INTERNATIONAL ATOMIC ENERGY AGENCY
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INTERNATIONAL CENTRE FOR THEORETICAL PHYSICS
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SMR/382- 30

WORKSHOP ON SPACE PHYSICS:
"Materials in Micorgravity"
27 February - 17 March 1989

"Transparent Model Experiments on the Separation of Monotectic Alloys"

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The Separation of Binary Alloys with Miscibility Gap in the Melt

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Abstract

Different mechanisms contributing to separation of monotectic metals are considered. The main reasons for the separation regularly found under microgravity conditions are wetting and spreading, capillary forces and Marangoni convection. Several transparent model experiments performed in the KC-135, in sounding rockets (TEXUS 7 and 9) and in Spacelab-D1 (WL-FPM-04) are discussed in detail.

1 Introduction

This paper is concerned with various attempts to produce finely dispersed mixtures of monotectic alloys under microgravity conditions as well as with the theoretical interpretation of the results obtained. There exist several hundreds of such metallic pairs and many of them hold out a prospect of practical application. Microgravity experiments hitherto have been flown with aluminum/indium, aluminum/lead, lead/zinc, bismuth/zinc and a few other systems /1-11/. Aluminum/lead, for instance, is a most promising material for producing bearings. Tests with sputtered samples have revealed excellent quality. Sputtering, however, is even more expensive than space production.

Fig. 1a shows the finely dispersed mixture as expected from experiments under microgravity conditions, whereas Fig. 1b shows a real result from an experiment in a SPAR rocket /2/. SPAR stands for the US microgravity sounding rockets (<u>Sp</u>ace <u>A</u>pplication <u>R</u>ockets), which were cancelled after six successful flights in the early seventies. The corresponding German program

TEXUS (Technologische Experimente unter Schwerelosigkeit) has, on the contrary, been expanded and has had about sixteen very successful flights. Looking at Fig. 1 we have to ask ourselves: What went wrong with the expectations and which mechanisms caused the obvious separation under microgravity conditions?

Fig. 2 shows a phase diagram of a monotectic pair of metals, namely the miscibility gap of aluminum/indium /12/. If these two metals are melted and heated to a temperature above 830°C, their melts mix without any restriction on composition. On the other hand, when a mixture of 20 percent indium in 80 percent alumimum is cooled down below 810°C, the melt separates into two phases: An aluminum-rich phase and an indium-rich phase. The composition of these two phases during further cooling down follows the consolutal curve limiting the miscibility gap, until at 660°C aluminum solidifies from the aluminum-rich phase. The indium-rich phase, which still contains a small amounts of aluminum, does not solidify until the temperature has come down to 156°C.

During cooling under terrestrial conditions, gravity usually dominates the separation: The heavier component, the indium-rich phase, sinks to bottom. Fig. 1b indicates, on the other hand, that cooling under microgravity conditions does not bring much advantage: Indium has been found outside and aluminum inside the flight-sample. A similar separation has been found with the other systems mentioned above. (In most of the sounding rocket experiments performed with monotectic alloys, the samples have been heated to a temperature above the miscibility gap before launch and have been cooled down to solidification during the six minutes of microgravity available. Two experiments have been flown applying acoustic mixing /13-15/.)

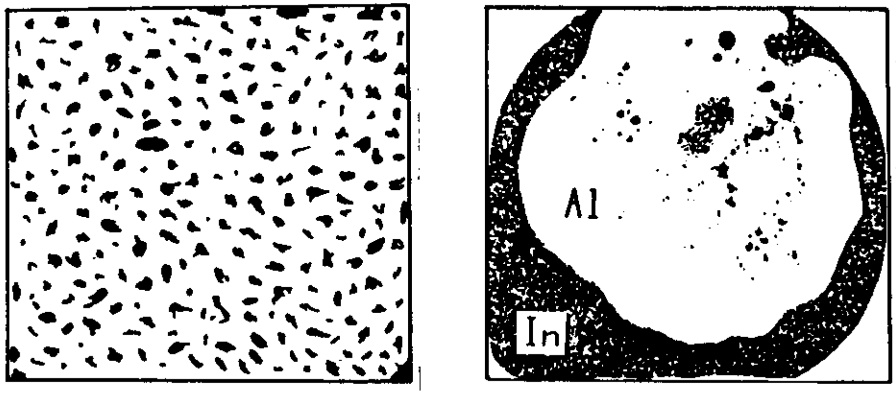


Fig. 1: Expected and obtained separation of monotectic systems under microgravity conditions

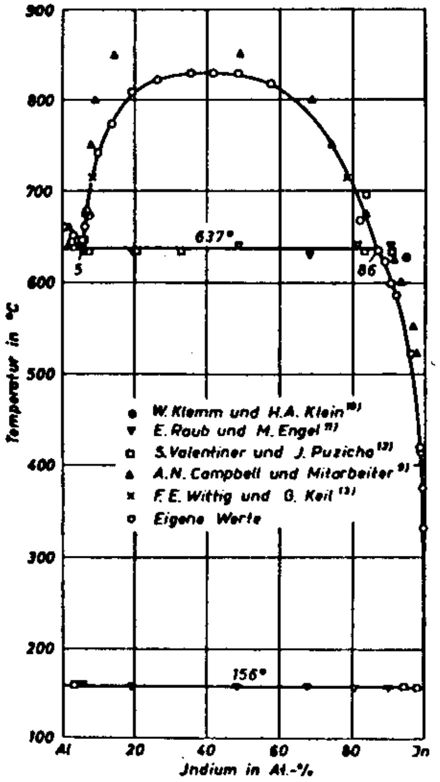


Fig. 2: The phase diagram of the monotectic system aluminum/indium

Fig. 1b suggests that wetting effects play a dominant role under microgravity conditions. There are other mechanisms strongly contributing to the separation as well. Table 1 presents a list of sixteen relevant mechanisms /16, 17/.

Table 1: Mechanisms of Separation. Those typed in capital letters are considered to be more important than those typed in lower case letters.

free convection	(gravity-dependent)
sedimentation	(gravity-dependent)
DIFFERING TENDENCIES OF COAGULATION	
DIFFERENCES IN WETTING	
DIFFERING INTERFACE TENSIONS	
CAPILLARY FORCES	
INTERFACE (MARANGONI) CONVECTION	
DIFFUSION GROWTH	
momentum due to oriented growth	
momentum due to directed diffusion	
minimization of internal energy	
Ostwald ripening	
REPULSION BY SOLIDIFICATION FRONT	
VOLUME SHRINKING DURING SOLIDIFICATION	
VOLUME CONTENT OF MINORITY COMPONENT	

Two of these, free convection and sedimentation, do not apply in microgravity. Some are important ones, and others less so. There are fast ones like wetting and slow ones like Ostwald ripening. However, in order to produce finely dispersed mixtures (if this is possible at all), one has to be aware of all of the effects listed.

2 Spreading along Edges

In the edges of the container shown in Fig. 1b there exist gas volumes. The contact angle between the indium-rich melt and the container, which consists of alumina, is about 150°. It is only roughly maintained during indium solidification (see Fig. 3).

Wetting of the container wall by aluminum is even worse than by indium. As a result, any gas enclosed in a container in microgravity spreads along its edges.

From the capillary equation the general law has been derived that a fluid must spread along a solid edge, if half the dihedral angle α of the solid edge plus the contact angle γ of the fluid is less than 90° /17/. (By a fluid, one means either a liquid or a gas.) With $\alpha = 45°$ and $\gamma = 30°$, this condition is obviously satisfied for the gas volume enclosed: Capillary forces or wetting effects cause the general shape of the solidified sample shown in Fig. 1b.

