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Keywords

liquid interfaces, surface rheology, microemulsions, emulsions, foams

Abstract

Soft matter is a field of condensed matter physics that began to develop in France in the 1970s under the impulse of Pierre-Gilles de Gennes. I had the chance to participate in this adventure, and I describe in this article some of the memorable events. Soft matter is not only linked to physics but also to chemistry and biology, and working in this multidisciplinary field is quite stimulating. My particular expertise deals with liquid surfaces, an area that considerably expanded with the advent of miniaturization, i.e., when surfaces begin to matter. I was able to benefit from the French and European network systems, as well as from many interactions with young students and industrial partners. I show how these favorable conditions contributed to successes in my research.

THE EARLY YEARS

How did I become a physicist? None of my family members were scientists, and neither were those of my husband. Langevin is a rather common name in the French region of Normandie from which his family originated. All the adult women around me were housewives or planning to become one, but I always thought that I should earn a living once I'd grown up. I was fond of mathematics: I liked solving problems, and math problems have only one solution; they looked much simpler to me than problems in social sciences. My father encouraged me and suggested that I become an engineer.

I then completed the usual courses to be admitted in engineering schools in France. Instead of joining a university after completing my baccalaureate, I took preparatory classes in a high school. My physics professor suggested I apply to Ecole Normale Supérieure (ENS) Sèvres. I was not planning to become a professor, but she said that I could also become a research scientist. At that time, I had no idea what research was. There were, of course, the well-known examples of Albert Einstein and Marie Curie, but it was not clear to me how they worked in their laboratories. However, I applied to ENS to please my professor. All my applications were accepted, and the choice was difficult. After passing exams in engineering schools, I realized that there were very few women there, whereas ENS Sèvres accepted only women. There were other ENS for men only; fusion between men's and women's ENS occurred much later. I had always studied in girls' schools, and I felt that I would be happier in a similar environment. I then bet that I would like research as much as engineering and I chose ENS. I never regretted this choice. Then I faced a second choice, between math and physics. At university level, math looked quite abstract to me. Physics seemed closer to the real world, although in preparatory classes, physics was not very attractive. I made the second bet that physics could become more interesting, another choice that I never regretted either. I had extraordinary physics professors, among them Alfred Kastler, who reconciled me with thermodynamics; Jean Brossel, with whom I discovered atomic physics; Yves Rocard, whose lectures and books have always been a source of inspiration; and Claude Cohen-Tannoudji, whose great quantum mechanics lectures are still vivid to me despite never having worked with quantum systems.

FROM SPECTROSCOPY OF RARE GAS MOLECULES TO LIGHT SCATTERING BY LIQUID SURFACES

After obtaining my diploma, I started a one-year thesis (called third-cycle thesis) to get introduced to the world of research. I chose to apply to the Laboratory of Hertzian Spectroscopy (now called Laboratoire Kastler-Brossel, LKB), part of the physics laboratory of the ENS. In this lab, the proportion of women researchers was greater than average; there were no or very few women in most physics labs at that time. My choice was certainly wise: I never felt I was considered differently from my male colleagues and realized only later that I have been privileged.

The Hertzian Spectroscopy Lab was founded by Alfred Kastler and Jean Brossel around the time of their discovery of optical pumping. Alfred Kastler had not yet been awarded the Nobel Prize; that happened when I was in the lab, and it was a great moment. My research topic was infrared and Raman spectroscopy of rare gas molecules (short-lived molecules), and my thesis adviser was Marie-Anne Bouchiat. Marie-Anne gave me papers and books, and I spent a full month in the library reading them. I realized that research progress would be slow; I had the awkward feeling that I was already losing time. After this reading period, I was asked to calculate the spectra of my molecules, an activity that I liked better. Sometime later, we were told that the infrared or Raman spectrometers would not be available for months. My thesis topic had to change.

At the time, the discovery of the helium-neon laser opened new research fields, in particular inelastic light scattering, because very small-frequency shifts can be detected with lasers. Jean Brossel felt that his lab was well prepared to tackle this new field. He proposed to Pierre Lallemand, just back from a postdoc in the United States, to undertake light scattering studies of gases and to Marie-Anne light scattering studies of liquid surfaces. As with bulk light scattering, surface light scattering (SLS) originates from thermal fluctuations, thermally excited capillary waves in the surface case, with wavelengths linked to scattering angles.

