

STRUCTURAL CHARACTERISATION OF SUPPORTED THIN POLYMER FILMS

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CHAPTER I. INTRODUCTION

1. INTRODUCTION

Thin polymer films on solid substrates are ubiquitous in modern technology. Understanding the structure and dynamics of polymers near solid walls is important in areas such as polymer processing, lubrication, adhesion and material properties. Surfaces and interfaces indeed play an important role in modern materials. Many high performance materials contain organic-polymer or inorganic-polymer interfaces. In addition, with the development of nanotechnologies and the increased trend to miniaturization, the need to understand polymer at interfaces is further increased. This is for instance important for thin and ultra-thin polymer films, which are technologically important systems, whose behaviour may be dominated by interfacial effects since their ratio surface/volume becomes increasingly important.

Their stability is a critical issue for many processes. Owing to the importance of this topic, numerous studies have concentrated on the perturbations of the dynamical properties of polymers near solid interfaces, either on filled polymers¹⁻⁵, either on model systems like thin films⁶⁻¹². This thesis precisely plans to investigate in more details the structure of the two interfaces of thin supported polymer films, the buried one at the substrate side, and the free one in contact with air. Below, we recall briefly the main properties of thin polymer films and polymers near interfaces, and the physical bases of the reflectometry techniques we will use to analyse the interfaces.

Glass transition temperature and dynamics of polymer chains

Long ago, dynamic mechanical measurements of various silica filled polymers^{1,2} showed two glass transitions for the concerned polymers : one related to the T_g of the bulk polymer, while the second was ascribed to regions containing chains of reduced mobility, due to the presence of solid walls, and was occurring at a higher temperature. Also, dynamic mechanical properties of polystyrene and polymethylmethacrylate filled with glass beads and mica flakes³ have been investigated and modifications of the dynamic properties were observed and related to the extent of polymer-filler interaction energy. Keddie *et al*^{6,7} described a dependence on thickness for the glass transition temperature. A decrease of T_g compared to the bulk value was observed for polystyrene films deposited on passivated silicon. Also, polymethylmethacrylate films (on gold surfaces) exhibited a T_g decreasing with decreasing film thickness. They ascribed this behaviour to the presence of a liquid-like layer at the air surface of the film. However, only a slight increase in T_g is observed for films of decreasing thickness spin-coated on silicon wafers with their native oxide layer, which is attributed to possible hydrogen bonds between the substrate and the film, that could reduce the chain mobility and by consequence increase the T_g of the film. Reiter^{8,9} studied the dewetting of polystyrene films (on floated glass substrates) thinner than the unperturbed size of the polymer chain. He put into evidence a dewetting at temperatures much lower than the bulk T_g of the polymer. This increase of mobility is larger when the film is thinner. By contrast, increased T_g of P2VP films were measured, compared to the bulk value, when deposited onto silicon oxide¹⁰. The authors attributed their measurements to the presence of a region of reduced

chains mobility near the solid substrate/polymer interface, due to the favourable interactions between polymer and substrate. Forrest *et al*^{11,12} were interested in the study of three geometries for thin polystyrene films : freely standing films, films supported onto a SiOx surface with one free film surface and films supported onto a SiOx surface with the film surface covered by a SiOx layer. The Tg of these films shows large modifications compared to the bulk value, putting into evidence the polymer/substrate interaction as a major factor influencing Tg. Other studies¹³ of the same systems support the existence of enhanced surface dynamics in the polymer and also that the free surface has a strong influence on the measured properties of thin polymer films. These experiments give evidence that when the effects of the free surface are removed, bulk-like behaviour is recovered in all measured quantities.

The glass transition behaviour of stacked layers of thin films was also investigated. Stacked thin films of polystyrene and poly(2-chlorostyrene)¹⁴ exhibit glass transition dynamics that are similar to those observed for single thin films. The glass transition temperature of as-stacked thin films is lower than the one of the single thin supported films of same thickness as the one of the single layers in the stacked thin films, and is higher than the one of freely standing films. Correlations have been proposed between the modification of Tg for thin polymer films and other dynamic properties of the film^{15,16}. Experimental reports show that the viscosity of polystyrene films supported by oxide-coated silicon decreases with decreasing film thickness, which is consistent with the observations made for the Tg of the same films¹⁶. Measurements of Tg of polymer films together with the dewetting rate of the films on different substrates¹⁵ put into evidence that there is no relation between Tg and the dewetting rate of the film.

Evidence for the distribution of Tg's across polystyrene film was given in ¹⁷, revealing that the enhancement of dynamics at a surface affects Tg several tens of nanometres into the film. When polymer films are sufficiently thin for a reduction in thickness to lead to a reduction in overall Tg, the surface-layer Tg actually increases with a reduction in overall thickness, whereas the substrate-layer Tg decreases.

Napolitano *et al*¹⁸⁻²² observed modifications of the dynamics of thin polymer films and postulated the presence of a layer characterised by a reduced mobility (later called "dead layer") in ultrathin films of poly(ethylene terephthalate) capped with aluminium, due to the strong interaction between polymer and substrate at the interfaces. The structural dynamics of the films is slowed down when the thickness is reduced. In the case of extremely thin films of polystyrene¹⁹, and poly(2-vinyl pyridine) capped with aluminium²⁰ they observed a gradual defreezing of the interfacial zone between the so-called dead layer and the bulk. The defreezing process, appearing before the glass transition, is responsible for the temperature dependence of the deviations from bulk behaviour. Analysis of freely standing films of PS²¹ revealed a reduction in the glass transition temperature. This is seen as an experimental evidence of a gradient of glass transition temperatures across the film thickness induced by an enhanced molecular mobility at the two free surfaces of the membrane. The glass transition behaviour of thin poly (bisphenol-A carbonate) films sandwiched between two aluminium layers²² was investigated. The thermal glass transition temperature is rather independent of the film thickness down to 20 nm. For thicknesses below 20 nm, an increase of Tg is observed. There exists a strong interfacial interaction of polycarbonate chains in the vicinity of the interface with aluminium, which results in a reduced molecular mobility with respect to bulk PBAC behaviour.

Fluorescence intensity measurements²³ have been used to determine the effects of decreasing film thickness on the glass transition temperature and on the relative strength of the glass transition, in supported, ultrathin polymer films (poly(styrene), poly(isobutyl methacrylate), and poly(2-vinylpyridine)). Positive deviations from bulk T_g are observed in ultrathin PiBMA and P2VP films on silica substrates while substantial negative deviations from bulk T_g are observed in ultrathin PS films on silica substrates. The strength of the glass transition was seen to decrease in thinner films. The temperature dependence of fluorescence intensity also provides useful information on the effects of processing history as well as on the degree of polymer-substrate interaction.

Lateral force microscopy (LFM) was used to probe the molecular motions at the surface of thin polystyrene films²⁴. LFM measurements were performed as a function of temperature in order to detect the relaxations at the surface and indicated a large enhancement of the surface molecular motions.

The glass transition of thin resist films and homopolymers (PS, PMMA) has been studied by two techniques: spectroscopic ellipsometry and multi wavelength optical interferometry²⁵. The film T_g values were compared with DSC measurements of the bulk material. A variation of the glass transition temperature was detected with both techniques for PS and PMMA when the thickness of the film decreases below 100 nm. It can be observed that the surface characteristics of the substrates exert an influence on the thermal properties of the films, especially when the polymer and the substrates have a strong affinity.

Fukao²⁶ et al studied the dynamics of thin films of poly(vinyl acetate) (PVAc) and poly(methyl methacrylate) (PMMA) by dielectric relaxation spectroscopy. The alpha relaxation, which is the main

component of the glass transition, is observed for thin films of PVAc and PMMA as a dielectric loss peak at a temperature T_α . For PVAc, T_α decreases gradually with decreasing thickness, and the thickness dependence of T_α is almost independent of the molecular weight. For PMMA, T_α remains constant as thickness decreases down to a critical thickness d_c , at which point it begins to decrease with decreasing thickness. For both PVAc and PMMA, a broadening of the distribution of the relaxation times in thinner films was observed. Also, the relaxation strength is depressed as the thickness decreases for both polymers.

The dynamics of chains at the surface of PS films have been extensively studied by Kajiyama *et al*²⁷⁻³². The scanning viscoelastic microscopy (SVM) and lateral force microscopy (LFM) were applied to examine the surface relaxation processes of the monodisperse PS films with various molar masses. The surface T_g was found to be much lower than the bulk T_g for the entire molecular weight range, and was strongly affected by the chain length of PS. It was insensitive to the film thickness. Such an intensive activation of the thermal molecular motion at the PS surfaces can be explained in terms of an excess free volume in the vicinity of the film surface induced by the preferential segregation of the chain end groups. Thermal segmental motion of supported PS thin and ultrathin films was studied by dynamic viscoelastic measurement. The range of temperature corresponding to the segmental motion in the ultrathin films is broadened, being toward both lower and higher temperature sides. Also, the activation energy for the segmental motion is reduced for ultra thin films probably due to a surface effect. The segmental motion in polymer ultrathin films is also strongly influenced by surface and interfacial effects. The surface relaxation behaviour of atactic poly(propylene) (aPP) film was examined by LFM³³. The surface T_g

of the film was lower than the bulk Tg of the polymer. This put in evidence that molecular motion at the aPP surface was more active than that in the bulk as for the case of PS.

Surface molecular motion of P2VP films was studied by LFM³⁴. It revealed that the surface Tg was much lower than the corresponding bulk Tg, as observed previously for other polymers. The surface Tg increased with decreasing thickness but remained lower than the bulk Tg even for the ultrathin films. In that case, since molecular mobility on the substrate might be restricted owing to the polar attractive interaction between polymer segments and the hydrophilic substrate, the activation of surface molecular motion seemed to be reduced for such an ultrathin film.

Dewetting of polymers films

While the glass transition is related to the freezing/defreezing of the motion of chain segments of limited length (a few to a few tens of monomer units), the dewetting of thin films concerns the motion of the entire chain.

Considerable efforts have been also devoted to the understanding of thin film dewetting from solid substrates, both experimentally³⁵⁻⁵⁶ and theoretically⁵⁷⁻⁶⁵.

Poly(ethylene propylene) films of various molecular weights, which would normally wet native-oxide silicon surfaces, were observed to dewet the surface when the film thickness became less than the polymer radius of gyration³⁶. PDMS films on silanised silicon wafers³⁷ were used to study the dewetting of ultrathin polymers films. The dewetting here was interpreted as a slippage of the polymer chains on the solid surface. The hole formation in thin polystyrene films process before rupturing is described to occur in two stages⁵⁵, each characterized by distinct dynamical and morphological features. This

has implications regarding the transition from the formation regime to subsequent hole growth regime on the underlying substrate.

Experiments were realised to suppress the rupture of thin films on non-wetting surfaces³⁸. To that aim, a polystyrene brush was attached to the silicon surface and films of oligostyrene together with free chains of polystyrene became stable for months. The effect would arise from entanglements of free chains with the immobilised brush.

As a matter of comparison, for liquid metals films on fused silica⁴⁰, two modes of dewetting are observed. First, heterogeneous nucleation of dry circular patches that are growing in diameter during the melting period. Second, spinodal dewetting, characterised by an instability of the liquid film against the growth in amplitude of surface waves (with characteristic wavelengths). The final structure of the film depends on the dominant rupture process.

Reiter^{35,41,49} and Sharma³⁹ studied the dewetting of thin polystyrene films on different substrates. These films dewet when annealed above T_g , following three stages. First, the films break up creating randomly distributed holes. Second, the holes then grow and the rims ahead of the holes eventually merge forming cellular structures. Third, the resulting ribbons are unstable and decay into droplets. They show adequation between experiments and theoretical predictions for instabilities and dewetting of polymers films.

Also, they put into evidence the importance of dispersion forces that are present everywhere, whose importance is largely neglected because directly at a surface or at an interface they are mostly weak compared with specific interactions of short range. They show that these forces are relevant and may have drastic consequences on the stability of thin films through the temporal evolution of different morphologies of unstable thin liquid polymer films caused by

destabilising intermolecular forces⁴⁹. Further work⁵⁰ presented real time observation of the pattern evolution during the self-destruction of thin polymer films, based on experiments with polydimethylsiloxane films sandwiched between silicon wafers and aqueous surfactant solutions. One more stage of pattern evolution was identified, namely the first that consists of an amplification of surface fluctuations. So, self-destruction of a thin polymer film would be a combination of two serial processes, amplification of initial surface fluctuations and subsequent dewetting of the underlying substrate. Sferrazza *et al*⁴⁵ studied the interface between deuterated poly(methyl methacrylate) films on polystyrene substrates. They put into evidence the earlier stages of the interfacial instability that finally leads to the spinodal dewetting of one polymer film by another. This dewetting is attributed to dispersive forces that amplify thermally excited capillary waves at the polymer/polymer interface.

Investigations of the opening of holes in thin glassy polystyrene films deposited onto silicon wafers coated with a polydimethylsiloxane monolayer revealed strong deviations from the behaviour of pure liquids⁵³. These experiments demonstrated that a thin film does not need to be purely liquid in order to dewet. Intermolecular interactions responsible for capillary forces may be sufficiently strong to deform even quasi-solid films. These results imply that phenomena like changes in film morphology or apparent thickening may also occur below the glass transition temperature (T_g) and can therefore not be taken as a criterion for determining T_g .

Imaging of the processes of spinodal decomposition and particle nucleation leading to dewetting of polystyrene films from non-wetting silicon substrates was realised⁴². Both spinodal decomposition and particle nucleation were observed to initiate dewetting. Under clean room conditions, spinodal decomposition dominates the nucleation

process while particle nucleation increases in higher aerosol concentration environments. Dewetting in thin polymer films can also be promoted by thermal cycling (anneal-quench cycling) producing delamination or loss of adhesion. The three mechanisms of defect formation were described and compared to theories of defect formation during drying of thin liquid films on non-wetting substrates. By contrast, others authors⁴³ suggested that during dewetting of polystyrene films on silanised surfaces, spinodal dewetting would not play any significant role. On the contrary, it could be demonstrated that rupture is dominated by nucleation from defects. Furthermore, strong evidence was given that these defects are intrinsic to the polymer due to its peculiar morphology, as opposed to other materials (such as metals).

Attention was paid to the surface of island structure of dewetted poly(ethylene propylene) films⁴⁴ and it was possible to identify capillary waves on the island surfaces. The wave number spectrum of these waves is modified by a cutoff introduced by the van der Waals substrate-film interactions.

Dewetting of films of polystyrene of low molar mass on a silicon substrate was investigated as a function of film thickness⁴⁵. Observation of the nucleation of holes in the early stage of dewetting for relatively thick films ($h > 100$ Å) were made, but the breakup of thinner films occurs through the growth of uniformly distributed surface undulations ("spinodal dewetting"). The average amplitude of these undulations increases exponentially up to the film rupture. This behaviour is predicted by a capillary waves instabilities model.

Studies of a similar system were realised⁴⁷ with emphasis put on the structure of the "dry" zones of the dewetted films. These observations put into light the existence of a remaining ultra-thin polymer film, with a structure consisting of small dimples with a diameter in the

nanometer range. The global structure of the dewetted film was similar to observations already made. The existence of an ultrathin residual film was also found when polyethylene oligomers were dewetted from a rough silicon oxide substrate^{66,67}. In contrast, no residual film was found when the film dewetted from a smooth oxide, indicating the importance of substrate roughness on dewetting. The crystallization of the oligomers was also observed, and the stability of the crystals was discussed depending on their interfacial energies. Kim *et al*⁴⁸ studied the dewetting of films of a perfluoropolyether polymer on silicon substrates. The disjoining pressure (negative derivative of the free energy with respect to film thickness, which arises from the interaction energies of molecules in a film being different from that in the bulk) of these films was determined, for a dewetting system. The determined disjoining pressure explains the different dewetting processes observed for different initial film thicknesses and is dominated by structural forces and by the inability of the polymer to spread on its own monolayer.

Seeman *et al*⁵¹ studied the dewetting of thin films of liquid polystyrene of low molar mass from solid surfaces. They demonstrated the interplay between short- and long-range interfacial forces. Observations comprised nucleation and spinodal dewetting, as well as thermal nucleation of holes. These results show, both experimentally and theoretically, that the stability of polystyrene films, or rather the wettability of silicon wafers, can be tuned by the variation of the oxide layer thickness. Polystyrene films on top of pure, clean Si surfaces are stable, whereas they are unstable on infinitely thick oxide layers. On top of Si substrates with a finite oxide layer thickness, polystyrene films are metastable or unstable. The authors found experimental evidence for all three rupture mechanisms within one system. The morphological characteristics of

the dewetting patterns could be assigned to the three possible dewetting mechanisms.

Homogeneous nucleation and spinodal dewetting were also observed by Wang *et al*⁶⁸. They studied the temporal growth pattern of surface fluctuations on a series of spinodally unstable polymer films and deviations from the attended behaviour were observed. They ascribed these deviations arise from large-amplitude fluctuations induced by homogeneous thermal nucleation.

Dewetting of thin polystyrene films with small height fluctuations⁵⁴ (imposed by rubbing with a rayon cloth) has been investigated as a means to distinguish spinodal dewetting and heterogeneous nucleation and to determine the effects of pre-existing topographical fluctuations on film rupturing. It was demonstrated that samples with a thickness below a certain value rupture predominately by a spinodal mechanism whereas the thicker samples rupture primarily by heterogeneous nucleation. The result shows that perturbations from rubbing do not produce changes in the free energy of the films that will alter the prevailing dewetting mechanism or the characteristic wave vector in spinodal dewetting. Nonetheless, the rubbing-induced defects do affect the rupturing process, in manners depending on the dominating dewetting mechanisms.

In the same idea, chemically patterned substrates with arrays of progressively narrower stripes were used to investigate the influence of pattern size on the morphology of ultrathin dewetting polystyrene films⁵⁶. The coupling of the dewetting patterns to the pattern scale and frequency at a relatively early stage influences the evolution to the final dewet morphology.

In a recent article, Reiter and Napolitano⁶⁹ address the central question of the way of obtaining and preparing polymer films used for the multiples studies made on this major experimental system.

According to them, understanding properties of thin polymer films requires that film preparation would be explicitly considered as a key factor. To that end, they suggest a simultaneous combination of approaches, *i.e.* dewetting studies, measurements of density profiles across the film, determination of the glass transition temperature, ... taking into account all the parameters linked to the sample preparation. The out-of-equilibrium state of annealed spin-coated polymer films would be a major reason for the large breadth of sometimes contradictory results reported for such films.

Theoretical approaches

From a more theoretical point of view, work realised on this topic predicted and described the behaviour of liquid and polymer films. Vrij and Overbeek⁵⁷ demonstrated that surface fluctuations having a wavelength larger than a critical value will grow spontaneously, due to the actions of van de Waals forces, and that these films will become thinner and break. Also, Brochart *et al*^{58,59} predicted the same behaviour. A non-wetting film is unstable. Below a critical thickness the film will dewet in a spinodal way, with a characteristic wavelength. The following steps are the appearance of dry patches that are going to generate a cellular pattern. The rims around each patch are going to coalesce and finally break into droplets.

