Soft Matter (Nobel Lecture)**

By Pierre-Gilles de Gennes*

What do we mean by soft matter? Americans prefer to call it "complex fluids". This is a discouraging expression, but it does indeed incorporate two of the major features:

1) **Complexity.** We may, in a certain primitive sense, say that modern biology has proceeded from studies on simple model systems (bacteria) to complex multicellular organisms (plants, invertebrates, vertebrates...). Similarly, from the explosion of atomic physics in the first half of this century, one of the outgrowths is soft matter, based on polymers, surfactants, liquid crystals, and colloidal grains.

2) **Flexibility.** I like to explain this through one early polymer experiment, which was initiated by the Indians of the Amazon basin. They collected the sap from the hevea tree, put it on their feet and let it "dry" for a short time whereby they had boots. From a microscopic point of view, the starting point is a set of independent, flexible polymer chains. The oxygen in the air forms a few bridges between the chains, and this results in a spectacular change: We shift from a liquid to a network structure which can resist tension—what we now call a **rubber** (in french: caoutchouc, a direct transcription of the Indian word). What is striking about this experiment, is the fact that a very mild chemical action induces a drastic change in mechanical properties: a feature typical of soft matter.

Of course, with some other polymer systems we tend to build more rigid structures. An important example is an enzyme. This is a long sequence of amino acids, which folds up into a compact globule. A few of these amino acids play a vital role; they form the "active site" which is built to perform a specific form of catalysis (or recognition). An interesting question (raised long ago by Jacques Monod) is the following: We have a choice of twenty amino acids at each point in the sequence, and we want to build a receptor site in which the active units are positioned in space in some strict way. We cannot just put these active units next to one another, because, if linked directly, they would not realize the correct orientations and positions. So, in between two active units, we need a "spacer", a sequence of amino acids which has enough variability to allow a good relative positioning of the active sites at both ends of the spacer. Monod's question was: What is the minimum length of spacers?

It turns out that the answer is rather exactly defined.[1] The magic number is 13 or 14. With less than 13 units, you will not usually succeed in getting the desired conformation, whereas with more than 14 units, you will have many sequences with can adopt it. The argument is primitive: It takes into account excluded volume effects, but it does not recognize the need for a stable enzyme—namely that the interior should be built preferably with hydrophobic units, while the outer surface must be hydrophilic. However, my guess is that this cannot change the magic number by much more than one unit. Indeed, when we look at the spacer sizes in a simple globular protein like myosin, we see that they are not far from the magic number.

Let us return now to **flexible polymers** in solution and sketch some of their strange mechanical properties. One beautiful example is the four-roller experiment set up by Andrew Keller and his co-workers.[2] In this experiment, a dilute solution of coils is subjected to a purely longitudinal shear. If the exit trajectory is well chosen (in the symmetry plane of the exit channel), the molecules are stressed for long periods. What is found is that, if the shear rate $\dot{\gamma}$ exceeds a certain threshold value $\dot{\gamma}_c$, an abrupt transition takes place, and the medium becomes birefringent. This is what I called a "coil–stretch transition".[3] When the shear begins to open the coil, it offers more grip to the flow, and opens even more... leading to an abrupt transition. Here, we see another fascinating aspect of soft matter—the amazing coupling between mechanics and conformations. Indeed, Keller showed that the chains break rather quickly (at shear rates $\dot{\gamma} > \dot{\gamma}_c$), and do so very near to their midpoint—a spectacular result.

Another interesting feature of dilute coils is their ability to reduce the losses in turbulent flows. This is currently called the Toms effect, although in actual fact, it was discovered even before Toms by Karol Mysels.[4] Together with M. Tabor, we tried to work out a scaling model of coils in a turbulent cascade,[5] but our friends in mechanics think that it is not realistic. Time will tell which answer is correct.

I have talked a lot about poylmers, let me now switch to **surfactants**—molecules with two parts, a polar head which likes water, and an aliphatic tail which hates water. Benjamin Franklin performed a beautiful experiment, using surfactants: On a pond at Clapham Common, he poured a small amount of oleic acid, a natural surfactant which tends to form a dense film at the water–air interface. He measured the volume required to cover all the pond and since he knew the area, he was able to calculate the height of the film—something like three nanometers in our current units. This was (to my knowledge) the first measurement of the size of molecules. Nowadays, when we are spoilt with exceedingly complex toys, such as nuclear reactors or synchrotron sources, I particularly like to describe experiments of this Franklin style to my students.

Surfactants allow us to protect a water surface and to generate beautiful **soap bubbles**, which delight our children. Most of our understanding of these soap bubbles is due to a remarkable team: Mysels, Shinoda, and Frankel who wrote *the* book on this subject.[6] Unfortunately this book is now very hard to find; I very much hope that it will be reprinted.

