of the binding of the inhibitor molecule can be obtained.
- Guest Investigators J.P. Wery and D. Clawson (Eli Lilly) obtained the largest crystal ever grown of onogene product, Raf Kinase, a drug target for cancer therapy. Unfortunately, the crystals were still too small for structural determination.

- Human Antithrombin III is important on the control of blood coagulation by forming complexes with thrombin and other coagulation proteases, a process that is accelerated by heparin. On a previous Shuttle flight, guest Investigator M. Wardell (Cambridge University, UK, now Washington U., St. Louis), had obtained crystals of this molecule which allowed the refinement of the structure so that the region of the heparin binding site to be seen for the first time. Unfortunately, the protein deteriorated during the delay in launching STS-73.
- Guest Investigators J. Rose and B.C. Wang (U.Georgia) obtained the largest crystal of neurophysin/vasopressin complex grown to date. The crystal exhibited a high degree of optical perfection. X-ray analysis is in progress.
- Guest Investigators J-P Declercq (Universite Catholique de Louvain, Belgium) obtained the largest crystals of L-alanine dehydrogenase ever grown. Unfortunately, the resolution is still not sufficient to obtain structural information.

G.K. Bunick (ORNL) used Carter's DCAM to crystallize nucleosome core particles which have a total molecular weight of 102 kD. Because of the launch delay of STS-73, most of the nucleosome core particles crystallized on the ground. However, a few of the DCAM units were set for longer times and the produced large crystals with a new morphology that diffracted to a higher resolution than any crystals grown previously.

MSL-1 (STS-83)

- Despite the early termination of MSL-1, several protein systems grew crystals large enough for X-ray analysis. However, The primary value of this flight was the optimization of the growth conditions for the next flight. Guest Investigator C. Chang (Dupont Pharmaceuticals) grew diffraction size crystals of HIV Protease complex with a proprietary inhibitor, but the crystals were twinned. There was not sufficient protein to support the STS-94 flight, but the system was reflowed on STS-85 under more optimal conditions. The crystals from this mission were the largest ever grown and provided data to 1.8 Å. With this resolution, a detailed image of the inhibitor bound to the active site was obtained.

MLS-1R (STS-94)

- Guest Investigators J-P Declercq (Universite Catholique de Louvain, Belgium) grew the largest and highest quality crystal of Pike Paralbumin ever grown. This protein is of interest to fundamental biochemistry. Previous diffraction limit for Pike Paralbumin is 1.7 Å and for all paralbumin structures in the Brookhaven Data Bank the highest resolution is 1.5 Å. Declercq's crystal diffracted to the limit of measure of the Hamburg synchrotron, which is 0.9 Å. Based on the number of reflections at this angle, it is estimated that the actual resolution is closer to 0.6 Å. He crystals were also subject to neutron diffraction studies at Grenoble.

- Crystals of lysozyme and ferritin were grown under special condition to support fundamental research by B. Thomas and P. Vekilov (University of Alabama in Huntsville, Center for Microgravity and Materials Science) into why crystals some grow better in microgravity. Hopefully, this line of research will lead to improvements in terrestrial growth processes.

McPherson (University of California) was also selected as a flight Principle Investigator by NASA and he developed a simple crystallization module designed to take advantage of the long duration microgravity environment on the Mir station to grow crystals by liquid-liquid diffusion. The protein and precipitant solutions are flash frozen separately and the frozen solids are placed next to each other in a small container. These individual experiments are formed into 3 bundles that are stacked in a sealed aluminum cylinder. The cylinder is then placed inside an aluminum vacuum jacket, or dewar, lined with a calcium silicate absorbent. The absorbent was filled with liquid nitrogen to delay crystal growth until thawing occurs aboard Mir. After the Shuttle docks with Mir, the crew secures the dewar in a quiet area of the Mir station to minimize vibration. The liquid nitrogen continued to boil off into Mir's oxygen/nitrogen atmosphere. In orbit, the samples thaw after the nitrogen evaporated allowing the liquids to slowly interdiffuse. The gradual increase in concentration of the precipitant within the protein solution causes the proteins to crystallize. This occurs very slowly, allowing formation of large crystals with highly uniform internal order. Growth by liquid-liquid diffusion is not practical on Earth because the differences in solution densities will cause rapid mixing by gravity-driven convection. Furthermore, the greater density of the crystals will cause them to settle to the bottom of the container.

The GN2 dewar was flown on 6 MIR docking missions; however only one of these, SL-M (STS-71) was considered a Spacelab mission. On this mission, 167 individual experiments involving 18 different growth systems were carried in a single dewar.

A number of proteins have been successfully crystallized by this method resulting in larger crystals with considerable improvement in resolution. Examples include Leg Hemoglobin, Catalase, Canavalin, STMV, Cellulase, Concanavalin B, and Thaumatin.

McPherson also developed a hand-held diffusion test cell (HHDTC) which was flown on USML-2, MSL-1 and MSL-1R. The unit consists of a gang of 8 cells that use the liquid-liquid diffusion method for crystallization. The cells are backlighted for observation of the growth process. The cell design is a forerunner of a more sophisticated system to be used on the ISS with more diagnostic measurements.

The European Program

Littke carried out his landmark experiment using a liquid-liquid diffusion apparatus in the Cryostat facility on Spacelab-1. Unfortunately, his attempt to obtain diffraction quality

β -galactosidase crystals on D-1 failed because of equipment problems. A third attempt on IML-1 yielded crystals that were too small for X-ray analysis.

The Cryostat on IML-1 provided McPherson the opportunity to compare crystals of canavalin and STMV grown by liquid-liquid diffusion with identical systems grown in the VDA on the same mission. Differences were noted in the kinetics of crystallization by the two methods. A crystal of SMTV was grown in the cryostat that was an order of magnitude larger in volume than had ever been grown on Earth. The diffraction resolution was improved from 6 Å to 4Å. This represents the best resolution ever obtained from a virus crystal. The best canavalin crystals were grown in the VDA. They were of superior optical quality and exhibited increased diffraction efficiency, but showed no significant increase in resolution. (See previous section, US Program Results)

The development of the Advanced Protein Crystallization Facility (APCF) on IML-2 made it possible to accommodate a larger number of samples (up to 48) and allows its users to choose their method of crystallization between (1) Liquid/liquid diffusion or free interface diffusion (FID), in which the protein and a salt solution are separated by a buffer and are allowed to flow together when activated (the method used in the Cryostat); (2) Dialysis (DIA), in which protein and salt solutions are separated by a membrane through which the salt will diffuse slowly into the protein; and (3) Vapor diffusion or hanging drop (HD), where crystals will form inside a drop of protein solution as solvent evaporates from the drop to a reservoir (similar to the VDA). It also provided a capability for real-time video recording of the growth process and was enhanced for the LMS mission by the addition of a Mach-Zehnder-Interferometer which could measure changes in the concentration field as the crystals grew, thus providing better insight into the crystal-growth process in microgravity.