Marie-Anne was supervising the “thèse d’Etat” (a 4–5-year thesis) of Jacques Meunier and had asked Jacques to build a set-up. Because the intensity scattered by a liquid surface decreases very rapidly with scattering angle, only angles smaller than 1 deg could be studied in practice. A serious protection against mechanical vibrations was thus necessary. Antivibration tables not being commercially available, Jacques mounted a heavy oak table on six truck air chambers and loaded it with concrete blocks and lead bricks, obtaining remarkable stability. He-Ne lasers were in turn commercially available, and the largest one available (60 mW) was purchased. The set-up was operational after only about six months, and Jacques studied two liquids, a low-viscosity one, ether, on which capillary waves propagate, and a large-viscosity one, glycerol, on which they are damped. As a result, the spectrum of the scattered light is frequency shifted from that of the laser in the first case, and in the second, just broadened. My new thesis task was to study the light scattering by the surface of a liquid with an intermediate viscosity, ethylene glycol.

Home-made instruments were common in physics labs at the time, and I began experiencing their frequent breakdowns. There were no computers, and the scattering spectra were recorded by mechanical devices equipped with ballpoint pens that frequently dried up, especially when I was not close by. After completing the experiments, I saw that the frequencies and line widths were not related simply to the roots of the dispersion equation of capillary waves as in the limiting cases studied by Jacques. Marie-Anne attributed the deviations to the white noise of the fluctuations and, indeed, the spectrum of a thermally excited harmonic oscillator agreed with my results.

Marie-Anne then proposed to continue this research with a National Centre for Scientific Research (CNRS) position. Thus far, I’d found the interest of my thesis work to be somewhat limited, probably because I had not mastered its scientific context, but I assumed that more excitement would come later (it did, of course). Marie-Anne wrote the proposal, and sometime after, she came and told me that I was hired by CNRS. I was not yet 22 years of age, and I had a permanent position. This story is hard to believe for young students nowadays, who rarely get permanent positions before a longer thesis and postdoctoral work. I could raise a family in comfortable conditions (I have four daughters), with convenient day-care facilities in France. I owe a lot to my husband, who is a mathematician. He works at home most of the time, so he could take care of the girls during the unavoidable periods when the children were ill.

LIQUID CRYSTALS

I then began a thèse d’Etat. At the time, Pierre-Gilles de Gennes was interested in the new field of liquid crystals. These liquids showed potential for displays and were used soon after in small screens, (watches, car displays, videogames). De Gennes suggested to Brossel that light scattering by liquid crystal surfaces would be of interest. This topic became my thesis topic, and I started with para-azoxy-anisole (PAA), a compound that was solid at room temperature and nematic liquid crystal above 118°C. Heated above this temperature, the surface was rapidly covered by a crust, likely due to impurities and/or oxidation. Brossel suggested a distillation, then sealing the cell under vacuum to avoid crust formation. He used to fill glass tubing with gases for the spectroscopy investigations in the lab, and he allowed me to borrow his gas pump. The procedure was not easy, but it solved my problem. Salvation came a few months later when I went to my first conference

in Montpellier, which gathered liquid crystal specialists. I met a German corporate chemist who synthesized a new room-temperature liquid crystal, MBBA (methyl benzylidene butyl aniline) and offered to send me a sample. The surface crust problems ended with MBBA, and my experiments became much easier.

I used to go every week to Orsay to follow de Gennes' lectures. He was building the hydrodynamic theory of liquid crystals that I needed to analyze my data. My plan was to investigate the anisotropy in bulk viscosities by studying the propagation of capillary waves in directions parallel and perpendicular to the magnetic field used to orient the molecules. I began noticing deviations between the spectra of the capillary waves and those of the thermally excited harmonic oscillator. The signal-to-noise ratio was better than with simple liquids because the refractive index of liquid crystals is large. Marie-Anne was at first surprised but found out that the correct spectrum had to be derived from the fluctuation-dissipation theorem. The harmonic oscillator spectrum, established for bulk scattering, did not satisfy the limit conditions at surfaces.

A still open question at the time was the orientation of liquid crystal molecules at the surface. We considered using light reflectivity and its variation with the angle between laser polarization and the magnetic field. It took me half a day to make the measurements and another half-day to write the paper; this was the fastest publication in my career (1).

I defended my thesis in 1974 and ended my liquid crystal studies. TV screens remained a challenge for many years, the response time of the devices was not fast enough at the time. Solutions were found in the following years, and TVs with liquid crystal screens are in the market, but OLED (organic light-emitting diode) devices are now taking over.

