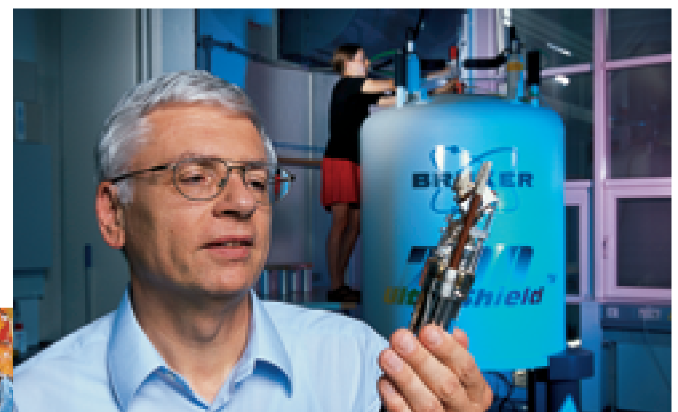
Hard Work on Soft Matter

What do silk blouses, diskettes, and the membranes of living cells have in common? All three are made from soft matter: if individual molecules are observed, they appear disordered, however, on a larger, supramolecular scale, they form ordered structures. Disorder and order interact, thereby affecting the properties of the soft material. At the MAX PLANCK INSTITUTES FOR POLYMER RESEARCH *in Mainz and of* COLLOIDS AND INTERFACES *in Golm, scientists are focussing on this "soft matter".*



Hans Wolfgang Spiess with the probe-head of a NMR spectrometer (in the background)

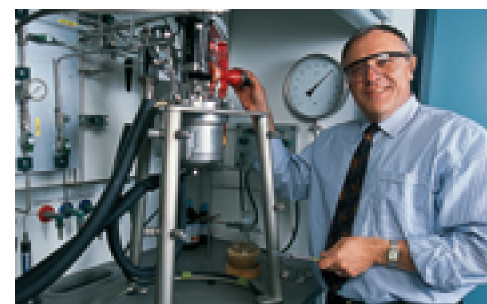
„The cultural development of mankind is inseparably linked to the development of new, high-performance materials," says Prof. Hans Wolfgang Spiess, Managing Director of the Max Planck Institute for Polymer Research in Mainz; "it is not without reason that we speak of the Stone, Bronze or Iron Age." After this hard prehistoric past, we have now arrived in the age of soft matter: leather and natural fibres such as wool and silk or paper have been important economic commodities for centuries. And over the past fifty years, synthetic materials have embarked on an unparalleled triumphal march. Even information, which today frequently tends to be described as one of the most important raw materials, can only be generated, stored, and disseminated on a massive scale via artificial soft materials. Without light-sensitive coatings, there would be no microchip - and nor would there be diskettes, CD-ROMs, and videotapes, which are all made from coated plastics.

PHOTOS: WOLFGANG FILSER

It is nature, however, which has really perfected the art of creating soft matter. For billions of years, since the existence of life on earth, highly complex structures have originated from soft matter. The ways in which they arise are typically very elegant; the molecules organise themselves into complex cellular membranes which perform vital functions. Or they form extremely strong fibres that give plants shape and support. Biologists, chemists, material scientists, and physicists are trying to understand and emulate nature's incredible structures and production processes.

"The term soft material relates to the states of aggregation which lie between the ordered structure of solids and the highly disordered gas. These are typically supramolecular structures and colloids in liquid media. Particularly complex examples occur in the area of biomaterials," says Prof. Reinhard Lipowsky, director of the "Theory" Division of the Max Plank Institute of Colloids and Interfaces in Golm near Potsdam (MPIKG). Prof. Hans Wolfgang Spiess says, "Soft material reveals its complex combinations of properties due to the precise interplay between areas of order and disorder of the building blocks." And Prof. Helmuth Möhwald, director of the "Interfaces" department at the MPIKG adds, "To put it in rather simplified terms, soft matter is unusual because its structure is determined by several weaker forces. For this reason, its properties depend very much upon environmental and production conditions."