The IML-2, USML-2, and LMS missions offered multiple flight opportunities to a number of investigator: a necessary commodity for success in this area of research since it is often necessary to adjust or refine an experiment since growth conditions optimized for normal gravity may not be optimum in microgravity. As with many of the US investigators, the stay time on orbit was not long enough in a number of cases to grow large enough crystals for diffraction studies. Also, the some of proteins loaded into the experiments on USML-2 degraded during the 23 day delay in the launch that was due to weather and technical problems. However, there were some noteworthy successes.

G. Wagner (U. Giessen) crystallized bacteriorhodopsin on IML-1, IML-2, and USML-2. Bacteriorhodopsin converts light energy to voltages in the membrane of photoenergetic microorganisms that are chemically and genetically distinct from bacteria and higher living organisms. Resolution of the three-dimensional structure of this protein will help scientists understand the mechanisms used to convert light energy to energy for growth. Crystals from their IML-1 experiment improved the resolution from 8 Å (from previous ground-based work) to 6 Angstroms. Using the APCF on IML-2, two different growth techniques were explored and larger cubic crystals were obtained. In a new experiment protocol, first used under microgravity conditions during the USML-2 mission, both the

compact alignment of the crystalline filaments of bacteriorhodopsin and the crystal size were greatly improved which resulted in an increase in diffraction power to 3.8 Å.

Ribosomes are responsible for the translation of the genetic code to proteins. While they are the only organelles in living cells to have been crystallized, most of the Earth-grown crystals are very thin and crack upon handling, causing severe difficulties in data collection

Yonath and H. Hansen (Max-Planck Laboratory for Ribosomal Structure, Hamburg) grew crystals of a ribosome particle on D-2, IML-2, and on USML-2. In all cases, the space-grown crystals tended to be somewhat rounded and bulkier than their Earth-grown counterparts, which seems to make them less fragile and easier to handle. However, none of the crystals were large enough for X-ray diffraction analysis.

On D-2, IML-2, USML-1, and LMS, V. Erdmann, and S. Lorenz (Freie Universität of Berlin) crystallized the nucleic acid 5S rRNA from *Thermus flavus*, an essential component of the ribosome that is needed for biosynthesis. The crystals on IML-2 were fewer in number, but larger than the ground-controls but diffracted only to the same resolution (15 – 20 Å). It was noted, however, that 7 weeks had lapsed before the space crystals could be analyzed, which may have caused some degradation. Similar results were obtained on USML-2, although, in this case, the material is known to have deteriorated during the launch delay. Engineered 5S rRNA (modified to reduce internal motions) grew larger in space than their ground controls, but did not diffract to as high a resolution as the best ground grown crystals. (Erdmann later was able to get crystals that diffracted to 7.4 Å using the VDA-2 On MSL-1R. See Section on US program.)

N. Chayen (Imperial College, London) and co-workers crystallized the protein Apocrustacyanin C on IML-2, USML-2, and on LMS. Apocrustacyanin C is a member of the lipocalin family of proteins, which binds to certain pigments that are widely distributed in plants and animals. Knowledge of the structure of the lipocalins will enable scientists to engineer these proteins to produce carriers that will bind more strongly to the pigment crocetin, which has anticancer properties. On IML-2, She found no significant increase in resolution in her flight samples, but did report seeing “halos” around the growing crystals which would correspond to the region of depleted blue-colored protein near the growth interface, indicative of growth under diffusion-limited transport conditions. She also reported motion of the crystals, which she attributed to Marangoni convection driven by concentration gradients along the surface of the hanging droplet and suggested that crystals growing from a surface, as in a dialysis chamber, might have better order (contrary to the findings of M. Long (UAB-CMC in the PCF). Mosaicity (rocking curve) measurements on the crystals grown on USML-2 showed a spread in data with no significant difference between space and ground based growth. The space grown crystals on LMS diffracted to much higher resolution than the ground controls, but were 12 times larger (by volume). Mosaicity measurements and X-ray topographic measurements have not yet been reported.

W. de Grip, (University of Nijmegen) was interested in the structure of visual pigments such as rhodopsin, which are the primary photoreceptor proteins for a variety of light-regulated processes. Knowledge of the structure of this protein may help understand the

signal transduction on the molecular level. Crystals grown on IML-2 were somewhat larger than the ground controls, but were not large enough for X-ray diffraction studies. Unfortunately, no useful crystals were obtained from the USML-2 flight because of problems with the reactor.

Broutin, M. Ries-Kautt, and A. Ducruix (CNRS, France) crystallized collagenase and Photoreaction Center (PRC) proteins on UML-2. The PRC crystals diffracted poorly because they degraded while being stored at 20°C prior to launch. However, the space-grown collagenase showed a dramatic increase in diffraction efficiency, although there was no significant increase in resolution.

Broutin, M. Ries-Kautt, and A. Ducruix (CNRS, France) extended their study of the effects of microgravity on the growth of hen egg white lysozyme (HEWL) on USML-2. Using the APCF on Spacehab-1, they grew the tetragonal form that diffracted to 1.3 Å. This was better than any previous published data, but there was no significant difference between the ground and space-grown crystals. On USML-2, they grew the monoclinic and triclinic form of HEWL. The ground and space-grown crystals of both forms diffracted to 1.45 Å, better than any previously published, although there are unpublished reports of 0.99 Å resolution for the triclinic form grown on the ground. The original plan was to also crystallize the protein Grb2, an adapter protein involved in the transfer of signals from one cell to another. However, this protein was found to be unstable before the final loading for the USML-2 flight.

The bacteriophage Lambda lysozyme is a small protein of 158 amino acids involved in the dissolution of the cell walls of bacteria. J-P Declercq and C. Evard (Université Catholique de Louvain, Belgium) grew crystals of this protein on USML-2 hoping to learn more about the method of destruction employed by this organism from the structure of its lysozyme. However, they obtained only small needle-like crystals and concluded that optimum crystallization conditions must be different in microgravity than on Earth.

J. Helliwell (U. Manchester) grew crystals of hen egg white lysozyme (HEWL) on IML-2. This type of lysozyme is easy to grow and it was one of the first proteins whose structure was determined. Therefore, it has been widely used as a model protein for studying the growth of proteins. In this experiment, rocking curves (a measure of crystal long range order) from space-grown crystals were found to be reduced from 0.0067 degrees for earth grown controls to 0.0017 degrees. It was noted that the decrease in rocking width is proportional to the increase in peak height of reflections with, after corrections for volume in the beam, the microgravity crystals displaying peak intensity levels three to four times that of the earth grown counterparts. It was readily possible to find reflections for the microgravity-grown case at 1.2 Å resolution.