Sharma⁶⁰ studied the relationship between film stability, morphology and macroscopic parameters of wetting, taking into account apolar and polar interactions. The conditions under which growth of instability leads to the film breakup, or to spatially non homogeneous films, were discussed.

Suh *et al*⁶¹ presented a criterion for determining the dynamic instability of a thin polymer film that is strongly confined to a substrate. They assert that when such a polymer film is heated above its glass

transition temperature, it dewets from the substrate by a spinodal dewetting.

Thiele *et al*⁶² have analyzed the evolution of a thin liquid film under the influence of long- and short-range interactions by determining the stable, metastable, and linearly unstable thickness ranges for flat films. They have shown that the linearly unstable film thickness range comprises nucleation- dominated and instability-dominated subranges.

Another work⁶⁴ established conditions under which instability and dewetting of a thin liquid film can be engendered by the density variations related to changes in the local film thickness. An increase in the density with the increasing film thickness can stabilize a thermo-dynamically unstable film and a decrease in the density with increasing film thickness can render a thermodynamically stable film unstable.

As well, the stability with respect to dewetting of thin films deposited on a substrate they thermodynamically wet was considered⁶³. It was shown that if density fluctuations with a sufficiently large amplitude appear in a film, the resulting gradient of disjoining pressure in the film destabilizes the free surface which can lead to the breaking up of the film in droplets.

Becker *et al*⁶⁵ put into evidence that the full spatial and temporal evolution of the rupture of ultrathin films can be modelled in quantitative agreement with experiment. It was accomplished by combining highly controlled experiments on different film-rupture patterns with computer simulations using novel numerical schemes for thin-film equations.

Objectives of this thesis

The dynamics of chains is not without importance when studying structural properties, since dynamics govern the parameters that allow a system to be driven to equilibrium. The study of the structure of thin films is precisely what will be the focus of this thesis.

In contrast to all the experiments described above, much less experimental work has been devoted to the characterisation of static properties of polymers in their condensed state near solid substrates, although theoretical works have predicted perturbations of polymer chains near solid walls (coil shapes, segment density, radii of gyration, conformations...) ⁷⁰⁻⁷⁶, which have as a consequence an effect on the dynamic properties of the polymer chains ⁷⁷. However, the experimental detection of such perturbations remains elusive. Yet, such issues may be important to consider before trying to explain the dynamical behaviour of polymers near interfaces. Also important is the characterisation of the free interface.

In this context, the objectives of this work are the following:

First, we will address experimentally the question of the density evolution of polymers near solid substrates, by determining density profiles on thin polymer films using X-ray reflectometry. Because we are interested in relatively minor perturbations, careful analysis procedures had to be followed. These are described in the data analysis section. Different anionic polymers of different molecular weights have been used in this study, while the substrate selected is the native silicon oxide layer of a clean silicon wafer.

Second, we will try to characterise the structure of free surfaces of polymers and to compare it to laws predicting the behaviour of small

molar mass liquids. AFM is the technique retained here because of its relevancy for the systems studied. Also, we will describe the root mean square (rms) roughness of the free surfaces of polymers. Knowledge of this value allows to lift uncertainties in interpreting X-ray reflectometry (XRR) data and as a consequence, to use less free variables during model fitting. In this context, we will also check for the stability of thin polymer films, which is, under specific circumstances, related to the surface roughness.

In a third part, using the results from the structural analysis of chapters II and III, we will try to refine and complete the study of structure of thin polymer films, using a complementary technique, namely neutron reflectometry, in order to probe with more precision the buried interface.

CHAPTER II. STRUCTURE DETERMINATION OF THIN POLYMER FILMS BY X-RAY REFLECTOMETRY

1. INTRODUCTION

In this chapter, we will address experimentally the question of the density evolution of polymers near solid substrates, by determining density profiles on thin polymer films using X-ray reflectometry. Because we are interested in relatively minor perturbations, careful analysis procedures have to be developed. These are described in the data analysis section. Different anionic polymers of different molecular weights have been used in this study, while the substrate selected is the native silicon oxide layer of a clean silicon wafer. Before entering into the results, the reflectometry technique will be presented in more details.

2. REFLECTOMETRY TECHNIQUE AND PRINCIPLES

X-ray reflectometry is an analysis method based on X-ray scattering. It compares the intensity of an incident beam of X-rays on a sample with the reflected intensity by the sample, as a function of the angle θ_0 which is the angle complementary to the incident angle.

Reflectivity is given by $R = \frac{I_{reflected}}{I_{incident}}$. Reflectivity is generally

expressed as a function of $k_{z0} = \frac{2\pi}{\lambda} \sin \theta_0$, the component of the wavevector perpendicular to the interfaces (λ is the wavelength in air). This allows to compare easily measurements realised at different angles with different wavelengths.

A. Experimental system

The experimental system used is described in Figure II-1.

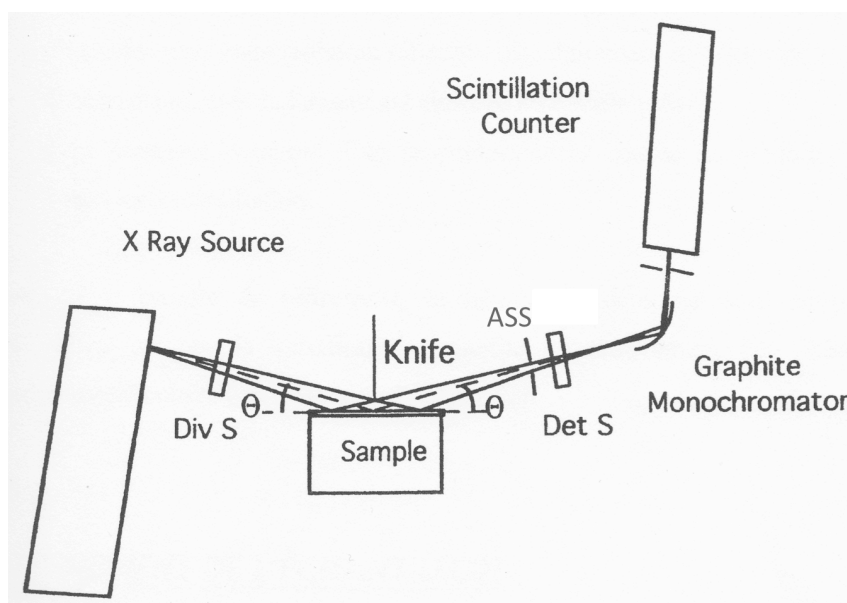


Figure II-1 : schematic representation of the reflectometer used in this work.

This device is based on a two-circle diffractometer (D5000 Siemens). It consists of

- a X-ray source with a rotating copper anode, with a maximal electrical power of 12kW ;
- divergence slits (div S) which allow to control the divergence in the incident plane, during the measurements of powder diffraction. In the case of reflectivity measurements these slits do not play a significant role and are closed so as to reduce parasite radiations. A sharp knife edge which is placed a few micrometers above the sample surface, and defines the effective divergence of the incident beam. The position of the knife is set with a micrometer screw.

- anti-scatter slits (ASS) that play the same role as divergence slits, on the detector side;
- Soller slits (that are not depicted on the figure), one at the end of the tube, the other before the monochromator. There are used in order to reduce the beam divergence in the direction perpendicular to the incident plane ;
- Detector slit, before the detector, that is used to define the direction of collected and is set so as to maximise the ratio signal/noise and to ensure that all the reflected intensity is detected ;
- A detector composed of a graphite curved monochromator and of a scintillation counter.

B. Reflectivity by perfectly sharp interfaces

Principles described in the following concern X-ray reflectometry (XRR). Nevertheless, they can be easily generalised to neutron reflectometry (NR). This is not an in-depth review of this technique, but essentially a description focused on the way we used this technique in the case of polymer thin films. T. P. Russell⁷⁸ and M. Tolan⁷⁹ provide detailed accounts of the theory of reflectivity. These works mainly inspired what follows here.

Single substrate

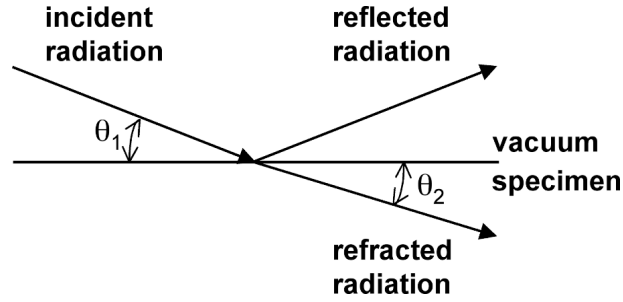


Figure II-2 Schematic representation of the incident, reflected and refracted beams on a surface⁷⁸.

Consider an incident radiation on a surface (Figure II-2). If refractive indexes of both sides of the interface are different, this incident radiation will undergo refraction and reflection. In the wavelength domain of X-rays, the refraction index is slightly less than unity and is given in good approximation by :

$$\eta = 1 - \delta + i\beta \quad \text{equation II-1}$$

where $\delta = \frac{\lambda^2 \rho_e r_0}{2\Pi}$ and $\beta = \frac{\mu \lambda}{4\Pi}$,

with :

- λ the wavelength of the incident radiation [$\text{\AA}$];
- ρ_e the material electron density [$\text{\AA}^{-3}$];
- r_0 the electron classical radius ($2.82 \cdot 10^{-15}$) [m];
- μ the material absorption coefficient [$\text{\AA}^{-1}$].

For both X-rays and neutrons, δ_X and δ_N are on the order of 10^{-6} . β_X is 10^2 to 10^3 smaller than δ_X . In the case of neutrons, the absorption coefficient is not significant enough to be considered, *i.e.* $\beta_N = 0$ ⁷⁸.

At the interface separating two media 1 and 2 with respective refractive indexes η_1 and η_2 , Snell's law gives the relation $\eta_1 \cos \theta_1 = \eta_2 \cos \theta_2$. This allows to determine θ_2 knowing θ_1 , the incidence angle. If medium 1 is air or vacuum, $\eta_1 = 1$ and $\cos \theta_2 = \frac{\cos \theta_1}{\eta_2}$.

For materials studied here, $\delta > 0$, which means that $\eta_2 < \eta_1 = 1$. As a consequence, $\theta_2 < \theta_1$, and there exists a critical angle, θ_c , under which total external reflection occurs. Only an evanescent field penetrates the matter below θ_c . θ_c is defined by $\cos \theta_c = \eta_2$.

It can be shown, within a good approximation, that $\theta_c \propto (2\delta)^{1/2}$. As a consequence, $\theta_c \propto \rho_e^{1/2}$ and $\theta_c \propto \lambda$. Over a wide range of materials, θ_c varies from 0.05 to 0.3 ° for typical values of λ .

The extent to which radiation is reflected at a surface or an interface depends on the difference of the wavevectors in the media on each side of the interface. As the incidence and reflected angles are equal (which is the case for specular reflectivity), the radiation undergoes a modification in its wavevector only perpendicular to the interface. For incident radiation in air, the perpendicular component of the wavevector is given by $k_{z0} = \frac{2\pi}{\lambda} \sin \theta_0$, where λ is the wavelength of the incident radiation in air and θ_0 the angle of incidence. The subscript 0 denotes the surrounding media, air in our case. In a medium i, the z component of the wavevector is modified and reads :

$k_{zi} = (k_{z0}^2 - k_{c0/i}^2)^{1/2}$, where $k_{c0/i}$ is the critical value of k_{z0} for the medium i in air, under which total reflection occurs ($k_{c0/i} = \frac{2\pi}{\lambda} \sin \theta_c$).

The reflectance or reflection coefficient of the electrical field at an infinitively sharp interface separating two media i and $i+1$, with wavevectors perpendicular to the interface k_{zi} and k_{zi+1} is given by the Fresnel law¹ :

$$r_{i,i+1} = \frac{k_{zi} - k_{zi+1}}{k_{zi} + k_{zi+1}}. \quad \text{equation II-2}$$

In the more specific case of an interface between air (0) and a polymer (1), this yields $r_{01} = \frac{k_{z0} - k_{z1}}{k_{z0} + k_{z1}}$, and the Fresnel reflectivity

due to the interface is then $R_F = r_{01} r_{01}^*$, where $*$ denotes the complex conjugate.

¹ Note that for the investigation of polymeric films by NR or XRR, the polarisation of the incident radiation is not of importance, since the reflectivity of both p and s-polarised waves is almost identical for grazing angle of incidence.

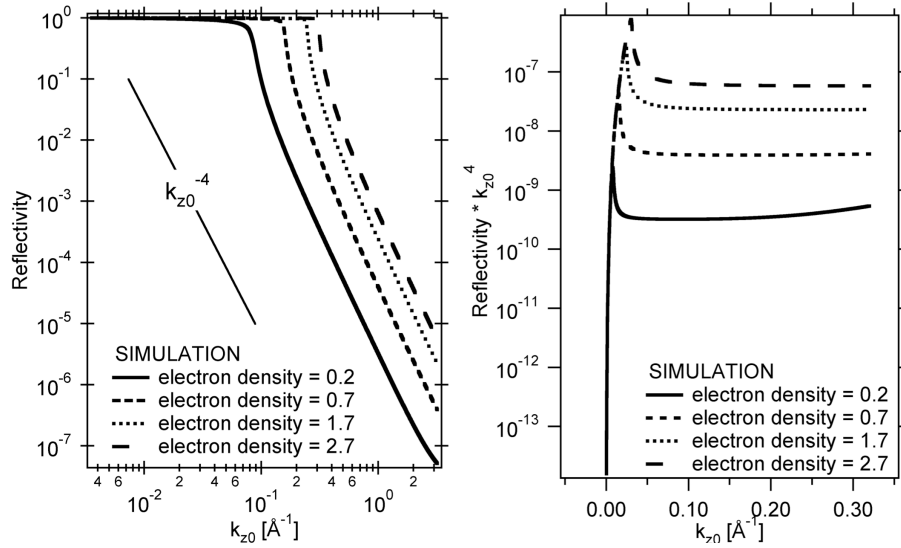


Figure II-3 Right : simulation of reflectivity profiles of flat materials of different electron density, showing the influence of electron density on the critical angle and illustrating Porod's law when $k_{z0} > k_c$; Left : the same curves, multiplied by k_{z0}^4 , which allow to emphasise the power law describing reflectivity at high angles.

At high values of k_{z0} , well above the critical angle θ_c , $R_F(k_{z0})$ varies as $\sim k_{z0}^{-4}$; this is called Porod's law (Figure II-3). Also illustrated in Figure II-3 is the effect of the film electron density, *i.e.* the nature of the material probed, on the value of the critical angle. We indeed see that $k_{c0/i}$ (value until which total reflection occurs), which is related to θ_c , varies with the nature of the film measured.

Film over a substrate

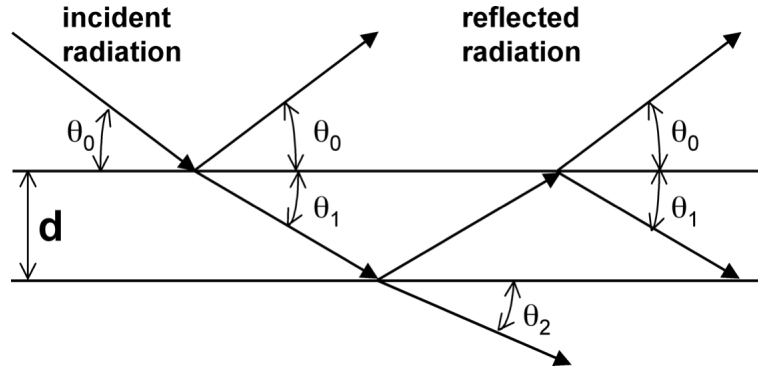


Figure II-4 : Schematic representation of the incident, reflected and refracted beams in a film of thickness d deposited onto a substrate⁷⁸.

Consider now the case of a polymer film of thickness d (medium 1), deposited onto a substrate (medium 2) with air as surrounding medium (medium 0) (Figure II-4). The reflectances to be taken in account are the following :

- r_{12} , reflectance between substrate and polymer film;
- r_{01} , reflection coefficient between specimen and air.

r_{01} and r_{12} are defined following by equation I.2.

The reflectance of the entire system is

$$r = \frac{r_{01} + r_{12} \exp(2ik_{z1}d)}{1 + r_{01}r_{12} \exp(2ik_{z1}d)}, \quad \text{equation II-3}$$

where $\exp(2ik_{z1}d)$ takes into account the influence between the rays reflected at the different interfaces.

Then, the exact Fresnel reflectivity is

$$R_F(k_{z0}) = rr^* = \frac{|r_{01}|^2 + |r_{12}|^2 + 2\text{Re}\{r_{01}r_{12}\exp(2ik_{z1}d)\}}{1 + |r_{01}|^2|r_{12}|^2 + 2\text{Re}\{r_{01}r_{12}\exp(2ik_{z1}d)\}} \quad \text{equation II-4}$$

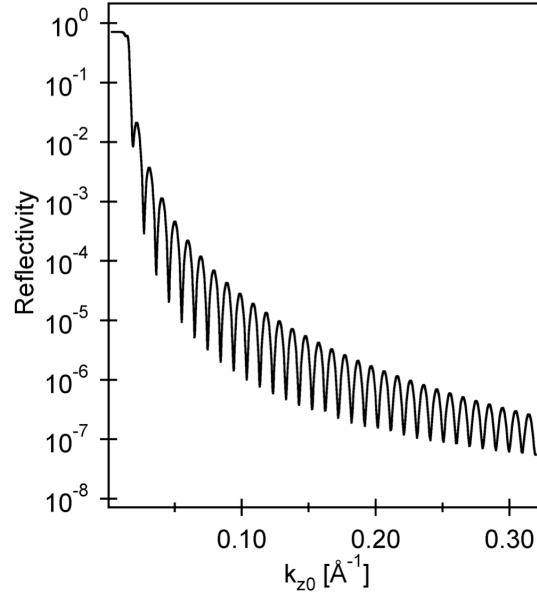


Figure II-5 : Simulation of a typical reflectivity curve for a PS film on a silicon substrate.

Figure II-5 shows a simulation of a typical reflectivity curve for a flat PS film on a flat silicon substrate, considering that interfaces are infinitively sharp. The reflectivity curve presents a series of fringes, called Kiessig's fringes. These are representative of the sample thickness. The position of two successive minima allows the determination of film thickness, following the relation :

$$d = \frac{\pi}{\Delta k_{z0}}. \text{ This expression neglected refraction, and is only valid}$$

when $\theta_0 \gg \theta_c$.

For incidence angles well above θ_c , the relation between electron density and reflectivity can be expressed by :

$$R_F(k_{z0})k_{z0}^4 \propto \delta_1^2 + (\delta_2 - \delta_1)^2,$$

which means that $R_F(k_{z0})k_{z0}^4$ is proportional to the square of the differences in electron density of the concerned interfaces, in the case of perfect interfaces. This illustrates clearly the sensitivity of reflectivity to the local variation in electron density and not to absolute values.