Capillary effects, in addition, are fast effects. For proving wetting effects it is sufficient to have a few seconds of microgravity, i.e. such effects can be studied during the parabolic flight of an aircraft or even during free fall in a drop tower. Figs. 4 and 5 show the results of two wetting experiments performed during parabolic flights of the KC-135 aircraft over the Gulf of Mexico /19, 20/. Fig. 4 shows a transparent cell with 40 mm x 20 mm x 10 mm, which also has been used for studying separation in two TEXUS flights (see Section 8). During the KC-135 flights in June 1985 this cell was filled with 2/3 methanol and 1/3 cyclohexane and was observed both by a normal camera and a video camera. Methanol is slightly denser than cyclohexane (ρmethanol = 0.79 g/cm^3, ρcyclohexane = 0.78 g/cm^3), such that during normal flight (1 g) and upward acceleration (1.8 g) of the aircraft methanol rested on the bottom of the cell. However, methanol wets the container walls much better than cyclohexane does. Therefore, during reduced gravity (10^{-3} g) methanol rapidly spread along the container's edges. From the stopwatch mounted next to the container it is obvious that wetting takes less than 10 s.

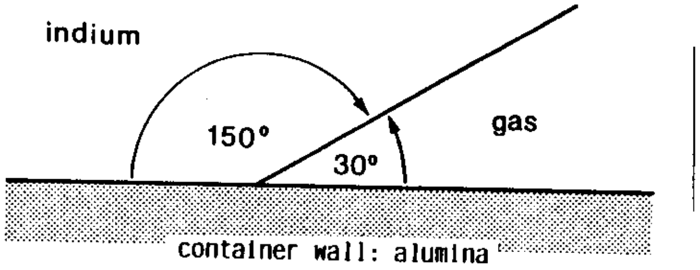


Fig. 3: The contact angle of indium versus gas at the container wall of alumina

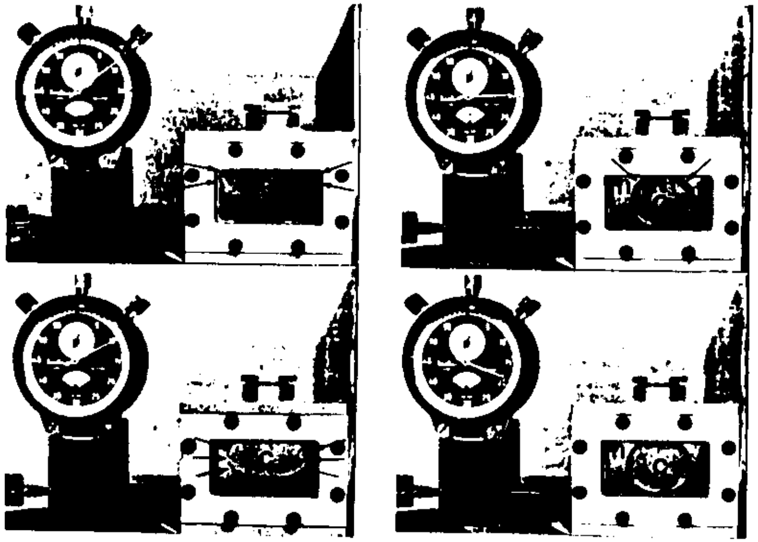


Fig. 4: The spreading of methanol around cyclohexane under reduced gravity (during a KC-135 flight)

Fig. 5 shows a cylindrical 80 mm x 10 mm x 10 mm container of plexiglas. It was filled to 1/8 with fluorinert, a liquid with density 1.8 g/cm^3 and a very low contact angle γ on glass, plexiglas and several other solids. The series of pictures taken during the KC-135 flights in May 1988 show that spreading along the edges of the container is very fast /21/. After about 10 s the final configuration is reached.

3 Volume Balancing Systems

The message from these wetting experiments is that any gas volumes should be strictly avoided during experiments on the separation of monotectic alloys. On the other hand, there is volume expansion during heating and melting and volume shrinking during cooling and solidification, with a few exceptions (e.g., bismuth and antimony). Thus, in order to avoid gas volumes it is necessary to use a volume balancing system. Up to now various systems have been tested, see Table 2.

Table 2: Systems used or considered for volume balance

pistons squeezed by quartz, metal or graphite springs
non-wetting crucibles with conical ends
non-wetting capillaries made from ceramics
non-wetting conically or stepwise narrowing capillaries
viscoelastic springs based on glas bulbs
porous materials surrounded by flexible materials
volume balancing on the basis of memory metals

Fig. 6 shows the volume balancing system based on capillary pressure which was used during melting and resolidification of a copper sample in the Spacelab-D1 experiment WL-IHF-06 /22/. The copper sample contained 1 volume percent of molybdenum particles that were 2 µm to 3 µm in size. It was intended to observe the displacement of the molybdenum particles by the melting and the solificiation fronts of copper. The melting and solidifi-

Fig. 5: The spreading of fluorinert in cylindric containers with rhombic cross-section under reduced gravity (during a KC-135 flight)

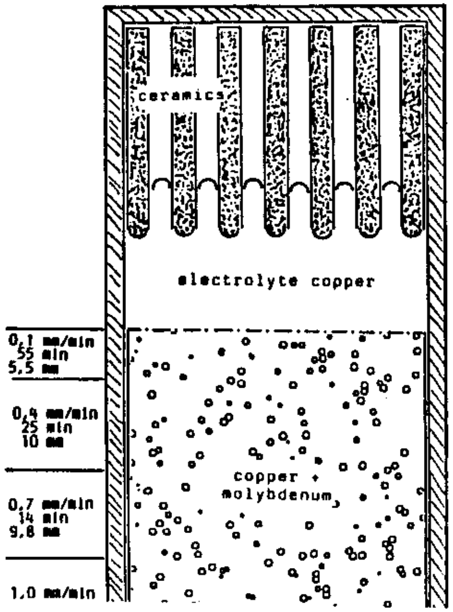


Fig. 6: The capillary volume balancing system used in the Spacelab-D1 experiment WL-IHF-06

cation rates were chosen within the theoretical range for pushing particles. Due to time delays during setting up of the isothermal heating facility (IHF) and again during installation of the gradient cooling block, the slow melting of the sample starting at the side of the volume balancing system had to be cancelled. The sample became rapidly molten from the centre to both ends instead.

The capillary volume balancing system consisted of a cylinder of magnesium silicate 10 mm in length, into which 19 holes, each 1 mm in diameter, had been drilled. Since molten copper has a contact angle $\gamma > 90°$ on magnesium silicate, it assumes a convex meniscus within the holes. It penetrates into the holes during melting, but is pushed back by capillary pressure during solidification. Due to rapid melting of the sample from its centre, the volume balancing system was not able to pick up the molten copper in the beginning, but perfectly fullfilled its tasks once the melting front had reached the upper end of the sample. Due to small differences in the hole's diameters, the copper melt was pressed out of the thinner holes prior to the thicker holes. Thus, in future microgravity experiments holes with conically or stepwise narrowing diameters will be used.

4 The Influence of the Cartridge Material

Once gas volumes are properly excluded the contact angle between the two metallic melts and the cartridge material gains primary importance. As a rule, the component with the lower contact angle nucleates at the wall first. This is what the Gibbs theory of nucleation claims. Once a droplet of the component with the lower contact angle has formed, it spreads out along the cartridge wall. In particular, it spreads along the edges.

As already stated, in Fig. 1b indium wets the cartridge material better than aluminum does. The contact angle of indium on the cartridge material alumina is less than 90°, if the second fluid is aluminum, see Fig. 7a.

The effect of the contact angle gains credibility from the complete wetting argument. There is theoretical reasoning that close to the consolutal point of a pair of immiscible liquids, the interface tension between one component and the container wall becomes so small that Young's boundary condition on the contact angle has no solution, and the other component completely wets the container wall instead. This is even truer between a liquid and the corresponding solid: spreading of a liquid on the corresponding solidification front is most likely. We will reraise this argument in Section 10.

The wetting situation is reversed if the cartridge is made from titanium nitrate, see Fig. 7b. In that case aluminum wets the cartridge wall better than indium /23/. Systematic investigations on the influence of the cartridge material on the separation of monotectic alloys are still missing.