The experiment was repeated on LMS in a chamber with a Mach-Zehnder interferometer and video imaging capability. Stability problems with the laser caused some difficulty in interpreting the interferograms, but depletion regions around the crystals were evident. Growth rate and crystal motion were monitored using the CCD video camera. All crystals seemed to follow a general drift at the rate of ~40 Å/sec., although occasionally there were spurts where they moved ~0.2 mm over a 2 hour period which corresponds to

a rate of 300 Å/sec. Unlike Chayen's experiment, which used the hanging drop method, these experiments used the dialysis method, hence there was no free liquid surface that could support Marangoni convection. (The observed drift was most likely due to the quasi-steady residual accelerations (atmospheric drag plus gravity gradient) and the sudden spurts could be the results of changes in attitude of the Shuttle.) Periods of increased growth rate were also noted that could be correlated with crew exercise periods.

J. Martial (Universite de Liège) and L. Wyns (Universite de Bruxelles) synthesized a series of *de nova* proteins, named Octarellins, that are designed on the basis of an alpha/beta barrel structure in order to understand the molecular forces that stabilize their structures. Attempts to crystallize several of these systems on IML-2 and on USML-2 produced only needle-like crystals, too small for X-ray analysis. However, some crystals produced in the ground control units were able to provide low resolution diffraction data.

L. Sjölin (U. Göteborg, Sweden) crystallized Ribonuclease S using the vapor diffusion method in the APCF on IML-2. The crystals grown in space were similar in size and number to those grown terrestrially; however, the space-grown crystals tended to have flatter faces which is generally a sign of greater perfection. Also, some of the control samples had cracks that were not found in any of the flight crystals. Ten data sets were then collected from both earth-grown and space-grown crystals. The results from the statistical analyses of the ribonuclease S crystal data indicate that, when crystal growth conditions are optimized, the space-grown crystals of ribonuclease S show a smaller mosaic spread than crystals under comparable conditions on earth. Analysis of the three-dimensional X-ray data from all ten crystals of ribonuclease from both space and earth clearly shows that the variance between the different data sets is less for the space grown crystals. A similar experiment was attempted on USML-2 using Glutathione S Transferase. Unfortunately, technical problems prevented the return of useful crystals.

J. Ng (now U. Alabama in Huntsville), B. Lorber, A. Théobald-Dietrich, D. Kern, and R. Giegé (CNRS, Strasbourg) grew Thermophilic Aspartyl-tRNA Synthetase on IML-2, USML-2, and LMS. Aminoacyl-tRNA synthetases are the enzymes that attach specifically the amino acids to transfer RNA, and thus are responsible for the correct expression of the genetic code. On IML-2 it was found that the crystallization conditions used on the ground were not proper for microgravity. Only small crystals were observed which appeared to be growing by Ostwald ripening. These results were used to set the crystallization conditions for the USML-2 experiment. Unfortunately the protein denatured during the launch delay and no usable crystals were produced on this flight. On the LMS flight, only one dialysis reactor contained crystals. However, this reactor contained three unusually large, high quality crystals, the largest being over 3 mm in length and free of any visual imperfections. These crystals produced almost twice the number of Bragg reflections than the Earth-grown crystals (93% increase in diffraction efficiency) but did not extend the resolution significantly. The mosaicity spread (rocking curve width) was reduced by a factor of 8 in the space-grown crystals, implying a dramatic increase in internal order.

Giege and his co-workers added thaumatin, a plant sweetening protein, to their experiment on USML-2 and found fewer, but substantially larger crystals in the space reactors. The space crystals, especially those that grew suspended in the fluid, were perfectly formed and free of any visual imperfections. They reported an improvement in resolution from 1.7Å to 1.5Å with improved diffraction properties as judged by relative Wilson plots. The rocking curve width was reduced from 0.055° to 0.023° for the crystals grown in space. Similar results were obtained from the LMS flight. In this case the rocking curve width (FWHM) was reduced from 0.047° to 0.018°.

McPherson used the liquid-liquid diffusion capability of the APCF on IML-2 to crystallize canavalin, STMV, Satellite Panicum Mosaic Virus (SPMV), and Turnip Yellow Mosaic Virus (TYMV). Both rhombohedral and hexagonal forms of canavalin grew in the same flight chambers; a highly unusual situation on the ground which was not seen in the control experiments. The crystals were quite large (>1 mm) and exhibited high optical quality, free of any imperfections. Previous flight had produced canavalin crystals of similar optical quality, but showed little or no increase in X-ray diffraction resolution. Relative Wilson plots of these crystals showed marked improvement over the best canavalin crystals ever grown on Earth. These crystals also diffracted to higher resolution and provided data to refine the structure of canavalin. Very large (>1.5 mm) cubic crystals of STMV grew in the flight reactor ; as much as 30 times the volume of the largest cubic STMV ever grown on Earth. Again these crystals diffracted to 2 Å better than the best cubic STMV grown on Earth. The TYMV crystals exhibited a different morphology attributed to diffusion controlled vs. convective transport. They did not show any improvement in X-ray diffraction resolution, however. No useful crystals of SPMV were returned. This system uses PEG as the precipitating agent, and as was discovered by DeLucas, its slow diffusion time for this liquid does not provide adequate mixing in microgravity in the time frame of these experiments.

McPherson added thaumatin, catalase, concanavalin B, and Tomato Aspermy Virus to the materials to be crystallized on USML-2. The thaumatin in this experiment was grown by liquid-liquid diffusion to compare with the result of the Strasbourg team who used the dialysis growth method (See Giege above). Only thaumatin grew high-quality crystals with sizes as large or larger than those grown on Earth. It was suspected that the other materials deteriorated during the launch delay of USML-2.

The thaumatin experiment was repeated on LMS. In both flights, the quality of the thaumatin crystals was excellent in all cases, except those where the crystals grew with faces against walls. These showed extensive striations. The thaumatin crystals increased in size with increasing protein concentrations. This interesting observation points out another advantage of growth in microgravity. On Earth, convection would continuously expose the growth interface to the high concentration, causing very rapid growth leading to many growth imperfections. In microgravity, the diffusion field limits the transport and keep the growth rate slow even at high protein concentrations. The flight crystals diffracted strongly to the maximum resolution that the data collection system could achieve, approximately 1.5 Å, an improvement of 0.2 Å from the best Earth-grown crystals. An improvement of 30% in diffraction efficiency was also noted. The mosaicity

of the flight crystals was measured at 0.020° FWHM vs. 0.048° for the best terrestrially grown thaumatin crystal. (Note: ground control experiments cannot use liquid-liquid diffusion because of the very rapid convective mixing of the two fluids.)