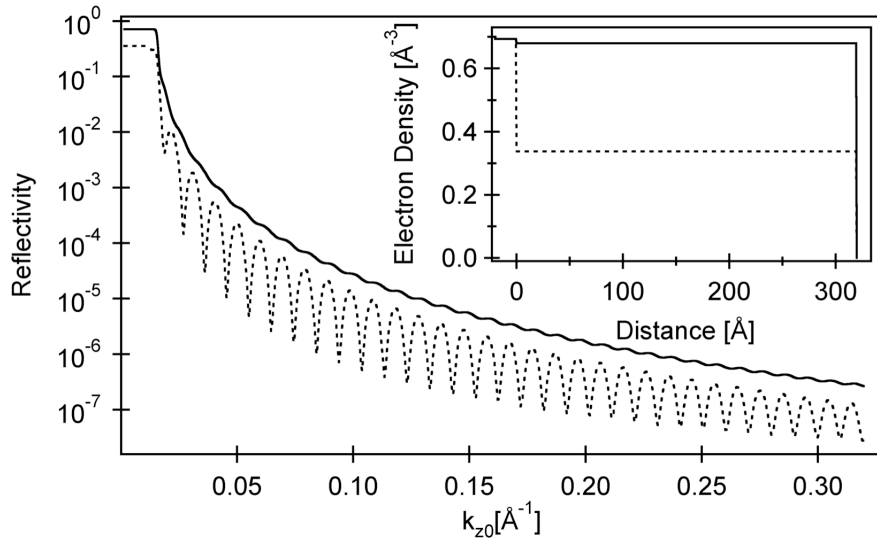


Figure II-6 : Simulation of typical reflectivity curves on a silicon substrate : effect of density contrast. The reflectograms are associated to the model electron density profiles showed in the inset. For the clarity of the figure, curves were shifted from each other by a factor 10.

The oscillations in the reflectivity profile result from the thickness of the film. The amplitude of the oscillations will depend upon the contrast in density at both interfaces. Indeed, if we look at equation I.4, we see that the real part of the third factor at the numerator is multiplied by both r_{01} and r_{12} . As a consequence, the amplitude of the oscillations will be more important if the contrast at both interfaces

is more pronounced. If there are no Kiessig's fringes in the reflectogram, this does not necessarily mean that no layer is present on the surface, but it can also signify a matching of the density at the interfaces, as depicted in Figure II-6.

Multilayered film over a substrate

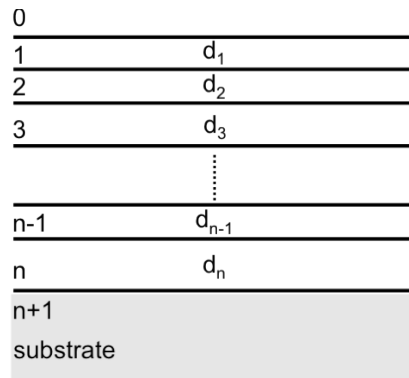


Figure II-7 : Schematic representation of a system consisting of n layers with $n+1$ interfaces.

Consider now a specimen containing an arbitrary number n of layers, deposited on a substrate (Figure II-7). The reflectance is calculated by considering first the reflectance between the substrate ($n+1$) and the n^{th} layer that is $r_{n,n+1} = \frac{k_{zn} - k_{z,n+1}}{k_{zn} + k_{z,n+1}}$. The reflectance is computed following equation I.3. Then the reflectance between the n^{th} layer and the $(n-1)^{th}$ layer is

$$r_{n-1,n} = \frac{r'_{n-1,n} + r_{n,n+1} \exp(2id_n k_{zn})}{1 + r'_{n-1,n} r_{n,n+1} \exp(2id_n k_{zn})},$$

where r' denotes the reflectance given by equation I.2 and $r_{n-1,n}$ includes internal reflections at the $n-1/n$ and $n/n+1$ interfaces of

the single layer film. $r_{n-1,n}$ is then used to compute the reflectance for the next layer by

$$r_{n-2,n-1} = \frac{r'_{n-2,n-1} + r_{n-1,n} \exp(2id_{n-1}k_{zn-1})}{1 + r'_{n-2,n-1}r'_{n-1,n} \exp(2id_{n-1}k_{zn-1})}.$$

This recursion is followed until $r_{0,1}$, the reflectance at the air/specimen, is obtained; the reflectivity is then computed using equation I.3. The theory here above is called "Dynamical Theory", and uses Parratt's formalism⁸⁰ for arbitrary multilayers. This model can be used to describe the scattering by many films, when the film can be modelled by different stratified multilayers.

An alternative approach, developed by Als-Nielsen^{78,81}, is the "Kinematical Approximation". This approach relates the reflectivity to the derivative of the electron density, yielding :

$$R(k_{z0}) = rr^* = \frac{(4\pi\rho_f)^2}{k_{z0}^2} \left| \int_{-\infty}^{+\infty} \frac{d\rho_e(z)}{dz} \exp(2ik_{z0}z) dz \right|^2,$$

where ρ_f is the average electron density in the film. This expression can also be expressed in the form :

$$\frac{R(k_{z0})}{R_F(k_{z0})} = \left| \int_{-\infty}^{+\infty} \frac{d\rho_e(z)}{dz} \exp(2ik_{z0}z) dz \right|^2, \quad \text{where } R_F(k_{z0}) \text{ is the}$$

reflectivity of the bare substrate. This result is only valid for $k_{z0} > k_{c0/i}$, that is to say, far from the critical angle. This corresponds to the first Born approximation of the complete scattering equation⁸².

C. Influence of roughness on reflectivity

So far, we considered only perfectly sharp interfaces, which is far from reality. The changes in density are never abrupt or discontinuous, nor at a surface, nor at an interface. Gradients of

density are observed instead of discontinuities. In the case of a perfect interface, we saw that

$$R_F(k_{z0})k_{z0}^4 \propto \delta_1^2 + (\delta_2 - \delta_1)^2,$$

If the interface between air and film is rough, whatever the source of this roughness, this relation is not true anymore. This is the case of all "real systems". $R_F(k_{z0})k_{z0}^4$ is still proportional to $(\delta_2 - \delta_1)^2$, which represents the density contrast between the film and the substrate. But, in the case of a rough surface, $R_F(k_{z0})$ decreases more rapidly than k_{z0}^{-4} , for $k_{z0} > k_c$. The Porod's law can be rewritten in the following form :

$$R(k_{z0}) = R_F(k_{z0}) \exp(-4k_{z0}k_{z1}\sigma^2),$$

where σ is the rms roughness of the surface or interface.

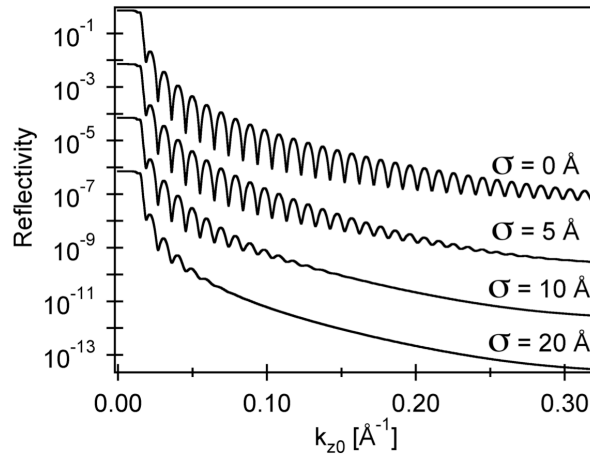


Figure II-8 : Simulation of typical reflectivity curves on a silicon substrate. Effect of roughness. For the clarity of the figure, each curve was shifted from the previous by a factor of 100.

In the case of specular reflectivity, only σ influences the reflectivity value. The lateral evolution of roughness does not affect the specular reflectivity. σ is determined by averaging laterally over a distance (surface) of size comparable to the radiation coherence length (area). The coherence length, l_c , is essentially the longest separation

distance on the specimen from which emerging X-rays will interfere coherently at the detector. Otherwise said, this is the length over which the density will be averaged. It can be determined from the uncertainty principle, which relates the uncertainty on the photon momentum to the uncertainty on its position, following :

$$\Delta k \Delta x = 2\pi.$$

equation II-5

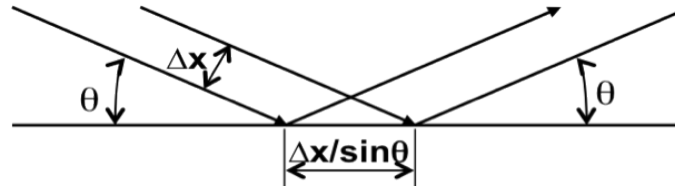


Figure II-9 : Two rays of an Incident plane wave, separated by a distance Δx , impinging on a specimen surface⁷⁸.

Consider two rays impinging at a surface, separated by a distance Δx , with an incidence angle θ (Figure II-9). At the surface, the distance between the two rays is $\Delta x / \sin \theta$. The rays are then reflected to a detector. In the conditions of specular reflectivity, there is no path length difference between them and the coherence length is determined by the effective width of the wavefront. l_c depends on the factors directly affecting Δk and Δx , as the wavelength, the incidence angle, the beam divergence. This length is macroscopic, from 1 to 100 μm . So the experimental resolution will be of critical importance to determine l_c .

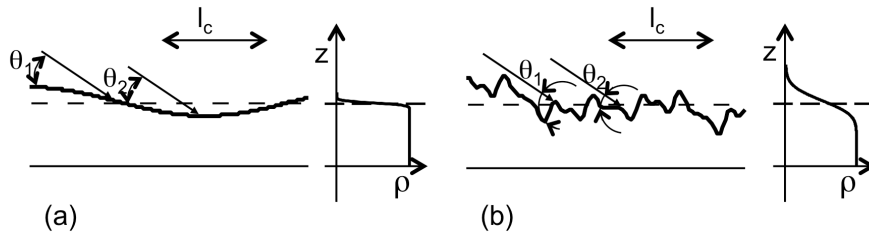


Figure II-10 : definition of: (a) waviness and (b) roughness of a surface compared with the coherence length l_c ⁷⁸.

Knowing the value of the coherence length is an important issue. Indeed, l_c allows to distinguish between roughness and waviness (long range roughness) of a surface. If the surface curvature has a wavelength larger than l_c , one speaks of waviness (Figure II-10a). In the other case, the surface presents undulations of characteristic length smaller than l_c : this is roughness (Figure II-10b)). The vertical electron density projection "felt by these X-rays" will be different in the two situations. In the case of waviness, the density variation at the air/film interface remains sharp despite surface undulations (Figure II-10a)). These undulations give the same effect as varying the incidence beam divergence on a flat surface. In the presence of roughness, the averaged electron density profile shows a slow variation from zero in air to the average value in the film. Surface or interfacial roughness causes a reduction of the measured reflectivity related to this surface or interface.

D. Reflectivity analysis: pseudo auto-correlation function

The correlation function used is the self-correlation of the derivative of the electron density profile $\rho(z)$, which is defined as:

$$P(r) = \frac{1}{\rho_s^2} \int_{-\infty}^{+\infty} \frac{d\rho(z)}{dz} \frac{d\rho(z+r)}{dz} dz,$$

where ρ_s is the electron density of the substrate.

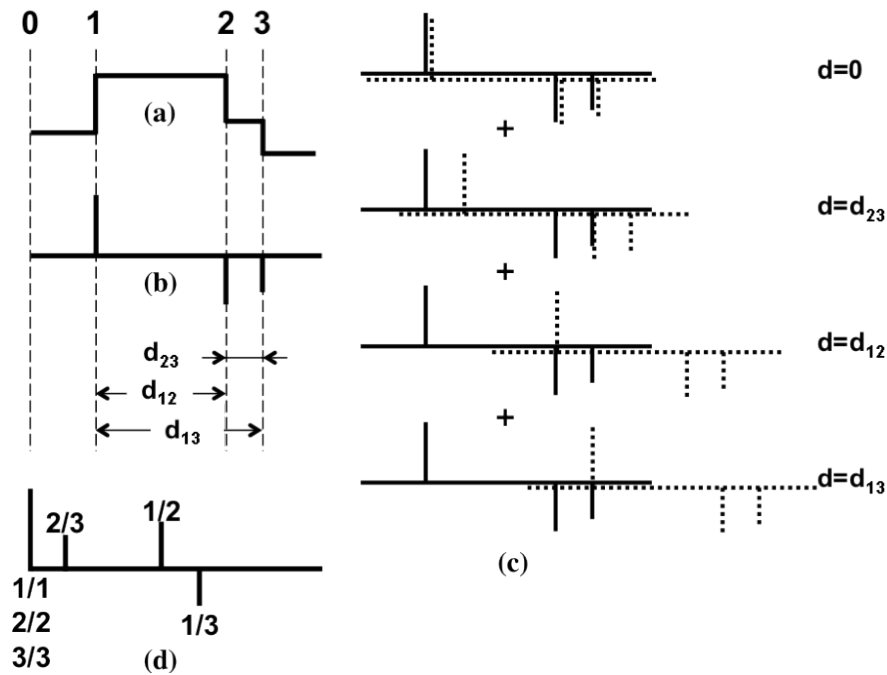


Figure II-11 : Intuitive approach of the auto-correlation function of the electron density profile derivative. a: discrete profile. b: derivative of the density profile. c: the four steps of computing the auto-correlation of the derivation density. d: sum of the different non-zero values obtained in c.

Let us have a sight at the physical meaning of this function, using the discrete density profile presented in Figure II-11 a. The first step to compute this correlation function is to take the derivative of the density profile (Figure II-11 b). Then, the derivative profile is convolved with itself (Figure II-11 c). Intuitively, it means that if we slide the derivative along the x-axis and multiply it by the unslided original derivative, we will obtain non zero values only for a few x values. These values are all the possible distances between interfaces. The correlation function is simply the integral of this product (Figure II-11 d). This function is in fact an interface distribution function. It allows us to get more information about distances *between the different interfaces* characterising the measured system.

Under the validity conditions of the first Born approximation, the autocorrelation function can be computed from reflectivity data $R(k_z)$, by means of a Fourier transform^{78,83,81} :

$$P_R(r) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} \frac{R(k_{z1})}{R_F(k_{z1})} \exp(2ik_{z1}r) dk_{z1}, \quad \text{equation I-6}$$

where k_{z1} is the component perpendicular to the interface of the wave vector *in the film* (i.e. we operate a refraction correction as suggested by others^{84,85}) and $R_F(k_{z1})$ is the Fresnel reflectivity of the bare and perfectly smooth substrate computed at k_{z1} ⁸⁶.

Since the first Born approximation is not valid near the critical angle for total external reflection, $P_R(r)$ is not strictly equal to $P(r)$. We thus call $P_R(r)$ pseudo auto-correlation function.

3. DATA ANALYSIS

XRR data will be analysed by an iterative procedure performed in reciprocal and real space. The procedure is based:

- on the comparison between measured reflectivity and reflectivity computed from a density profile to be optimised;
- on the comparison between an experimental correlation function and the correlation function computed from the simulated reflectivity.

These two ways of analysis will be described in the two following sections. They allow to be sure that errors are distributed uniformly in both direct and reciprocal spaces.

A. Reflectivity analysis: simulation of experimental curves

The construction of the density profile from the reflectivity data was done in the following way. We first select an a priori model for the density profile, consisting of one layer, which describes the film as a continuous slab of constant density. We calculate the reflectivity associated with this particular model using Parrat's formalism⁸⁰, and adjust the different parameters (thickness, roughness and electron density) of the slab and substrate, in order to minimize

$$\chi^2 = \sum_{j=1}^N \left(\frac{R_{meas,j} - R_{calc,j}}{w_j} \right)^2,$$

where $R_{meas,j}$ is the measured reflectivity, $R_{calc,j}$ is the computed reflectivity and w_j is a weight equal to the standard error on point j .

At this stage of the process, if the control parameter χ^2 has an acceptable value, we stop the fit.

If χ^2 is too high, we restart the fitting procedure with a more complex model for the density profile. That is to say we introduce one or two more layers, usually at the interfaces. These layers do not have a physical meaning as such, but have as goal to introduce a perturbation (by comparison to the initial homogenous layer) in the density profile. Again, we fit the parameters. This procedure is repeated with increasing complex models (e.g. obtained by dividing each layer situated at the interfaces in two) until we have a low value for χ^2 . If this condition is fulfilled for models containing an important number of layers (more than six), we try finally to simplify this model in order to keep the main features of the density profile, while reducing the number of parameters. In some instances we found useful to use a regularisation technique during the fits, as described elsewhere⁸⁶.

Unfortunately, we have to face the phase problem inherent to all scattering techniques. Since we measured the amplitude of reflectivity and not the reflectance, the phase information is lost. As a consequence, it is not possible to define unambiguously a single electron density profile related to a reflectivity measurement. To allow a better analysis of the measurement, we used another complementary approach to determine the density profile associated with a particular reflectivity measurement.

We can calculate and compare the pseudo ACF $P_R(r)$, computed from fit, and the pseudo ACF $P_{R,\text{exp}}(r)$, computed from the experimental data. Note that we do not compare directly the self-correlation of the electron density, $P(r)$, with $P_{R,\text{exp}}(r)$, since these two functions always differ slightly due to the failure of the first Born

approximation at very low angles. Because the Fourier transform in equation I-6 has the virtue to accumulate at the same spatial location small periodic differences between R_{meas} and R_{calc} , the comparison between $P_R(r)$ and $P_{R,exp}(r)$ reveals clearly such differences that are not easily detectable in reciprocal space. The comparison between $P_R(r)$ and $P_{R,exp}(r)$ is performed qualitatively : all the features (peaks, valleys) of $P_{R,exp}(r)$ must be found in $P_R(r)$.

B. Reflectivity analysis: combined approach

The construction of the density profile from the reflectivity data was done in different steps. We first selected an a priori model for the density profile, consisting in one layer of constant density. If χ^2 has an acceptable value, we compared the shapes of $P_R(r)$ and of $P_{R,exp}(r)$. If all the features present in $P_{R,exp}(r)$ are also displayed in $P_R(r)$, we stop the fit.

If χ^2 is too high, or/and the shape of $P_R(r)$ and $P_{R,exp}(r)$ show noticeable differences, we restart the fitting procedure with a more complex model for the density profile. Again, we fit the parameters and compare $P_R(r)$ and $P_{R,exp}(r)$. This procedure is repeated with increasingly complex models until we have together a low value for χ^2 and a qualitatively good agreement between $P_R(r)$ and $P_{R,exp}(r)$. If the agreement between the two functions is qualitatively good and χ^2 is low enough, we stop the adjustment procedure. The obtained density profile is, following a very good probability, the most appropriate to describe the structure of the film, perpendicular to its surface.

4. EXPERIMENTAL PART

A. Polymers

The polymers used in this study are PS (poly(styrene)), PMMA (poly(methyl methacrylate)) and P4VP (poly(4-vinyl pyridine)). PS was obtained from Polymer Laboratories, UK. PMMA and P4VP were obtained from Polymer Source Inc, Canada. Samples used in this study are described in Table II-1. These polymers were selected for the potential differences in the way they interact with the substrate considered. PS is an apolar polymer, whereas PMMA and P4VP are more polar and hydrogen-bonded to the Si-OH groups present on the surfaces of a clean silicon wafer.