The answers given by the three scientists are typical in that their perspectives all differ. Some scientists define soft matter as being almost liquid, whilst others also include very strong materials such as natural or artificial fibres. However, whether liquid or solid – there are properties that all forms of soft materials have in common. What the three scientists have outlined in



Klaus Müllen also achieves mastery over polymers in the form of a football...

technical terms (explained on page 60) can be roughly expressed in layman's terms as follows:

- Firstly, the molecules form a much more disordered structure in soft matter than the atoms or molecules in the crystal lattice of a true solid. On the other hand, they do not swirl around in a disordered fashion as they do in a gas. Soft materials are also not true liquids, although areas that are liquid can affect their properties significantly.
- Secondly, the structures of soft matter are both flexible and stable.
- Thirdly, soft matter can form supramolecular structures spontaneously through self-organisation. Without this particularly interesting characteristic, no natural organism would be able to exist or survive.

At the Max Planck Institute for Polymer Research in Mainz, the scientists are investigating a type of soft material without which life – and our everyday existence as we know it today – would be unimaginable: natural and artificial materials consisting of polymers. Polymers are large molecules in which hundreds or thousands of similar, fundamental building blocks, the monomers, are strung together. Every artificial material, from the contact lens to the most modern woven fibre, is a polymer. Nature conceals an even more tremendous variety of polymers. The carriers of the hereditary information of life, the nucleic acids, are polymers. Proteins are polymers, as is the starch from potatoes or grains. Polymers also lend animal tissue elasticity and stability in the form of collagen fibres. Other polymers, cellulose fibres, perform this function in plant tissue.

In Mainz, two research groups are playing a special role in the analysis of the properties of polymers. They are developing increasingly precise instruments which allow them to look into the world of molecules. Thanks to these tools, the researchers in the laboratories are far better able to understand the properties of the polymer molecules. They are in a much better position to investigate materials and develop new ones with greater accuracy than previously.

One of these tools is computer simulation. The experts in this area are members of the "Theory of Polymers" research group, headed by one of the Institute directors, Prof. Kurt Kremer. The scientists construct the simulated polymer material from individual, virtual molecules and calculate its properties. Soft matter is still too complex to be easily reproduced in all its detail on a computer. But the theorists are able to simulate the most important properties amazingly well (Fig. 1). In the process, they are learning how the individual molecules behave in the polymer. Despite the simulation being virtual, they are able to zoom into the molecular processes that take place in real polymers.

For the computer simulations to be able to draw a realistic picture of the material being studied, they must also be provided with reliable data from measurements in order to have firm ground to stand on. This data is being provided by the "Polymer Spectroscopy" research group under Hans Wolfgang Spiess. Spectroscopy is the second tool for the developer of new materials. This is where the new samples are investigated using various analytical methods. NMR (Nuclear Magnetic Resonance) spectroscopy is particularly important. NMR makes use of the fact that many atomic nuclei behave like tiny magnets. Placed in a strong magnetic field, these atomic magnets can be excited by an NMR spectrometer to receive and transmit electromagnetic signals. From this, the scientists are able to deduce how the material is constructed. Spiess and his colleagues have developed new solid state NMR methods, which are particularly suitable for explaining the structure of polymer materials.

By working with the theorists and spectroscopists, the material scientists in Mainz are able to experiment very effectively. Besides, pure research, applied research – the aim of which is to develop marketable products – is also important at the Mainz Institute. The scientists at Mainz are even able to further develop conventional mass-produced plastics so that they get completely new properties; for example, pipes made from polyethylene, the artificial material from which plastic bags are made.

One successful example of industrial co-operation by the Max Planck Institute for Polymer Research is the development of an artificial material for renewing pipes in collaboration

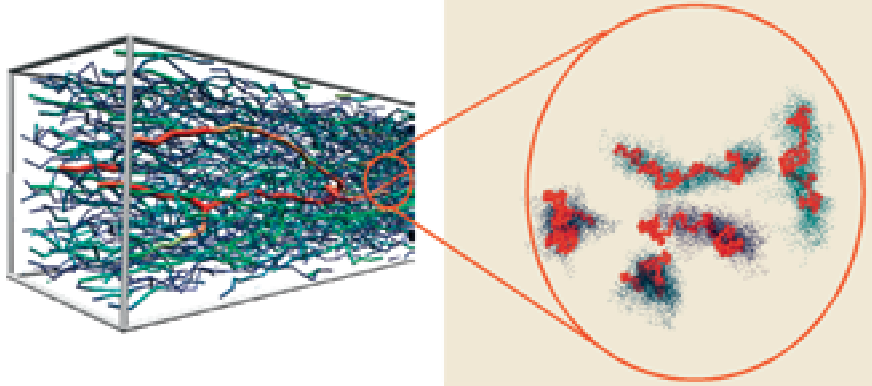


Fig. 1: This three-dimensional "snapshot" from a Mainz computer simulation shows how the long polymer chain molecules move in a polymer melt.