W. Weber (U. Eppendorf) and Ch. Betzel (European Molecular Biology Lab, Hamburg) continued their work on the various forms of receptors of Epidermal Growth Hormone that they began using the VDA on SL-J. However, now they used the European APCF that was flown on the USML-2, and LSM missions. Diffraction data from three crystals grown on USML-2 again showed a maximum resolution of 6 \AA with a remarkably high quality of Bragg reflections, confirming the SL-J results. The best Earth-grown crystals of this particular receptor had yielded comparable results but required larger sizes and much more time to grow. The crystals grown on LMS did not produce usable diffraction data.

P. Fromme (Max Volmer Institute) and W. Saenger (Freie Universitat Berlin) crystallized the protein complex, Photosystem I, which is responsible for the primary conversion of visible light into chemical energy in water-oxidizing photosynthesis. The objective of this experiment was to determine the complete arrangement of chlorophyll molecules that perform this conversion process. On Earth, the largest of the hexagonal rod-like crystals grew on the dialysis membrane and was 2 mm long and 0.5 mm \varnothing (volume of 0.4 mm^3). The USML-2 flight produced crystal that were 4 mm long and 1.5 mm \varnothing (volume of 7 mm^3) even though, for technical reasons, the flight crystals could not grown be at their optimum growth temperature. In spite of this, the crystals still diffracted to 3.8 \AA , and the mosaic spread reduced slightly to approximately 0.7° . The experiment was repeated on LMS and, for reasons unknown, the flight reactors failed to nucleate crystals even though all the ground control reactors produced diffraction quality crystals.

L. Wyns, M.H.D. Thi, and D. Maes (Universite de Bruxelles) investigated the growth of CcdB crystals, a protein involved in the control of cell death which may lead to the design of new antibiotics and anti-tumoral drugs. The quality of terrestrially grown crystals of this protein was not sufficient to obtain high resolution diffraction data and twinning was a serious problem. In addition, they wanted to crystallize two specific serine-to-cysteine mutants (Ser74Cys and Ser94Cys), proteins which have not produced crystals large enough for data collection. Small needle shaped crystals of CcdB were obtained in the hanging drop reactors on both USML-2 and on LMS, but they diffracted no better than Earth-grown counterparts and twinning is still a problem. No useful crystals of the mutants were obtained on either mission.

Zagari (U. Napoli) and coworkers crystallized *Sulfolobus Solfataricus* Alcohol Dehydrogenase on the USML-2 and LMS missions. Alcohol dehydrogenase (ADH) is an enzyme that occurs in large amounts in the livers of mammals, where it plays an important role in several physiological functions, including the breakdown of alcohol. Mammalian ADH is unstable at high temperatures or in the presence of organic solvents, properties that limit its biotechnological application to the synthesis of organic compounds. ADH from *Sulfolobus solfataricus*, a bacterium that thrives at high temperatures, has greater thermal stability, however, and is scarcely affected by the presence of organic solvents. Given these properties, the enzyme is a good candidate for industrial applications.

Crystals of useful size can be grown on Earth, but are badly twinned, thus preventing the collection of diffraction data. Some success had been obtained with growth in gels, which also reduce convective effects, which prompted the experiments in microgravity.

Since the protein is known to be very stable, it was not reloaded during the 23 day delay in launching USML-2. However, both flight and ground control experiments which were activated at the same time as the flight experiments produced only small crystals that diffracted poorly, suggesting that degradation of the protein did occur. The experiment was repeated on LMS with much better results. The space-grown crystals diffracted to significantly higher resolution and exhibited increased stability in the X-ray beam. Unfortunately, analysis of the X-ray data revealed that the space-grown crystals were still twinned.

T. Richmond and A. Mader, (Institut für Molekularbiologie und Biophysik, Zurich) crystallized nucleosome core particles. The nucleosome shapes the DNA molecule by twisting and bending it and form higher order structures on the scale of genes. The laboratory crystals have an anisotropic mosaicity spread, which they hope to reduce by growing crystals of these particles in microgravity. Unfortunately, the growth conditions they had to use in the APCF were not optimum for this material. Consequently, the space-grown crystals showed no significant improvement over the ground control growth experiments, and neither produce as good results as their optimized laboratory growth methods.

J. Garcia-Ruiz, F. Otalara, D. Rondon, and M. Novella (U. Granada, Spain) used the APCF on LMS to test the Mach Zehnder interferometer, measure growth rate and crystal motion, investigate the use of high protein concentration in liquid-liquid diffusion growth, and to explore the concept of growing protein crystals in X-ray capillary tube. The protein chosen was HEW lysozyme, which is one of the standard proteins, used for investigating the growth of protein crystals. They were able to record interferograms, but also ran into difficulty in interpreting them because of instabilities in the laser. Their observations of particle motion were similar to those described by Helliwell (see above). Growth rates were observed to increase initially, and then decline with time as would be expected from growth under diffusion-limited transport condition as the diffusion field spreads out.

Since crystals ultimately have to be mounted in X-ray capillary tubes for analysis, this operation raises the possibility of damage to the fragile crystal. The confined growth environment may offer another advantage. One of the arguments for why protein crystals grow better in microgravity is that diffusion limited growth slows the rate at which nutrient is transported to the growing crystal so that growth becomes transport limited rather than kinetics limited. This gives surface kinetics a chance to go to equilibrium, assuring that each ad molecule has a chance to find its lowest energy configuration, which would produce greater order in the lattice. An analogy would be the filling of an arena for a rock concert or a soccer match. If the doors were opened wide, the crowd rushes in, there is great confusion in finding the proper seats, and many fans do not wind up in their assigned seats. Here, the filling of the seats is limited by the rate at which people can

find any old seat, which would correspond to crystal growth under kinetics limited conditions. On the other hand, if only a few people were allowed in at any one time, the filling of the arena would be transport limited and the people would have a much better chance of being in the right seat, which would correspond to admolecules finding their right position and orientation in the lattice.

When a crystal grows on Earth, the nutrient next to the growth interface is depleted and the lighter solvent rises, bringing more solute to the growth site. Since growth kinetics are slow for most proteins, the convective flows always bring nutrient to the crystal faster than it can be incorporated into the lattice. Thus the growth in normal gravity is generally kinetics limited. In space, solute must diffuse in from the surrounding region, which slows the transport to the growing crystal. However, the laws of diffusion are such that this depleted region (so called diffusion length) is approximately the radius of the growing crystal and the diffusion limited transport may not be slow enough to be the limiting factor in the growth rate of the crystal. In fact, Vekilov et al. recently showed that growth instabilities may arise when transport and kinetics are in competition, and that this situation could explain why some proteins produce inferior crystals when they are grown in space. See. Vekilov, et al., *Physical Review* 54/6 (1966) 6650-6660). Growing crystals in X-ray capillary tubes in space may have the added benefit of extending the diffusion length and assuring that growth actually becomes transport limited.