The size of the chains is computed as $R_g = \sqrt{\frac{n}{6}}b$, where n is the number of repeat units and b the statistical segment length. The statistical segment length can be taken from values from the literature or computed from values of the characteristic ratio⁸⁷ C_∞ according to $b = \sqrt{2C_\infty} l_{cc}$, where $l_{cc} = 1.54$ Å is the length of the C-C bond in the main chain. Given values of C_∞ are comprised between 9 and 12 for PS, 6 and 9 for PMMA and 11.2 for P4VP, that gives b values of 6.5-7.5 Å, 5.3-6.5 Å and 7.3 Å respectively for PS, PMMA and P4VP. This indicates a slightly more flexible chain for PMMA. These values are in good agreement with the experimental values of b for PS (6.8 Å⁸⁸), and P4VP (8 Å⁸⁹). However, the value of b published for PMMA by Sato et al⁸⁸, which is 4.9 Å, is slightly lower than what can be computed from the tabulated value of C_∞ . In this work, the experimental value was used for the determination of the estimated

value of R_g . Table II-2 gives the characteristics of the different polymers used in this study.

Polymer	Molar Mass (M_n) [g/mole]	R_g [Å]	Polydispersity Index	Tg of bulk polymer [°C]
PMMA	$528.4 \cdot 10^3$	~ 142	1.11	133
	$88.6 \cdot 10^3$	~ 58	1.03	135
PS	$1030 \cdot 10^3$	~ 277	1.05	109
	$66 \cdot 10^3$	~ 70	1.03	104
P4VP	$81.5 \cdot 10^3$	~ 91	1.18	152

Table II-1 : Characteristics of the polymers used in this study. Radii of gyration were computed from the following statistical segments lengths: $b_{PS} = 6.8 \text{ Å}^{88}$, $b_{PMMA} = 4.9 \text{ Å}^{88}$, $b_{P4VP} = 8 \text{ Å}^{89}$.

B. Substrate

The substrates used are silicon wafers with their layer of native oxide ($\sim 13 \text{ Å} \pm 2 \text{ Å}$ as measured by ellipsometry), obtained from Wacker (n-type, <100> orientation). Prior to spin coating, these wafers were cleaned by immersion for 20 minutes in a freshly made solution [1:1vol/vol of sulphuric acid (98%, Merck) and hydrogen peroxide (27% Vel) (piranha solution)]. The wafers were then thoroughly rinsed in milliQ water and dried by spinning at 3000 rpm in a clean room environment. This procedure efficiently removes the organic contaminants without introducing measurable roughening of the surface. This cleaning procedure has been reported^{90,91} to produce a highly hydrophilic surface by leaving on the silicon oxide layer a relatively dense layer of Si-OH functions.

C. Film Preparation

The polymer films were prepared by spin-coating (speed: 3000 rpm) from polymer solutions of different concentrations directly after having cleaned the substrate, in a clean room environment. In the case of

PS and PMMA, the solvent used was toluene (Merck, p.a.). In the case of P4VP, the solvent used was pyridine (Acros, 99+%, spectrophotometric grade). These solvents allow the deposition of smooth and homogeneous films, which is a prerequisite for X-ray reflectometry. To obtain the relationship between film thickness and solution concentration, a series of films were measured by ellipsometry. From these calibrations, we then selected spin-coating concentrations giving thicknesses around $4R_g$ (radius of gyration) for each polymer. This allows minimizing confinement effects on film structure.

The samples were measured by XRR before and after annealing. The annealing took place in a vacuum furnace equipped with a trap for oil vapours. The samples were annealed for 5 hours at temperatures from 35°C to 50°C above the T_g of the bulk polymer, and then quenched in air at room temperature.

D. Measurements

XRR measurements were performed with a $\theta - 2\theta$ goniometer (D5000 from Siemens, radius of the goniometer = 30 cm), which is mainly composed of a $Cu K\alpha$ source ($\bar{\lambda} = 1.5418 \text{ \AA}$), a graphite secondary monochromator, a scintillation counter and a Siemens reflectometry stage modified in house. The divergence of the beam in the incidence plane was set by a variable $1 \text{ }\mu\text{m}$ -precision slit; typical divergences of 0.0084° were used. The reflected beam was collected through a $200 \text{ }\mu\text{m}$ wide detector slit. Soller slits in the incident and reflected beam limited axial divergence to 0.02° . A special automated alignment procedure allowed the sample to be positioned within a few micrometers from the goniometer sample⁹¹. The incident intensity and

reflected intensity at low angles of incidence were measured through a calibrated filter to avoid overexposure of the detector.

The reflected intensity was divided by the measured incident intensity to obtain reflectivity. The data were corrected for background scattering and invariance of the illuminated area at very low angles of incidence (below $\cong 0.125^\circ$, depending on sample size). The data are reported as a function of k_{z0} , the component perpendicular to the interface of the wave vector in vacuum of the incident photons

($k_{z0} = \frac{2\pi}{\lambda} \sin \theta$, where λ is the X-ray wavelength and θ is half the angle between incoming and outgoing beams).

E. Results

PS

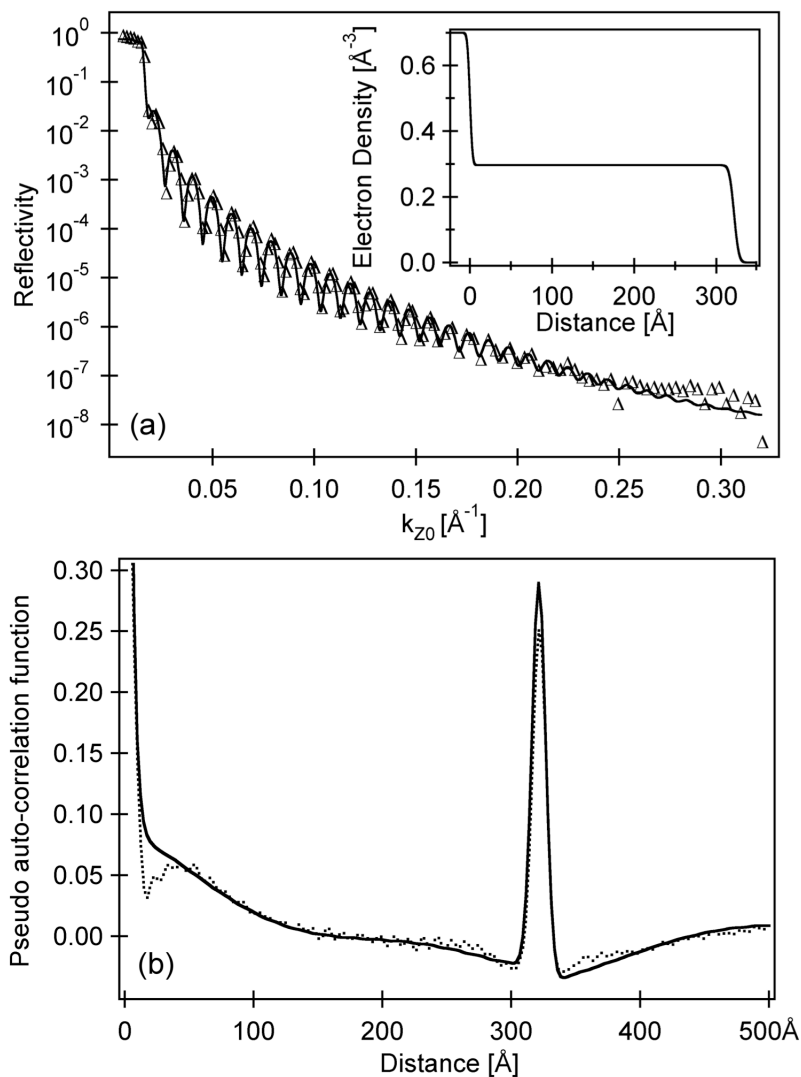


Figure II-12: (a) X-ray reflectogram, fit (one layer model) and density profile for PS 66 k. The film was measured after annealing during 5h, at 150°C. For the clarity of the figure, only every fifth point has been represented in the reflectogram. (b) pseudo auto-correlation function calculated from the experimental data (dashed line) and from the fit (continuous line).

We present in Figure II-12 the XRR data pertaining to sample PS 66k, together with a fit using a simple model (homogeneous film of ~ 320 Å thickness). Although the fit reproduces quite well the data in reciprocal space (Figure II-12 (a)), the comparison between $P_R(r)$ and $P_{R,\text{exp}}(r)$ (Figure II-12 (b)) reveals a major difference in real space: the simulation clearly lacks a dip in the region $15 \text{ Å} < r < 50 \text{ Å}$. This indicates that the model should include a density fluctuation near one of its interface. Because of the symmetry properties of auto-correlation functions, one can envision two possibilities, either a decrease of density near the substrate, either density excess near the free interface. The latter possibility can be excluded, as no evidence for this kind of behaviour can be found in the literature. In addition, this selection could not explain the results obtained on other samples (see below).

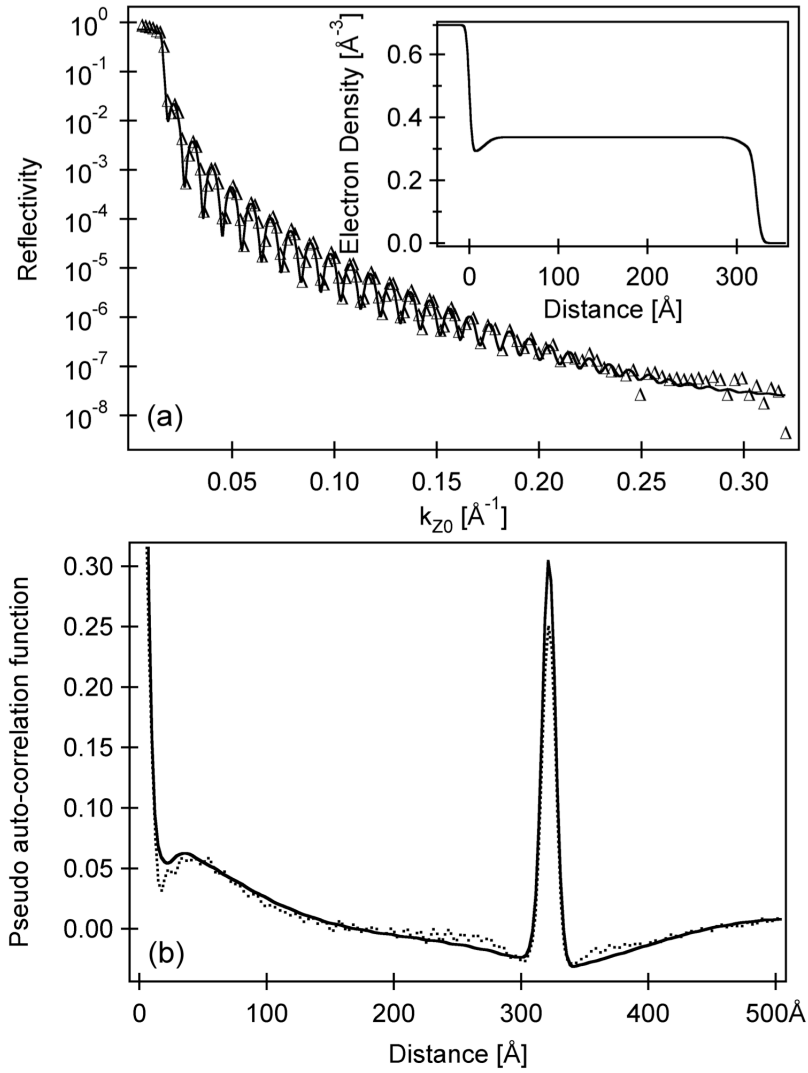


Figure II-13 : (a) X-ray reflectogram, fit (three layers model) and density profile for PS 66 k. The film was measured after annealing during 5h, at 150°C. For the clarity of the figure, only every fifth point has been represented in the reflectogram. (b) pseudo auto-correlation function calculated from the experimental data (dashed line) and from the fit (continuous line).

Figure II-13 presents the fits and pseudo-correlation functions obtained with a more complex model, in which we have added two supplementary layers, one at the substrate interface, one at the free

interface. The best fit coincides with a model where the electron density of the film decreases near the substrate interface, as shown in the inset of Figure II-13 a. The pseudo correlation functions now show a much better agreement (Figure II-13 b), with all the features of $P_{R,\text{exp}}(r)$ being reproduced by $P_R(r)$: the main peak due to the correlation between the two interfaces near 320 Å, and the depression of $P_R(r)$ near the origin, due to the dip in electron density at the substrate interface. Note that the roughness of the free interface differs also slightly from a pure Gaussian roughness, as can be detected by comparing the inset of Figure II-12 a and of Figure II-13 a. We will come back to this in a later chapter.

We have estimated the extent and the dimension of the perturbation of density near the substrate by computing the integral width (w_d) and surface (A_d) of the dip, using as baseline the film electron density far away from the substrate (ρ_f), as reported in Table II-2. Also reported are the values found for a PS having 1030 k as molecular mass (data in annexes). It is important to realise that the precision on these parameters is low, due to the limited sensitivity of XRR to the exact shape of the density perturbation at the interface. As can be seen in Table II-2, the characteristics of the dip are not significantly modified when increasing the molecular mass by a factor of about 15.

Polymer	$A_d [\text{\AA}^{-2}]$	$w_d [\text{\AA}]$
PS 66k	-0.66	15.0
PS 1030k	-0.37	12.2
PMMA 88.6k	-0.28	13.3
PMMA 528.4k	-0.61	11.7
P4VP 81.5k	+0.58	26.9

Table II-2 : Integral (A_d) and integral width (w_d) of the density modification near the substrate. Positive values of A_d indicate an increased density near the substrate, while negative values indicate depletion.

P4VP

We then determined the density profile and the pseudo correlation function of a film of poly(4-vinylpyridine) (P4VP) spin-coated onto Si/SiO_x . As before, we used two models to fit the data: a simple homogeneous film (Figure II-14) and a more complex model (Figure II-15) by introducing one or more thin layers near the two interfaces. By contrast to PS, a denser layer had to be introduced near the solid interface in order to fit correctly the experimental data, in the reflectivity profile and in the pseudo auto-correlation function (compare Figure II-14 with Figure II-15). The height and extent of this bump are reported in Table II-2. The spatial extent of this bump is somewhat higher to what was found for the density depletion in PS.

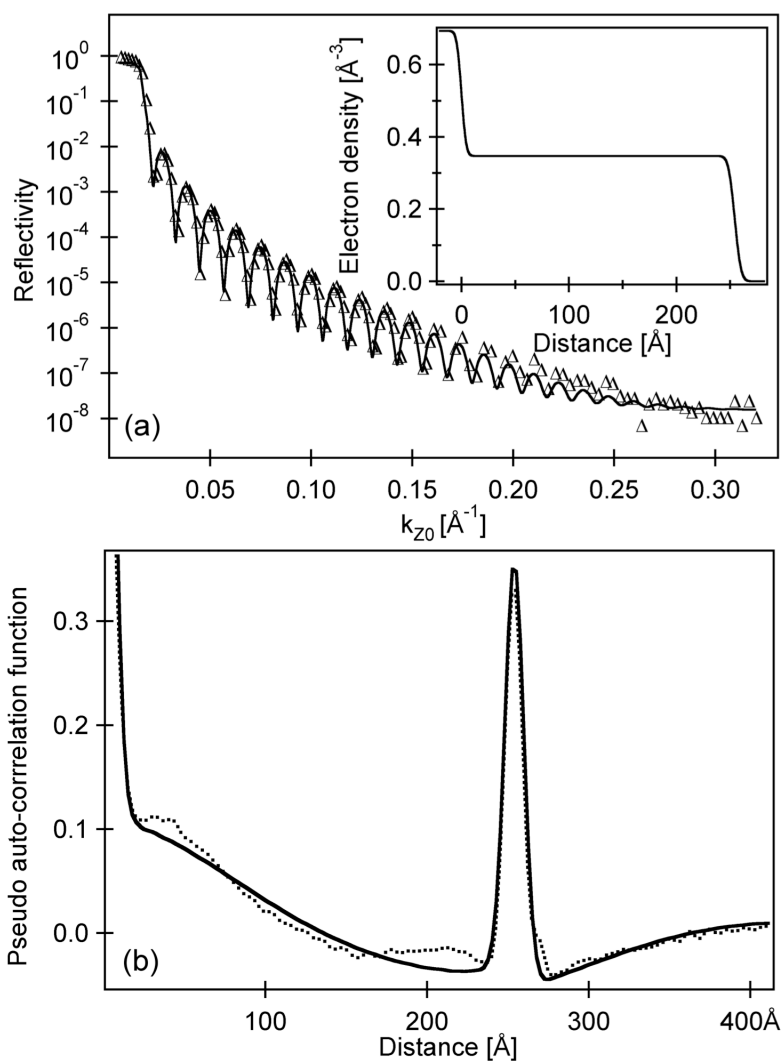


Figure II-14 : (a) X-ray reflectogram, fit (one layer model) and density profile for P4VP 81.5 k. The film was measured after annealing during 5h, at 190°C. For the clarity of the figure, only every fifth point has been represented in the reflectogram. (b) pseudo auto-correlation function calculated from the experimental data (dashed line) and from the fit (continuous line).

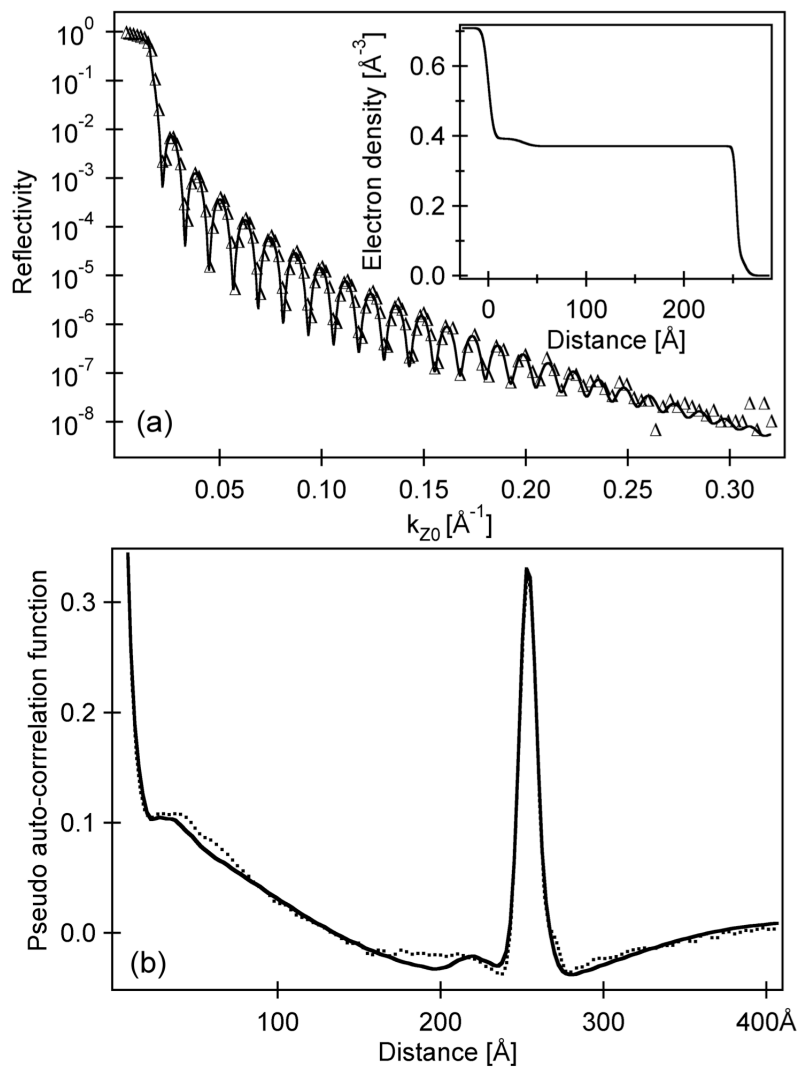


Figure II-15 : (a) X-ray reflectogram, fit (three layers model) and density profile for P4VP 81.5 k. The film was measured after annealing during 5h, at 190°C. For the clarity of the figure, only every fifth point has been represented in the reflectogram. (b) pseudo auto-correlation function calculated from the experimental data (dashed line) and from the fit (continuous line).