5 Coagulation

Another important class of mechanisms has to do with coagulation. Once a droplet of the minority component has been formed, it gives rise to a concentration gradient, a region of depletion, through which further material diffuses towards the droplet. The droplet grows. The question has to be raised, to what extend do the two droplets of the minority component with a small spacing take notice of each other. They may mutually lose surface energy by coagulation and joining to form a single droplet. However, this either requires an external action, e.g. Brownian motion or a macroscopic convective flow, or a direct interaction via an overlap of the depleted regions.

The effects of pressure and convection on coagulation are exhibited in Fig. 8. It shows the transparent cell, which was filled with methanol and cyclohexane during the KC-135 flights in June 1985. The cell was shaken by hand before one of the parabolas following the wetting experiment shown in Fig. 4, such that an emulsion of cyclohexane in methanol was caused. During the rest of the 1g-phase and the 1.8g-phase, the less-dense cyclohexane droplets moved upwards and rapidly coagulated. However, in reduced gravity, during the 20 s to 30 s with 10^{-2} g shown in Fig. 8, both convection and coagulation fully came to rest /19, 20/. The message from this experiment is that coagulation is strongly reduced under microgravity conditions. Two droplets of the same component may swim close to each other without any mutual notice.

The reservation must be stated that coagulation in a transparent system like methanol/cyclohexan is not necessarily representative of coagulation in metallic systems like aluminum/indium, etc. Transparent organic liquids consist of oriented molecules which, along a surface, may assume preferred orientations. It has been observed, for example, that methanol droplets in cyclohexane have a much stronger tendency to coagulate than cyclohexane droplets in methanol, see Section 10. A methanol/cyclohexane interface may look different from each side. Metallic melts, on the other hand, are made up from atoms which are stripped off their electrons. The miscibility gap between two metallic melts usually arises from the differing electronic states, by the valence bands and conduction bands not fitting to each other, or by the differing atomic diameters. This hampers quantitative comparison of coagulation in transparent organic and metallic systems.

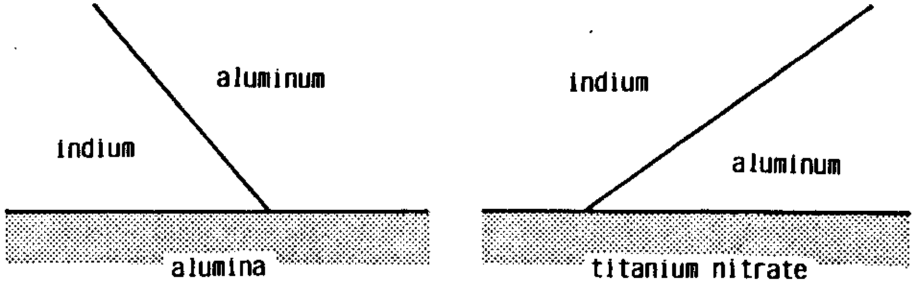


Fig. 7: The contact angles of indium versus aluminum at alumina and titanium nitrate

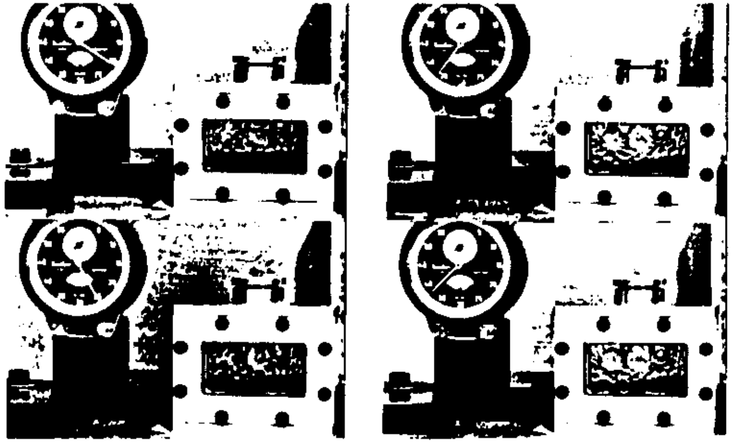


Fig. 8: The reduction of coalescence of cyclohexane droplets in methanol under reduced gravity (during a KC-135 flight)

6 Effects Supporting Coagulation

There are several hypotheses on the effects caused by the mutual overlap of the depleted zones. On a molecular basis one may argue that a liquid mixture exhibiting concentration gradients assumes a state of lowest energy if there is maximum attraction between atoms of the same species, i.e. if the surfaces of equal concentration (the isopleths) assume a spherical shape. This hypothesis treats regions with different concentration like different liquids and the isopleths like interfaces with infinitesimal interface energy. If the isopleths around two growing droplets contract to spheres, they bring the droplets enclosed into contact and thus favour coagulation /24/.

Another hypothesis makes use of Ostwald ripening and Marangoni convection. A small droplet generally has a higher solubility than a large one. The former tends to increase the concentration of the respective component in the outer liquid, whereas the latter tends to decrease it. There arises a concentration gradient directed from the small to the large droplet. The growing of the latter at the cost of the former is known as Ostwald ripening. It depends on diffusion and therefore generally is slow in comparison to the other mechanisms discussed in this paper. However, it strongly gains weight if looked at in connection with Marangoni convection: Once the large droplet notes the concentration gradient caused by the small droplet, it migrates towards the latter due to Marangoni convection. This is a fast mechanism. (Marangoni convection will be discussed in detail in the next Section.) And, of course any stirring in the liquid due to coagulation further favours coagulation.

Coagulation becomes more likely the higher the volume percentage of the minority component becomes /17, 25/. This is a matter of statistics, of randomly filling a given volume with spherical droplets. Fig. 9 shows cross-sections of random distributions of drops with equal diameter. In the upper row, which corresponds to 5 volume percent, most droplets are singles, in the middle row corresponding to 10 volume percent are a lot of pairs and triples, in the lower row corresponding to 20 volume percent singles form the minority. In Fig. 10 the percentage of droplets (particles) which exist as singles, pairs, triples, etc. is plotted versus the volume percentage. At 8 volume percent less than 50 percent of the droplets exist as singles.

In Figs. 9 and 10 random distributions of droplets were assumed without regard for the fact that droplets growing in demixing melts are more uniformly distributed than random: Close to a growing droplet, the probability of a new nucleus is strongly reduced.

7 Marangoni Convection

One of the most important contributions to the separation of monotectic alloys, Marangoni convection, has been mentioned only marginally. It represents the main topic through the rest of this paper.

Whenever a gradient in interface tension along a fluid interface arises, the regions with high interface tension pull more strongly than those with low interface tension, such that a shear force parallel to the gradient of the interface tension results. A gradient in interface tension may be caused by temperature differences, concentration differences or electric or magnetic fields. One uses the terms thermocapillarity, solutocapillarity and electrocapillarity, respectively. The original effect observed by Marangoni /26/, the formation of regular convection rolls, as when wine or cognac creeps up a glass and again slides down, is basically solutocapillarity.

