

Super Computer Plays with Strings of Pearls and Liquid Crystals

How do polymers behave and what structures do they form in different solutions?

This is the question that is currently being investigated by scientists from the

*Theory Department headed by **PROF. KURT KREMER** at the **MAX PLANCK***

INSTITUTE FOR POLYMER RESEARCH in Mainz. A most important tool for the

scientists is a powerful computer, which enables them to simulate the "glass pearl

game" involving atomic and molecular building blocks from dissolved polymers.

"The overall vision is to achieve an integrated structural design", says Kurt Kremer with regard to the future in his field of research work. "This would directly link the experiment with a simulation which both traces and controls the formation and behaviour of complex, nanoscopic structures. The result would be a tailor-made material." However, Kremer does not venture to offer any predictions on when this might become possible. Whatever the time scale may be, the Theory Department at the Max Planck Institute for Polymer Research is now working on making this a reality. Junior scientists such as Hans Jörg Limbach and Thomas Soddemann are simulating the be-

haviour of complex systems made up of large polymer molecules. They are using the Cray T3E parallel computer at the Max Planck Society's computing centre in Garching for these simulations. Examples of polymers include large biomolecules such as DNA, which carry the genetic code, and synthetic materials (see MAX-PLANCKRESEARCH 3/2001, Pg. 52ff). Their design is simple: consistently identical, basic molecular modules – known as monomers – form a chain with a length that can vary strongly. However, the size of the molecules produces complex characteristics. Alone the diversity of shapes, the "conformations", poses a challenge to the researchers. The chain contains many chemical bonds which

are able to move like joints or hinges. A computer simulation must therefore start by creating a large variety of possible molecule conformations, for the most part in a "start-up phase". Only after this phase will it simulate the situation under investigation.

According to Kremer, these complex systems can no longer be calculated using "pencil and paper". Experimental methods are also not sufficient: they yield an average over many molecules and provide no direct data on the behaviour of an individual molecule. This information, however, is extremely important to the researchers, as it allows them to gain a proper understanding of these systems. Computer simulations pro-