PMMA

The same procedures were applied to analyse PMMA films spin-coated onto Si/SiO_x . Here, we simply present the results obtained for fits with the finally selected models in Figure II-16 for PMMA 88.6 k. As for PS, the introduction of a dip in the electron density profile near the substrate was found necessary to allow a complete reproduction of the experimental data in reciprocal and direct spaces. These dips were found to be slightly comparable in their spatial extents and in their amplitudes to those of PS films (see Table II-2).

One should note that similar dips were found by us necessary to reproduce the X-ray reflectograms of a series of other polymers spin-coated onto Si/SiO_x : chlorinated poly(butadiene)⁹¹, poly(methyl hexyl silylene)⁹², atactic poly(propylene)⁹², chlorinated poly(propylene)⁹².

Also, it should be mentioned that this was found true for measurements performed with two different reflectometers, differing in their X-ray source and beam collimation systems, and for films produced by different persons in different environmental conditions. Finally, it is important to mention that such dips were not found when analysing polyelectrolytes multilayers⁹³ deposited by self-assembly onto similar Si/SiO_x substrates. This effectively rules out the possibility that the reported density perturbations be due to an improper handling of the substrates after cleaning, or to artefacts in our analysis methods.

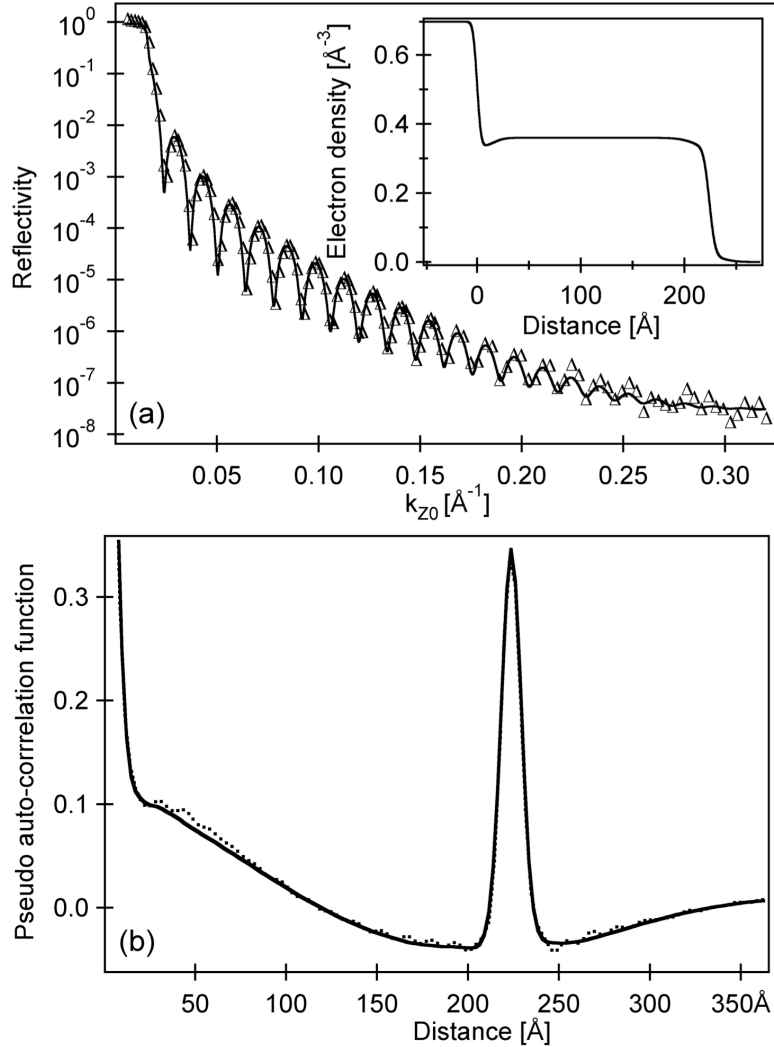


Figure II-16 : (a) X-ray reflectogram, fit (three layers model) and density profile for PMMA 88.6 k. The film was measured after annealing during 5h, at 150°C . For the clarity of the figure, only every fifth point has been represented in the reflectogram. (b) pseudo auto-correlation function calculated from the experimental data (dashed line) and from the fit (continuous line).

F. Discussion

For the different systems analysed in this study, local perturbations of the density profile were observed near the substrate interface (either

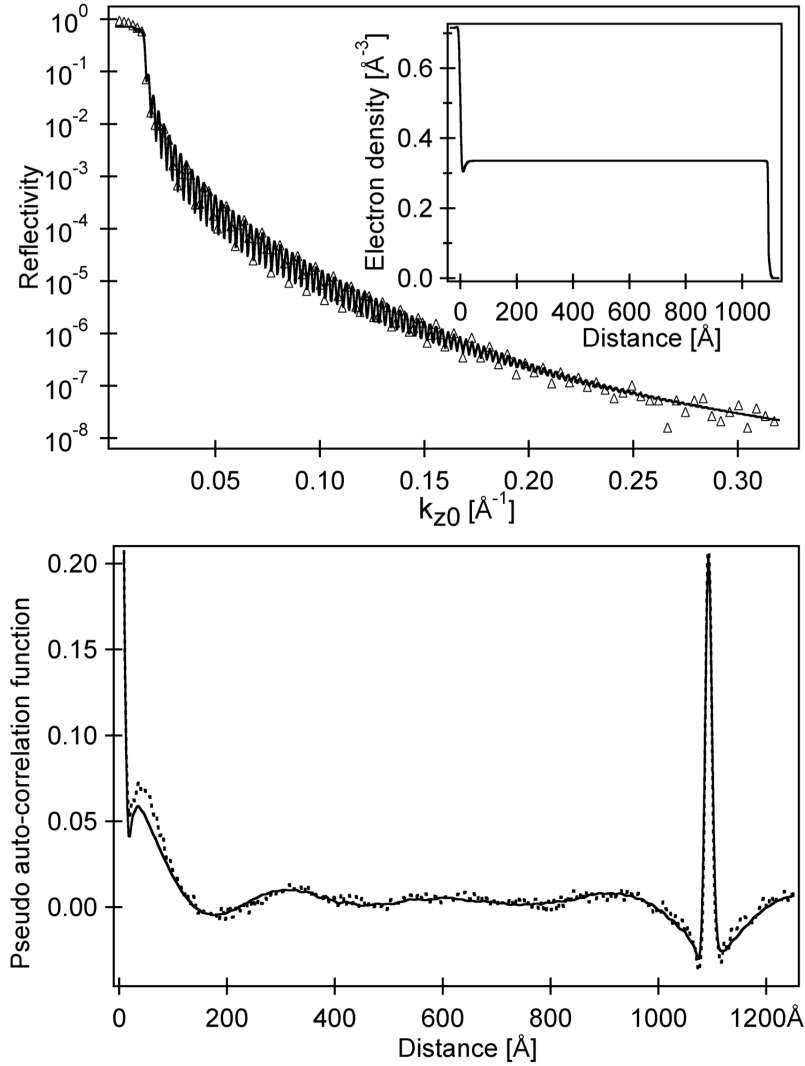
a depletion or an increase). The reproducibility of our experiments, and the quantitative differences observed between P4VP and PS, exclude the possibility that our observations be due to artefacts or surface contamination. Therefore, their origin should be sought into a variation of free volume (excess or depletion) near the substrate. Perturbations of the macromolecular conformations near the substrate are the most probable cause for these density fluctuations. Indeed, several simulations and theoretical work predict a perturbation of the local segmental distribution near surfaces : a decrease of density is expected for non-adsorptive surfaces^{71, 94} while an increase of density is predicted for strongly adsorptive surfaces^{71,94,74}. According to these studies, the density perturbations near a solid wall span a distance of about 2 statistical segment lengths, and depend on the strengths of the surface-monomer potential. Except for P4VP, where the experimental integral width of the density modification is slightly larger than 3 statistical segment lengths (Table II-2), the experimental integral widths of the density perturbations are indeed about two statistical segment lengths, which is in good agreement with theoretical predictions. The independence of this width with molar mass is also in agreement with the predicted localized nature of the density perturbations, which do not scale with the radius of gyration of the statistical coil. Finally, the strength of the density perturbations (Table II-2) evolves qualitatively consistently with the strength of the surface-monomer potential. Indeed, interactions between PS and silicon oxide (a polar substrate and a non-polar polymer) are weak, and the monomer-surface potential is dominated by weak non-adsorptive van der Waals interactions. Accordingly, a depletion of density near the substrate is observed. By contrast, P4VP is capable to develop acid-base interactions with the acidic silicon oxide surface. Accordingly, density increases near the

interface. The behaviour of PMMA would be expected to be intermediate between PS and P4VP, since PMMA interacts mildly with silicon oxide, possible hydrogen bonds between PMMA and silicon oxide being weaker than acid-base interactions, but stronger than purely dispersive van der Waals interactions. However, due to the limited sensitivity of XRR, we were not able to detect significant differences between PMMA and PS in this study. Other experimental techniques should be used to distinguish PMMA from PS.

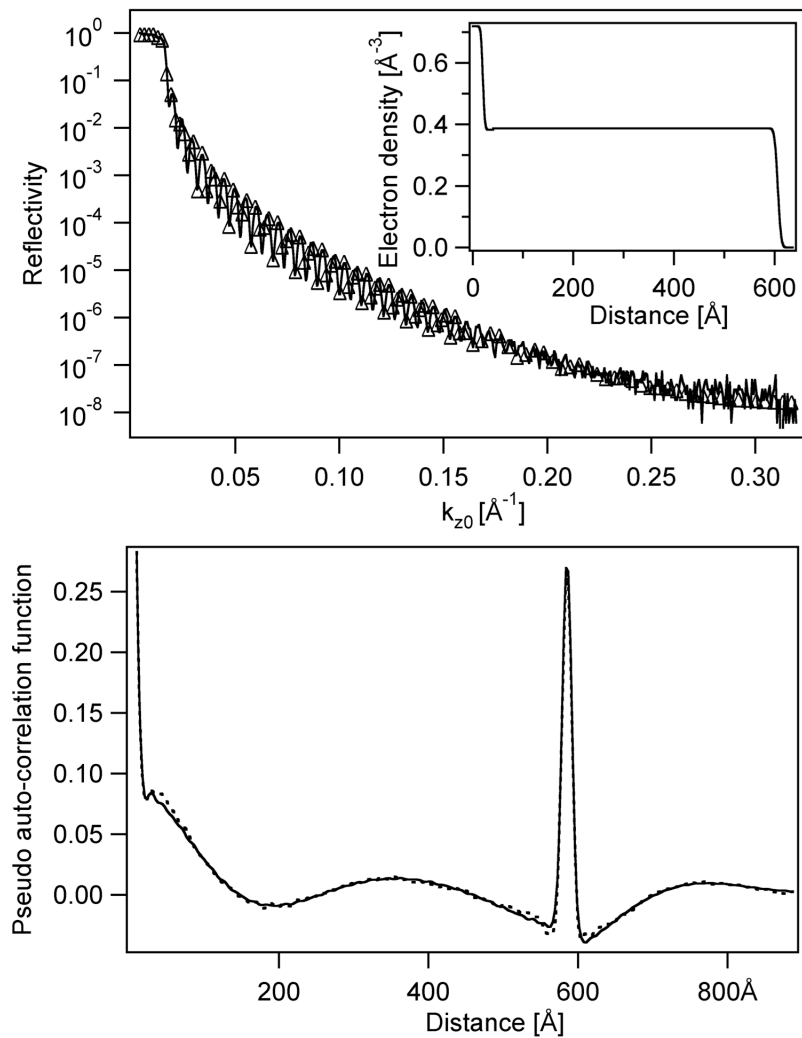
5. CONCLUSIONS

XRR studies of different polymer films (PS, PMMA, P4VP) deposited onto silicon wafers covered with their native oxide indicate perturbations of the density profile near the solid substrate, either a depletion (PS, PMMA), either an increase of density (P4VP). The importance of these effects correlates with the strength of the interactions developed between the polymer and silicon oxide, weak and non-adsorptive in the case of PS, and strong and adsorptive in the case of P4VP. The limited sensitivity of XRR did not allow, however, revealing differences between PS and PMMA. The presence of these thin layers of modified density near the substrate was supported by the calculation of the pseudo auto-correlation functions. The determination of these functions is directly based on the experimental data and is therefore not affected by fitting artefacts. The spatial extent of these perturbations spans 2-3 statistical segment lengths, and is independent of the molecular weight of the polymer. These observations are in relatively good agreement with earlier theoretical predictions^{74,94}. The results of this first chapter, however, provide a confirmation that more thorough investigations of the structure of thin supported films is warranted. This will be performed in the next chapters.

6. ANNEXES



(a) X-ray reflectogram, fit (three layers model) and density profile for PS 1030 k. The film was measured after annealing during 5h, at 150°C . For the clarity of the figure, only every sixth point has been represented in the reflectogram. b: pseudo auto-correlation function calculated from the experimental data (dashed line) and from the fit (continuous line).



(a) X-ray reflectogram, fit (three layers model) and density profile for PMMA 528 k. The film was measured after annealing during 5h, at 150°C . For the clarity of the figure, only every sixth point has been represented in the reflectogram. b: pseudo auto-correlation function calculated from the experimental data (dashed line) and from the fit (continuous line).

CHAPTER III. THE FREE SURFACE OF POLYMER FILMS : IS ROUGHNESS DUE TO CAPILLARY WAVES ?

1. INTRODUCTION

The aim of this chapter is to characterise the structure of free surfaces of polymer films and to compare it to laws predicting the behaviour of small molar mass liquids. AFM is the technique retained here because of its relevance for the systems studied. A second objective is to describe the root mean square (rms) roughness of polymer free surfaces. Knowledge of this value allows, as will be seen in the next chapter, to decrease uncertainties in interpreting X-ray reflectometry (XRR) data and as a consequence, to use less free variables during model fitting. This would help consolidate our temporary conclusions on the density perturbations of films at the vicinity of the substrate. As a side benefit of this chapter, we will investigate the stability of thin polymer films, which is, under specific circumstances, related to the amplification of the surface roughness.

2. THEORETICAL ASPECTS

A. Statistical description of a rough surface

Before starting the experimental analysis of polymer surfaces, it is worthy to focus on the different parameters that characterise a surface. Daillant⁹⁵ gives an exhaustive description of this kind of surfaces, which inspired the following paragraphs.

A random rough surface is completely characterised when each point of this surface is known by its three space coordinates, *i.e.*, $z(x,y)$ or $z(\vec{x})$ where $z(\vec{x})$ is the height of the surface. This height is determined in comparison with a reference $z_{ref}(\vec{x}) = 0$.

The same surface can also be described as the sum of waves, with different frequencies and amplitudes, as shown in Figure III-1 for a one-dimensional case. The height of the surface, z , is a function of the local coordinates $\vec{x}$, with $z(\vec{x}) = \sum_i z_i(\vec{x})$; each $z_i(\vec{x}) = A_i \exp j(2\pi\vec{s}\vec{x} + \varphi_i)$, with $|\vec{s}| = 1/\lambda_i$, represents the contribution of a particular wavelength λ_i of phase φ_i .

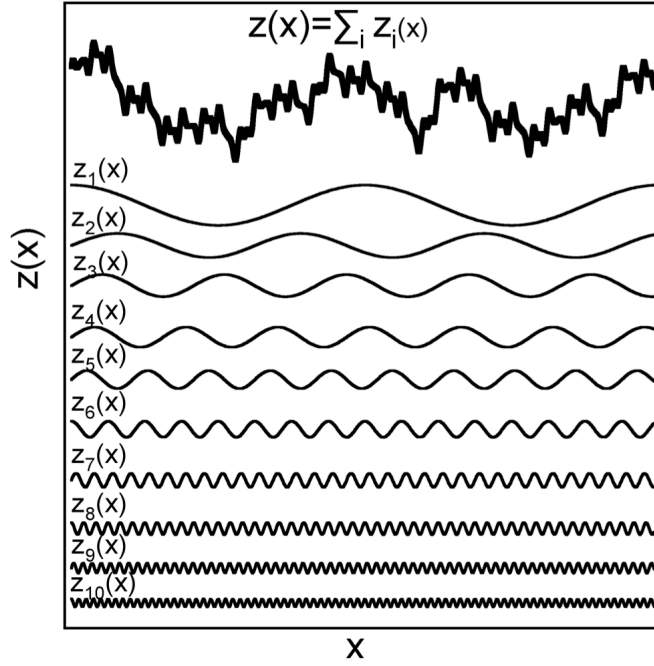


Figure III-1 : Random rough 1D surface viewed as the sum of waves of different amplitudes A_i and different wavelengths λ_i .

Another important characteristic of the surface is its roughness, which gives an indication of the deviation of the studied surface in comparison with the surface of reference $z_{ref}(\vec{x})$. The root mean square (rms) roughness of a surface, σ , is defined as follows :

$\sigma^2 = \langle (z(\vec{x}) - z_{ref}(\vec{x}))^2 \rangle$, where $\langle f(x) \rangle$ indicates averaging over the whole surface. This value gives a gross indication of the degree of roughness of the surface.

It is also interesting to describe more completely a surface as a function of the characteristic spatial frequencies (or wavelengths) and their respective intensities. To that aim, the square norm of the Fourier transform of the surface height profile can be computed, according to⁹⁵ :

$$P(\vec{s}) = \frac{1}{S} \left| \int_{\text{surface}} z(\vec{x}) \exp(-2\pi j \vec{s} \cdot \vec{x}) d\vec{x} \right|^2,$$

S being the area of the considered surface.

This gives the intensity of each wave as a function of the spatial frequency. This function is called the power spectral density (PSD). The power spectral density provides an indication about the strength of height fluctuations of the surface, associated with a particular wavelength (or spatial frequency), as schematically depicted in Figure III-2.