Fig.: MPI for Polymer Research

Fig. 2: The pushed-in repair tube before inflation.

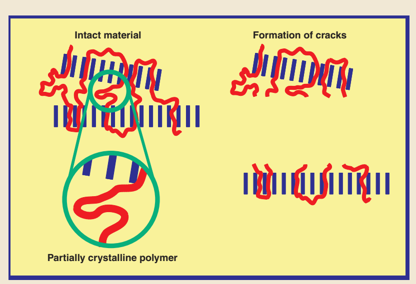
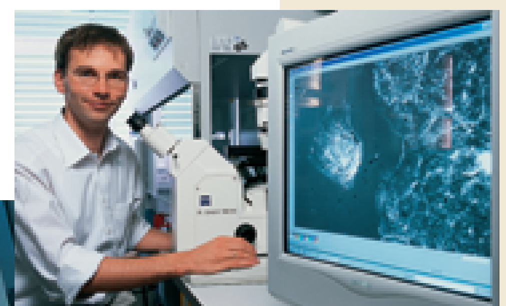


Fig. 3 left: The long chain molecules (red) hold the crystalline (blue) together in the undamaged plastic. Right: Under stress the chains tear and a crack opens.

Joachim O. Rädler is head of the polymer physicists in Mainz. His group is studying the interaction between molecules in order to use them for building nano-systems, and is hot on the trail of nature's fascinating strategies, one of which is the self-organisation of molecules into complex structures.



Kurt Kremer is head of the Theory Division in Mainz.

with a subsidiary of the former Hoechst Corporation. Who hasn't had big problems with pipes at one time or another? And not just with ceramic or metal pipes: plastic pipes can also crack or become porous. "American pipe manufacturers have already had to pay a billion US dollars in compensation, a figure equal to the Max Planck Society's annual budget", Hans Wolfgang Spiess mentions in passing.

A FIELD OF RESEARCH IN ITS INFANCY

When the French physicist Pierre-Gilles de Gennes was awarded the Nobel Prize for Physics in 1991, a scientist commonly described as the "father of soft matter" was honoured. He had made significant theoretical contributions to a young field of research that only became more defined in the eighties. Besides new theoretical models, development also progressed due to better measuring techniques and the growing capabilities of computers. This resulted in the scientists discovering that the properties of very varied and structurally complex materials all had a common factor: the interaction of order and disorder on a molecular level. Whether virtually liquid or very strong – these materials are always flexible. It was for this reason that they were christened "soft matter".

HIGH-TECH-PLUMBERS

His group made a significant contribution to the development of a product that cleverly simplifies the repair of gas and water pipes. It is a flexible polyethylene pipe. The repairers first push it, folded up, into the old pipe. Once it is in position, they inflate it – and that's it! The new pipe nestles up to the wall of the broken pipe, bridges leaky seals and cracks, thus sealing it completely (fig. 2).

Despite the incredible simplicity of this idea, it does impose strongly conflicting requirements on the plastic used; on the one hand, it must be very flexible, whilst on the other, it must be capable of withstanding great pressure. As it must not deteriorate with time over decades, flexibility creates a problem. Flexibility does in fact depend on high mobility of the molecules in the artificial material. For this reason, the molecules do gradually tend to give way under stress. The pipes age and can crack at places subjected to intense pressure.

The scientists in Mainz first had to establish how these cracks develop in the polyethylene material (PE) used. To this end, they developed a special NMR experiment that showed them what happens to the molecules during the ageing process. PE is a typical form of soft matter that owes its properties to the interaction between order and disorder. It consists of crystalline areas in which the long molecular chains of polymers lie highly ordered, just like spaghetti in a bag. Long chain molecules wind themselves round these crystallites, just like tangled knots of thread. They support the structure. Under stress – such as excessive pressure – these chain molecules can tear. If several neighbouring chains give way, a weak spot develops in the material. With time, these weak spots grow until cracks open up (fig. 3).

