Gentner-Kastler-Preis

Complex Fluids in Confined Environments

Stratifications of thin films of polymer solutions

Dominique Langevin

Thin liquid films have properties that can be different from the bulk material. We have studied freely suspended films of polyelectrolyte solutions, that means films with two liquid-air surfaces. We were able to show that the forces between surfaces are oscillatory, revealing stratification, i. e. a structuring in layers of thickness equal to the polymer network mesh size. The stratification kinetics reveal interesting differences when the surface conditions are changed.

It is now well recognized that materials which are made of a small number of atoms or molecules have properties very different from the bulk material. For instance, gold nanoparticles do not produce the usual metallic reflection of bulk gold, their solutions are violet instead! Similarly, the properties of matter close to surfaces can be very different from bulk properties: crystals have to adjust the periodical array of their atoms to that of the surface, liquids become ordered, etc. [1]. These problems are nowadays extensively studied, in view of the fast developments of nanotechnologies, which require a good understanding of the consequences of confinement. Recently the franco-german network „Matter in dimension 2.5“ was created, associating German and French teams, including ours, that are working on complex fluids in confined environments.

In the case of liquids, the field of microfluidics is nowadays quite active, because of the development of miniaturized detectors in Analytical Chemistry and of diagnostics in Biology, such as DNA chips. The aim is to build „labs on a chip“ and to possibly extend the field towards Nanofluidics.

A number of studies of the behaviour of liquids close to surfaces have been reported in the literature. In their pioneering work with the Surface Force Apparatus (SFA), the „ancestor“ of the Atomic Force Microscope (AFM), Israelachvili, Ninham and coworkers evidenced an ordering phenomenon of liquids close to solid surfaces. This is illustrated in Fig. 1. On the top left side, one sees that the molecules have to order along the surface, because they cannot cross it. In liquids, the pair correlation function (which is the probability of finding a molecule at a distance r from another molecule) is oscillatory as in solids, because liquids are locally ordered. However, this order rapidly dies away exponentially with a characteristic length ζ called the correlation length1), which is only a few times the molecular size. A typical pair correlation function is shown on the bottom side of Fig. 1a. Here the liquid order extends at a distance of the surface equal to the correlation length ζ. If a second surface approaches close to the first one (Fig. 1b), the two ordered regions may overlap (Fig. 1c). As a consequence, the matter between the surfaces is no longer strictly speaking a liquid; it is more ordered. The forces between the surfaces are then oscillatory functions of their distance h, with a period and damping length close to those of the pair correlation function [2], as shown in Fig. 2. Recent work focuses on particular liquids such as water [3], whose behaviour close to surfaces remains unclear, despite its importance. An important field is also lubrication, as the dynamic behavior of these oriented liquid layers is unusual [4]. A question which still remains controversial is that of „slippage“ on a sub micrometric scale. [5]

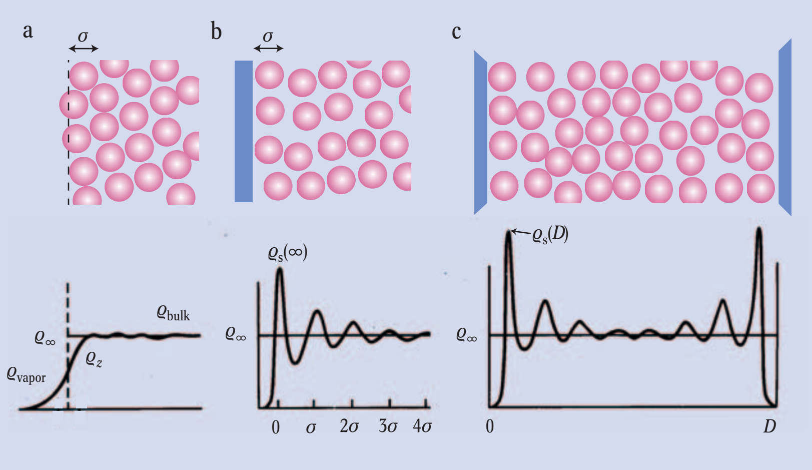

Fig. 1:
Ordering (top) induced by a wall (b) or two walls (c) on a liquid made of hard sphere molecules (a). Below each drawing, the corresponding pair correlation functions are represented [1].