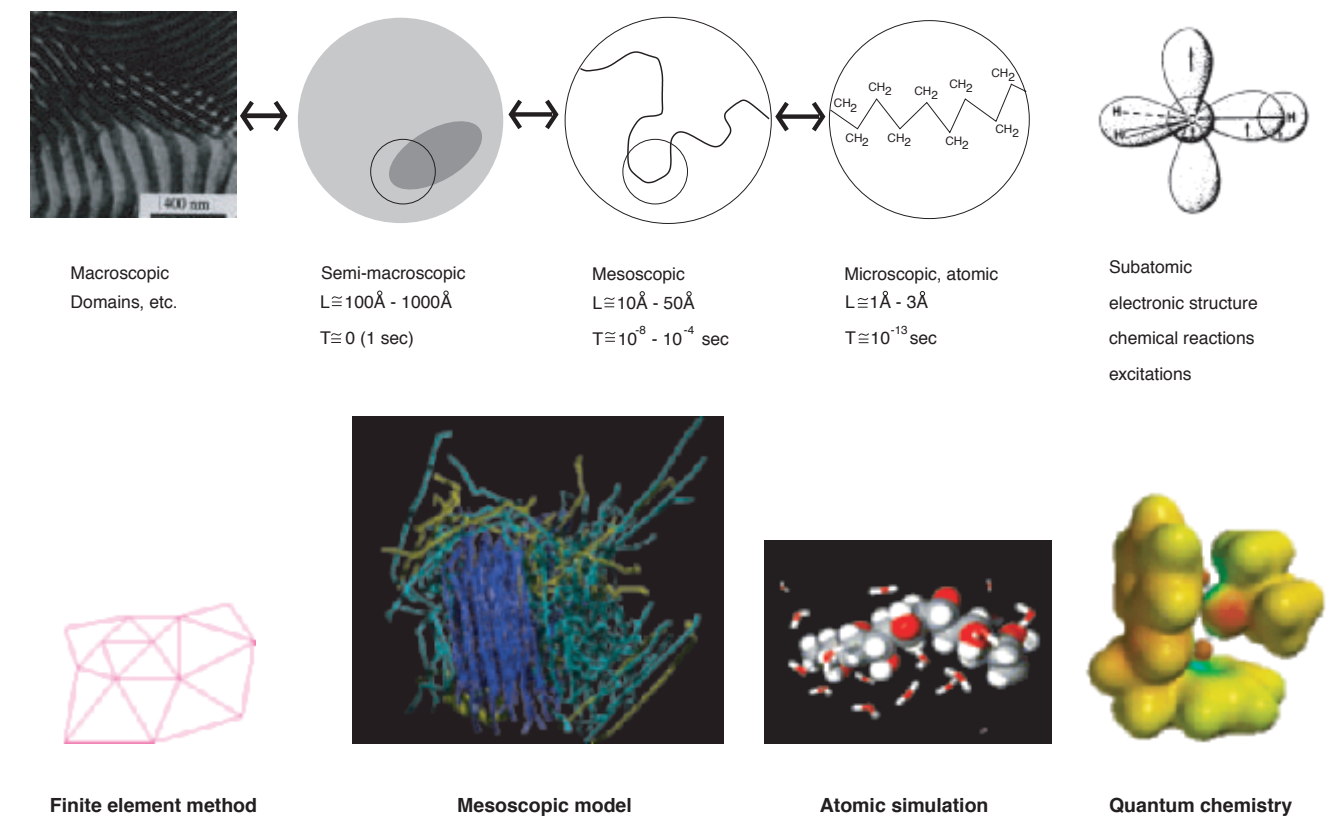


Fig. 1: The top row shows different scales from macroscopic to subatomic (L: length, Å = Ångström, T = time). The bottom row shows graphics from the simulation models on different scales. The finite element method does not take molecular structures into account.

vide the opportunity of bridging the gap between experiment and theory.

THE FASCINATION OF POOR QUALITY SOLUTIONS

The world of macromolecular material is governed by the law of scale. The large molecules are subject to interactions on size and time scales that vary immensely. Figure 1 (top) focuses in on the macroscopic scale (left), right through to the microscopic scale of tiny, subatomic structures (right). The medium, mesoscopic scale, located in between, is of particular importance to polymer systems. The focus sequence begins on the left with length scales of several hundred nanometres (a billionth of a metre) and time scales of only

seconds, and ends on the right below the Angström range (a tenth of a nanometre) with processes that last only femtoseconds (a thousandth of a billionth of a second). Individual polymer chains are detectable in the mesoscopic range. As illustrated in the lower section of Figure 1, a simulation of polymer systems contains a model for each of these scales and then links these models to a complete picture.

Hans Jörg Limbach is investigating the behaviour of "polyelectrolytes" in "poor" solvents. This might sound like a specialist niche for researchers who enjoy a particularly tough challenge, but it is actually an important area of research. In

the past, neither experiments nor theoretical models had been able to provide a precise explanation of how polymer chains behave in this type of poor solvent. In his PhD thesis, Limbach attempted to shed light on this unknown area. Using images created from his simulations, Figure 2 shows just how complicated this type of polymer solution is.

In contrast to normal polymers, polyelectrolytes are soluble in the very solvent of our environment: water. It therefore comes as no surprise to discover that many vital biomolecules are polyelectrolytes, including DNA and almost all proteins. When produced artificially, for example, they make environmentally-