Long ago Françoise Brochard, Jean-François Lennon, and I[7] became interested in some *bilayer* systems, in which we have two sheets of surfactant, each pointing towards the neighboring water. A related (although more complex) sys-

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[*] Prof. P.-G. de Gennes
Collège de France
11, Place Marcelin-Berthelo, F-75231 Paris Cedex 05 (France)
or
Ecole Supérieure de Physique et
de Chimie Industrielles de la Ville de Paris (ESPCI)
10, Rue Vauquelin, F-75231 Paris Cedex 05 (France)

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tem of this type is a red blood cell. For many years it has been known that, when observed under phase contrast, these cells *flicker*. It was sometimes believed that this flicker reflected an instability of a living system under nonequilibrium conditions. Actually it is much simpler: The essential property of insoluble bilayers is that they optimize their area at fixed surfactant number. Thus the energy remains stationary with respect to area, and the surface tension vanishes. This means that the fluctuations in shape of these deflated cells or "vesicles" are huge; the flicker is just an example of Brownian motion for a very flexible object. What Jean-François had done was to measure space–time correlations for the flicker. Françoise then showed that they could be understood from a model containing no surface tensions, but instead only curvature energies plus viscous forces—another good example of soft matter.

This was, in fact, one of the starting points for many studies on surfactant bilayers (pioneered by W. Helfrich) and, on a more formal side, on random surfaces (especially with D. Nelson). One of the great successes in this field has been the invention of the "sponge phase" of **microemulsions**.[8, 9] More generally, it is amusing to learn from these people that there is some overlap in thought between the highbrow string theories and the descriptions of soaps!

Let me now move to another corner in our garden, **liquid crystals**. Here, I must pay tribute first to two great pioneers: 1) Georges Friedel, who was the first to understand exactly what a liquid crystal is and what the main types are, and 2) Charles Frank, who (following some early work of Oseen) constructed the elastic theory of nematics, and described also a number of their topological defects ("disclinations"). Here I will only cover smectics. Observing certain defects ("focal conics") in smectics, Friedel was able to prove that the structure must be a set of liquid, equidistant, deformable layers.[10] From observations at the 100 µm scale, he was thus able to infer the correct structure at the 10 Å scale—an amazing achievement.

Smectics bring me naturally to another important feature of complex fluids, namely that nowadays it is sometimes possible *to create new forms of matter*. The sponge phase mentioned above was an example. Another striking case was the creation of **ferroelectric smectics** by R. B. Meyer (in Orsay, ca. 1975). He thought about a certain molecular arrangement with chiral molecules which should automatically generate a phase (the "C phase") carrying a non O electric dipole. Within a few months, our local chemists had produced the right molecule, and the first liquid ferroelectric was born![11] These materials have already become very important for display purposes; they commute 10^3 times faster than the nematics in our wristwatches.

Another case of far less importance, however amusing, concerns "ferro-smectic" materials constructed by M. Veyssié and P. Fabre. The starting point is a water-based ferrofluid, which is a suspension of very fine magnetic particles. (Ferrofluids were invented long ago by R. Rosensweig, and have amazing properties.) **Ferro-smectic materials** are a type of club sandwich formed from bilayer|ferrofluid|bilayer|... If a system like this is subjected to a magnetic field $\vec{H}$, it is happier when $\vec{H}$ is parallel to the layers. It is then interesting to observe the sandwich (with a polarizing microscope) in the frustrated situation where $\vec{H}$ is perpendicular to the layers. At very low fields, nothing is seen. However, beyond a certain weak threshold $\vec{H}_c$, figures like flowers grow in the field.[12] We understand this as a two-step process: a) Just above threshold there is a chemical undulation instability; b) later, focal conics appear with a basic size imposed by the original undulation, but also with smaller conics (which are required to fill space correctly). This "club sandwich" is reacting to rather weak magnetic fields (ca. 30 Gauss).

Let me mention yet another new animal: the **Janus grains**, first made by C. Casagrande and M. Veyssié. Like god Janus who had two faces, the grains have two sides, one apolar and the other polar. Thus they have certain features in common with surfactants. There is, however, an interesting difference if we consider the films which they make; for instance, at a water–air interface. A dense film of a conventional surfactant is quite impermeable. On the other hand, a dense film of Janus grains always has some interstices between the grains, and allows for chemical exchange between the two sides: that is, "the skin can breathe". This may possibly be of some practical interest.