After the Max Planck scientists had explained the mechanism of ageing, the industrial scientists were able to make specific improvements to the artificial material by strengthening the chain compounds between the crystallites. The industry is now using the modified plastic to produce new, flexible pipes with a life up to fifty times longer than before.

Wolfgang Knoll, Mainz Materials Research Director, must, like all other scientists, conquer mountains of paperwork.

Fig. 4: Dumbbell-shaped graphite islands arrange themselves on a graphite surface. Two neighbouring islands are approximately 3 nm away from each other.

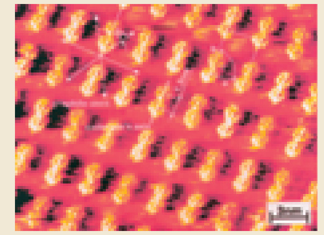


Fig. 5: How the Mainz chemists manufacture nano-objects: from the starting material, left above, blocks develop through differently controlled sources, which contain different nano-structures (yellow). Solvents dissolve the polymer block (blue) and release the nano-building blocks.

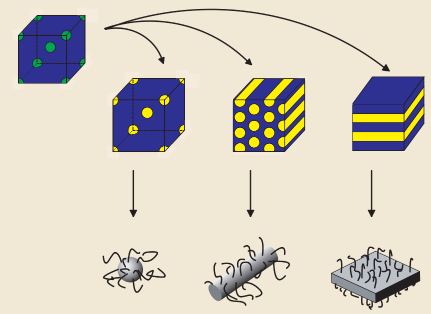
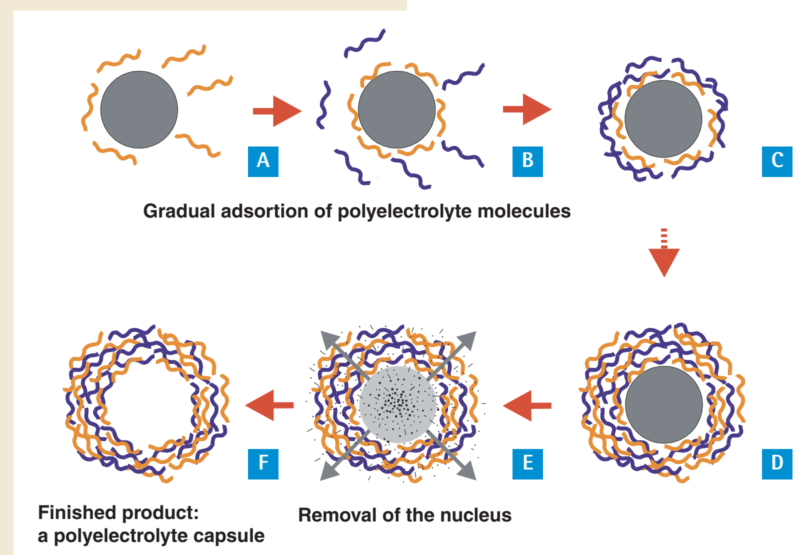


Fig. 6: A multi-layer nano-capsule is formed: the nucleus is coated with oppositely charged polymer molecules (red or blue) (A to D). Next, acid dissolves the nucleus (E), and the completed hollow capsule is left (F).



It may be that soft materials of the future will have completely new properties. For example, they might convert light into electric power. Solar cells have enormous potential for growth. Today they are made from silicon, a hard, brittle material with limited applications. If it were also to prove possible to manufacture solar cells in the form of light, pliable films, it would open up completely new areas of application.

SOLAR CELLS ON FILM

The research group headed by Prof. Klaus Müllen, another director at the Mainz Institute, is developing films from organic materials which are capable of converting light into electric power. The basic components of the new materials are carbon atoms in the form of graphite, which we commonly come across as soot or in pencils. The carbon atoms form honeycombed lattices in the graphite which can be easily pushed together. First the scientists synthesise tiny graphite islands on a graphite surface. These are in the shape of a dumbbell or a figure of eight. Fig. 4 shows the regular pattern formed by these islands on the surface.