Confinement in freely supended liquid films

We have focused our work on the confinement of liquids in freely suspended films, that is to say, films with two liquid-air interfaces. Such liquid films are normally unstable; their lifetimes are usually only a few seconds. We therefore use surfactants to stabilize them. Surfactants adsorb at both film surfaces, create a surface pressure π and lower the liquid surface tension $\gamma : \gamma = \gamma_0 - \pi$,

Prof. Dr. Dominique Langevin, Laboratoire de Physique des Solides, Université Paris Sud, Orsay, France – Plenary talk on the occasion ot the conferment of the Gentner Kastler Prize at the DPG Spring Conference 2004 in München

---

1) ζ is the length after which the amplitude has decreased by a factor e and is close to σ.

1617-9439/04/0808-67

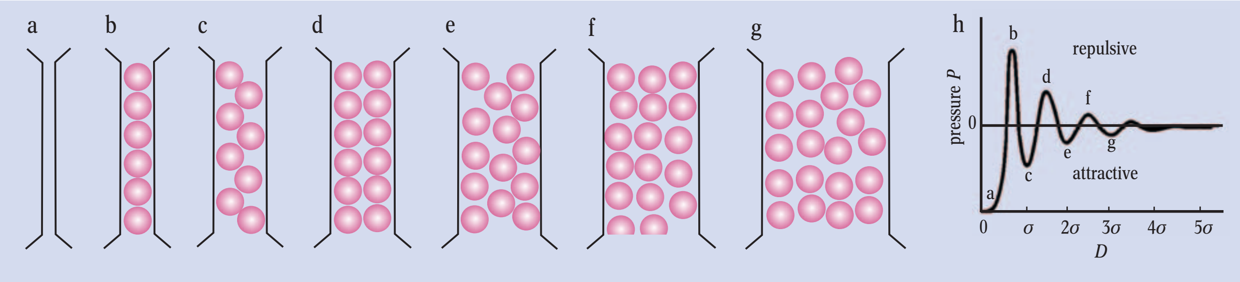

Figure 2:
Schematic representation of a liquid made of hard sphere molecules confined between two walls (top) and corresponding surface forces (bottom) [1].

γ_0 being the pure liquid surface tension. The surface pressure π depends on the number of adsorbed molecules. When the film surface is locally stretched, π decreases in the stretched regions; surface pressure gradients then build up and act as restoring forces (called „Marangoni forces“), protecting the film against rupture. These films are present in foams, usually made from surfactant solutions, the films separating adjacent bubbles (Fig. 3).

We work with films on frames, by using the so-called „porous plate method“ (Fig. 4) [5]. The film is formed in a small hole (diameter ~1 mm) drilled into a porous glass disc onto which a glass capillary tube is fused. The free end of the capillary tube is at atmospheric pressure and the disc is enclosed in a pressurized cell. The pressure is regulated by a syringe pump, which allows us to change the difference in pressure ΔP between the cell and the exterior, which is also the difference in pressure between the gas surrounding the film and the liquid in the film; ΔP is measured by transducers covering various pressure ranges. Once formed, the film thins because of the applied pressure, flattens and eventually reaches an equilibrium thickness. At equilibrium, ΔP is compensated by the disjoining pressure $\Pi_{\rm d}$, which is the force between the two surfaces counted per unit area. The film thickness h is measured by using micro-interferometry: a white light beam is focused onto the film, the reflected beam is filtered at 632 nm and its intensity is measured with a photomultiplier. The whole film area is imaged by a video camera and the images recorded on a computer.

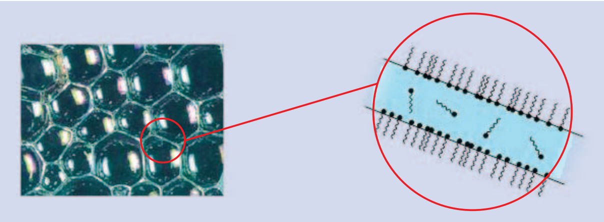

Fig. 3:
Thin soap film in a foam (left), and enlarged representation showing the two surfactant monolayers at the film surfaces.