MONOLAYERS ON WATER

In the midst of my thesis, I started studies of monolayers on water. The propagation of capillary waves was expected to be modified by the surface compression modulus E and an associated surface viscosity of the layers. I first calculated the theoretical spectrum, including these additional parameters. I learned the preparation procedures from Lisbeth Ter-Minassian, whose lab was in the medicine faculty. I used a small circular trough filled with water and successive depositions of surface-active substances to increase their surface concentration. Surface contamination is a crucial difficulty in monolayer experiments, but following the wise tips given by Lisbeth, I obtained reproducible results. For liquids with small viscosities such as water, the spectra are broadened by instrumental effects (finite width of the laser beam and residual vibrations). Another group, who did not account for this broadening, concluded that the viscosity of water close to the surface was four times larger than its bulk viscosity. Making corrections for instrumental broadening were not easy at the time because computers were not available. I approximated the experimental spectra by Lorentzian curves and the instrumental function by Voigt functions, convolution of Gaussians and Lorentzians. The experimental spectra were then also convolutions of Gaussians and Lorentzians, and I could do the analysis by hand. I then obtained the correct viscosity for water (2). The spectra with monolayers are much more difficult to analyze, and the differences with the spectrum of pure water are not very large. **Figure 1** shows an example for which the difference is the largest.

Because of the influence of the surface rheological parameters in the spectrum, it was necessary to perform in situ surface tension measurements to reduce the number of fitting parameters. A few years later, I designed a homemade Langmuir trough and studied various fatty molecules and polymers that are able to spread on water. I submitted a paper with the results to the *Journal of Colloid and Interface Science* and the two referees rejected it; one said that the theory was wrong and the other that the data analysis was biased. Most of my papers were published at the time in the *Comptes Rendus de l'Académie des Sciences* or in the *Journal de Physique*. I was invited in 1979 to attend the Gordon Research Conference on Chemistry at Interfaces and realized that my work

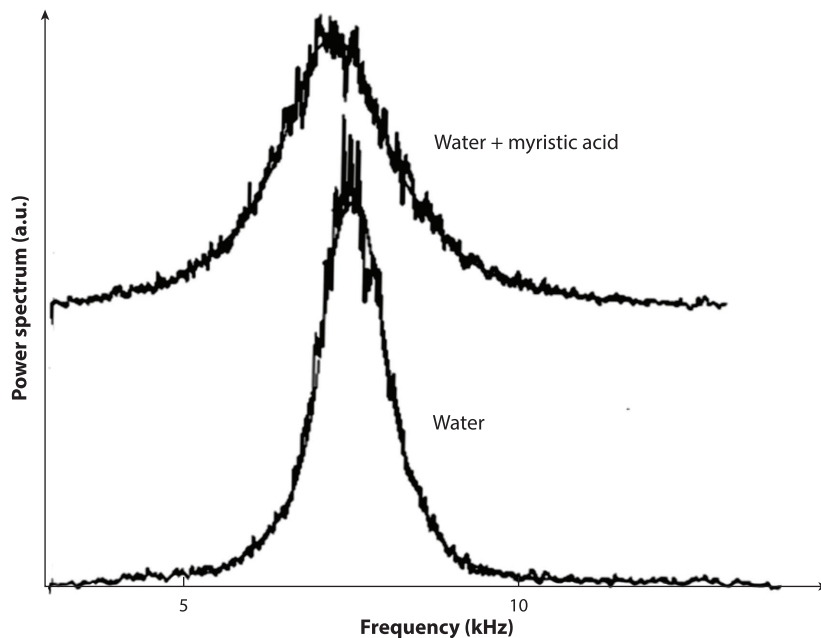


Figure 1

Spectra of the light scattered by the surface of pure water and of water covered by a monolayer of a fatty acid. The wavelength of the capillary wave selected is 200 μm . Figure adapted from Reference 46 with permission.

was mostly unknown by the community gathered at this conference, which included great names in the *Journal of Colloid and Interface Science*. Hence, my attempt to publish in one of their favorite journals failed. I did not agree with the referees and wrote to the editor to explain why. He decided to accept the paper, which is now one of my most cited (3).

The accuracy of the SLS method is unfortunately limited by instrumental broadening. It was not as widely used as bulk light scattering; commercial SLS instruments were never available.