Now the island structures develop remarkable behaviour: they stack themselves up into microscopic twin columns. These columns can convert the captured light into electric power. The shape of the columns is crucial to their efficiency. The scientists once again struck on the characteristic property of soft matter: a well defined "ordered disorder" in the stacks makes the columns such good electrical conductors that they are ideally suited for solar cells. This development is still in its early stages, but perhaps one day we will even wear jackets which are capable of charging mobile phones or Walkman batteries using solar power.

There is little that fascinates scientists more today than nano-objects, which measure just a few billionths up to several hundred billionths of a metre. Work on nano-objects is expanding our knowledge of the chemical, biochemical, and physical processes which are responsible for the diverse nature of our world. And yet, the scientists are only really just beginning to get into the nano-world (MAX PLANCK RESEARCH 3/2000). And it is therefore hardly surprising that today's research is sometimes reminiscent of small children at play: by playing around with building blocks, children "come to grips" with the world - by playing with tiny nano-building blocks, scientists become acquainted with and master the nano-world. Although even the manufacture of the nano-building blocks themselves is a challenge to today's scientific technology.

In collaboration with colleagues from the group led by Hans Wolfgang Spiess, Dr. Ulrich Wiesner, currently at Cornell University in the USA, has produced nano-objects such as these from organic/inorganic hybrid materials. Such materials are used to manufacture contact lenses, scratch resistant coatings, and dental fillings. They are based on two phases, which are mixed together. The first phase, termed "organic" in the chemical world, consists of long-chain polymer molecules. For the sake of simplicity we shall call this phase O. The other phase is "inorganic", and we shall call this phase A. A is formed from smaller molecules that contain metal atoms (aluminium) and a compound called hydrosilicon. Hydrosilicons consist of hydrogen and the basic element of sand, silicon. They are, incidentally, the inorganic counterparts of the hydrocarbons in organic chemistry.

Phase O is a soft material, whereas A is hard, like glass or pottery. In simplified terms, the clever synthesis process developed in Mainz is carried out as follows. First, the chemists dissolve phase O in an organic solvent, and add a given quantity of A. Then they condense the resulting composite to make it solid. Amazingly, self-organisation results in the formation of very regular nano-structures. Even more incredible: the shape of the structures can be precisely controlled by the mixing ratio of phases A and O. Provided that phase A is not dominant, a polymer block is formed. It contains the nano-structures produced from A and O. Depending upon the mixing ratio of the phases during synthesis, these can be spheres, cylinders or cuboid layers (fig. 5, above). In order to release these nano-objects, the chemists now only have to dissolve the polymer block (fig. 5, below).

Besides being minuscule, the Mainz nano-building blocks have another characteristic feature: long

Reinhard Lipowsky and his colleagues design tiny membrane machines.

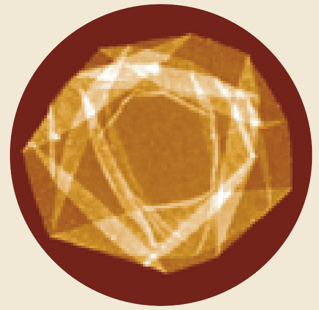


Fig. 7: Scanning force microscope photograph of a completed nano-capsule. This requires a vacuum in which the capsule caves into folds.

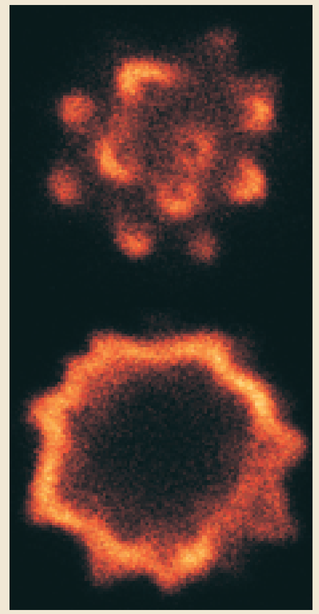


Fig. 8: Two sectional drawings through different levels of a capsule, created by coating a red corpuscle in the "thorn-apple form" (erythrocyte).

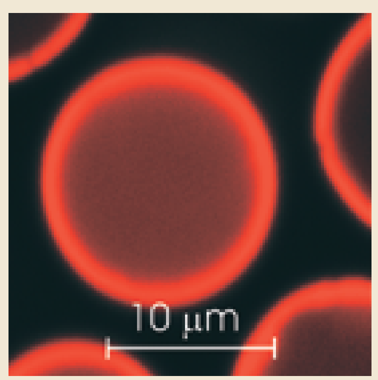


Fig. 9: These capsules measuring approximately ten micrometres (millionths of a metre) are filled with a polymer (red). Chemical reactions resulted in the formation of the polymer which was built up from smaller molecules that had penetrated the wall of the capsule.

chain molecules stand out from their surfaces like hairs. Who knows what surprises these hairs might have in store for us...