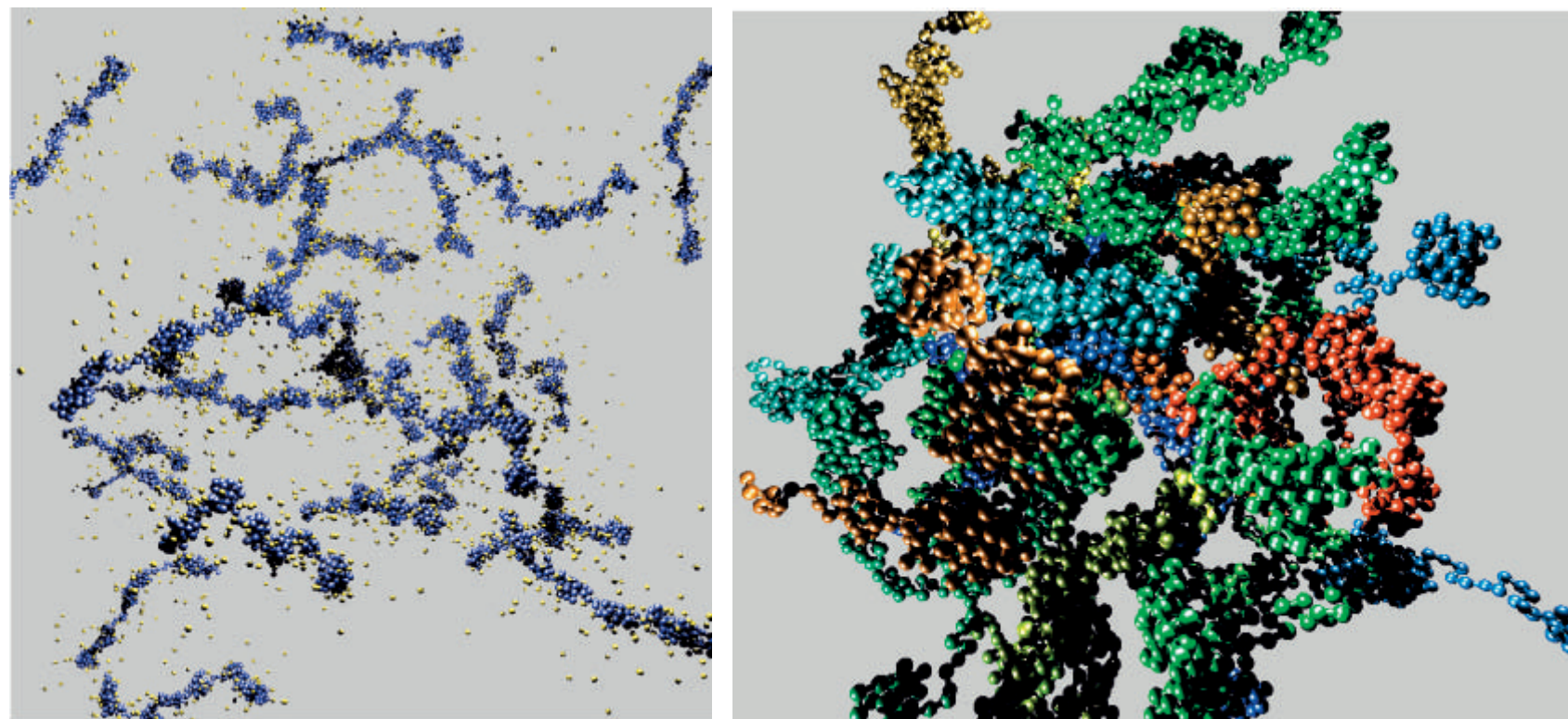


Fig. 2, left: Extract from the simulation model for a diluted solution. It contains 32 polyelectrolyte chains of 200 monomers each and 3,200 separated counter ions (yellow spheres), therefore 9,600 particles in total. Right: the same system at a greater density. The polymers that are pushed closer together are shown here in different colours, and the counter ions have been cut out.

friendly disperse dyes water-soluble, stabilize foodstuffs, or ensure that the body can absorb pharmaceutical substances. We are confronted as early

on as babyhood with polyelectrolytes in the form of “super absorbers” in nappies. Polyelectrolytes react on water or other “polar” solvents in the same way as salts. At certain positions, their chains split off electrically charged atoms – counter ions – thus acquiring the opposite charge at these sites. The counter ions buzz around the molecule like a swarm of excited bees. The electrical charges produce strong long-range electrical “Coulomb” fields, which superimpose

in many ways. In the sizing picture, these forces are effective from the microworld of ions right up to the macroscale.