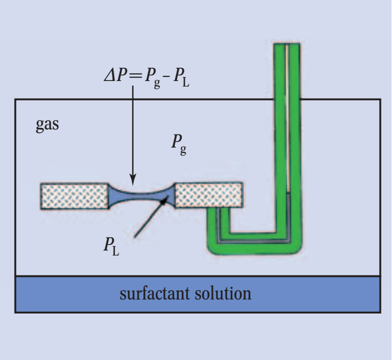

Fig. 4:
In the „porous plate method“ for studying thin films a liquid film is formed in a small hole. The hole is drilled into a porous glass disc onto which a glass capillary tube is fused.

Electrostatic and van der Waals forces

The described experimental setup can be used for the study of film thinning and for the measurement of the surface forces. Let us discuss the second. Typical interactions between surfaces in freely suspended films are van der Waals forces (attractive) and electrostatic forces if the surfactant is ionic (repulsive). Short range forces (steric, hydration) become important at small thicknesses. The disjoining pressure is the sum of the corresponding terms counted per unit area:

$$\begin{aligned}&\Pi_{\rm vdw} \sim -A/6\pi h^3\\&\Pi_{\rm elect} \sim {\rm B}\ {\rm e}^{-\varkappa h}\\&\Pi_{\rm steric,\ hydration} \sim {\rm C}\ {\rm e}^{-h/\lambda}\end{aligned}\tag{1}$$

where A is the Hamaker constant, B and C are constants, λ is the range of the short range forces, typically a few tens of nm, and $\varkappa^{-1}$ is the Debye-Huckel length such that:

$$\varkappa^2 = 4\pi l_{\rm B} \sum Z_i^2 n_i \text{ with } n_i = N c_i / M_i \tag{2}$$

where n_i the number concentration of the ionic species i, c_i its concentration by weight, M_i its molecular weight, and Z_i its valency. When the electrostatic repulsion is strong enough, an energy minimum can be found for thicknesses of a few tens of nanometers. Figure 5 shows a schematic diagram of the disjoining pressure, in which the contribution of short-range repulsive forces has also been included. If a pressure ΔP is applied, the thickness of the film decreases down to h_i (Fig. 5), and the corresponding equilibrium film is called „common black film“. If the pressure ΔP is larger than the electrostatic barrier, after drainage one reaches a very small film thickness where the water layer thickness is of order λ: this is the so-called „Newton black film“. Both types of films are called „black“ because their thickness is smaller than the optical wavelength and they reflect little light.

Oscillatory forces

In addition to electrostatic and van der Waals forces, oscillatory forces can also be observed, if their period is large enough. Indeed, the resolution is not as good as with the SFA. Such forces have been measu-

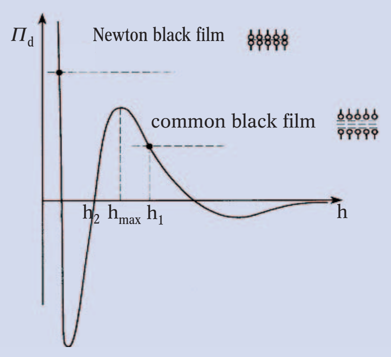

Fig. 5:
Variation of the disjoining pressure $\Pi_{\rm d}$ with film thickness h. The dotted lines correspond to different applied pressures ΔP and show the final equilibrium thicknesses of the film.