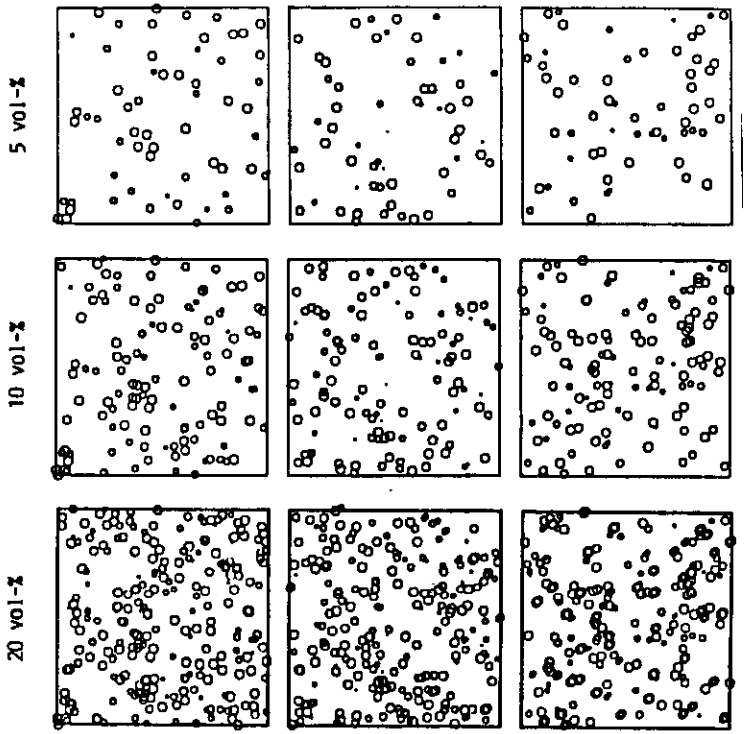


Fig. 9: 3-dimensional random distributions of spherical particles. top: 5 vol-%; centre: 10 vol-%; bottom: 20 vol-%

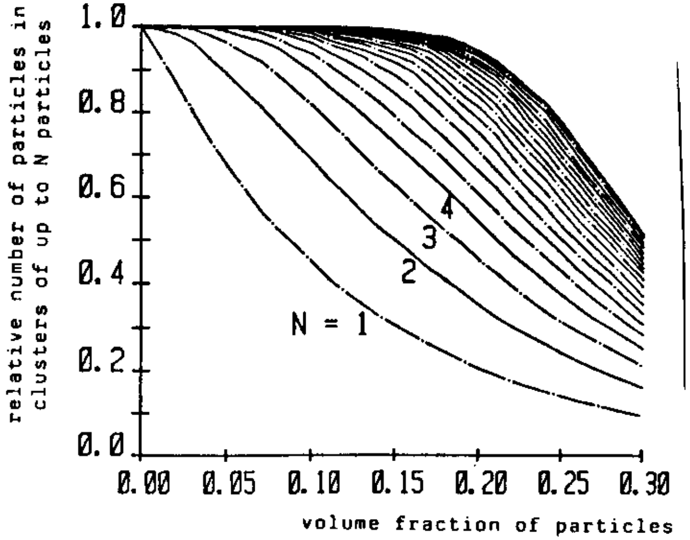


Fig. 10: The relative number of multiples arising in a random distribution of spherical particles

Gradients in temperature or concentration usually give rise to density gradients, such that Marangoni convection always appears together with gravity driven convection under terrestrial conditions. Under microgravity Marangoni convection is the only type of natural convection left. During the separation of monotectic alloys it causes a migration of droplets from cold to hot regions. The migration of droplets actually is from regions with high to regions with low interface tension. This means a decrease in energy of the fluid system. The velocity v of migration is proportional to the negative gradient in interface tension times the droplet's radius over the dynamic viscosities of the fluids involved. By expanding the flow field around the migrating droplet in terms of spherical harmonics one obtains /27/: $v = (-\nabla\sigma)R/(2\eta_o+3\eta_1)$, where η_o and η_1 are the dynamic viscosities of the outer fluid 0 and the droplet 1, respectively. Fig. 11 exhibits the flow field in a coordinate system moving with the droplet. The gradient in interface tension is made up of both the thermal and the solutal gradient.

A cartridge containing melts of two monotectic metals necessarily has to be cooled from the outside. The first droplets of the minority component arise at or close to the container wall. They experience the temperature and concentration gradient from the wall to the centre, i.e. Marangoni migration of the growing droplets is directed inwards. The distribution of components shown in Fig. 1b (and that observed with all other samples solidified under microgravity conditions) clearly suggests that Marangoni migration together with wetting plays a dominant role.

There is continuing discussion whether it is more favourable to cool a sample fast or to cool it slowly. Fast cooling causes strong temperature and concentration gradients and strong Marangoni migration during a short time. During slow (so-called isothermal) cooling Marangoni migration is slow as well, but solidification takes a long time. The considerable reduction of coagulation nevertheless is a strong argument in favour of the latter procedure.

8 Sounding Rocket-Experiments with Cyclohexane/Methanol

In order to discriminate between the different mechanisms listed in Table 1 and in particular to demonstrate Marangoni migration of droplets, two TEXUS-experiments with the transparent model system methanol/cyclohexane have been performed /28, 29/. Fig. 12a shows the phase diagram of this pair of liquids. The consolutal temperature is 46°C, which to achieve is easier than the 800°C to 1200°C required for melting and mixing monotectic alloys. The disadvantage in doing model experiments with transparent systems is that the thermal diffusivity is lower than that of metals by two orders of magnitude. The Prandtl number is correspondingly higher. With the penetration of cooling into a transparent sample being slower, the droplets have more time for growing to sizes at which Marangoni convection becomes effective.

A great advantage of the system methanol/cyclohexane for terrestrial investigations is that the densities of these two liquids are very similar (see Section 2). The densities may even be matched by adding deuterated cyclohexane, C_6D_{12} with density 0.89 g/cm^3. With the temperature gradients of the densities being similar as well, it is possible to severely reduce gravity effects also during terrestrial investigations into separation.

Methanol (as are all alcohols) is very hydrophilic. Fig. 12b shows the dependence of the miscibility gap on a possible water content. When working with methanol/cyclohexane the water content has to be carefully watched.

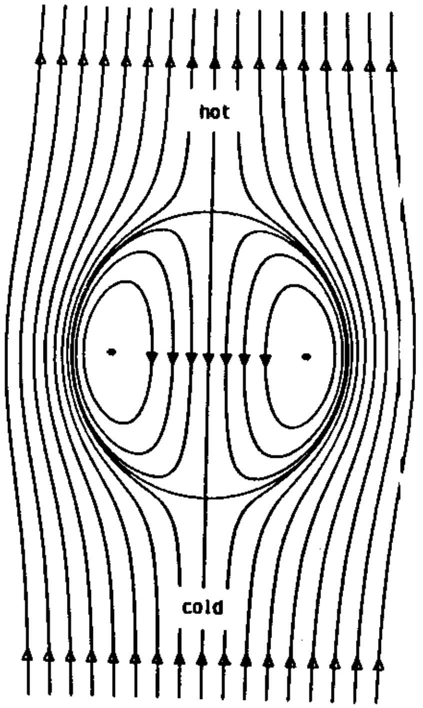


Fig. 11:
The flow field inside and outside a droplet undergoing Marangoni migration in a temperature field

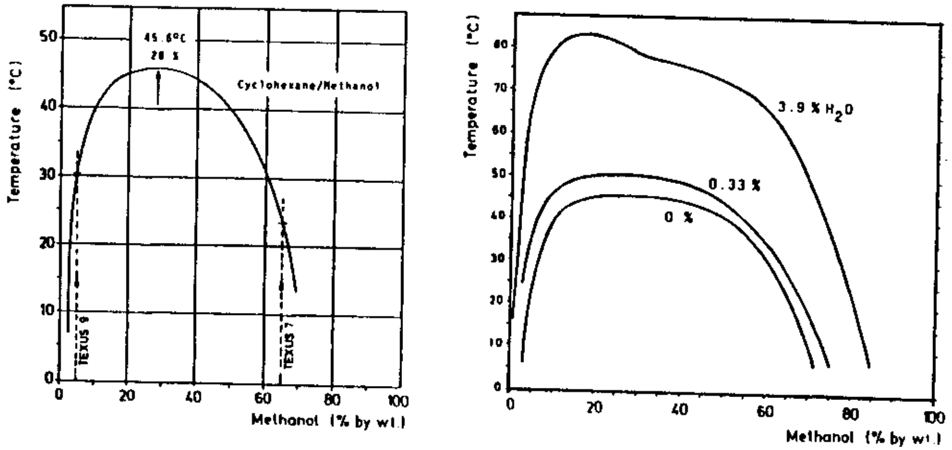


Fig. 12: The phase diagram of the transparent system cyclohexane/methanol

a) The mixtures used in missions TEXUS-7 and TEXUS-9

b) The dependence of the miscibility gap on the water content

Fig. 13 exhibits the principle of the TEXUS experiments performed. Before launch of the rocket the liquid mixture is heated to a temperature above the consolutal point, to 50°C. After beginning microgravity it is unidirectionally cooled to 5°C and -10°C in missions TEXUS-7 and TEXUS-9 respectively. The right-hand side shows the penetration of cooling within 40 s. Only close to the bottom, within a region of about 5 mm, does a temperature gradient exist. After 160 s the region of penetration has doubled, and the temperature gradient has fallen correspondingly. Even after 360 s, at the end of the microgravity time, cooling has not really proceeded to the upper region of the cell. In the region between 15 mm and 20 mm, the temperature is still close to 50°C.