The first technique used to make the Janus grains was based on spherical particles half embedded in a plastic and silanated on the accessible side.[13] This produces only microquantities of material. A group at Goldschmidt research developed a much cleverer pathway: The starting point is a collection of *hollow* glass particles (which are commercially

Pierre-Gilles de Gennes was born in Paris in 1932. From 1955 to 1959 he was a research engineer at the Atomic Energy Center (Saclay), where he completed his doctorate on neutron scattering and magnetism under the supervision of A. Abragam and J. Friedel in 1957. After a postdoctoral year with C. Kittel at Berkeley in 1959, he became assistent professor in Orsay in 1961, and soon started research on superconductors and later (1968) on liquid crystals. In 1971 he accepted a professorship at the Collège de France, where his attention turned to polymer physics. Starting in 1980 he became interested in interfacial problems, in particular the wetting and adhesion phenomena. Among the many honors he has received are the Ampère prize of the French Academy of Science, the Harvey and Wolf prizes (both from Israel), and the Nobel prize for Physics. He is member of several societies, including the French Academy of Sciences and the National Academy of Sciences of the USA.

available). There the outer surface is hydrophobized, and finally the particles are crushed! The resulting platelets are hydrophilic on one side and hydrophobic on the other. They are irregular but can be produced in tons.

I would now like to consider the style of soft-matter research. One of the most important features is the possibility of carrying out very simple experiments in the spirit of Benjamin Franklin. Let me mention two examples. The first concerns the **wetting** of fibers. Usually a fiber after being dipped in a liquid, shows a string of droplets, and thus, for some time, people thought that most common fibers were nonwettable. F. Brochard analyzed theoretically the equilibria on curved surfaces, and suggested that in many cases we should have a wetting film on the fiber, in between the droplets. J. M. di Meglio and D. Queré established the existence, and thickness of the film in a very elegant way.[14] They created a pair of neighboring droplets, one small, one large and showed that the small one emptied slowly into the big one (corresponding to the capillarity). By measuring the speed of the process, they could determine the thickness of the film which lies on the fiber and connects the two droplets; the Poiseuille flow rates in the film are very sensitive to thickness.

Another elegant experiment in wetting concerns the collective modes of a contact line, the edge of a drop standing on a solid. If one distorts the line by some external means, it returns to its equilibrium shape with a relaxation rate dependent upon the wavelength of the distortion, which we wanted to study. But how could we distort the line? I thought of very complex tricks, using electric fields from an evaporated metal comb, or other, even worse procedures. However, Thierry Ondarcuhu came up with a simple method. First he prepared the unperturbed contact line L by putting a large droplet on a solid. Then he dipped a fiber in the same liquid and obtained (from the Rayleigh instability) a very periodic string of drops. Subsequently, he laid the fiber on the solid, parallel to L, and generated a line of droplets on the solid. Finally he pushed the line L (by tilting the solid) until L touched the droplets; then coalescence took place, and he had a single, wavy line on which he could measure relaxation rates.[15].

I have emphasized experiments more than theory. Of course we need some theory when thinking of soft matter. In fact some amusing theoretical analogies sometimes arise between soft matter and other fields. S. F. Edwards is responsible for one important example.[16] He showed a beautiful correlation between the conformations of a flexible chain and the trajectories of a nonrelativistic particle, the statistical weight of the chain corresponding to the propagator of the particle. In the presence of external potentials, both systems are governed by exactly the same Schrödinger equation! This observation has been the key to all later developments in polymer statistics.

Another amusing analogy relates the smectic A phases to superconductors. This was discovered simultaneously by the late W. McMillan (a great scientist, whom we all miss) and by ourselves. Later, it was exploited artistically by T. Lubensky et al.[17] Here again, we see a new form of matter being created! We knew that type II superconductors let in the magnetic field in the form of quantized vortices. The analogy here is a smectic A phase into which we add chiral solutes. These play the role of the field. In some favorable cases, as predicted in 1988 by Lubensky, this may generate a smectic phase drilled by screw dislocations, the so-called A* phase. This was discovered experimentally only one year later by Pindak and coworkers[18]—a beautiful feat.

Let me now end this sentimental journey into soft matter, with a brief mention of my companions. Some were met along the way, like Jean Jacques, a great creator of liquid crystals, and Karol Mysels, the undisputed master of surfactant science. Some others were with me all the way: Henri Benoit and Sam Edwards, who taught me polymer science; Jacques des Cloizeaux and Gérard Jannink, who have produced a highly theoretical book on this subject. Finally an inner core of fellow travelers, over all forms of land and sea: Phil Pincus, Shlomo Alexander, Etienne Guyon, Madeleine Veyssié, and last but not least, Françoise Brochard, sans laquelle les choses ne seraient que ce qu'elles sont.

The final lines are not mine; they relate to an experiment on soft matter (taken from Eugène Boudin a French painter of the 18th century) which is shown in the figure below. No conclusion could be more appropriate.

Received: January 31, 1992 [A 873 IE]
German version: *Angew. Chem.* **1992**, *104*, 856

La Souffleuse de Savon.
Amusons-nous. Sur la terre et sur l'onde Malheureux, qui se fait un nom! Richesse, Honneurs, faux éclat de ce monde, Tout n'est que boules de savon.[*]

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[*] The portrait of the lady blowing soap bubbles is inscribed: "Have fun on sea and land. Unhappy it is to become famous. Riches, false glitters of this world, All is but soap bubbles."

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