red with solutions containing surfactant micelles [7]. Surprisingly, they were also seen with semi-dilute polyelectrolyte solutions, where the polymer chains form a network with a mesh size ξ [8]. The origin of the oscillatory forces in this case has been explained in ref [9]. The structure factor $S(q)$ of polyelectrolyte solutions has a peak: for large q, $S(q)$ is similar to the form factor of neutral polymers, but at the difference of these polymers, $S(0)$ is very small; this is because the osmotic pressure is essentially due to the counterions and is large. The position of the $S(q)$ peak is such that $q_{\max} \sim 2\pi/\xi$. The pair correlation function is the Fourier transform of $S(q)$; it is therefore oscillatory, with a period ξ, because of the presence of the peak. As in the earlier discussion for simple liquids (Fig. 2), the forces are also oscillatory, with a period close to ξ. When the film thins under the influence of an external pressure, the local film thickness changes discontinuously between the different branches of the disjoining pressure curve. Circular domains of smaller thickness nucleate in the thick film, expand and cover the whole film area (Fig. 6). This process is a particular case of dewetting. It should be noted that only repulsive forces can be measured with this technique, at the difference of the SFA. When the polymer concentration is increased, additional branches appear [9-12] (Fig. 7). In all these experiments, which involved various polymers (polyacrylamide sulfonate (PAMPS), polystyrene sulfonate (PSS), carboxymethylcellulose (CMC), xanthane), the period ξ was found to be inversely proportional to the square root of the polymer concentration, as expected from theory (Fig. 8). The same forces can be measured with an AFM, in which case it is not necessary to add a surfactant; with this instrument, larger portion of the branches can be measured [13]. At larger pressures and smaller thicknesses, one would again find the transitions „common black film“ and „Newton black film“.

Stratification in polymer networks

The existence of structuring at a nanometric scale is therefore a general phenomenon in thin films containing complex fluids. Although the forces have not been measured, other experiments evidenced the phenomenon of stratification in solutions of colloidal particles [14]. Whereas it is easy to conceive the kinetic process as an expulsion of layers of micelles or colloidal particles in the film border, it is less obvious to understand how the polymer network evolves during film thinning. A surprising observation was that the velocity of opening of dark spots, such as those shown on Fig. 6, depends on the surfactant used: if the surfactant has a charge of the same sign as the polymer, the kinetics are faster than when the surfactant has a charge of opposite sign [12]. Since the amount of surfactant used is extremely small, the difference should be associated with different surface conditions. Indeed, surfactants of the same charge as the polymer repel the polymer chains and create non-adsorbing conditions, whereas surfactants of opposite charge form mixed surfactant-polymer layers at the film surfaces [15].

This behaviour is coherent with that observed recently with thin polymer films (polymer melts). The dynamic behavior of polymer films, and in particular the description of viscous dissipation in thin films, is presently an active field of research. Israelachvili et al. [16] found by using an SFA that the viscosity of polystyrene (PS) films increases with decreasing film thickness (of the order of nanometers), which suggests an increase of the entanglement density. Neutron scattering experiments on thin PS films [17] show, on the contrary, a decrease of the entanglement density with decreasing film thickness. However, in the SFA experiments, both interfaces of the films are constrained by hard substrates, whereas in the neutron scattering experiments, the films had a free surface. Masson and Green [18] have studied dewetting of PS films on silicon substrates, and shown that the viscosity decreases with decreasing film thickness, which is consistent with the neutron scattering results. Valignat et al. [19] studied dewetting of another polymer, polydimethylsiloxane (PDMS), and showed that the local friction is independent of the polymer molecular weight, in a range where the bulk viscosity varies by a factor of 50. The few existing