The left-hand side shows the growing of droplets of the minority component in the cooled region, their upward migration due to thermocapillary and solutocapillary convection. If they move faster than the cooling penetrates, they shrink in the upper, still-hot region.

Fig. 14 shows the TEXUS flight cell, which was also used during the parabolic flights in June 1985. On top and on bottom heaters are mounted for heating the liquid mixture to 50°C and to achieve complete mixing before launch. After beginning microgravity, the lower heater is switched off and the meander cooling system is used instead. The movie camera was directed towards the lower centre part of the test cell. Magnification was 1:1, i.e. a section with 10 mm x 7 mm was observed.

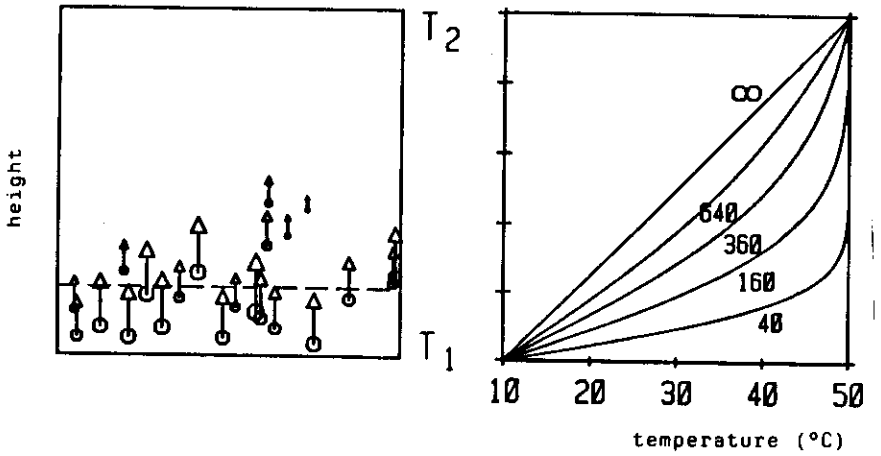


Fig. 13: Growth, migration, and shrinking of droplets during unidirectional cooling

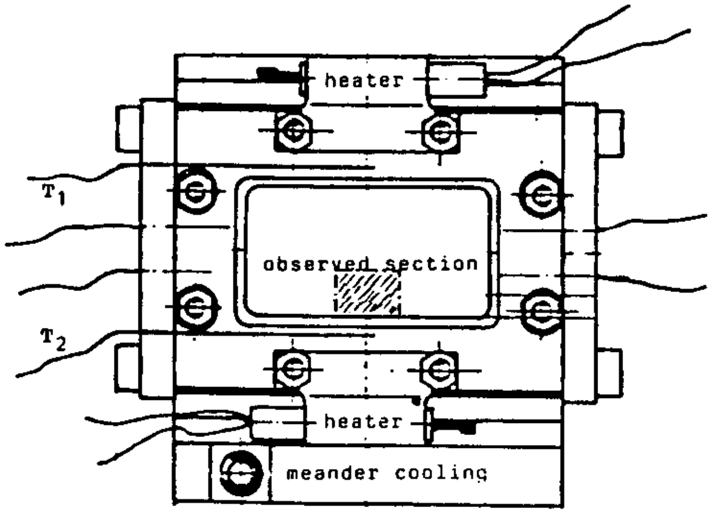


Fig. 14: The TEXUS flight cell with the heaters and the cooling device

9 The TEXUS-7 Experiment

In mission TEXUS-7 the mixture used was 35 percent cyclohexane in 65 percent methanol. This composition was selected according to reference experiments on the ground, which showed only a very few cyclohexane droplets for lower concentrations. In the opposite case, for higher concentrations, the number of cyclohexane droplets became so large that transparency of the cell was lost.

The flight film shows an extending fog zone at the cell bottom during the first 30 s of cooling. The fog is formed by tiny cyclohexane droplets. The fog front moves upwards as the cooling front penetrates, see Figs. 15 and 16. After 35 s cyclohexane droplets of about 50 µm to 200 µm appear, which rapidly migrate to the fog front. They have grown at the cooled cell bottom and now undergo Marangoni migration in the upward temperature gradient. At the cooling front, which is nearly identical with the fog front, migration stops due to the vanishing temperature gradient. Subsequently, the number and size of the migrating particles rapidly increase and the fog zone becomes partly transparent again, see Fig. 16.

The migrating cyclohexane droplets carry along coolness from the bottom of the cell to the cooling front. This additional transport of coolness causes the cooling front to move faster than predicted by the heat conduction equation: There arises a moving droplet front, see Fig. 15. The droplets move in the temperature gradient which they carry along in a collective manner. The situation is even more complex since the droplets also bring along concentration. According to the consolutal curve, their cyclohexane equilibrium content at the cooled cell bottom is higher than at the cooling front, where they dissolve cyclohexane

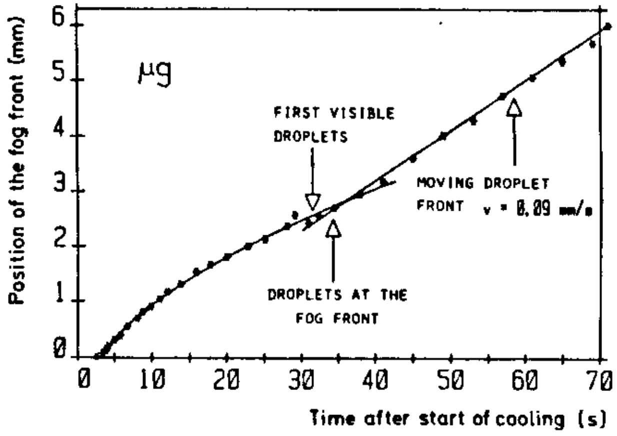


Fig. 15: The position of the fog front caused by cyclohexane droplets during mission TEXUS-7

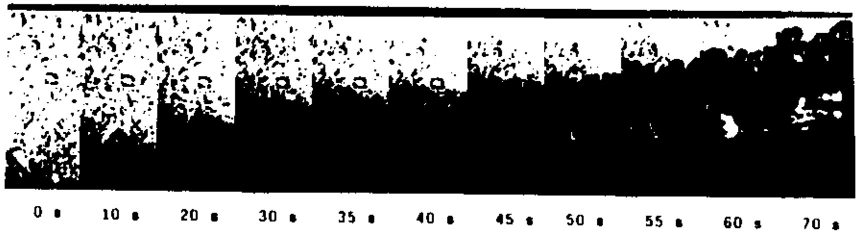


Fig. 16: The motion of the fog front and Marangoni migration of cyclohexane droplets during mission TEXUS-7

or else take up further methanol. The droplets thus increase the cyclohexane concentration at the cooling front. The decrease in interface tension from bottom to top is due to temperature and concentration as well.

Due to these transport effects droplet migration in the TEXUS-7 experiment is faster than in the 1g-reference experiments. In the latter experiments the cyclohexane droplets enter the upper hot region due to buoyancy, where their dissolution does not further decrease the interface tension: It is zero anyway. The theory of the joint droplet migration in a temperature field has been tackled only recently /30-32/.