Garcia-Ruiz et al. grew HEW lysozyme, which has come to be a standard protein for studying growth phenomena. The space grown crystals typically diffracted to 1.25 Å (one crystal diffracted to 1.15 Å), which is comparable to the best lysozyme crystals grown on Earth with highly purified material. The longer diffusion length provided by the X-ray capillary may have acted as an effective filter for the higher molecular weight impurities usually found in lysozyme. The Garcia-Ruiz team found a spread of mosaicities (rocking curve width) ranging from 5 arc seconds (0.0014°) to 20 arc seconds (0.005°), depending on the part of the crystal they examined. These roughly correspond to the flight and ground-based values obtained by Helliwell. Since the first growth incorporates the nearby impurities before the diffusion field has a chance to develop and act as a filter or to limit the growth rate, this could explain why different part of the crystal exhibited different mosaicities. Similar results have been seen in ground based work by Garcia-Ruiz using the gel-acupuncture method for growth.

Other Biotechnology Experiments

Electrophoresis

Electrophoresis, and its related electrokinetic separation processes such as isoelectrofocussing, are widely used for separation of proteins on an analytical scale. The protein molecules take on a particular surface charge (zeta potential) in a buffer solution. When an electric field is applied, the molecules will be move under the influence of the applied field. Usually, the proteins are caused to migrate through a gel. The combination

of the attraction by the applied field and the drag through the pores of the gel give each protein a specific mobility so that they will become separated spatially as the process is continued. Because this process is limited to microgram quantities, it is used primarily as an analytical tool.

Attempts to scale electrophoresis to a preparative scale by replacing the gel with a continuous flowing sheet of sample plus buffer solution has enjoyed only limited success on the ground, primarily because buoyancy driven convection places severe restrictions on the sample concentration and the thickness of the flowing buffer sheet. These factors limit the throughput of continuous flow electrophoresis (CFE); consequently, it has largely lost favor to other methods, such as column chromatography, as a preparative separation method. There are certain potential advantages to CHE, however. It is a universal method, as opposed to column chromatography, where the columns have to be designed to separate specific proteins. Also, it can be applied to cell separation without having to tag the cells as is required by various cell sorting techniques.

The potential advantages of CFE prompted the McDonnell Douglas Corporation to develop a space continuous flow electrophoresis device (CFES) with the hopes of carrying out preparative electrophoresis on a commercial scale by widening the flow chamber and using a highly concentrated sample stream. The CFES flew seven times on the early Shuttle flights and worked reasonably well, but the separation was never as clean as was hoped for. Eventually, their commercial partner found a ground-based alternative to separate their product, and the project was dropped.

The unexplained broadening of the concentrated sample stream prompted Snyder and Rhodes at NASA/MSFC together with Saville at Princeton University to carefully examine the electrohydrodynamics involved in the distortion of a concentrated sample stream because of the mismatch in conductivity and dielectric constant between the sample and the surrounding buffer. Such effects had gone unnoticed in the development of CFE machines for terrestrial use because they were usually masked by convective effects. None-the-less, these electrohydrodynamic effects had to be operating, even though on a scale of lesser importance, but they could ultimately become a significant factor as other limitations were overcome by clever designs.

Interest to re-evaluate the potential of CFE in space on the part of the Japanese and the French led to the inclusion of two CFE systems on IML-2. The Japanese Free Flow Electrophoresis Unit (FFEU) was designed primarily as a separation device and was first flown on the Spacelab-J mission during which Kuroda and his team from Osaka University Medical School attempted to separate a group of standard proteins (horse cytochrom C, chicken conalbumin, and bovine serum albumin) in order to test the resolution as a function of concentration, flow rate, and operating voltage. Their results were inconclusive due to technical difficulties. On the same mission, Akiba (Institute of Physical and Chemical Research) attempted to separate three strains of *Salmonella typhimurium* LT2 cells, each of which has a different surface charges, which corresponds to its sensitivity to antibiotics. A clean separation was obtained for one of the cell types,

but the peak of the third cell line unexpectedly overlapped with the second, thus preventing their separation.

On IML-2, Kobayashi (JOSAI University) successfully separated two types of nematode DNA from a DNA mixture using the FFEU with a special buffer to operate in the isoelectric focussing mode. The sample detector indicated sharp, well defined sample streams. However, a bubble in the separation chamber caused some irregularity in the collection.

Okusawa (Hitachi Ltd.) also used the FFEU on IML-2 to extract IgG from a culture medium of STK1 cells. He reports that the cells cultured in space produced twice as much IgG as their ground control. The sample detector indicated the separation was much more stable in space than on the ground, however bubbles in the chamber caused difficulty in the sample collection.

Hymer (Penn State University) used the Japanese Free Flow Electrophoresis Unit (FFEU) on IML-2 to separate rat anterior pituitary organelles with aim of separating out those vesicles that contained growth hormone (GH). The vesicles were obtained from the lysate of pituitary cells cultured in space. Due the absence of sedimentation, he was able to use a higher concentration of the lysate in space, hence was able to increase the throughput by a factor of 5.6. He did notice a wider band spread of the GH-producing particles that were separated in space. The plan to separate the GH-producing cells from other cells using the FFEU could not be carried out due to equipment problems, but was performed on the ground at KSC 8 hours after landing. Pituitary cells that were fed in space, for unknown reasons, produced 5 times as much GH as the ground control. Further, it was found that their electrophoretic mobility had increased by a factor of 2 as compared to cells that had been cultured on Earth.

The other electrophoretic device flown on USML-2 was the French "Recherche Applique sur la Methodes de Separation Electrophorese Spatiale" or RAMSES. This instrument was designed as a research tool as well as a separation device. It could be operated with AC fields to examine the electrohydrodynamic sample stream distortion without the complicating cross flows involved in the actual separation process.

Sanchez and Clifton (Universite Paul Sabatier, Toulouse), characterized the separation ability of the RAMSES system by separating various standard proteins, hemoglobin, and dyed BSA. A much broader range of operating conditions are available in microgravity and the flows were stable under all conditions studied, confirming that gravitational effects limit the operating range on Earth. Dilute samples differing in mobility by only 3×10^{-9} m²/Volt/sec could be separated. However, the more concentrated samples spread so that their peaks overlapped. This electrohydrodynamic phenomenon is due to the difference between the conductivity and dielectric constant of the sample and the buffer. The Investigators were, however, able to increase the throughput of a biologically active sample by a factor of 5 by concentration and still get as good a separation as on Earth. All of these results were supported by extensive computer modeling.

Snyder and Rhodes had also planned to investigate the effect of high sample concentration and electrohydrodynamic instabilities in the absence of shear flow. Unfortunately, their experiment could not be run due to an electrical failure in the RAMSES equipment.