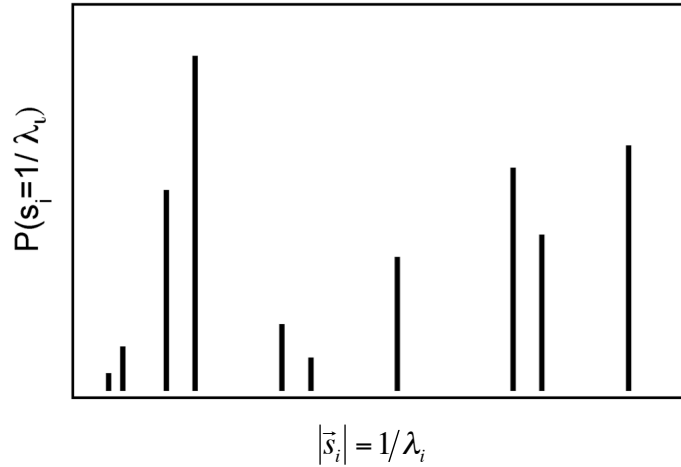


Figure III-2 : Schematic representation of the power spectral density of a surface. Each P_i represents the strength of the surface height fluctuations associated to a given wavelength (λ_i) or a reciprocal wavelength (s_i).

Now, from a more general statistical angle, a random rough surface can be described with the help of height probability distributions like $p_1(\vec{r}, z)$ and $p_2(\vec{r}_1, z_1, \vec{r}_2, z_2)$.

$p_1(\vec{r}, z)$ gives the probability for the surface point with coordinates $\vec{r}$ to be at the height between z and $z + dz$ and $p_2(\vec{r}_1, z_1, \vec{r}_2, z_2)$ gives the probability for the surface point with coordinates $\vec{r}_2$ to be at the

height between z_2 and $z_2 + dz_2$ if the point of coordinates $\vec{r}_1$ is simultaneously at a height between z_1 and $z_1 + dz_1$.

Using these probability functions, it is possible to determine⁹⁵ :
the mean height of the surface :

$$\langle z \rangle(\vec{r}) = \int_{-\infty}^{+\infty} z(\vec{r}) p_1(\vec{r}, z) dz,$$

the mean square height of the surface :

$$\langle z^2 \rangle(\vec{r}) = \int_{-\infty}^{+\infty} z^2(\vec{r}) p_1(\vec{r}, z) dz,$$

and the height-height correlation function of $z_1(\vec{r}_1)$ and $z_2(\vec{r}_2)$:

$$C_{zz}(\vec{r}_1, \vec{r}_2) = \langle z_1 z_2 \rangle(\vec{r}_1, \vec{r}_2) = \int \int_{-\infty}^{+\infty} z_1(\vec{r}_1) z_2(\vec{r}_2) p_2(\vec{r}_1, z_1, \vec{r}_2, z_2) dz_1 dz_2 .$$

This function allows to put into evidence the existence of a relationship between z_1 and z_2 as a function of $\vec{r}_1$ and $\vec{r}_2$ or $|\vec{r}_2 - \vec{r}_1|$. It can be used to define the distance required between different points for the values of z to be uncorrelated.

Random rough surfaces can have different characteristics. Among them, one can cite the following :

- Homogeneous surface : the character of height fluctuations does not change with the point considered on the surface;
- isotropic surface : the surface characteristics are the same along any direction. Average values of any functions characterising this kind of surfaces do not depend on absolute values $\vec{r}$, but only on the distance between points belonging to the surface.

For such a flat surface, the mean height of the surface $z(\vec{r})$ also does not depend anymore on $\vec{r}$. It is then possible to choose a reference

plane in such a way that $\langle z \rangle = 0$. The mean square deviation of the surface then becomes :

$$\langle z^2 \rangle = \int_{-\infty}^{+\infty} z^2 p_1(z) dz,$$

which is equal to σ^2 , the square of the rms roughness. The height-height correlation function can be rewritten as :

$$C_{zz}(\vec{r}_1, \vec{r}_2) = \langle z(0)z(\vec{r}) \rangle = C_{zz}(\vec{r}) = \int \int_{-\infty}^{+\infty} z_1 z_2 p_2(z_1, z_2, \vec{r}) dz_1 dz_2.$$

The power spectrum can also be computed from the height probability distributions :

$$P(\vec{s}) = \langle |\tilde{z}(\vec{s})|^2 \rangle,$$

with $2\pi\vec{s} = 2\pi(s_x, s_y)$ being the 2D wave-vector, and $\tilde{z}(\vec{s})$ being the Fourier transform of the variable z defined as $\tilde{z}(\vec{s}) = \int \int_{-\infty}^{+\infty} z(\vec{r}) \exp(2\pi j\vec{s}\vec{r}) d\vec{r}$. The power spectrum is the Fourier transform of the height-height correlation function (Wiener-Kintchine theorem)⁹⁵:

$$P(\vec{s}) = \int \int_{-\infty}^{+\infty} \langle z(0)z(\vec{r}) \rangle \exp(2\pi j\vec{s}\vec{r}) d\vec{r} = \tilde{C}_{zz}(\vec{s}).$$

Experimentally, we have only access to a single realisation (or random rough surface) for the ensemble of the random process. If each realisation carries the same statistical information about the homogenous random process, this process is said to be ergodic⁹⁵. The spatial average, computed for each realisation is then equal to the ensemble average. In other words, "measuring the same zone" of one realisation as a function of time or "measuring different zones" of the same realisation at a given time is statistically equivalent.

$$\text{Then, } \sigma^2 = \langle z^2 \rangle = \lim_{L_x, L_y \rightarrow \infty} \frac{1}{L_x L_y} \int_{L_x, L_y} z^2(\vec{r}) d\vec{r}, \quad \text{with } L_x, L_y$$

being the dimension of the surface, and

$$C_{zz}(\vec{r}) = \langle z(0)z(\vec{r}) \rangle = \lim_{L_x, L_y \rightarrow \infty} \frac{1}{L_x L_y} \int_{L_x, L_y} z(\vec{r}') z(\vec{r}' + \vec{r}) d\vec{r}' .$$

It will be assumed and not demonstrated that surfaces considered

here are Gaussian, *i.e.*, $P(z) = \frac{1}{\sqrt{2\pi}\sigma} \exp\left(-\frac{z^2}{2\sigma^2}\right)$.

The following section will deal with the statistical description of liquid surfaces, which fluctuate as a function of time.

B. Statistical description of liquid surfaces: the theory of capillary waves fluctuations

In this section, the microscopic description of the structure of the interfacial region of liquid surfaces will be described. The approach considered is the capillary wave model^{79,95}. Capillary waves are thermally excited height fluctuations that are always present on liquid surfaces and are responsible for surface deformations. A simple way to visualise such fluctuations is to look to the surface of a lake in the absence of wind. Such wavelets are ubiquitous over the surface. Depending on the wavelength of these ripples, one will speak of capillary or gravity waves (see below). In the theory of capillary wave fluctuations, a step-like profile is assumed for the liquid-vapour interface. However, due to waves on the surface, the interface appears as broadened when averaged laterally (Figure III-3).

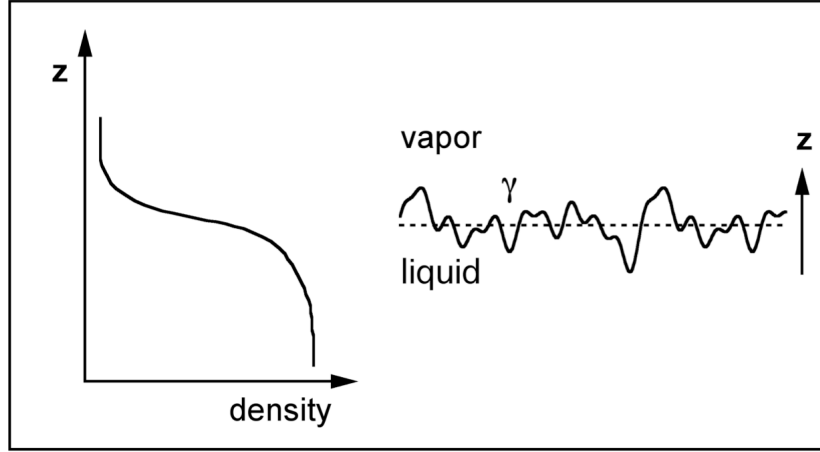


Figure III-3 : Capillary waves. Left : averaged density profile. Right : Instantaneous surface profile : γ is the surface tension and z the interface height.

All the structural information of the interface is contained in the profile $z(\vec{r})$, which describes the height of a surface as a function of the position vector $\vec{r}$. Surface structural information can as well be given by height correlation functions defined previously, meaningful in the presence of random generated capillary waves. This means that interface fluctuations can be characterised by a power spectrum $\langle \tilde{z}(\vec{s}) \tilde{z}(\vec{s})^* \rangle$, where $\tilde{z}$ denotes the Fourier transform of function z and $2\pi\vec{s}$ is the wave vector. In the case of a finite surface,

$$z(\vec{r}) = \sum_{\vec{s}} \tilde{z}(\vec{s}) \exp(2\pi i \vec{s} \cdot \vec{r})$$

The work necessary to deform the interface $z(\vec{r})$ can be computed, according to the following equation :

$$W = \int_S \left[\int_0^{z(\vec{r})} \Delta \rho g z dz + \left(\gamma \sqrt{1 + \left(\frac{\partial z(\vec{r})}{\partial \vec{r}} \right)^2} - \gamma \right) \right] d\vec{r},$$

where the first term in the integral denotes the energy necessary to work against gravity considering the difference between liquid density and the density of the surroundings $\Delta \rho$ (gravific energy), and the

second term represents the energy necessary to create an extra-surface for the liquid with surface tension γ , due to the local curvature of the surface by the waves.

Developing this equation, ones obtains :

$$W = \gamma S + \frac{1}{2} \sum_{\vec{s}} \sum_{\vec{s}'} \tilde{z}(\vec{s}) \tilde{z}(\vec{s}') \int_S [\Delta \rho g - 4\pi^2 \gamma \vec{s} \vec{s}'] \exp(2\pi j(\vec{s} + \vec{s}') \cdot \vec{r}) d^2 \vec{r}.$$

The wave vectors $2\pi\vec{s}$ are the modes of the surface, that is to say, the possible spatial frequencies, multiples of $2\pi/L$, with L being the surface dimension. Another way to say this is that the maximum wavelengths composing a surface are limited by the surface size (see Figure III-1). For an isotropic homogeneous rough surface as a liquid, this equation simplifies in :

$$W = \gamma S + \left[\frac{1}{2} \sum_{\vec{s}} \tilde{z}(\vec{s}) \tilde{z}(-\vec{s}) \left(\frac{\Delta \rho g}{\gamma} + 4\pi^2 s^2 \right) \right].$$

Using the energy equipartition theorem to distribute thermal energy among the different modes, the power spectrum can be determined :

$$P(s) = \frac{1}{S} \frac{k_B T}{\Delta \rho g + \gamma (2\pi s)^2}. \quad \text{equation III-1}$$

The power spectrum of thermally excited capillary waves of low molar masses liquids is thus easily determined. This equation shows that height fluctuations are the result of a balance between thermal energy ($k_B T$) and the cost to deform the surface (gravitation energy due to the mass of the crests of the waves, plus extra-surface energy due to the increased surface of the waves interface). For waves having $s = 1/\lambda \ll \sqrt{\Delta \rho g / \gamma}$ (i.e., for typical values of γ and ρ for organic liquids : $\lambda \gg 1-2$ mm), $\Delta \rho g$ dominates the denominator in equation III-1. One then speaks of gravity waves. For waves having $s = 1/\lambda \gg \sqrt{\Delta \rho g / \gamma}$ ($\lambda \ll 1-2$ mm), the surface tension term

dominates in equation III-1, and one may speak of thermally excited capillary waves.

In the case of viscoelastic liquids, one more important factor has to be taken in account : the bending rigidity κ . In the case of a polymer surface, the energy necessary to deform this surface will also depend on the ability of the polymer chain to be bent. The creation of a wave surface stretches locally the material. The bending rigidity takes into account the capacity of the polymer chain to resist to this stretching, which depends on the rate of sollicitation compared with the characteristic relaxation times of the chain. A similar method as the one described above for the derivation of the power spectrum leads to⁶⁰:

$$P(s) = \frac{1}{S} \frac{k_B T}{\Delta \rho g + \gamma (2\pi s)^2 + \kappa (2\pi s)^4}.$$

C. Case of thin liquids films

The power spectrum determined in the former section concerned bulk liquids. But actually, if bodies considered are thin or very thin films, one has to take into account supplementary forces or potentials that develop through the films, due to van der Waals interactions of the atoms of the film with the substrate. In that case, these forces are taken into account by a supplementary constant term in the equation of the power spectrum, involving the Hamaker constant A for the system. This gives :

$$P(s) = \frac{1}{S} \frac{k_B T}{\Delta \rho g + \frac{A}{2\pi d^4} + \gamma (2\pi s)^2 + \kappa (2\pi s)^4} \quad \text{equation III-2}$$

d being the thickness the film considered. It is appropriate to discuss in more details the Hamaker constant in order to provide a firm basis for the discussion to come. In full generality, the van der Waals (VDW) interaction energy between two bodies can be expressed as a function of characteristic dimensions and distances describing the system, and of Hamaker constants, representing the interactions between the atoms of the bodies considered⁹⁶. This constant is defined according to :

$$A = \pi^2 C \rho_1 \rho_2 [J], \quad \text{equation III-3}$$

where ρ_1 and ρ_2 are respectively the volumic atom density of bodies 1 and 2 and C is the proportionality coefficient in the VDW atom-atom pair potential, $W(d)$ ⁹⁶, as described by the following equation (Figure III-4) :

$$W(d) = -\frac{C}{d^6}.$$

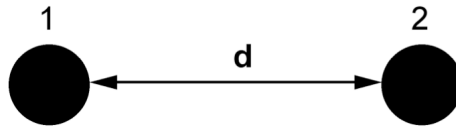


Figure III-4 : Two atoms of different nature, separated by a distance d .

Now consider one semi-infinite body, consisting of two different materials in planar contact, as described in Figure III-5. Near the interfaces, atoms of each material interact through VDW potentials with the atoms of the other material. Atoms in the gray region in Figure III-5 thus feel a potential different from what they would have experienced in the absence of the interface (continuous bodies). This extra-energy, integrated over the whole shaded area, and normalised

to unit surface area, is called the VDW component of the surface energy, γ_{32}^{LW} (Figure III-5 top). Apart from this component, local specific interactions (γ_{32}^{sp}) also contribute to the total surface energy which is equal to $\gamma_{32} = \gamma_{32}^{LW} + \gamma_{32}^{sp}$.

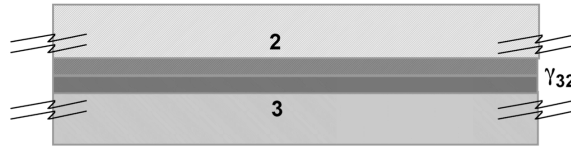


Figure III-5 : Semi-infinite bodies consisting of two different materials brought into planar contact. The gray areas represent the zones over which act the VDW potentials due to the presence of the interface

Now, consider the case of a film of thickness d on a semi-infinite substrate. For films thick enough as compared to the range of VDW interactions (a few tens of nanometers), as shown in Figure III-6, the free energy of the system, per unit surface, may be written as :

$$G_{132} = \gamma_{13} + \gamma_{23} + \frac{\rho g d^2}{2} \quad \text{equation III-4}$$

where $\rho g d^2/2$ is the gravitational surface energy associated to the film.

If the film thickness decreases to the point where the gray regions in Figure III-6 invade each other, equation III.4 is no more valid, as atoms of body 2 now feel atoms of body 1, while atoms of the top most surface of the film also experience the potential of body 1 through the film. Consequently, equation III.4 must be corrected :

$$G_{132} = \gamma_{13} + \gamma_{23} + \Delta G_{132}^{LW} + \frac{\rho g d^2}{2}$$

where ΔG_{132}^{LW} takes into account the interaction of 1 and 2 through the film 3.

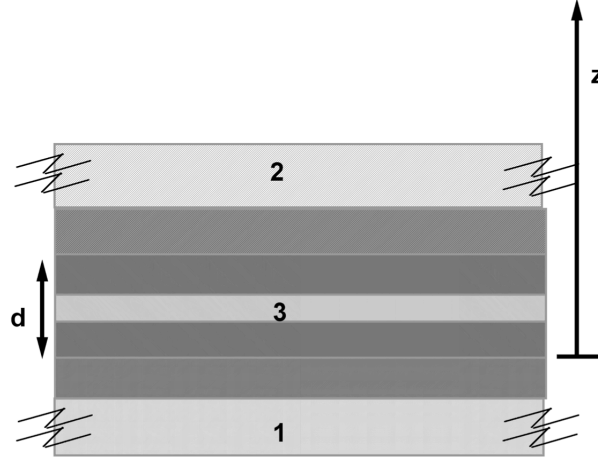


Figure III-6 : A thick film on a surface. The gray area is the distance over which VDW perturbations due to the presence of interfaces extend.

ΔG_{132}^{LW} can be viewed as an energy correction term taking into account the specific VDW interactions linked to the new geometry of the system. ΔG_{132}^{LW} is the excess free energy due to the new configuration of the system and is given by⁹⁶ :

$$\Delta G_{132}^{LW} = -\frac{A_{132}}{12\pi d^2},$$

where A_{132} is the Hamaker constant characterising the 1/3/2 system. ΔG_{132}^{LW} can be negative or positive, depending on the value of A_{132} . If the film becomes so thin as having specific, local interactions established between interfaces 1/3 and 3/2, this effect must also be taken in account. This could generally be the case for films thinner than 20-30 Å.

The problem now is to determine the value of A_{132} . The definition given in equation III.3 does not take into account the influence of neighbouring atoms on the interaction between any pair of two atoms, and in the case of condensed media, computing A_{132} becomes complicated.

One way to determine the Hamaker constants is by using relationships established between A_{132} and the wetting behaviour of corresponding macroscopic drops. This seems reasonable since macroscopic parameters (surface and interfacial tension) governing the wettability (contact angle) also derive from the sum of intermolecular interactions, both VDW and specific local interactions^{60,96}.

In the case of the geometry described in Figure III-6, of two bulk phases 1 and 2 separated by a film of fluid 3 and of thickness d , not considering the role of specific local interactions but only non retarded Lifschitz-van der Waals (LW) interactions, the effective Hamaker constant A_{132} can be defined in terms of Hamaker constants for binary interactions between slabs of materials i and j in a vacuum⁶⁰:

$$A_{132} = A_{33} + A_{12} - A_{13} + A_{23}. \quad \text{equation III-5}$$

In the particular case of a polymer film deposited onto a silicon substrate in air, equation III.5 can be simplified in⁶⁰ :

$$A_{132} = A_{33} - A_{13}.$$

In this case, A_{132} can also be expressed as a function of the individual Hamaker constants of each material^{39,97} :

$$A_{132} = \sqrt{A_{33}}(\sqrt{A_{33}} - \sqrt{A_{11}}),$$

which indicates that unstable films (positive A_{132}) may only be obtained for liquids deposited on substrates of lower Hamaker constant (this treatment ignores the role of polar interactions, a valid approximation for films of apolar polymers with vacuum as one of the bounding media⁶⁰).