10 The TEXUS-9 Experiment

In order to verify the results obtained in the TEXUS-7 mission and to study the additional effects of a solidification front (volume shrinking, wetting), the concentrations of methanol and cyclohexane were reversed in the mission TEXUS-9. The 1g-reference experiments showed that a reasonable, but still-not-too-high, number of methanol droplets could be obtained by applying 5 percent methanol in 95 percent cyclohexane. The melting temperature of cyclohexane is 6°C. The cooling temperature thus was lowered to -10°C. Fig. 17 shows the beginning of cooling in the TEXUS-9 experiment. A fog of methanol droplets arises (instead of the fog of cyclohexane droplets observed in the TEXUS-7 experiment) which moves upwards with the speed of the cooling front. About 10 s after the beginning of cooling a second, darker fog front arises. It moves upwards faster than the first one and passes it after about 15 s. This fog front turns out to be formed by small methanol droplets undergoing collective Marangoni migration. After about 30 s larger methanol droplets migrate from the bottom to the cooling front. They may even pass it by 1 mm to 2 mm. This is particularly true for some large droplets, which migrate along the same trail. The transport of coolness and concentration causes local changes of the temperature and concentration field.

After 36 s, when the cell bottom assumes the solidification temperature of cyclohexane, the distribution of the migrating methanol droplets becomes more uniform. The average droplet size decreases. This can be ascribed to a change in the wetting conditions. The migration of many droplets along the same trail obviously has been caused by nucleation centres at the cell bottom, by small scratches or even dirt. At these positions large methanol droplets grow, detach and undergo Marangoni migration. However, when the nucleation centres are blocked by the solidification front of cyclohexane, a more uniform growth of methanol droplets and a more uniform Marangoni migration results. As stated in Section 2 (see Fig. 4), methanol wets the cell bottom better than cyclohexane does. This means that methanol droplets generally must grow to a larger size in order to detach than cyclohexane droplets. This changes completely, when the cell bottom gets covered with solid cyclohexane. Cyclohexane now wets the bottom much better than methanol. Even complete wetting of liquid cyclohexane at solid cyclohexane may happpen, even though the solidification temperature and concentration of cyclohexane are far away from the critical point.

Due to the fog zone formed by methanol droplets, the solidification front of cyclohexane is not actually visible in the TEXUS-9 flight film. Its position was calculated theoretically and verified by the 1g-reference experiments. The final position of the solidification front became visible during reentry of the payload, when there was strong stirring and the cell became transparent again. The position still agreed with the calculations.

The TEXUS-7 and TEXUS-9 films reveal several additional effects. There is a much faster coagulation of methanol droplets in the cyclohexane matrix than of cyclohexane droplets in the methanol matrix, in spite of the fact that in both cases the same interface tension is working. Another effect noticed was the formation of regular convection rolls during the TEXUS-9 mission. They evolve more and more clearly after about 3 min and may be ascribed to a correlation between the growth front of cyclohexane and the nucleation and migration of the methanol droplets.

11 The D1-Experiment WL-FPM-03

In order to reduce the observed contributions to separation, two approaches have been suggested:

- to lower heterogeneous nucleation at the crucible by changing the material of the crucible, or preferably, by containerless processing. This procedure bears the risk of increasing capillary effects and Marangoni convection along the free surface.
- to cool very slowly in order to achieve uniform nucleation within the sample and to minimize Marangoni convection. The latter may, however, be jeopardized by the much longer cooling time required.

The D1-experiment WL-FPM-03 was a first step toward a free fluid surface and toward slow cooling as well /33/. A free liquid column between coaxial disks was established and the mechanisms causing mixing during active heating and demixing during passive cooling were observed. A closed liquid container adapted to the Fluid Physics Module (FPM) was developed, see Fig. 18. The two circular disks holding the column are concave in order to avoid high flow velocities during liquid injection. Separation of the disks is achieved by rear plate rotation of the FPM. The liquid

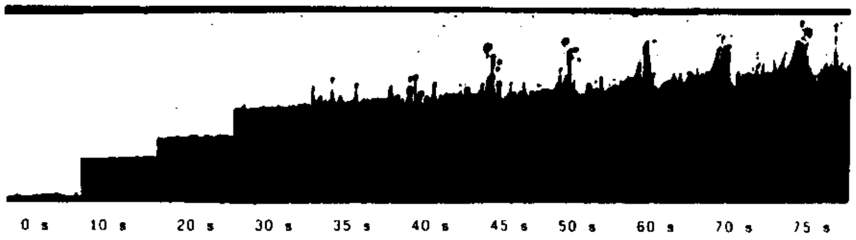


Fig. 17: The motion of the fog front and Marangoni migration of methanol droplets during mission TEXUS-9

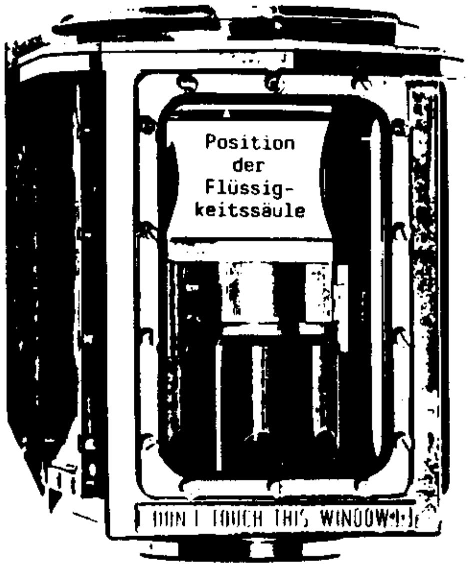


Fig. 18: The flight-cell of the experiment WL-FPM-03

volume required for achieving a cylindrical column is simultaneously injected from the reservoir. The front disk contains the heater whose operation is redundantly controlled by two thermistors. Cooling of the liquid column is passive by heat radiation and conduction.

For safety reasons it was not possible to use the liquid system cyclohexane/methanol in Spacelab-D1. Methanol is toxic, its flammability temperature is 11°C, its boiling temperature is 65°C. Benzylbenzoate/paraffin oil was chosen instead. The miscibility diagram of this liquid pair, which was obtained by volumetric methods, is shown in Fig. 19.

The surface and interface tensions of the two liquids and their contact angles with aluminum and teflon have been determined by the sessile drop method. The sum of the interface tensions benzylbenzoate/paraffin oil plus paraffin oil/air turns out to be much smaller than the interface tension benzylbenzoate/air, such that spreading of paraffin oil along the free fluid surface of the column was expected. In addition, benzylbenzoate wets the supporting aluminum disks better than paraffin oil. Therefore, this component would either form two separated spherical segments at the disks, or an inner liquid column in an outer liquid column made up from paraffin oil. In view of the low contact angle of both liquids on aluminum, the supporting disks had sharp edges. They were equipped with teflon rings, which also served as seals during storage, launch and landing. Several wetting tests in parabolic flights with KC-135 were performed with this design.

With the configuration of the two liquid components being unknown during heating of the column and diffusion being very slow, Marangoni convection is a necessary requirement for mixing and unmixing. The temperature coefficient of the surface tensions paraffin oil/air and benzylbenzoate/air is about 10^{-4} N/mK. Depending on the temperature profile this may lead to flow velocities of up to 30 mm/s along the free fluid surface and to migration of bubbles up to 1 mm/s. This suggested using 20 min for heating and 40 min for cooling of the column.