Electrofusion

Electrofusion has emerged as an important new hybridization technique on the cellular level for the formation of hybridomas for making monoclonal antibodies as well as for somatic hybridization in sexually incompatible plants. In the later application, hybridization and exchange or recombination of organelles can be achieved by fusion of protoplasts by the reversible electric breakdown of their plasma membranes. With this method, protoplasts are first brought into close membrane contact by a weak alternating electrical field and then subjected to a high voltage pulse of short duration to induce local membrane reorganization at the contact area. However, for this process to be successful, it is necessary for the two electrically-aligned cells to remain in the same relative positions for a certain time after the application of the high voltage pulse. Gravity tends to interfere with this process, especially when the protoplasts have different densities. This consideration prompted a number of microgravity experiments using the TEXUS suborbital rocket program, which led to the electrofusion experiments on the D-2 Spacelab mission.

During the D-2 mission, Hampp and his team at Universität Tübingen performed electrofusion experiments on three different systems; 1. tobacco as a model system, 2. *Helianthus* (sunflower) as an important crop, and 3. *Digitalis* as a plant of pharmacological interest. The resulting fusion products were cultivated (along with parental cells) for 10 days under microgravity, and subsequently regenerated on the ground for biochemical analysis.

The alignment times were shortened for all three systems, however, for some reason, the tobacco did not respond to the first pulse and increased voltage had to be applied. Consequently, the heterofusion yield for the tobacco was only 0.3-1.5% in both flight and ground control experiments. However, the yield for *Helianthus* was increased by 4-fold in microgravity and the yield for *Digitalis* was increased by a factor of 10.

ASTROCULTURE

ASTROCULTURE™ is a state-of-the-art plant growth chamber for space as well as terrestrial research that was developed by the Wisconsin Center for Space Automation and Robotics (WCSAR), a NASA-sponsored Commercial Space Center (CSC) located in the College of Engineering at the University of Wisconsin-Madison. This chamber uses many of the technologies developed by WCSAR and its industrial partners which includes the ASTROPORE® humidity control system, high intensity LED light sources, a porous tube water-nutrient delivery system, a unit for removing ethylene which does

not require consumable materials, and proprietary software to coordinate and monitor operation of these subsystems. This chamber represents an integration of agriculture and automation, two of WCSAR's core technical strengths. The traditional method of studying plants has been in their natural environment. Over the past few decades that approach has changed to one of research in a controlled environment such as the ASTROCULTURE™ where scientists are able to control each variable.

The primary missions of the WCSAR are: 1. to support industry in the identification and development of new products and new technologies for the commercial marketplace, 2. to support NASA in the development of technologies that will contribute to the human exploration and development of space, and 3. to support dissemination of WCSAR program experience for educational purposes.

The ASTROCULTURE™ facility first flew on USML-1 and subsequently has flown on a number of Shuttle flights including the USML-2 Spacelab mission. The earlier flights were primarily tests of the various subsystems in microgravity, which culminated in an actual demonstration of the growth of potato tubers on USML-2 that could be used as a source of food on later extended duration missions. The potato tubers developed normally, despite the lack of gravity, and the starches they produced were very much the same as the starches produced by potatoes grown on Earth except for the reduced activity of the enzyme, ADP-glucose pyrophosphorylase. This later finding is not understood and requires further study.

Later flights investigated the growth of other plants as possible food sources for extended manned missions including the growth of dwarf wheat plants from seed-to-seed on the MIR station. It was also demonstrated during the STS-95 mission that the microgravity of space provides a particularly suitable environment for transgenic plant alterations. A scaled-up version of the ASTROCULTURE™ facility is being developed for the International Space Station to provide food to the crew.

A number of the technologies that went into the development of the ASTROCULTURE™ flight hardware have found their way into the commercial market. For example, owners of large commercial nurseries nationwide are now using the module's water and nutrient delivery tubes. The project also developed a system of air humidification/dehumidification that does not need a gas or liquid separator as other systems do. The LED arrays used for lighting in the facility produce an average continuous output of 4 - 6 watts at a wavelength of 660 nm. This output is equivalent to the terrestrially sensed output of the sun at this wavelength at high noon. These LED chips are arrayed on an alumina tile substrate that may be formed to provide optical power focused on a specified target area which can be used as energy efficient lighting systems for large scale commercial nurseries. These arrays also offer a low cost alternative to laser light sources in a wide range of medical applications such as measuring blood sugar levels or use in photodynamic cancer therapy.

BioServe

BioServe Space Technologies is a NASA Center for Space Commercialization located jointly at the University of Colorado in Boulder, Colorado, and Kansas State University in Manhattan, Kansas. The primary mission of BioServe is to facilitate commercial use of the unique environment of space. BioServe focuses on research in biomedical, pharmaceutical, bioprocessing, bioproducts, agricultural, and environmental areas. Areas of investigation can be categorized to include studies on whole organisms, mammalian cells, viruses, plants, microorganisms, biocrystal growth, biomaterials, bones/skeletal materials, and other related topics. In general, reduced gravity has been shown to alter one or more aspects associated with each of the above categories. Ongoing research is directed towards identifying the underlying causes of the altered outcomes and exploring the potential of related commercial applications.

A Generic Bioprocessing Apparatus (GPA) payload was flown for the first time on USML-1 (STS-50). The GPA module replaces a middeck locker and provides confinement and environmental control for up to 72 Fluid Processing Apparatuses (FPAs). Each FPA can be thought of as an automated test tube in which up to three different fluids can be mixed at different times in order to perform an individual experiment. (For example, an activator can be added to a culture medium at the beginning of the experiment and a fixative added at the termination.). On USML-1, the FPAs were activated individually by the crew. On later flights, the FPAs were packaged in groups of 8 so that the entire group could be activated manually or automatically. Individual FPAs can be placed into an optical density measurement device inside the GBA to collect turbidity data providing real-time experimental reaction rates. Variations of the standard FPA configuration include a Gas-Exchange FPA (GE-FPA), a Plant-FPA (P-FPA) and an Insect FPA (I-FPA). Inserts are also used to facilitate protein crystal growth experiments. The different designs address specific experimental requirements such as providing larger habitats (insects) or allowing gas exchange within the GAP atmosphere to increase the available amount of oxygen / carbon dioxide. The T-GAP (toroid) contains a single volume insert (no activation or termination) that replaces the 8 FPAs to provide a larger experimental volume for specific applications. Other modifications can be considered on an "as needed" basis.

The Commercial GBA can either be flown as an isothermal containment module (GBA-ICM) with a set temperature ranging from 4°C to 37°C, or as an incubator (GBA-INC). A Fluid GBA was designed to dispense carbonated beverages on STS-77 and a Plant GBA designed to support plant growth was flown on STS-77 and on MSL-1 and 1R. All told, GBAs have been flown on 18 Shuttle flights, including two extended stays on MIR. More than 100 plant experiments have been conducted, more than 2500 space experiments have been performed in FPAs and another 120 experiments have been performed in Bioprocessing Modules (a JSC-developed device whose function is similar to the FPA).