As the Coulomb forces act on all scales and, as a result of superposition, form a fluctuating total field with a complex shape, the simulation approach which is successful in the case of neutral polymers fails to succeed here: the researchers can no longer carry out computational calculations of individual models for each particular scale involved and subsequently link them together. Fortunately, Limbach was able to use a special mathematical procedure to help him reroute the contributions of the individual ions

to the total field. He was able to carry out parallel calculations of these individual contributions on the Cray T3E and therefore to considerably shorten computing times.

The researcher in Mainz carried out systematic simulations of polyelectrolytes in different solutions ranging from poor to better quality. If, for example, the same charges are located in the polyelectrolyte chain in the solution, then these will repel each other. In the presence of these “repulsive” forces, the chain would really like to extend itself. However, at this point the counter ions come into play: they gather around the chain and partially screen the electrical fields and so too the repulsive forces. In water, which is a poor solvent, other attractive forces conse-

quently gain the upper hand and want to draw the chain together. This interplay not only changes the length of the chain but also its shape. Limbach was able to show that the appearance of polyelectrolytes in poorer quality solutions resembles a chain of pearls and strings (Fig. 4). Each “pearl” contains a mass of monomers. In the simulation the counter ions are shown as small yellow spheres.

In highly dilute solutions the repulsive forces dominate and the molecule chains extend (Fig. 3). Only at the ends of the chains is the attractive force strong enough to form small pearls. If the concentration of the solution increases and with this the number of counter ions, then well-defined strings of pearls will

occur (Fig. 4). These strings of pearls exist until the concentration of the counter ion becomes too high. Then the string will clump together to form a more compact shape without pearls (Fig. 5).

PEARLS ARE FORMED UNDER TENSILE FORCE

Limbach also investigated the reaction of a string of pearls whose ends are pulled apart by a tiny fraction of the molecular length. “In this way we can, for example, become better acquainted with the behaviour of hydrogels. What happens to the chain conformation when they swell?” asks Limbach. Figure 6 shows the outcome using the example of a “two-pearl” string. When subjected to a tensile force, a new

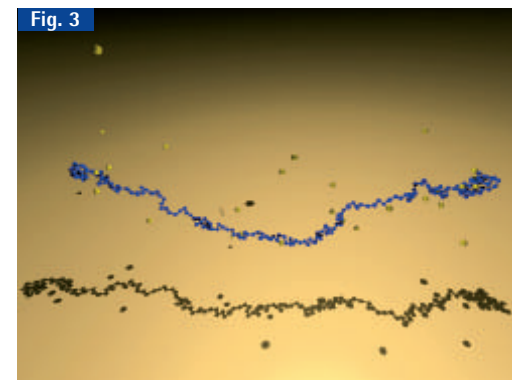


Fig. 3

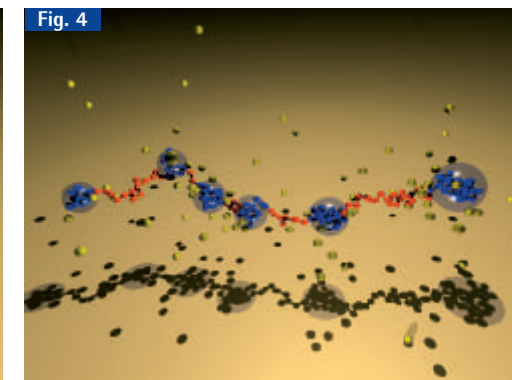


Fig. 4

The conformation of polyelectrolyte chains in a poor quality solution with varying concentrations from very low (Fig. 3) to relatively high (Fig. 5). The string of pearls structure in Fig. 4 is a compromise between the Coulomb repulsion of the charged string modules and the tendency of the chains to precipitate in poor quality solvents.