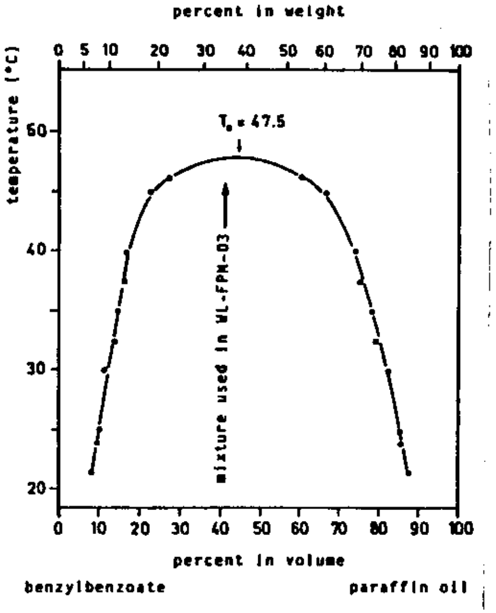
12 Results of Run A of WL-FPM-03

Fig. 20 shows the different steps of WL-FPM-03 and the actual position of Run A in the D1-timeline. Real-time TV and on air-to-ground loop were available for 46 minutes. A fruitful cooperation between payload specialist Ernst Messerschmid in the Spacelab and the experimentator on ground resulted. Both sides pointed out important phases of the experiment and discussed steps to be taken.

The most important observations of the experiment were:

- Thermal and solutal Marangoni convection along the free fluid surface during heating. The fog regions resulting from mixing migrate to the lower, cold end of the column with speeds up to 3 mm/s. This speed, which is about 20 % of the estimated value, further decreases in the course of heating, when the stationary temperature profile is reached (Fig. 21).

- Downward Marangoni convection along the free fluid surface causes on upward counterconvection inside the column, which takes along the bubbles. The latter eventually rupture when they reach the surface. The inclusion of bubbles was by no means planned, but turned out to be very helpful for observing the flow velocity and proving the effectiveness of bubble expulsion by Marangoni convection (Fig. 21).



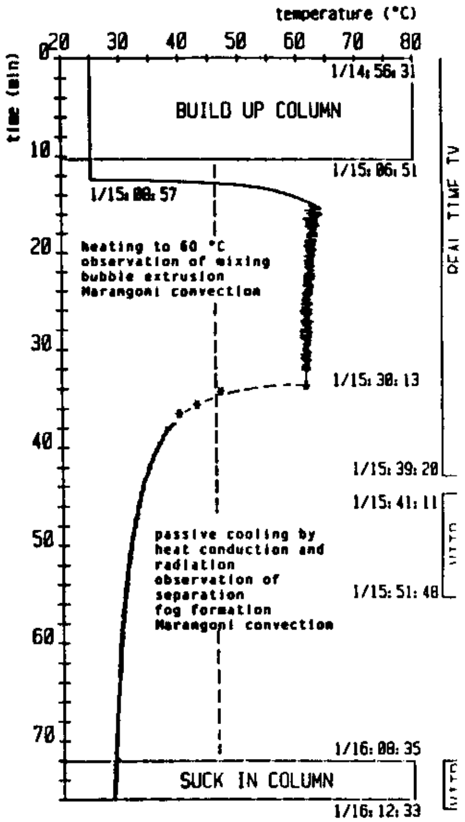


Fig. 19: Miscibility diagram of the transparent model system benzylbenzoate/paraffin oil

Fig. 20: The steps of Run A and its schedule in the D1-timeline

- Spreading of benzylbenzoate along the heated disk. This spreading, which is due to complete wetting of aluminum by this component, brings about the expected axisymmetric configuration of the liquid column. The speed of spreading and the dynamic contact angle clearly decrease with the approach of the symmetric configuration (Fig. 22).

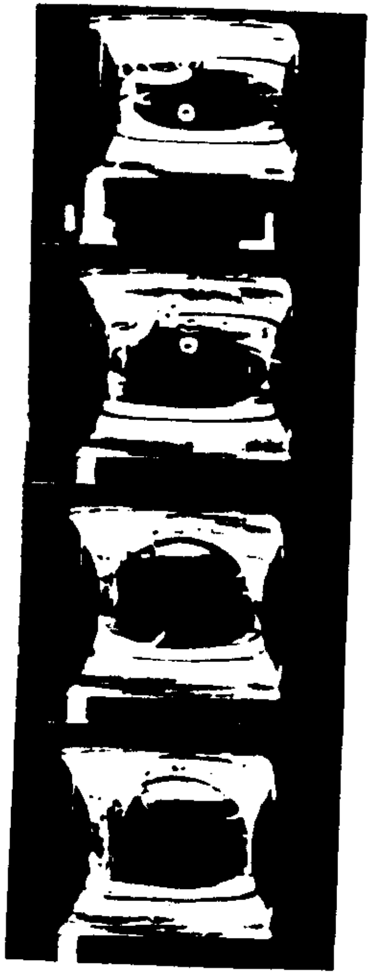
- Capillary effects together with a Rayleigh instability. The inner column of benzylbenzoate, which is caused by the preceeding spreading, broke into two spherical segments at the supporting disks (Fig. 23). Breakage started at the relative height $H/2R = 0.8$ and the relative neck radius $R_n/R = 0.5$ of the inner column, a much larger neck radius and liquid volume than is predicted by theory.

- Continuing mixing due to diffusion and Marangoni convection (Fig. 24) until full dissolution of the spherical segment of benzylbenzoate at the upper disk.

- Progressive demixing during the cooling phase. As in the beginning of the heating phase there arose fog regions which moved downwards due to Marangoni convection. The demixed region eventually extended over the upper half of the column (Figs. 25, 26).

The final recovery of the column into the reservoir worked as intended.

Since the liquid mixture spread across the teflon rings surrounding the supporting metallic disks, the liquid column formed an unduloid rather than a cylinder. The neck to disk ratio was $R_n/R = 0.7$. This shape of the liquid surface represents a convex-concave lense. Radially all distances are enlarged, whereas axially all distances shrink. Fig. 27a shows the image of a



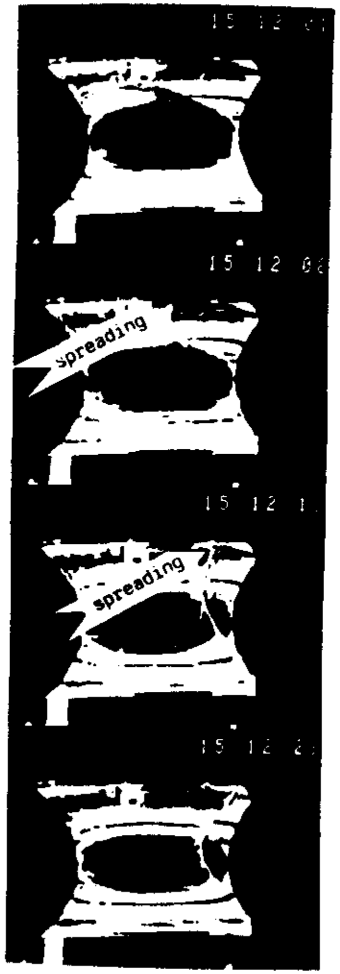
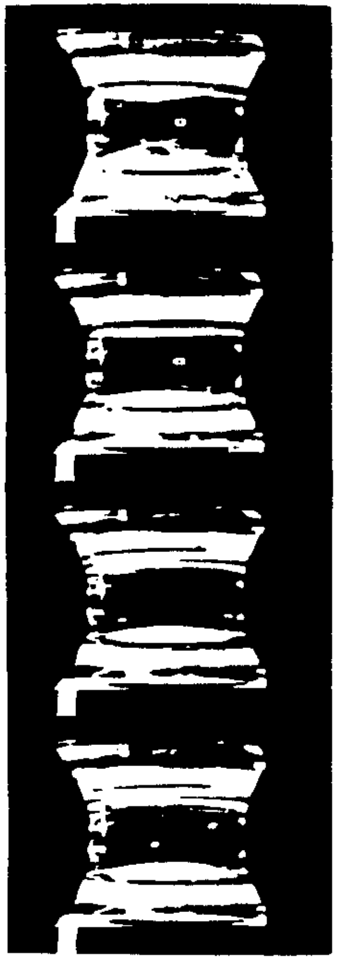


Fig. 21: Downward Marangoni convection of fog regions and upward migration of bubbles in the beginning of heating

Fig. 22: The spreading of benzylbenzoate along the upper, heated disk

Fig. 23: The breakage of the inner column of benzylbenzoate in the outer column of paraffin oil due to a Rayleigh instability