These flights have been used to investigate a wide variety of microgravity effects, many of which were totally unexpected and could not have been predicted from simple fluid mechanical arguments. A few examples are:

1. Accelerated growth of microorganisms. Many experiments have demonstrated that bacteria, paramecia, and other microorganisms grow faster in microgravity. One argument that has been suggested is that since the organism does not have to swim against gravity, more resources can be devoted to growth. The BioServe experiment, which demonstrated enhanced growth of a nonmetal strain of *E. coil* (ATCC 4157), shows that other factors are responsible. Growth in suspension cultures as well as on agar substrates were enhanced in microgravity.
2. Enhanced cellular production. The production of the antibiotic monorden by the fungus *Humicola fuscoatra* was increased by 190% in microgravity, which is consistent with reports of increased production of cell products from other cell lines in a weightless environment.
3. Altered development of organisms. In one set of experiments, the development of brine shrimp was significantly increased in microgravity. However, in another set of experiments, the differentiation of bone marrow macrophages was retarded, although their growth was enhanced.
4. Enhanced enzymatic activity. Enzymes such as plasmin, collagenase, and cellulase were shown to degrade fibrin, collagen, and cellulose respectively 30-50% faster in microgravity than in normal gravity. A smaller enhancement was also observed in clinostat experiments.
5. Enhanced expression of auxin-regulated genes. Plant growth and development is highly sensitive to auxin and altered sensitivity can have dramatic effects on such things as root growth and the production of metabolites of pharmaceutical interest.
6. Plant growth and development in absence of gravitational cue. The role of the statocytes (specialized cells though to be the gravity sensors) in gravitropism is reasonably understood, but not the mechanism by which the gravity force is turned into a biochemical signal. BioServe is interested in how plants, in the absence of gravitational cues, signal for ethylene production, cell wall thickness, lignin production, and the partitioning of carbohydrate between lipid and starch production. This knowledge might allow them to manipulate plants to optimize plant products, both in space as well as on Earth.
7. Magnetic combing of collagen. Collagen can be grow in vitro on Earth, but it is disordered at the fiber level making it undesirable for implants. BioServe demonstrated that it could be "combed" in microgravity by drawing fixed magnetic bacteria through it with a strong magnetic field as it is being polymerized.
8. Growth of biocrystals. BioServe has demonstrated that different growth techniques; e.g. osmotic dewatering, dialysis diffusion, microdialysis, etc. can

also produce biocrystals that are of higher quality in microgravity as evaluated by X-ray diffraction resolution, mosaicity, and stability in an X-ray beam.

Science Assessment

Biomolecular Crystal Growth

The growth of protein and other macromolecular biomaterials has been and still is more of an art than a science. There are many variables that can affect the growth process, many of which are not well understood, are not always under control. Furthermore, nucleation is a stochastic event so that there is always a certain amount of randomness involved, even if all other variables are controlled. As a result, it is not unusual for apparently identical experiments to yield quite different results. Traditionally, structural molecular biologists have set up large arrays of growth experiments, not just to screen for optimum growth conditions, but also to improve their chances of obtaining at least one growth chamber with usable crystals. Since their primary job was to obtain molecular structure, not to investigate growth processes, these workers seldom had the opportunity or the background to investigate the fundamentals of the growth process.

There is no question that some growth systems have produced crystals of outstanding quality in microgravity and, in a number of cases, the space-grown crystals were superior to the best crystals of those particular systems that had ever been grown on Earth. These findings have attracted the attention of some of the theoreticians who study the formation of crystal structure in small molecule systems. Exactly how does gravity affect the growth process? Why do some protein systems seem to benefit from microgravity and others do not? Can we apply this knowledge to improve the growth of protein crystals on Earth? NASA is now vigorously supporting this avenue of research. Consequently, this growth problem is being attacked by a multi-disciplinary approach, which includes protein chemists, solid state physicists, surface scientists, fluid dynamists and computational process modelers. International meetings sponsored by several crystal growth societies are now being held on an annual basis and are attracting an increasing number of participants.

There are a number of theories and conjectures that have been set forth as possible explanations for this phenomenon, several of these have already been discussed in the preceding sections. One of the more paradoxical findings has been the fact that the space-grown crystals in many cases have been both larger and better organized. Generally better internal order requires slower growth rates, which would be the case if diffusion controlled transport became the rate limiting step in the growth process. Therefore, the growth rate in space should always be equal or less than the growth rate on Earth where convection provides additional transport. How then can the space-grown crystals grow larger in the same length of time as their ground control counterparts?

One possible answer is that the space crystals continue to grow while the growth of their Earth counterparts slows and eventually ceases. This well-known, but poorly

documented, phenomenon of growth cessation had been one of the factors that limited the size of many protein systems and it has been demonstrated that the problem is exacerbated by forced convection (see Pusey et al. *J. Crystal Growth* 90 (1988)105-111). It was speculated that the convective flows bring contaminants to the vicinity of the growing crystal where they may poison the growth interface. For this theory to hold, the contaminants must be incorporated into the crystalline lattice in preference to the protein monomers; otherwise, convective flows would have the beneficial effect of sweeping the build-up of the partially rejected impurities away from the growth front. It is known that protein growth solutions are frequently contaminated by higher order oligomers of the native protein that form spontaneously. Whether these oligomers are preferentially incorporated and, if so, how their presence might poison the growth interface is still not clear. However, the results obtained by Garcia-Ruiz from growth in X-ray capillaries lend credence to the hypothesis that the diffusion field actually do make an effective filter for higher molecular weight contaminants and that their reduction does in fact improve the growth and quality of the crystal. Subsequently, it has been found that by paying more attention to the purity of the starting material, dramatic improvements can also be made in terrestrially grown crystals. . Progress such as this may ultimately prove to be the most valuable contribution the space experiments can make to the field of macromolecular crystal growth and structure-based drug design.

Another issue that must be addressed is why so many space experiments have failed to produce high quality crystals. One to two weeks is marginal for the growth of many systems and a number of flights have returned crystals that were simply too small for X-ray diffraction analysis. Longer duration flights, which will be possible on the ISS, should help this situation immensely, as evidenced by the successes McPherson has had with his GN2 dewar experiments on the Mir station. In addition, there seems to be some evidence that growth conditions that have been optimized for growth in normal gravity may not be optimum growth under purely diffusion-limited conditions and some tinkering with the growth conditions in space may be required. The problem of maintaining control over the many possible variables, such as the presence of trace contaminants, plagues space experiments as it does terrestrial experiments, making it difficult to get reproducible results. Finally, according to Vekilov's theory, growth of some systems in microgravity may actually move the growth mechanism from a region of stability to an unstable one. Unfortunately, the physical properties of only a few protein systems are known well enough to be able to apply this theory, and a rigorous test of the theory has not yet been performed.