Although useful, this expression is not related to macroscopic surface parameters. It is however possible to establish a relationship between A_{132} and the VDW components of the surface energy in the following way. Consider two bulk materials 1 (silicon in our case) and 2 (air in our case), separated by a fluid film of material 3 (apolar polymer in our case) of thickness d . Suppose d is infinite. The free energy of the system per surface unit is :

$$G_{132}^{\infty} = \gamma_{13}^{LW} + \gamma_{23}^{LW},$$

ignoring gravitation.

Now, let us bring 1 and 2 closer together, thereby squeezing material 3. The free energy of the system per unit area rises to :

$$G_{132}^{\infty} = \gamma_{13}^{LW} + \gamma_{23}^{LW} - \frac{A_{132}}{12\pi d^2}.$$

By squeezing the film to the position where 1 and 2 come into contact, then

$$G_{132}^{\infty} = \gamma_{13}^{LW} + \gamma_{23}^{LW} - \frac{A_{132}}{12\pi d_0^2},$$

where d_0 is the equilibrium distance arising from the short range Born repulsion (r^{-12} term in the Lennard-Jones potential). The best average estimate for d_0 is about $1.58 \text{ \AA}^{60}$.

On the other hand, one can write the free energy of this system (1 in contact with 2) as :

$$G_{132}^0 = \gamma_{12}^{LW},$$

which provides :

$$\gamma_{12}^{LW} - \gamma_{13}^{LW} - \gamma_{23}^{LW} = -\frac{A_{132}}{12\pi d_0^2}. \quad \text{equation III-6}$$

The left-hand side of this equation is known as the VDW component of the spreading coefficient :

$$S^{LW} = \gamma_{12}^{LW} - \gamma_{13}^{LW} - \gamma_{23}^{LW}. \quad \text{equation III-7}$$

If S^{LW} is positive (A_{132} negative), a droplet of liquid 3 will tend to spread on body 1 immersed in the medium 2. If S^{LW} is negative (A_{132} positive), only partial wetting (finite values of contact angles) will occur. In this case, the contact angle can be derived as⁶⁰ :

$$\cos \theta = 1 + \frac{S^{LW}}{\gamma_{23}^{LW}}.$$

This equation must be corrected if specific (polar) interactions exist between 1 and 3, as :

$$\cos \theta = 1 + \frac{S^P + S^{LW}}{\gamma_{23}^{LW}}, \quad \text{where } S^P \text{ is the polar component of the}$$

spreading coefficient.

The Good-Girifalco-Fawkes combining rule says that⁶⁰ :

$$\gamma_{ij}^{LW} = ((\gamma_i^{LW})^{1/2} - (\gamma_j^{LW})^{1/2})^2,$$

which gives for the spreading coefficient :

$$S^{LW} = 2(\sqrt{\gamma_1^{LW}} - \sqrt{\gamma_3^{LW}})(\sqrt{\gamma_3^{LW}} - \sqrt{\gamma_2^{LW}}),$$

This equation allows, if surface tension values of the different components are known, to determine the sign of the LW component of the spreading coefficient, and thus of the Hamaker constant (which is opposite to the one of S^{LW} , as shown by equations III-6 and III-7).

As a consequence, this permits to decide about the stability or not of the film deposited on the substrate.

Indeed, consider the equation giving the energy per unit surface of the entire system consisting of a film 3 on a substrate 1 bounded by a fluid 2, in a gravitational field :

$$G_{132} = \frac{\rho g d^2}{2} + \gamma_{13} + \gamma_{32} - \frac{A_{132}}{12\pi d^2}.$$

Two cases can be distinguished, unstable and stable systems.

unstable systems : $S^{LW} < 0, A_{132} > 0$ **and** $d < d_c$

The free energy curve has the shape given in Figure III-7.

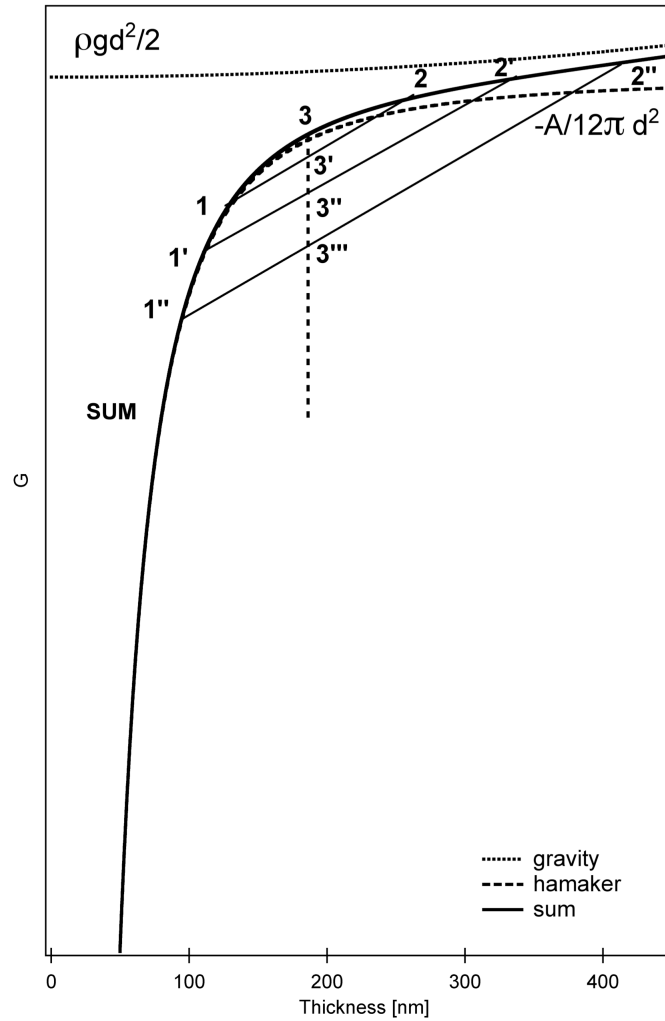


Figure III-7 : unstable systems : schematic representation of the different contributions to the free energy of the entire system.

As can be seen, the thicker the film, the higher the energy. Stability is related to the curvature of $G_{132}(d)$. Consider the system indicated by point 3 on $G_{132}(d)$. Random thermal fluctuations of the surface will

drive the system locally to points 1 and 2; in this state, the system has a free energy represented in Figure III-7 by point 3', lower than the energy of the film of uniform thickness. The phenomenon will thus be amplified, and the system will be driven to a state where very thin sections alternate spatially with thick regions. The system is said to undergo spinodal dewetting, similarly to polymer blends that undertake spinodal decomposition when the curvature (versus composition) of the free energy of mixing of the components is negative. Interestingly, for thicker films, the free energy curve will be dominated by the gravific energy that is of positive curvature, which shows that thick films will not dewet spinodally, above a critical thickness w . They may however dewet by hole nucleation and growth (this would be similar to binodal demixing for the case of polymer blends). The critical film thickness below which spinodal dewetting occurs is given by :

$$\left. \frac{\partial^2 G_{132}(d)}{\partial^2 d} \right|_{d_c} = 0, i.e., \rho g - \frac{A_{132}}{2\pi d_c^4} = 0,$$

giving :

$$d_c = \sqrt[4]{\frac{A_{132}}{2\pi\rho g}} = \sqrt[4]{\frac{-6S_{LW}}{\rho g}} d_0^2,$$

as shown by Brochard *et al*^{58,59}.

stable systems : $S^{LW} > 0, A_{132} < 0$ **and** $d < d_c$

The free energy curve has the shape given in Figure III-8. Due to the positive curvature of $G_{132}(d)$, it is now clear that the system is stable for all thicknesses.

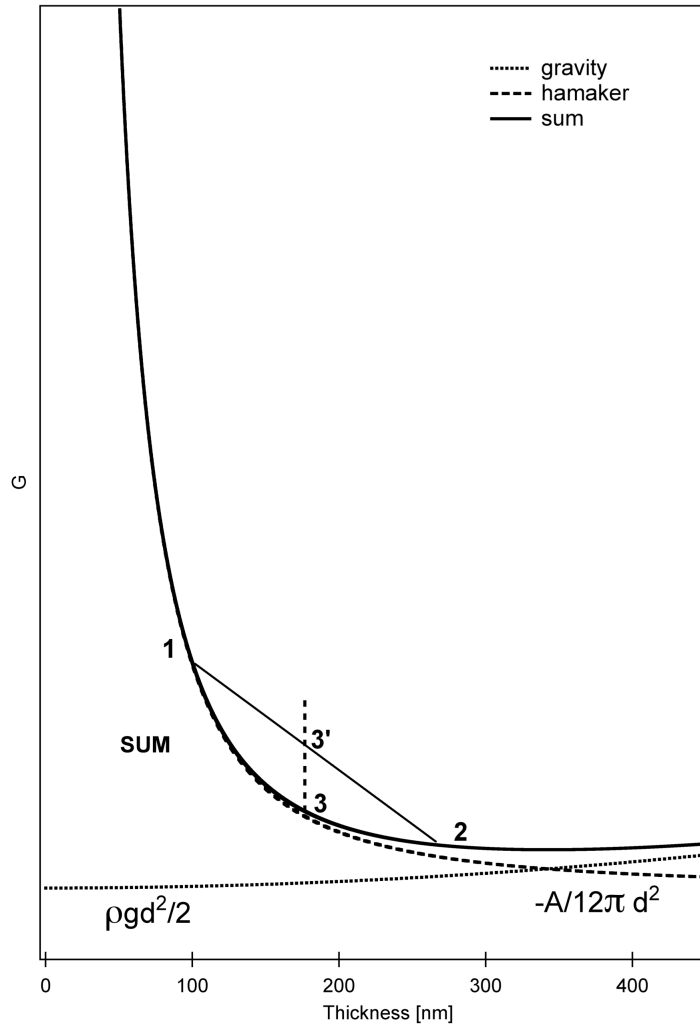


Figure III-8 : stable systems : schematic representation of the different contributions to the free energy of the entire system.

Now, the behaviour of polymer-based systems will also depend on kinetic factors, since parameters like molar mass, viscosity, entanglement limit are going to play an important role on the behaviour of the studied systems. Indeed, even if a system is, according to thermodynamics, unstable, kinetic factors can still prevent spinodal dewetting on the timescale of the experiment. Systems will then be unstable or metastable.

Then, when $A_{132} > 0$, the instability of thin films can manifest itself in two ways :

- by heterogeneous dewetting involving nucleation and growth of holes in the film, if the film is metastable, *i.e.*, if the time scale for the amplification of spontaneous height fluctuations is much larger than the time scale of the experiment;
- by spinodal decomposition which consists of a dewetting of the film by an amplification of capillary waves. The film breaks into droplets with a characteristic spatial frequency $|\vec{s}_c|$.

Which dewetting scenario will be followed depends on the initial thickness of the film.

In the case of films with thickness $d \ll d_c$, gravity does not play any role on the behaviour of the system. In that configuration, Brochard *et al*^{58,59} showed that height waves of the type $\xi = h(x,t) = h_0 + \Delta h \exp(jqx) \exp(-t/\tau_q)$ can exist on the surface of the film, provided :

$$\frac{1}{\tau_q} = \frac{d_3}{3} V(q^4 - 3 \frac{d_0^2 q^2}{d^4}),$$

where $V = \gamma_{13}/\eta$ is the dewetting speed with η being the viscosity of the concerned liquid. This relation describes all the possible modes for capillary waves, with wavelength $2\pi/q$, which are damped with a

characteristic time τ_q . If $q < q_c = \sqrt{12} \frac{d_0}{d^2} \sqrt[4]{\gamma_{13}/\gamma_{23}}$, then $|\tau_q^{-1}| < 1$ and the capillary waves are amplified with time. The fastest of unstable modes, that is to say the mode which will amplify preferentially, is characterised by ⁶⁰ :

$$q_c = \sqrt{12} \frac{d_0}{d^2} \sqrt[4]{\gamma_{13}/\gamma_{23}},$$

corresponding to the characteristic time :

$$|\tau_q^{-1}| = 12 \frac{d_0^4}{d^5} \frac{\gamma_{13}}{\eta}.$$

Sharma⁶⁰ has provided more complete expressions of these equations, taking into account polar components of the interactions energies.

3. EXPERIMENTAL DETERMINATION OF THE POWER SPECTRAL DENSITY

In this section, we present how power spectral densities can be obtained experimentally from atomic force microscopy (AFM) data.

The objective of this section is thus :

- first, to describe corrections applied to raw AFM data ;
- second, to emphasise the mathematical treatment applied to images, in order to extract the relevant information from the images.

All figures presented in this section concern a PS66k, 8Rg thick film, annealed for five hours in a vacuum, at a temperature 50°C above the bulk T_g . Topographic images $h_i(x,y)$ of the samples after annealing were obtained by AFM under ambient conditions using an Autoprobe® CP microscope (Thermomicroscopes, Sunnyvale, CA). The analyses were realised in intermittent contact mode (IC-AFM) using Pointprobe® cantilevers from Nanosensors with free resonance frequencies between 160 and 165 KHz, springs constants around 50 Nm⁻¹ and integrated silicon tips with a typical apex radius of curvature lower than 10 nm. For each samples, at least three different zones of the surface were analysed.

A. Raw data correction

Two types of correction are applied to raw images.

The first one is a line-by-line flattening of images. Indeed, as can be seen in Figure III-9 and Figure III-13 a, an inclination and a curvature of the surface are induced by the measurement. This is issued from the fact that the plane of the sample and the scanning plane are not parallel, which induced the inclination that can be observed. The

curvature results from the shape of the scanner, consisting of a tube which flexes during the scanning. As the surface roughness of measured samples is very low, these curvature and inclination hide the surface topography. It is then necessary to correct the raw image. To perform this, the surface average profile is computed and then subtracted (equation III-8). To that aim, a polynomial of order 2 to 6 is used to fit line by line the data, $z_y(x)$.

$$h(x,y) = z(x,y) - \langle z_y(x) \rangle \quad \text{equation III-8}$$

The flattened surface is presented in Figure III-10 and Figure III-13 b. As can be seen, outliers (dust or defects present in the film) prevent to distinguish clearly the topography of the film. The second correction consists thus of the suppression of these outliers (Figure III-11 and Figure III-13 c). Points suppressed are being given the average value of the height (Figure III-12 and Figure III-13 d), which effectively neutralises them. On some images, edges have also been suppressed, because of distortions caused by the change of the scanning direction of the AFM tip. In all cases, no image has been used for further analysis if the suppressed area exceeds 10 percents.

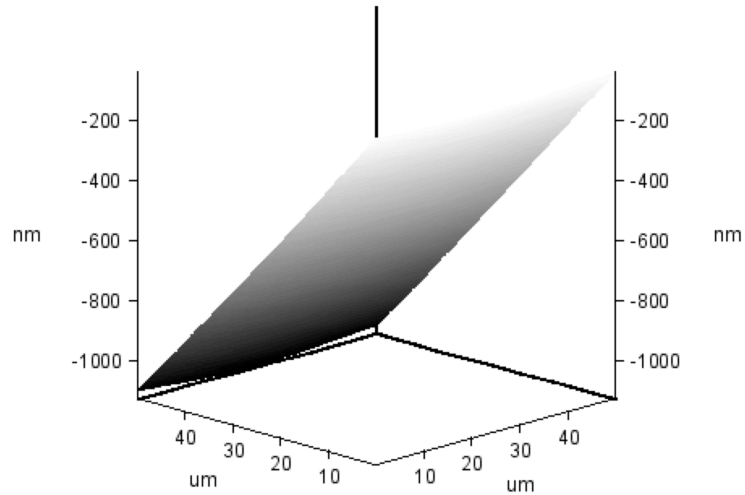


Figure III-9 : 3-dimensional IC-AFM topographic image of a PS 66k 8Rg thick film on a Si wafer covered by a 1.3 nm thick layer of native oxide, after 5 hours annealing at 155°C (50 x 50 μm^2 cell size; raw data).

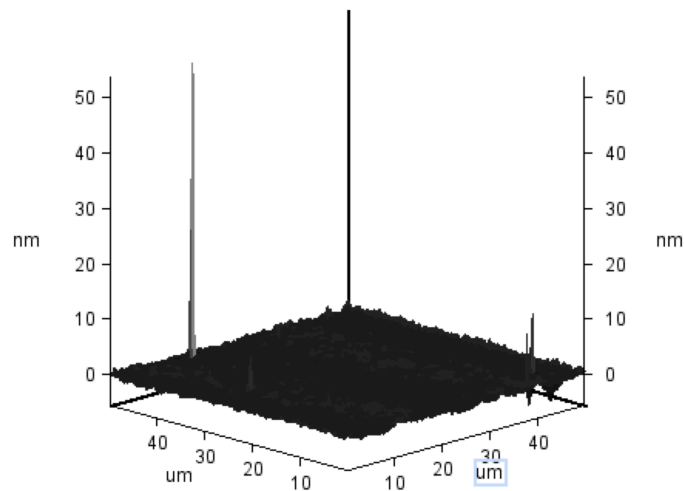


Figure III-10: 3-dimensional IC-AFM topographic image of a PS 66k 8Rg thick film on a Si wafer covered by a 1.3 nm thick layer of native oxide, after 5 hours annealing at 155°C (50 x 50 μm^2 cell size; AFM data after flattening).

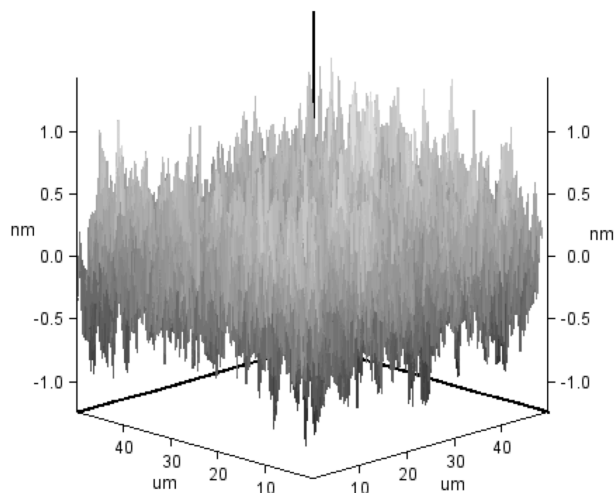


Figure III-11 : 3-dimensional IC-AFM topographic image of a PS 66k 8Rg thick film on a Si wafer covered by a 1.3 nm thick layer of native oxide, after 5 hours annealing at 155°C (50 x 50 μm^2 cell size; data after flattening and outliers suppression).