POLYMER SOLUTIONS

I was encouraged by the head of the CNRS physics department to plan a postdoctoral traineeship. I could not leave Paris, because my husband was a professor and sabbatical leaves were not possible. De Gennes had recently left Orsay for the Collège de France with part of his group and was starting polymer work. He was successfully applying renormalization group theories, used earlier for critical phenomena, and he established a number of scaling laws for polymers. He viewed semidilute polymer solutions as networks with a mesh size ξ varying with polymer concentration C as $C^{3/4}$. He predicted that the motion of small objects in the solution should be governed by the solvent viscosity when their diameter D is smaller than ξ and by the solution viscosity when D is larger, the effective viscosity varying as $\exp(D/\xi)$ in between. Francis Rondelez, a member of his group, learning that I had a postdoctoral stay in mind, proposed to perform a study of particle sedimentation in these solutions. For this purpose, he secured the access to an ultracentrifuge in the biophysics lab of the College. The rotor of the machine was quite big, the rotation velocity high at 60,000 rpm, and I was always afraid of making a mistake during its installation and seeing this rotor breaking the metal shielding and flying out into the room. The machine was equipped with a schlieren device and was taking pictures on a photographic plate that I had to develop in a

dark room. After a year of playing with different particles, proteins, viruses, and silica, I obtained results that were in agreement with de Gennes' predictions (4). When I showed him the results, I learned with stupefaction that the law that I painfully tested for one year had no theoretical foundation—it was just his guess. I came from a lab where the approach to problems was different: First, elaborate the theory, then build a setup and perform measurements to verify the theory. I thus learned that research could be performed differently. De Gennes' guess happened to be right. It has now been demonstrated theoretically and is widely used to predict the mobility of nanoparticles in the cytoplasm of cells and other gels.

MICROEMULSIONS

When I was in the Collège de France, de Gennes invited Marc Bavière from the Institut Français du Pétrole (IFP, now IFPEN) to exchange on the emerging problems of enhanced oil recovery (EOR). In EOR methods, water is injected to dislodge oil trapped in porous rocks of reservoirs; surfactant is added to lower the oil–water interfacial tensions (IFTs) and facilitate recovery by reducing local capillary pressures. At the time, there was no commercial instrument to measure low IFTs, but surface light scattering was well suited. Jacques Meunier also became interested and Marc Bavière gave us a commercial surfactant for the first trials. The surfactant was not pure, and the additives formed a crust at the oil–water interface that recalled those I'd seen with PAA. Measuring IFTs with light scattering was impossible.

I attended a conference on surfactants in Bordeaux in 1978 and met Pierre Lalanne and Anne-Marie Bellocq from the Centre de Recherche Paul Pascal (CRPP), headed then by Pierre Bothorel. Both Lalanne and Bellocq were working on model systems for EOR and showed me samples with beautiful clean interfaces (**Figure 2**). They were microemulsions (thermodynamically stable dispersions of oil and water made using surfactants), in equilibrium with excess oil, water or both. Jacques and I started studying the interfaces in this system. Anne-Marie Cazabat,

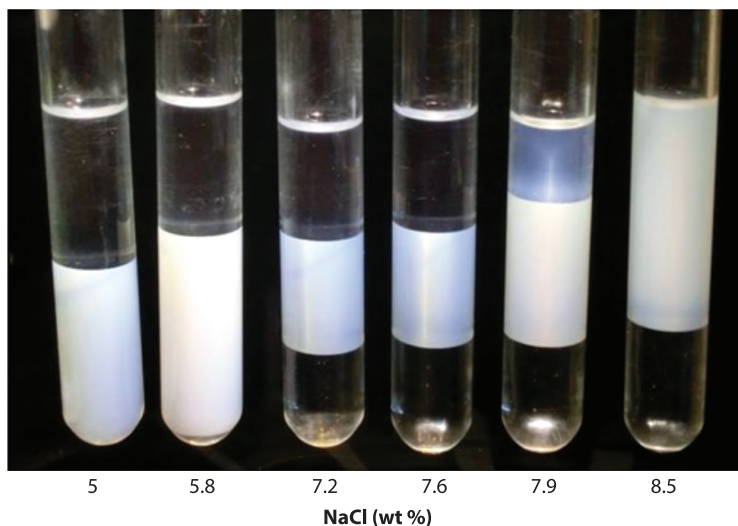


Figure 2

Model systems for enhanced oil recovery (EOR). The test tubes contain mixtures of water, toluene (model oil), sodium dodecyl sulfate (SDS, surfactant), and butanol (cosurfactant). Salt is added to obtain three-phase systems in which the interfacial tension is at a minimum, which is the optimal condition for EOR. Figure adapted from Reference 46 with permission.

who had been working with Pierre Lallemand on bulk light scattering, became interested in microemulsions and we started bulk studies together. We had been given funding for this work, so we hired a thesis student, Didier Chatenay. Alain Pouchelon was detached from the company Rhône-Poulenc to begin an engineering thesis with us. We were then five people in the team, and the work progressed quickly.