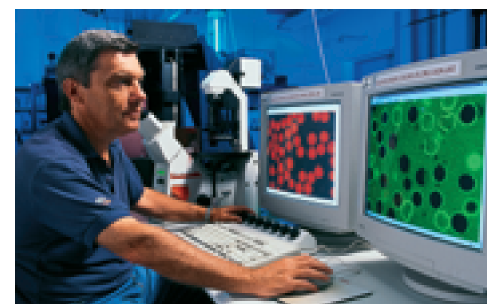
At the Max Planck Institute of Colloids and Interfaces in Golm, there is also close collaboration between experimenters and theorists from the chemical, physical and material sciences. Helmuth Möhwald's team are among the experimenters. They invented a modular system for nano-capsules, which can be used for nano-packaging. In recognition of this groundbreaking work, one of the young scientists involved, Dr. Gleb Sukhorukov, was awarded the 2.25 million Mark Sofja Kovalevskaja prize by the Alexander von Humboldt Trust (see page 94 of this edition). The manufacture of the Golm capsule is based on an idea, which is as irresistibly simple as it is experimentally demanding. The fundamental building blocks are microscopic nuclei. These can be inorganic particles, or alternatively polymer particles, crystals from a pharmaceutical agent or even biological cells. The researchers coat these nuclei with electrically charged polymer molecules, which are taken up in a solution. Once the first coating is completed, the resulting nano-capsule is put into a second solution with oppositely charged molecules. The molecules are attracted by the first coating and form a second layer. Using this method, the researchers are able to build up many alternately charged coatings like onions skins, thereby greatly varying the properties of the capsule.

What happens to the nucleus inside the capsule now? If it is not composed from the substance with which the capsule is to be filled, it must be removed from the capsule without it being destroyed. To do this, the scientists dissolve it into small molecules. The wall of the polymer capsule is in fact permeable to such small molecules and the capsule empties itself.

All that is left is the completed nano-capsule (Figs. 6, 7 and 8). The scientists at Golm can regulate the wall thickness of their hollow capsule with great precision to a billionth of a metre and can also greatly vary the chemical composition of the capsule wall. By this process, capsule walls can be formed which remain stable for years or, by contrast, can be made to readily decompose.

The permeability to different active substances can also be regulated. If, for example, the scientists vary the surfaces of the layers, they can cause certain chemical substances to accumulate within the capsule interior. The capsules fill themselves up, so to speak, with the desired active substance.

The nano-capsules even make it possible for the scientists in Golm to imitate the properties of biological cells in a simple way. In this case, it is a question of the outer layers of the cells acting as membranes to protect the interior of the cell. These membranes can make themselves permeable to certain substances. This is how they control the exchange of essential substances between the inside of the cell and the environment. To emulate this, the Max Planck scientists coat the walls of their nano-capsules with a double layer of lipid



Helmuth Möhwald and his department manufacture nano-capsules.

States of Aggregation

Materials can exist in three states of aggregation: solid, liquid, and gaseous. The fundamental building blocks of the substances – the atoms or molecules – are most ordered in solids. They form three-dimensional crystal lattices in which they have fixed places. If the solid matter becomes liquid, these rigid structures break up and the degree of order diminishes. The molecules are mobile and glide past each other. In gases, the atoms or molecules produce enough energy to detach themselves from each other and to fly through space (virtually) freely. Gases are therefore the least ordered.

Supramolecular Structures

How do supramolecular structures come into being? Let us imagine that the molecules are cars. The drivers of these cars have completely different destinations. If the drivers were simply able to drive to their destination in a straight line, there would be chaos. Individual traffic is fundamentally extremely disordered. Order is only created from the chaos by a superstructure of roads, traffic lights, and crossroads, which then guarantees a functioning traffic network. Supramolecular structures perform a similar role. In nature, these supramolecular structures come into being through the self-organisation of the molecules. The molecules behave as if they know their place within a complex structure and migrate there. For example, big molecules organise themselves in flowing liquids in such a way that they can flow faster. Or red blood corpuscles change their shape so as to be able to pass through the narrowest blood vessels. When they change their shape, the molecules of their membrane form a different supramolecular structure from before. Self-organisation is therefore a fundamental characteristic of nature, without which no life could exist. Self-organisation allows those big molecules that form the building blocks of living organisms to come into being. It also shapes the biochemical processes of all vital functions.