Even though the success rate of obtaining superior crystals by growing them in space is only 20-25% for a given protein (i.e., one or more of all the space experiments with that particular protein produced better crystals than had previously been produced on Earth), the scientific and industrial interest has been very high. Guest Investigators from a number of research foundations, medical schools, and pharmaceutical industries have committed their own resources to participate in the program. It should be understood that although these Guest Investigators do not pay NASA to fly their experiments, neither do NASA pay them for their efforts. They commit their own time and travel expenses as well as provide the highly valuable purified proteins to support the experiment. The

scientific output has also been impressive. The bibliography (see Appendix) cites a total of 283 publications, 211 of which appeared in refereed journals that deal with the background, flight preparation, flight results and their applications.

Electro kinetic Separation

Even though the flight experiments were hampered by equipment problems, it is fairly clear that enhanced throughput from a continuous flow electrophoresis device can be achieved in a microgravity environment by the use of more concentrated samples and wider spacing between the walls of the flow channel. However, increasing the sample concentration exacerbates the electrohydrodynamic effects caused by the mismatch in conductivity and dielectric constant between the sample stream and the buffer curtain, which tends to degrade the resolution. Understanding these effects may lead to the development of more efficient continuous flow electrophoresis machines for terrestrial use, but it appears unlikely that the gain in efficiency would be sufficient to justify carrying out such separations in space unless they were done in conjunction with materials that were already in space (e.g., products from some cell culture or fermentation process). The bibliography cites a total of 31 related publications, which include 19 journal articles.

Electrofusion

Although there have been only a limited number of space experiments (mostly rocket flights) to investigate the advantages of using microgravity in the creation of hybridomas and hybrid plants by electrofusion, the results look encouraging. The role of gravity in the process is clearly not understood, but given that the process seems to benefit from space, more research to understand the process is certainly merited. The bibliography cites 9 related publications including 6 journal articles.

Commercial Biotechnology

The WCSAR ASTROCULTURE™ effort is more of a technology development than a scientific endeavor. However, it has produced some very useful spinoff products such as their closed plant growth system that allows complete control of the growth environment, their proprietary water and nutrient delivery tubes as well as their air humidification /dehumidification systems for use in plant nurseries, and their efficient LED light source for plant growth and other medical applications. Their work on the use of microgravity for transgenic plant alterations is intriguing since the role of gravity is not understood in the process, but as in the case of electrofusion, it apparently is important and needs to be understood. The bibliography cites 10 related publications (no journal articles).

The BioServe effort is extremely broad based scientifically and is carrying out an extensive research program to catalog how various organisms respond to the microgravity environment with the goal of exploiting those characteristics they find useful for commercial purposes. Many of their findings, such as the accelerated growth

of certain organisms, enhanced production of cell products, enhanced enzymatic activity, etc. in microgravity are surprising and are not understood from simple fluid modeling of gravity effects in living organisms. Their academic collaborators at the University of Colorado, Boulder, and Kansas State University in Manhattan, Kansas have published a very impressive total of 265 papers, 160 of which appeared in peer reviewed journals.

Economic and Societal Impacts

Of all the NASA-sponsored microgravity endeavors, the Biotechnology effort offers by far the greatest promise of economic and societal benefit. Structure-based drug design, which requires improved methods for crystallizing biomolecular materials, has the potential to produce pharmaceutical compounds with fewer side effects. In today's highly competitive, cost-sensitive drug market, macromolecular crystallography can help pharmaceutical manufacturers bring exclusive, proprietary drugs to market faster and with significantly lower development costs. Therefore, any improvement in obtaining the crystals of interest that NASA can make, either in space or on the ground, translates into significant potential cost and health benefits. Crystals grown in space have already contributed to the direct solution of several protein and viral structures and to the refinement of many others. Some of the more promising drugs under development, in which space played a significant role, are summarized below:

- Pharmaceutical companies had been searching for way to control the release of human insulin so that diabetics could take fewer injections and have a more constant supply. One promising binding agent turned out to be toxic to humans. Space grown crystals provided the clue as to what was going on and led to a solution of the problem.
- Factor D is a protein that often stimulates the immune system to overreact from the trauma following open heart surgery. A particularly large crystal of this protein grown on USML-1, when merged with other data, provided the structural information. Drugs to block this protein are in Phase II clinical trials and may be available by 2001.
- Space grown crystals of Glyceraldehyde 3-phosphate dehydrogenase (GAPDH), an essential enzyme in the parasite that is responsible for Chagas' disease, were instrumental in refining this protein. Drugs based on the structure of this molecule are in pre-clinical trials.
- NAD-synthetase is a target for a wide spectrum antibiotic under development that pre-clinical trails have shown to be effective against anthrax, pseudomonas, and flesh eating bacteria. Space grown crystals played a role in obtaining its structure. A crystal grown on STS-95 improved the resolution from 1.6 Å to 0.9Å. These data should prove useful to help improve knowledge of the active site if it becomes necessary to adjust the design of the drug that is presently being tested.

The NASA-sponsored Center for Macromolecular Crystallography now employs more than 100 Scientists and engineers working on crystal growth, structure determination, and the next generation of flight experiments. They collaborate with 37 universities and have 21 industry partners that contribute over \$2 million per year in direct funding. There are now 4 spin-off companies (BioCryst Pharmaceuticals, Inc., Ibbex Pharmaceuticals, Inc. and Diversified Scientific, Inc., in Birmingham and New Horizons Pharmaceuticals in Huntsville) that have been created as a result of the NASA-sponsored work in this area.

BioCryst uses data from the space experiments to help design new structure-based drugs. Presently, they are developing drugs to treat cutaneous T-cell lymphoma (in phase I/II human clinical trials), psoriasis (in phase I/II human clinical trials), stroke and certain complications of open heart surgery (preclinical trials), viral influenza (preclinical trials), and AIDS (preclinical trials).

Ibbex has used the protein structures developed initially by the Center for Macromolecular Crystallography to develop drug for cystic fibrosis, bacterial vaginosis, and Chagas' disease, all of which are in preclinical trials. Chagas' disease is a devastating parasite disease that affects more than 18 million people in South America and 150,000 in the US. The high resolution data from the malic enzyme crystal obtained in the glovebox experiment on USML-1 played a major role in obtaining the structure of this protein.

Diversified Scientific is commercializing the improved crystallization techniques based on the knowledge gain from the space experiment. This equipment will allow other pharmaceutical companies to improve the crystals they grow in the laboratory in order to further stimulate the use of structure-base drug design.

Some of the technological benefits that has come from the other NASA-sponsored Commercial Space Centers that work in biotechnology, BioServe and WCSAR, have already been discussed. Their work on utilizing microgravity to improve the process of transgenic plant alterations could have significant societal and economic benefits by producing food crops that mature faster. BioServe's work on controlling the production of lignin in wooded plants could also have a major impact on the building as well as the pulp paper industry.

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