Another action that boosted the topic in France was the creation of a microemulsions GRECO (groupement de recherches coordonnées) by CNRS, chaired by Pierre Bothorel. This GRECO associated six teams, physicists and physical chemists, with comfortable yearly funding allowing for organization of two one-week meetings and for each team to buy an instrument (present cost of about EUR 50,000). During the first meeting, we had difficulties following the talks of the physical chemists, essentially because their vocabulary was not the same as ours. However, one year later, we were working together quite efficiently. The GRECO was recommissioned after four years, and four years after that evolved into several GDRs (groupe de recherche), with reduced funding. Despite funding restrictions, these GDRs continued to federate the French community, and no doubt all these structures were at the origin of the successes of the French soft matter community at the international level.

The microemulsion topic was quite new in the 1980s and most of the microemulsion properties looked mysterious. We first showed that the low IFTs were due to the surfactant monolayer adsorbed at the oil–water interfaces (5). Until that time, they were attributed to the vicinity of a critical point and it took time for people to trust our findings. However, our result made optimizing oil recovery more economical (microemulsions were not needed), despite large quantities of surfactant remaining necessary, because a lot was lost by adsorption onto the porous rocks.

The role of the monolayer had interesting consequences. The first Ising model of microemulsions was proposed by de Gennes, who replaced the then current models (droplets or Voronoi tessellation) with a cubic lattice and explained quite simply why microemulsions were stable. Ben Widom from Cornell University began working on Ising models of microemulsions and predicted that in the three-phase systems (**Figure 2**), the middle-phase microemulsion should not wet the oil–water interface despite the IFTs being ultralow. This was clearly different from systems close to a critical point, where critical wetting occurs (Antonov’s rule). During a visit in Paris, Ben asked if we could check his prediction and was thrilled seeing with us that, indeed, the middle phase was not wetting the oil–water interface. I established later a long collaboration with Reinhard Strey of the Max Planck Institute in Göttingen. We could locate the transition in wetting behavior by following the evolution of microemulsions toward molecular mixtures, which wet the oil–water interface (6).

When Jacques measured the reflectivity of the interfaces, he could not interpret the results with the method used for critical fluids, which considered only the fluctuations of wave lengths λ larger than the light wavelength λ_0 . In fact, the fluctuations with $\lambda < \lambda_0$ also affect the reflectivity, and their contribution is especially important for microemulsion systems. Jacques and I mentioned the problem to de Gennes, who advised we use the Debye Waller factor, which enabled the data analysis. We then sent a manuscript to *Physical Review Letters*, where it was rejected because it questioned the earlier work on critical fluids. It was subsequently published in *Journal de Physique Lettres* (7) and attracted the interest of Peter Pershan, who was starting X-ray reflectivity work on liquid interfaces. Peter used our result, which is now fully admitted. We realized that ellipsometry would bring more information, and Jacques started building an ellipsometer for oil–water interfaces. We could then measure the elastic modulus of curvature K of microemulsion surfactant layers.

We carried out in parallel bulk microemulsion studies. We found that the phenomenon of percolation in water-in-oil microemulsions (sudden increase in the electrical conductivity) occurs at a drop volume fraction typically between 10% and 30%, depending on the interaction forces

between drops; percolation is not observed when the forces are not attractive enough (8). It was soon realized that middle-phase microemulsions do not have a drop structure; they are bicontinuous (sponge like) with a characteristic size ξ_p . De Gennes postulated that ξ_p is the persistence length of the surfactant layer, which varies exponentially with K . Our measurements confirmed these predictions (9). We were also able to relate the low IFTs to K (10). There are actually two moduli of curvature, the mean modulus K and the Gaussian modulus \tilde{K} . I showed later that \tilde{K} can be measured by combining inelastic light and neutron scattering (11).

When the oil price went down, EOR methods being too expensive, microemulsion research became less active in the 1990s. I then started work with giant micelles and emulsions. Emulsions are thermodynamically unstable; hence, they are difficult to study. Microemulsions were discovered much later than emulsions, but a good understanding was rapidly achieved, whereas emulsion stability is still the object of active controversies.

GIANT MICELLES

I worked on giant micelles in collaboration with Wladimir Urbach and Albrecht Ott, who was then a PhD student. Micelles are surfactant aggregates, generally spherical, but they can grow very long when certain salts are added. They are interesting substitutes to polymers to obtain viscous solutions, because micelles break reversibly and are not damaged by shear as are polymer chains. Albrecht used the technique of photobleaching by fringes built in the lab by Didier Chatenay to measure self-diffusion coefficients. He observed small but systematic deviations from classical diffusion (average distance traveled proportional to the square root of time). We showed the results to Jean-Philippe Bouchaud, then a member of the statistical physics lab of ENS, to which my group belonged after 1988. Jean-Philippe suggested new experiments that confirmed that the diffusion was anomalously fast in certain conditions. This was the first experimental evidence of anomalous diffusion of the Levy type (12). This work has stimulated activity in the field, including for other types of experimental achievements.