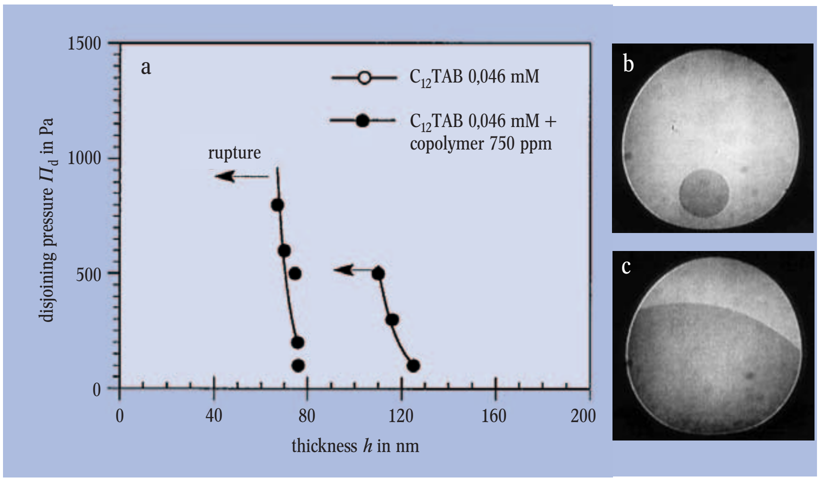

Fig. 6:
Disjoining pressure Π_d versus thickness measurements for a film made of a polyelectrolyte (PAMPS) solution (left) and successive images of the film taken during the discontinuous thickness change (lower arrow on the Π_d curve) [8]. The analogue of Fig. 5 would look like Fig. 2b in this case.

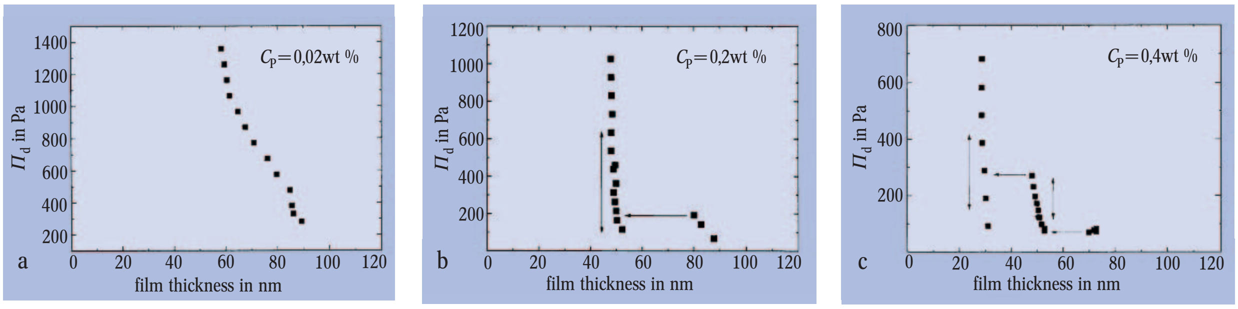

Fig. 7:
Disjoining pressure Π_d versus film thickness for polystyrene sulfonate (PSS) at different polymer concentrations C_p (a–c) [10]. When the polymer concentration is increased, additional branches appear.

experimental results tend therefore to show that local viscosity is smaller than the bulk viscosity if the film surfaces are free to move (non-adsorbing case), and larger than the bulk viscosity if the polymer stick to the film surfaces (adsorbing case). This behaviour is in line with our experiments on polymer solutions.

In conclusion, we have studied freely suspended films of polyelectrolyte solutions and shown that the forces between surfaces are oscillatory, revealing stratification, i.e. a structuring in layers of thickness equal to the polymer network mesh size. The stratification kinetics reveals interesting differences when the surface conditions are changed: the kinetics is faster when the polymer network is decoupled from the surfaces (non-adsorbing conditions). Recent results seem to show that the local viscosity tends towards the water viscosity, as if the network progressively disappears during the thinning process [20]. These conceptually important findings are currently being investigated in more detail.

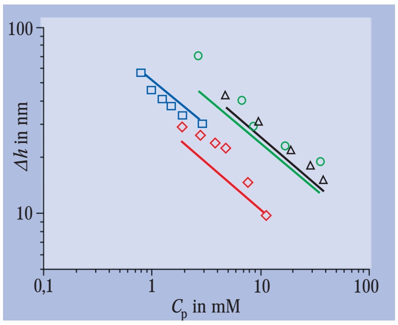

Figure 8:
Distance between disjoining pressure branches Δh versus polymer concentration for different polymers: PAMPS (squares); PSS (triangles); CMC (lozenges); xanthane (circles). The lines are the theoretical predictions for the network mesh size; according to [10] and [12].