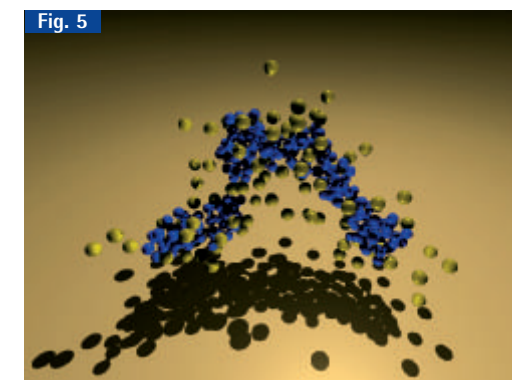


Fig. 5

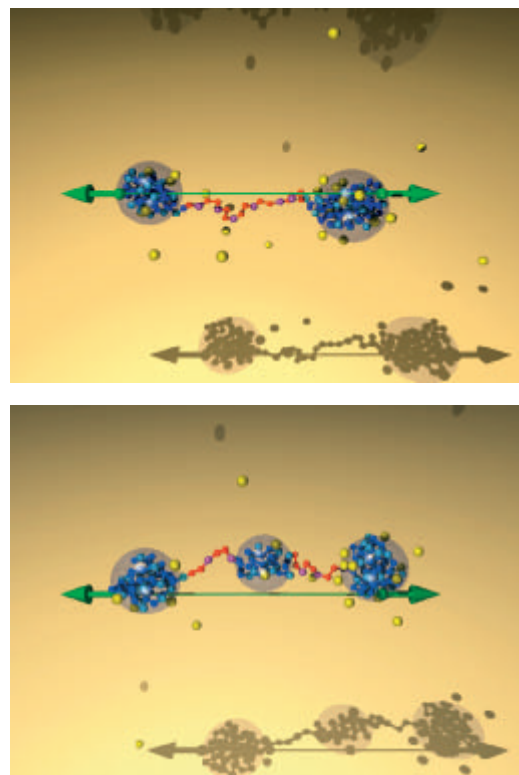


Fig. 6: Top, a string of pearls before the application of a tensile force, below afterwards.