SURFACE RHEOLOGY: TOWARD EMULSION AND FOAM STUDIES

Emulsions and foams are, respectively, liquid-liquid and gas-liquid dispersions stabilized by surfactants (or other surface-active agents, such as polymers or small particles). IFs in these dispersions are large, and the curvature surface energy no longer matters. My driving idea was that emulsion and foam stability should be controlled by surface compression rheology. As mentioned earlier, this rheology is accessible through SLS. Frequency dependences being important in rheology, I designed several devices to extend the frequency domain accessible by SLS: electrically excited capillary waves (13) and mechanically excited compression waves (14). I could then observe the huge variation of the compression viscoelastic coefficients of surfactant monolayers with the frequency of surface deformation: When the frequency is low and the surfactant is soluble in the underlying liquid, surfactant solubilizes into the liquid, and the resistance to compression is lowered; the lower the frequency, the smaller the resistance. I also designed a device for measuring surface tension as a function of time to access adsorption kinetics. I demonstrated the existence of adsorption barriers with ionic surfactants, due to the repulsive electrostatic surface potential (15). This result is now recognized as important in the elaboration of foams and emulsions. I showed with Emmanuelle Rio that the adsorption barrier is also one of the parameters controlling the thickness of films drawn by plates (Landau-Levich problem; 16) or frames (Frankel problem; 17).

I started foam studies with a question brought forward by the company Rhône-Poulenc: how to optimize antifoams, which are currently dispersions of small solid particles into silicon oil. This led me to study the mixed surface layers of surfactant and silicon oil, which have an uncommon

duplex structure, using neutron reflectivity in collaboration with Lay-Theng Lee (18). Later on, with Annie Colin, we explained to Rhône-Poulenc why the surfactant mixtures used in washing machines do not foam: The solution phase separates and the droplets of the minority phase act as an antifoam (19). I also proposed with Vance Bergeron a mechanism for antifoam aging (after some time, these products are no longer active). Using parabolic flights (that provide microgravity conditions), with Anniina Salonen, we recently showed that antifoams are not active in microgravity, explained why, and confirmed the validity of the mechanism of antifoam aging (20).

With the aim of completing surface characterizations, I purchased devices for imaging interfaces at the Brewster angle and for measuring surface shear rheology. I was then able to show that mixed surface layers of cationic surfactants and DNA (21) or nanoparticle layers (22) behave like soft three-dimensional solids. In collaboration with Francisco Monroy, from the Universidad Complutense de Madrid, we studied monolayers of various lipids. At the time, biophysicists considered that lipid bilayers were fluid, allowing membrane proteins to move freely. We found out that certain lipid layers are rather viscoelastic, even solid (especially in the “rafts” of biological membranes; 23). We also studied monolayers of neutral polymers and evidenced for the first time a phenomenon of quasi 2D reptation (24) as well as a glass transition, at a temperature well below the bulk transition (25).

SOAP FILMS

The behavior of emulsions and foams not only depends on the surfactant monolayers but also on the thin films formed between drops and bubbles, which are frequently called soap films. In order to study their drainage kinetics and the forces between their surfaces (disjoining pressure), I designed a video-microscopy device under controlled pressure. I first found out that many films drain much faster than currently predicted in models, which assume that films have immobile surfaces. Film surfaces are in fact mobile, and the drainage rate depends on the surface compression modulus E . I showed that the modulus to be considered was the high-frequency modulus, because with the film being thin, it does not contain enough surfactant to allow surface-volume exchanges (26). This result confirmed the origin of the rule proposed by Wilder Bancroft in 1940, and widely used since, which states that the continuous phase of the emulsion contains the surfactant. The films between drops containing the surfactant drain much faster, because this surfactant is directly accessible for exchanges, and E is small, whereas the films of the phase containing the surfactant drain much more slowly (large E).