Colloids

The term "colloid" is derived from the Greek word for "gluey". Colloids consist of microscopically small particles. They can be dispersed throughout another substance, the "dispersion medium". Examples of colloids are particles of cigarette smoke in the air, or of varnish, in which fine colour pigments are "dispersed" in a solvent. A colloid owes its properties to the fact that the particles are much larger than atoms or "normal" molecules, but still remain microscopic. Their diameter varies between a few nanometres (one billionth of a metre) and several tens of micrometres (millionth of a metre). Colloids have enormous economic and technical importance. In nature, for example, they play an important role in living cells.

molecules (lipids are fats). The capsule walls are then able to recognise selected molecules and make themselves permeable to them. In this way they become a simple model for the membrane functions of a living cell, which are, of course much more complex.

FROM THE NANO-CAPSULE TO THE VESICLE MEMBRANE

The Golm capsules are an example of how pure research can lead to completely new fundamental technology. They have tremendous potential for application in industry. For example, Möhwald highlights the fact that many cosmetics and pharmaceuticals are not readily soluble in water; for this reason our body cannot absorb them properly. The capsules could act like microscopic submarines to transport such substances into the body. Their shells could be configured to take them to precisely the place where their contents were to act and release the active substance in a controlled manner.

The system developed in Golm also opens up completely new avenues for pure research. Helmuth Möhwald cites as an example the study of chemical reactions or crystallisation under the special conditions offered by nano-cavities. Fig. 9 shows an example from the Golm "box of tricks". Here, the Golm scientists demonstrated that they can not only fill the capsules with smaller molecules – by using chemical reactions, they are even able to produce larger molecules from them within the capsule.

When talking to Reinhard Lipowsky, the term biomimetics keeps cropping up. This is how scientists describe the method of reconstructing biological subsystems in a simplified form and at the same time are learning something about them. Reinhard Lipowsky and his colleagues in Golm are specialists in theoretical biomimetics. They explore the fascinating world of membranes and imitate nature using their high power computers. The computer simulation in fig. 10 shows snapshots of how molecules form a simple membrane. To do this, the scientists place virtual amphiphilic molecules in virtual water and instruct the computer to calculate what happens.

Amphiphilic molecules have one end that attracts water, and one that repels it. The water-repellent end does its best to avoid contact with the water molecules and it is precisely this that drives the amphiphilic molecules to organise themselves into a bilayer membrane. Both layers of the membrane arrange themselves so that the ends that shy away from the water sit on the inside of the membrane.

The computer simulation also clearly illustrates the interplay between order and disorder which is characteristic of soft matter. The randomly distributed molecules are more ordered within the membrane than previously. In fig. 10, it can be seen how the order increases from snapshot to snapshot. But a remnant of disorder remains even in the finished membrane. The molecules are in fact not fixed firmly into the membrane structure, but can wander freely within the membrane surface and swap places. With its two dimensions the membrane surface behaves almost as if it were liquid. The membrane owes its flexibility to this mechanism.

A bilayer membrane like this is only four to five nanometres thick. Its surface can however have a significantly greater diameter. It can extend over several micrometres, i.e. millionths of a metre, even up to millimetres. In this case, the membrane is a million times more extensive than it is thick! The membranes of a nerve cell can even reach dimensions in the region of a decimetre. But however far the membrane might stretch, it has a problem, namely its edges. On one side the water-repellent molecules would be exposed and be in danger of coming into contact with the surrounding water. The membrane is only able to avoid this by simply forming no edges. It doubles itself up and closes itself up into a fluid filled blister, a vesicle.