Acknowledgments

This work was supported in part by CNES. More details can be found in the original references 9, 10, 12 and 15. The work was started at the Laboratoire de Physique de l'Ecole Normale Supérieure, Paris, and continued at the Centre de Recherche Paul Pascal, Bordeaux and at the Laboratoire de Physique des Solides, Orsay with many colleagues: A. Sonin, A. Asnacios, V. Bergeron, A. Espert, R. v. Klitzing, A. Colin, C. Stubenrauch, C. Marquez and A. Saint-Jalmes. They are all gratefully acknowledged.

References

[1] *J. N. Israelachvili*, Intermolecular and Surface Forces, Acad. Press, London (1985)
[2] *R. Roth, R. Evans* and *S. Dietrich*, Phys. Rev. E **62,** 5360 (2000)
[3] *U. Raviv, P. Laurat* and *J. Klein*, Nature **413,** 51 (2001)
[4] *C. Drummond* and *J. Israelachvili*, Phys. Rev. E **63**, 041506 (2001)
[5] *L. Leger,* J. Phys. Condens. Matter **15**, S-19 (2003)
[6] *K. J. Mysels* and *M. N. Jones*, Discuss. Faraday Soc. **42,** 42 (1966)
[7] *V. Bergeron* and *C. Radke,* Langmuir **8,** 3020 (1992)
[8] *V. Bergeron, A. Asnacios* and *D. Langevin*, Langmuir **12,** 1550 (1996)
[9] *A. Asnacios, A. Espert, A. Colin* and *D. Langevin,* Phys. Rev. Lett. **78**, 4974 (1997)
[10] *R. v. Klitzing, A. Espert, A. Asnacios, T. Hellweg, A. Colin* and *D. Langevin*, Colloids and Surfaces A **149**, 131 (1999); *R. v. Klitzing, A. Espert, A. Colin* uad *D. Langevin*, Colloids and Surfaces A **176**, 109 (2001)
[11] *B. Kolaric, W. Jaeger* and *R. v. Klitzing,* J. Phys. Chem B 104, 5096 (2000); *O. Theodoly, J. S. Tan, R. Ober, C. E. Williams* and *V. Bergeron*, Langmuir **17**, 4910 (2001); *R. v. Klitzing, B. Kolaric, W. Jaeger* and *A. Brandt*, Phys. Chem. Chem. Phys. **4**, 1907 (2002)
[12] *C. Marquez Beltran, S. Guillot* and *D. Langevin* Macromolecules **36**, 8506 (2003)
[13] *A. J. Milling*, J. Phys. Chem. **100**, 8986 (1996); *D. Qu, D. Baigl, C.E. Williams, H. Mohwald* and *A. Fery*, A. Macromolecules **36**, 6878 (2003)
[14] *D. T. Wasan, A. D. Nikolov, P. A. Kralchevski* und *I. B. Ivanov,* Colloid Surfaces 67, 139 (1992)
[15] *D. Langevin*, Advances in Colloid and Interface Science **89**, 467 (2001)
[16] *G. F. Luengo, J. Schmit* and *J. Israelachvili*, Macromolecules **30**, 2482 (1997)
[17] *R. L. Jones, S. K. Kumar, D. L. Ho* and *T. P. Russell*, Nature **400**, 146 (1999)
[18] *J.-L. Mason* and *P. F. Green*, Phys. Rev. E. **65**, 31806 (2002)
[19] *M. P. Valignat, G. Oshanin, S. Villette, A. M. Cazabat* and *M. Moreau*, Phys. Rev. Lett. **80**, 5377 (1998)
[20] *C. Marquez* and *D. Langevin*, in preparation

The author

Dominique Langevin is one of the leading scientists in the field of soft condensed matter. She graduated from the Ecole Normale Supérieure in Paris and received a doctorat d'état in Physics while working at the Physics Laboratory of the Ecole Normale Supérieure. After that, she did a postdoctoral stay at the Collège de France in 1976 and continued research at the Ecole Normale afterwards. She later served as director at the Centre de Recherche Paul Pascal in Bordeaux. Since 1998 Dominique Langevin has been working at the Laboratoire de Physique des Solides in Orsay.