By studying films containing charged polymers (polyelectrolytes), I observed and could explain the occurrence of a stratification, relating it to the pair distribution function of polyelectrolytes that is oscillatory, with a period comparable with the Debye length (27). The thickness of the film decreases step by step, after opening and expansion of areas of lower thickness. The study of stratification kinetics made it possible to trace a local viscosity in the film, which is very different from the viscosity of the polymer solution (28). I found that stratification is only observed if the polyelectrolyte has time to orient itself parallel to the surface of the film, and this period of time can be long, for example, for DNA, which is a very rigid polyelectrolyte (29). When the surfactant added to stabilize the film has a charge opposite to that of the polymer, I was able to explain why films containing flexible polymers are much more stable than those containing a rigid polymer, DNA, for example. Using microscopy at Brewster’s angle and shear rheology, I showed that the mixed layers were relatively fluid with flexible polymers, but solid and brittle with rigid polymers: With the latter, the layers can break due to sudden tensions in the film during drainage; without protection, the film breaks.

I also studied bulk complexation in mixed polymer-surfactant solutions with opposite charges, solutions often used in industrial formulations (30). In particular, I evidenced peculiar

monodisperse aggregates whose nanostructure is the same as that of the liquid crystal phases obtained beyond the precipitation threshold (31).

FOAM AND EMULSION STUDIES

Foam bubbles are usually much larger than emulsion drops, and the density contrast between phases is larger. Therefore, gravity induces rapid foam drainage. A theory was proposed in the 1990s by the team of Denis Weaire at Trinity College, Dublin. Denis is a condensed matter physicist and became interested in foams when he saw that Kelvin used crystallography to find the shape of bubbles with minimal area. When I met Denis at a conference, I was studying antifoams, and he was quite surprised to hear that such things existed. He convinced me to begin foam drainage experiments. Shortly afterward, the team of Howard Stone at Harvard University proposed another drainage theory, with different surface boundary conditions. Experiments made with commercial foaming solutions (different in Ireland and in the United States) agreed with each theory. By using mixtures of pure surfactants, I was able to show that both groups were right; the drainage regime depends on the rheological properties of bubble surfaces (32).

I continued foam studies investigating the ripening process, in which bubbles grow by gas transfer due to different internal pressures in the bubbles. The study of ripening is difficult because it is coupled with drainage. With Arnaud Saint-Jalmes, we used multiple light scattering experiments with a rotating cell as a first approach (33). More complete experiments in microgravity conditions have been initiated (see the section titled Microgravity).

In collaboration with Véronique Schmitt and Fernando Leal-Calderon from CRPP, we carried out a study with emulsions in which drainage is negligible. We showed that the ripening rate decreases when the compression modulus E of the interfacial layer increases (34). Foams made with the same surfactants showed that ripening also decreases with the gas permeability of films between bubbles (35). Though film permeability decreases when E increases (the surface layers become more compact), we do not know yet which is the relevant parameter. Experiments are planned to clarify the problem.

I also studied foams stabilized by nanoparticles and showed that they do not ripen, although the surface coverage was only 20%, thus excluding low gas permeability. However, E is high enough for ripening to be blocked: The criterion $E > \gamma/2$ established by Gibbs long ago for irreversibly adsorbed surface layers (nanoparticle case) is satisfied (36). I also studied foamed emulsions, in collaboration with Anniina Salonen; foamed emulsions are another interesting type of foams, combining emulsion and foam properties (37).

The third process of destabilization of foams and emulsions, coalescence of bubbles and drops, remains elusive. With Emmanuelle Rio, we have shown that the probability of coalescence is proportional to the area of the bubbles, which is a question that has long remained unproven, although important for selecting the different scenarios proposed for coalescence (38). I am presently trying to clarify the relationship between coalescence probability and surface rheology.

PETROLEUM

I maintained a collaboration with IFP (now IFPEN) and after microemulsion studies, I began working with Jean-François Argillier on heavy crude oils. These oils are mixtures of many components that were separated using distillation and heating, creating unpleasant smells in the lab. The 1999 Erika oil tanker wreck happened on one of the distillation days, and my reputation in the lab suffered seriously. During injection of water in petroleum wells, microemulsions are not formed, but rather very stable emulsions are, and it is quite hard to recover the oil afterward. Indeed, these oils contain asphaltene, which are efficient natural surfactants. With Jean-François, we were

able to link the stability of these emulsions to the surface compression modulus E (39). We have also shown by neutron scattering that the oil–water interface is covered by asphaltene aggregates adsorbed from the oil, a question much discussed before (40). We have also used flotation to remove residual oil from production water. We have shown that addition of salt promotes oil separation, favoring coalescence of oil drops (41). In collaboration with the small and medium-sized enterprise Teclis, and using one of their new devices, I was able to prove the irreversibility of the adsorption of asphaltenes at oil–water interfaces, another long-debated question (42). Work with Teclis on asphaltenes of different origins (petroleum, bitumen, and coal) is in progress.