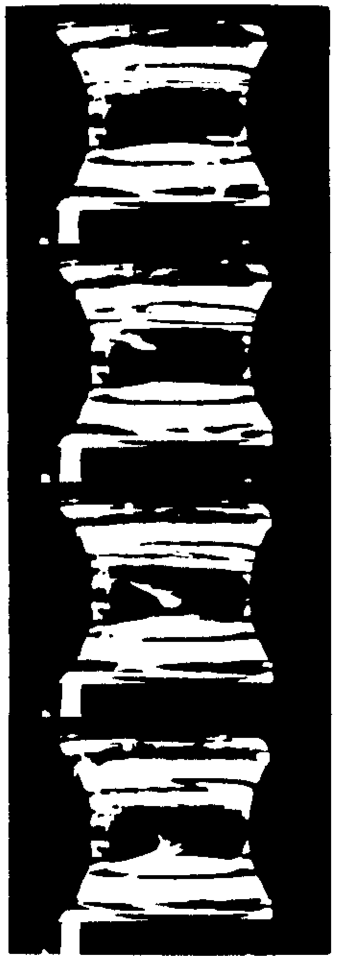


Fig. 24: Continuing mixing and bubble migration in the end of the heating phase

Fig. 25: Marangoni convection of fog regions in the beginning of the cooling phase

Fig. 26: Progressive demixing in the upper half of the liquid column

quadratic grid in the meridian plane. The dash-dot lines in Fig. 27b are the images of circles in the meridian plane, the full lines those of circles on the supporting disks. Comparison with the video pictures reveals that the dark horizontal rings repeatedly visible within the column are images of the non-illuminated concave disks.

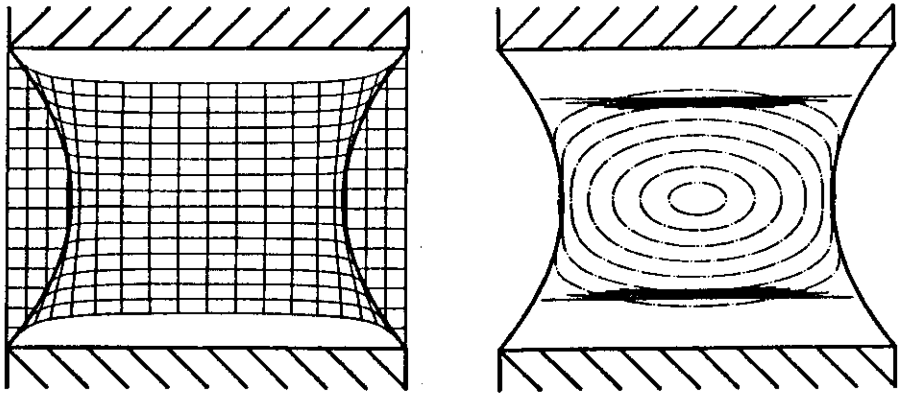


Fig. 27: Ray tracing in the unduloid obtained:

a) The image of a quadratic grid in the meridian plane

b) The image of circles in the meridian plane (dash-dot lines) and the image of circles on the supporting disks (full lines)

An analysis of the accelerometer data, which have been recorded within the Werkstofflabor, exhibits several obvious correlations. Some accelerations of about 5×10^{-3} g cause vibrations of the video camera or, rather, of the video picture. No response at all can be detected of many other perturbations with the same order of magnitude. The frequency dependence obviously is important. The typical resonance frequencies of the column considered have the order of magnitude of 1 Hz, which means that they are not resolved by the peak detection method used in the Spacelab.

13 Results of Run B of WL-FPM-03

Following the successful performance of Run A and the realization of many expected and unexpected effects, a second run was enabled by the science coordination team. The heater temperature was increased to 75°C in order to speed up Marangoni convection and to distinguish reproducible from irreproducible mechanisms. Due to insufficient coordination between JPL/Houston and GSOC/Oberpfaffenhofen only the last seconds of the heating phase, the cooling phase and the recovery of the column were recorded.

The first video pictures were rather surprising: Although the column was heated for 20 min and a stationary temperature profile resulted, there existed a clear interface between the two liquids. Paraffin oil formed a large asymmetric drop on one side of the column made up by benzylbenzoate. The contact line between this drop and the column is clearly visible in spite of the gradual shrinking of the former. Considering that the temperature at the upper disk equaled 75°C, the column assumed the critical temperature of 47°C at about 40 percent of its height. Therefore neither an interface tension nor an interface should exist in the upper half of the column.

Opposite to the drop's position, the column of benzylbenzoate shows a fog region extending between the two disks. In the course of cooling and demixing this fog region becomes narrower and clearer and assumes a line structure caused by Marangoni convection. During recovery, the column of benzylbenzoate breaks into two spherical sections at the supporting disks. Due to the volume reduction once more a Rayleigh instability has arisen.

14 Conclusions

Both runs of WL-FPM-03 clearly demonstrated the importance of capillarity, stability, and spreading during mixing and unmixing of liquids exhibiting a miscibility gap. In spite of being effective during short time intervals only, these mechanisms essentially affected the final distribution of the two liquids.

Marangoni convection along the free fluid surface turned out to be lower by at least one order of magnitude than had been expected from the reference experiments on the ground. This may be ascribed to

- a contamination of the liquid mixture due to its storage and transportation for several months. Contamination regularly lowers surface and interface tensions

- opposite effects of temperature and concentration on the surface tension due to the component having the lower surface tension (paraffin oil) getting enriched on the cold side.

If the latter explaination is correct the advantage of a free fluid surface, the suppression of heterogeneous nucleation, will not generally be balanced by the disadvantage of stronger Marangoni convection. In that case containerless processing appears commendable also for metallic alloys.

The liquid system benzylbenzoate/paraffin oil used in the Spacelab experiment WL-FPM-03 exhibits a much lower interface energy than the liquid system cyclohexane/methanol used in the TEXUS missions. This, together with the much lower cooling rate. strongly reduced Marangoni migration of the growing droplets. There was little contact and coagulation of these droplets, such that foggy regions lasted for the full cooling time. This suggests that slow cooling may reduce demixing also in the case of metallic alloys. Since Marangoni migration favours contact and coagulation and the speed of migration increases with droplet size, Marangoni migration exponentially speeds up demixing. It therefore appears advisable to reduce it by means of soluble additives.

15 Future Research

The realization of finely dispersed mixtures of monotectic alloys has recently led to a joint research program between German universities and industrial companies. The aim is to further elucidate the conduct of separation, and, by systematic variations, to enable production of compound materials /34/. In this context it is intended

- to quantitatively study the different mechanisms of separation in terrestrial and microgravity experiments,
- to improve the theories of the different mechanisms and to check them experimentally,
- to develop a general theory of separation, which fully integrates the hitherto isolated results,

- to produce samples with high technical potential, like aluminum/lead for bearings, silver/nickel for electrical contacts, aluminum/lead/zinc for superconductors.

A vital step will consist of measuring and collecting from literature (in dependence of temperature and concentration)

- the surface tensions and interface tensions between different metallic melts and their contact angles with the crucible material,
- dynamic viscosities, diffusion coefficients, thermal diffusivities (thermal conductivity and heat capacity),
- phase diagrams and thermodynamic data like enthalpy and entropy of mixing.

These basic studies will be paralleled by

- further investigations into transparent model systems and their compatibility with metallic systems,
- theoretical and experimental studies into homogeneous and heterogeneous nucleation and the effect of fast cooling,
- studies into droplet growth due to coagulation, Ostwald ripening and the mutual overlap of depleted zones,
- the effect of the volume content of the minority component, which appears to render differing droplet sizes in different systems,

- reconsideration and extension of existing theories of Marangoni migration inclusive of the inherent temperature and concentration transport,

- TEXUS and Spacelab experiments on the particle transport by a solidification front,

- theoretical and experimental studies on the influence of additives, which by affecting the inherent interface tensions and contact angles change the conduct of the separation.

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