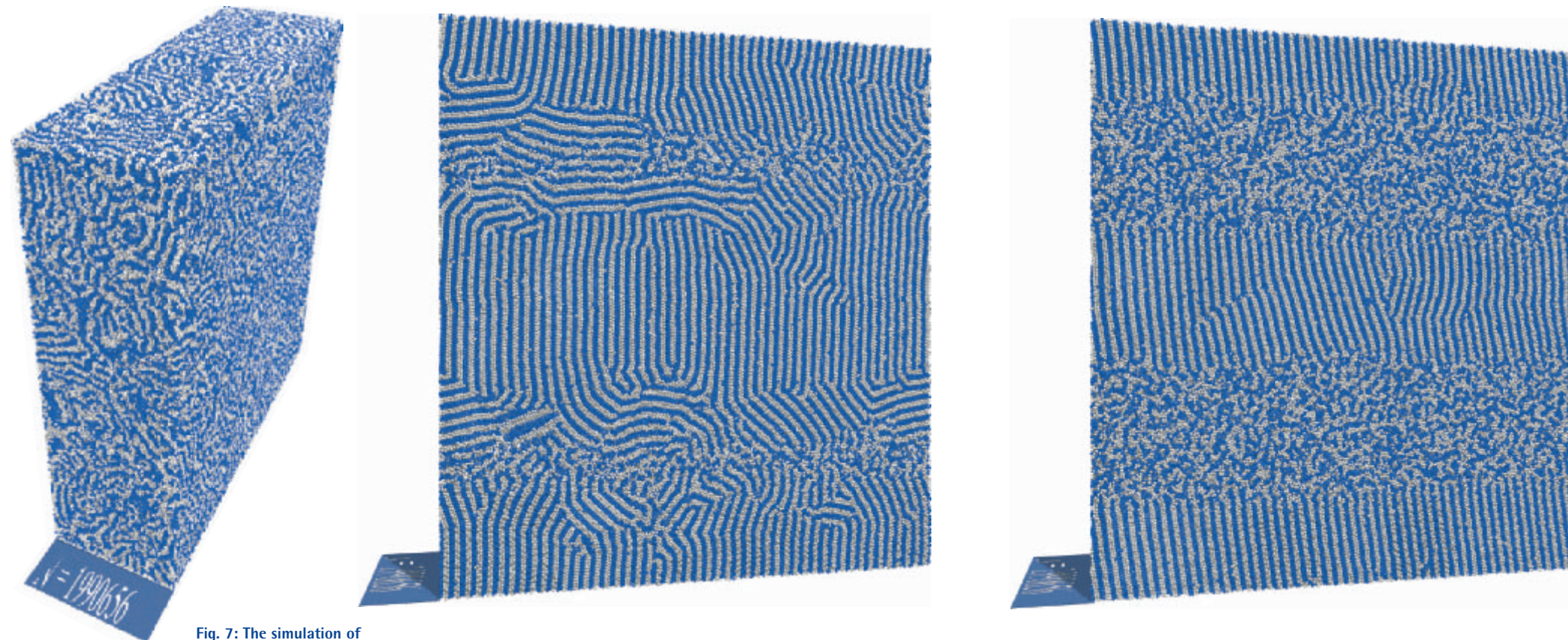


Fig. 7: The simulation of a lamellar system consisting of a million amphiphiles. The liquid lamellae shown in blue and yellow can be clearly identified (left). At a certain shearing rate the lamellar system forms shear bands (centre) which become more distinctly separated as the shearing rate increases (right).

lamellar-type layers within domains. The cigar-shaped form of the molecules plays a contributory role here. As a result of their chemical properties they are also called amphiphiles due to the fact that, in plain terms, they “like both”.

CHEMICAL CHAINS BIND UNEQUAL PAIRS

Soaps are a good example of this. Their molecules have one end that is hydrophilic and the other that is lipophilic. In water they form membranes out of two molecule layers. In this way they are able to keep their lipophilic heads inside the membrane away from the water. These systems are simple models of biological membranes, which enclose cells or cell organelles – and are therefore

of great scientific interest. Another system that can be applied to Sodde-mann’s model is that of liquid crystals. Liquid crystal molecules can also form well-ordered domains in the liquid phase. Electric fields can re-orientate these domains. This is how liquid crystal displays are able to control their light transmission.

A third system plays a central role in the work carried out by the researchers in Mainz. This system involves melts of “diblock copolymers”. These are macromolecules which consist of two different polymers. Below a certain temperature, this unequal pair becomes incompatible and would like to separate in the same way as oil and water. However, the strong chemical bond that exists between them forces them to stay to-

gether. They therefore only lightly separate into “microphases” which can form highly-ordered, three-dimensional nanostructures.

What distinguishes the lamellar systems is their ability to possess zones with a relatively high degree of order, even in a liquid state. In order to investigate this aspect, the researchers place these, for example, between two surfaces, which are only a few millimetres apart. They then rub these surfaces against each other, thereby exerting a “shearing

force” on the liquid. This forms lamellar patterns with a structure that is dependent on the speed and deflection of the shearing action. The researchers are attempting to learn about the interplay between the molecules from the interrelationship between the pattern formation and the shearing rate.

A MILLION MOLECULES INTERACT

A computer simulation on the basis of individual molecules can also help the scientists to increase their knowledge in this field. “We are able to simulate the shearing characteristics of lamellar systems with a million amphiphiles”, explains Kremer. Experiments show that so-called shear bands, which are sepa-

rated by sharp interfaces, can form in complex liquids. Thomas Sodde-mann was able to reproduce this effect in a simulation based on a single molecule.

Figure 7 shows this type of simulation with almost a million amphiphiles. Initially the system is highly disordered. It consists of numerous areas which are extremely small and in which the orientation of the lamella is varied. If the computer exerts a shearing force on this system, then the picture changes. Figure 7 (centre) shows how highly ordered zones occur which are separated by disordered zones. The separation becomes more defined (right) when the shearing rate is increased three-fold. Shear bands develop which run against each other as a whole.

Thomas Sodde-mann’s simulation model has made it possible, for the very first time, to gain detailed insight into the behaviour of individual molecules. The model has consequently been able to confirm fundamental theoretical model concepts. There is no doubt that it will be used further in the future.

Tailor-made material built from this molecular construction kit is certainly destined to remain a vision for the future for some considerable time to come. However, the success of the work carried out in Mainz demonstrates how researchers equipped with enough imagination, patience, and advanced technology can venture into the depths of the largely undiscovered world of large molecules.

ROLAND WENGENMAYR