In collaboration with Jean-Louis Salager in Venezuela, I recently used a new method for measuring surface rheology in low IFT systems. This work allowed us to explain the very low stability of emulsions in three-phase oil–water–microemulsion systems, a question that puzzled me and many others since the 1980s (43).

MICROGRAVITY

Foam studies in the International Space Station (ISS) were planned since 1999. We wanted to suppress foam drainage and study foams containing appreciable quantities of liquid (wet foams) unstable on ground. The project began with Denis Weaire's group and now involves several other groups. The foam module should have flown before 2010, but we faced numerous delays. EADS (European Aeronautic Defence and Space Company, now Airbus), which had to provide a prototype in 2007, was unable to do so. The project had to be completely redefined and is now focused on foam ripening. To prepare these experiments, we took advantage of parabolic flight opportunities. We were able to show that in microgravity, bubbles in pure water are stable if the gas fraction is less than 64% (spherical bubbles), but unstable above: Bubbles distort into polyhedra, films are formed between them, and capillary drainage is fast and leads to film rupture (44). The first ISS flight took place in 2020, followed by others in 2021 and 2022. We are currently analyzing terabytes of data and uncovering many unexpected and exciting results: Wet foams behave quite differently than dry foams. A picture of such a wet foam is shown in **Figure 3**. Many interesting features are observed close to the gas fraction of 64%, which is the jamming transition of bubbles.

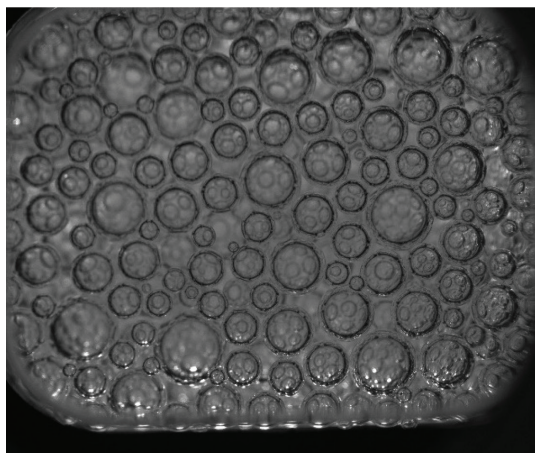


Figure 3

Picture of a wet foam in the International Space Station. Liquid fraction is 40%. The size of the image is 1 cm \times 1.4 cm.

CONCLUSION

My scientific career has been devoted to liquid interfaces. When I started, few studies of liquid interfaces were performed, because of both the lack of techniques and contamination problems making experiments cumbersome. Surfaces became more fashionable with the advent of miniaturized systems, such as micro- and nanofluidic devices: When the surface/volume ratio increases, at some point surfaces begin to matter. My work became therefore better coupled to that of others and, thus, more interesting as years went by.

As could be guessed from this article, the role of de Gennes was crucial in my career. There was not much research work in the field of colloid and interfaces in the 1970s in France; the topic was more active in England, Netherlands, and the United States, where it was carried out mostly by chemists and chemical engineers. De Gennes showed that the field, now called soft matter, was also attractive for physicists.

I stayed many years in the physics lab of the ENS, benefiting from an exceptional scientific environment. In 1994, I was offered to head the CRPP in Bordeaux. Seeing how difficult it was to remain invested in research, I decided to leave at the end of my four-year term. I then joined the Laboratory de Physique des Solides in Orsay, where I had many colleagues from the liquid crystal years and where I was offered space to start new activities. I retired officially in 2013 but still enjoy working there as an emeritus researcher.

I worked with Jacques Meunier and Marie-Anne Bouchiat to establish the experimental and theoretical bases of the surface light scattering method and edited a book on the subject (45). The method led me to study microemulsions, at a time when little was known about their properties. After only 10 years, many open questions were solved. I then turned to emulsions and foams, where the situation was quite different, as the field had been extensively investigated, but because these systems are not thermodynamically stable, their understanding was quite limited. I contributed to progress, and I've just finished writing a book on these topics (46).

I realized early that collaborations were useful and pleasant. Having colleagues and friends all over the world is a great opportunity for researchers. I largely benefited from the French and European network systems. These networks helped me to become more knowledgeable in chemistry. I ended up being a fan of molecules—they offer so many possibilities to discover new physics. The soft matter field is multidisciplinary, with interfaces not only between physics and chemistry but also biology. Biology seemed always too difficult to me—I only had brief excursions with a few DNA studies and a nanoparticle toxicity study (47). No doubt the soft matter interface with biology will successfully expand in the future.

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Errata

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