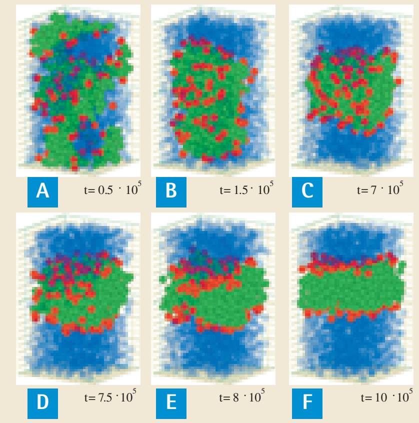


Fig. 10: A bilayer membrane organises itself. The computer simulation calculated a system of 100 amphiphilic molecules (in this case they consist of four green spheres with a red head) in 840 water particles (blue spheres). There is approximately a femtosecond between snapshots A, B and C to F (a millionth part of a billionth of a second).

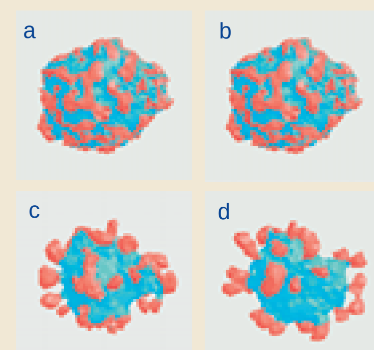


Fig. 11: A vesicle forms buds.

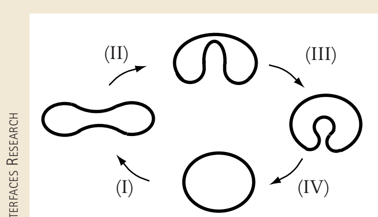


Fig. 12: A vesicle that assumes different shapes (schematic). If it runs through these forms cyclically, it will swim through the surrounding liquid like a living unicellular organism.

Fig.: MPI for Colloid- and Interfaces Research

This kind of vesicle can assume many different shapes. However, it always tends towards the shapes for which its membranes need to generate the least bending energy. The minimum level of energy – and hence the shape of the vesicle – depends upon the ambient temperature, the volume, and the nature of the vesicle's filling. Even molecules that cling to the two surfaces of the membrane can bring about a change in its shape.

What happens, for example, if there are two different types of molecule in one vesicle membrane which repel each other? These might perhaps be lipids and cholesterols, which are present in the membranes of red blood corpuscles. Fig. 11a shows what happens according to the computer simulation. The mutually "disagreeable" molecules collect in separate membrane domains which are coloured red or blue on the illustration. As the molecules migrate, these zones become larger. As this happens, the red zones behave extremely peculiarly. They form buds. Neighbouring buds are in turn attracted to each other and form even bigger buds (figs. 11b-d). In this way a "nano-blackberry", which looks as if it's been pecked at by birds, develops. The behaviour of this simple system gives an idea of how living cells form protuberances, for example at the start of a cell division.

Can a vesicle deliberately be switched between different shapes? Light-sensitive polymer molecules, termed azobenzene chromophores, do have this interesting potential. Ultraviolet light allows these molecules to jump from one spatial form – the "cis isomer" – to another – the "trans isomer". Infrared light switches them back again. If such molecules are present on the membrane surface, they change its curvature. The cis isomer bends the membrane differently from the trans isomer. If a vesicle were equipped with these molecules, the scientists really would be able to use light to switch them from one shape to another.

SWIMMING LESSONS FOR MEMBRANE MACHINES

This gave Reinhard Lipowsky a fascinating idea. He designed a model of a vesicle that can actively swim through an aqueous liquid. To do this, the microscopic membrane machine does however require a special swimming lesson: two different shapes, A and B, are not enough. The vesicle would just bob around in the water, but not move. To really cover any distance, it must go through a cycle of several changes of shape, as depicted in figure 12.

This is where biomimetics come on the scene again, because the principle of this swimming technique has been used successfully by single-celled organisms for hundreds of thousands of years. If, one day, it were to become possible for such a membrane machine to be built in the laboratory, the researchers would again have unravelled another mystery.

Throughout the ages, soft matter was and is a motor of human culture. Perhaps nanotechnology based on soft matter will give 21st century civilisation a big push as artificial materials did in the 20th century. Material scientists can still learn a lot from nature, as Hans Wolfgang Spiess emphasises: "Nature achieves tremendous complexity using just a few building blocks. In our work with synthetic materials, we use an amazing array of building blocks, but, at the moment, achieve relatively little."

Roland Wengenmayr