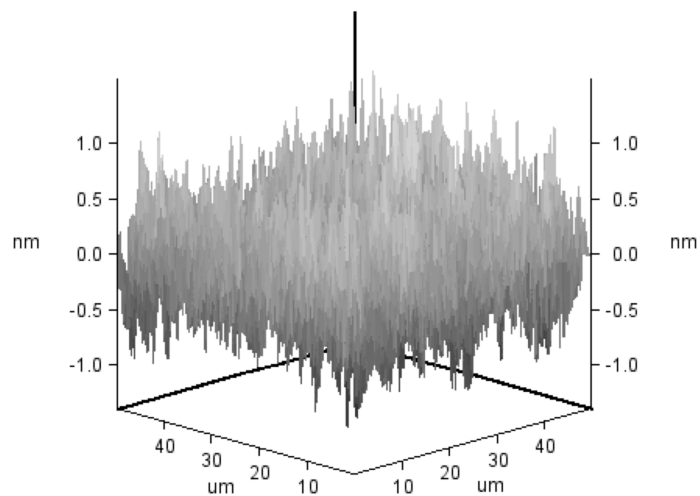


Figure III-12 : 3-dimensional IC-AFM topographic image of a PS 66k 8Rg thick film on a Si wafer covered by a 1.3 nm thick layer of native oxide, after 5 hours annealing at 155°C (50 x 50 μm^2 cell size; data after cleaning).}

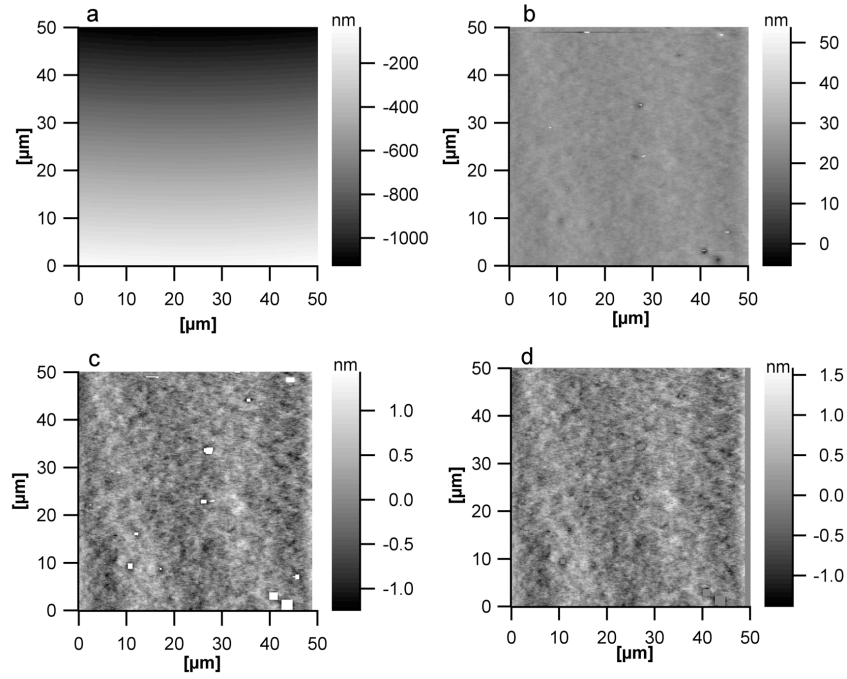


Figure III-13 : IC-AFM topographic image of a PS 66k 8R_g thick film on a Si wafer covered by a 1.3 nm thick layer of native oxide, after 5 hours annealing at 155°C (50 x 50 μm² cell size). a : raw data; b : data after flattening; c : data after outliers suppression; d : clean image.

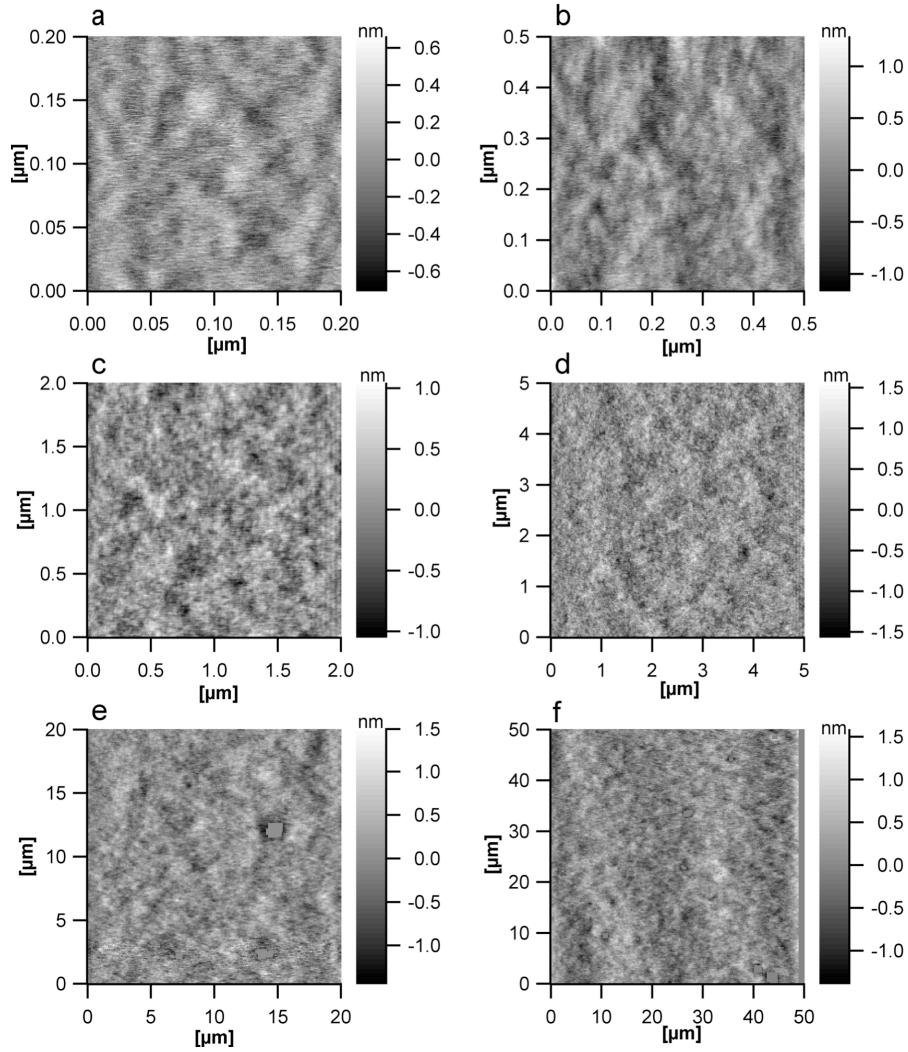


Figure III-14 : IC-AFM topographic image of a PS 66k 8Rg thick film on a Si wafer covered by a 1.3 nm thick layer of native oxide, after 5 hours annealing at 155°C. Six different cell sizes. Images after flattening, outliers suppression and cleaning.

Typical images of different sizes obtained after data correction are presented in Figure III-14, whereas Figure III-15 presents the histograms of the height of these images. It is obvious that all histograms are gaussian, as was assumed in the theoretical section. In the histogram of the 20 x 20 μm^2 and 50 x 50 μm^2 image, the point

corresponding to zero height is well above the expected gaussian. This is due to the elimination of outliers, originating from a defect in the image $20 \times 20 \mu\text{m}^2$, and from an edge effect in image $50 \times 50 \mu\text{m}^2$, as can be observed in the images of Figure III-14.

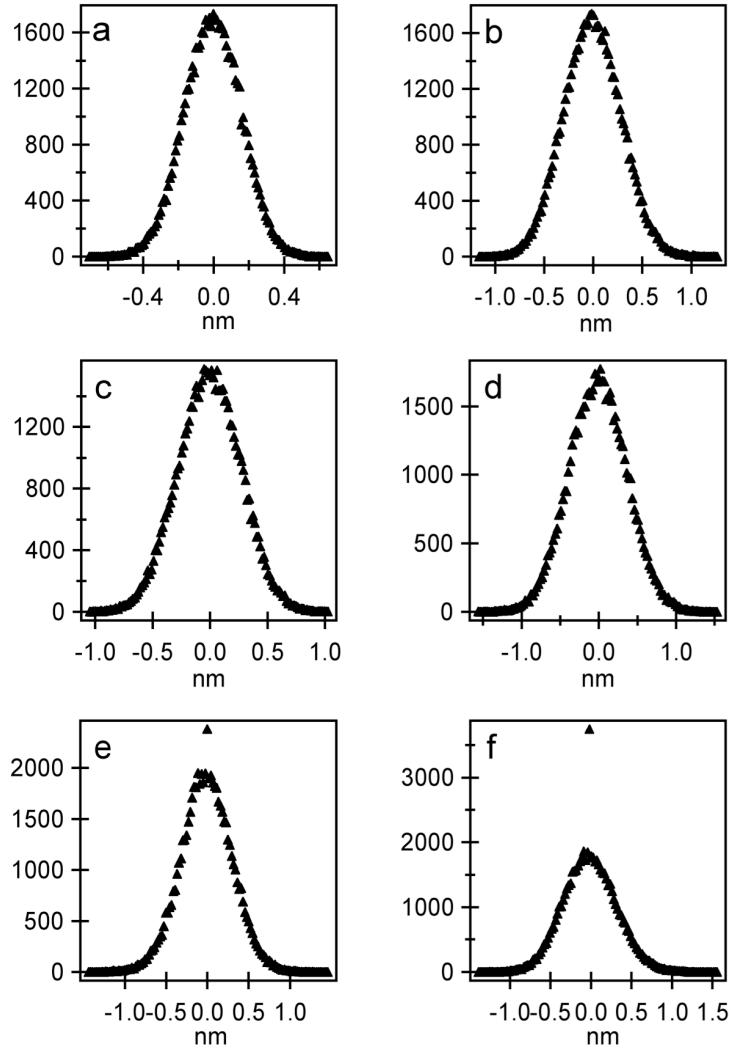


Figure III-15 : Height histograms corresponding to the bidimensional images of a PS 8Rg thick film, presented in Figure III-14, a corresponding to the $0.2 \times 0.2 \mu\text{m}^2$ cell size, b corresponding to the $0.5 \times 0.5 \mu\text{m}^2$ cell size, c corresponding to the $2 \times 2 \mu\text{m}^2$ cell size, d corresponding to the $5 \times 5 \mu\text{m}^2$ cell size, e corresponding to the $20 \times 20 \mu\text{m}^2$ cell size, f corresponding to the $50 \times 50 \mu\text{m}^2$ cell size.

B. Analysis of corrected data

After data correction, the analysis of images is performed. Different steps are followed.

The first one consists of a data windowing (Welch window), to prevent Fourier ripples entering the $P_1(s)$ ⁹⁸.

In a second step, a bidimensional Fourier transform is performed by a FFT algorithm, and the square of its amplitude computed, leading to the 2D power spectral density (2D-PSD) after normalisation by the surface of the image :

$$P_2(s_x, s_y) = (L_x L_y)^{-1} \left| \int_{L_x L_y} h(x, y) \exp(2\pi j(s_x x + s_y y)) dx dy \right|^2$$

Results are presented in Figure III-16. Since the 2D-PSD is isotropic, as expected, a circular averaging of the 2D-PSD is performed, giving the one-dimensional power spectral density :

$$P_1(s) = (2\pi)^{-1} \left| \int_0^{2\pi} P_2(s, \varphi) d\varphi \right|,$$

where φ is the azimuthal angle.

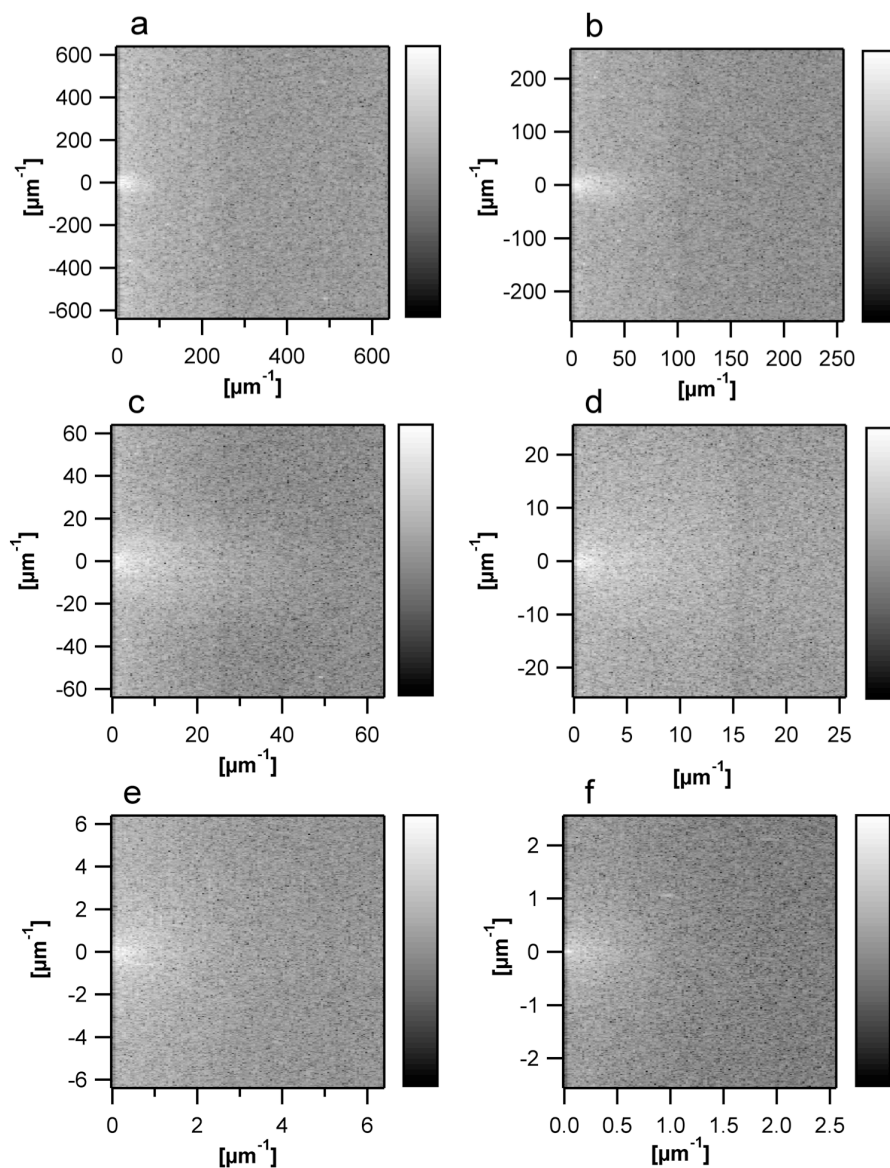


Figure III-16 : 2-D PSD for a PS 66k 8 Rg thick film, presented in Figure III-14, a corresponding to the $0.2 \times 0.2 \mu\text{m}^2$ cell size, b corresponding to the $0.5 \times 0.5 \mu\text{m}^2$ cell size, c corresponding to the $2 \times 2 \mu\text{m}^2$ cell size, d corresponding to the $5 \times 5 \mu\text{m}^2$ cell size, e corresponding to the $20 \times 20 \mu\text{m}^2$ cell size, f corresponding to the $50 \times 50 \mu\text{m}^2$ cell size. The grayscale is logarithmic.

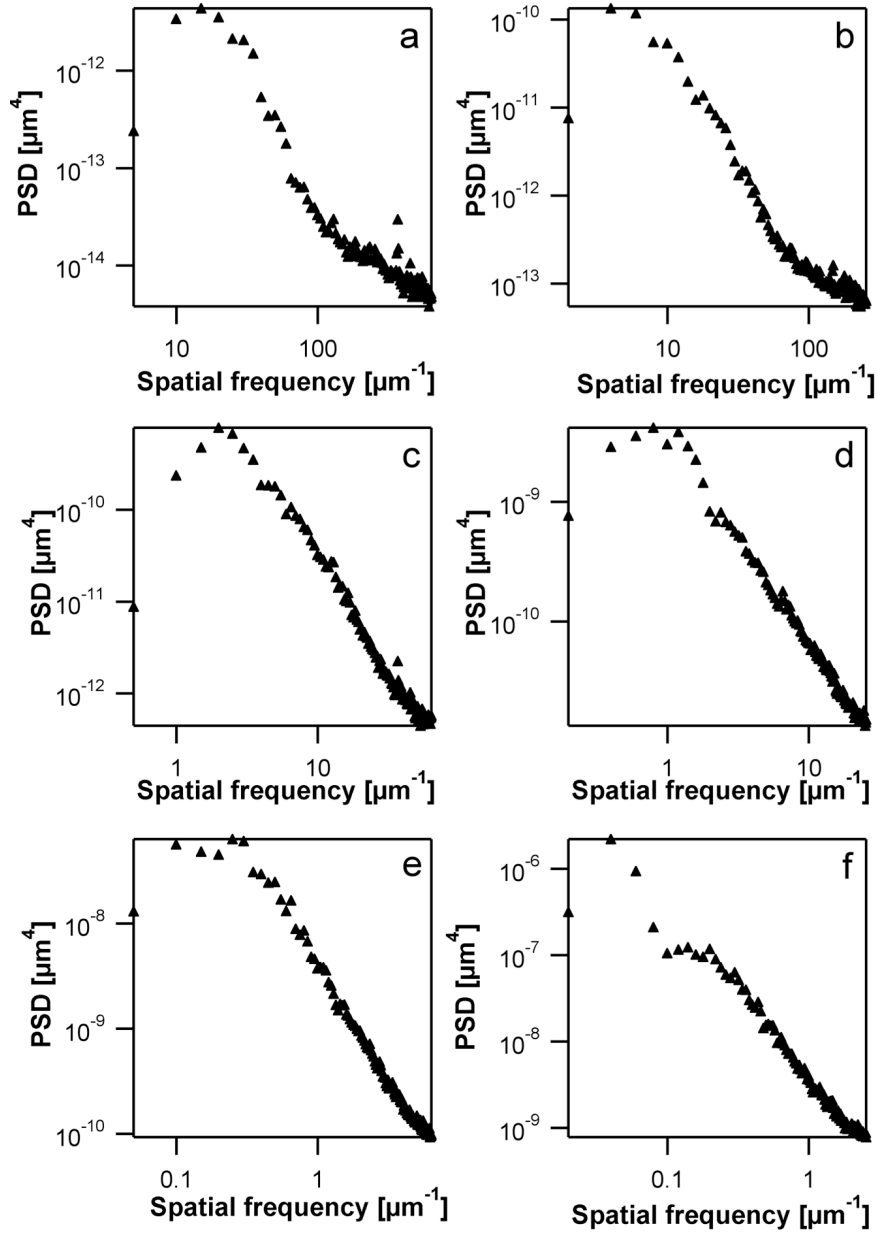


Figure III-17 : $P_1(s)$ for a PS 66k 8 Rg thick film, presented in Figure III-14, a corresponding to the $0.2 \times 0.2 \mu\text{m}^2$ cell size, b corresponding to the $0.5 \times 0.5 \mu\text{m}^2$ cell size, c corresponding to the $2 \times 2 \mu\text{m}^2$ cell size, d corresponding to the $5 \times 5 \mu\text{m}^2$ cell size, e corresponding to the $20 \times 20 \mu\text{m}^2$ cell size, f corresponding to the $50 \times 50 \mu\text{m}^2$ cell size.

Figure III-17 and Figure III-18 present the $P_1(s)$'s, obtained from images of different sizes of the same sample.

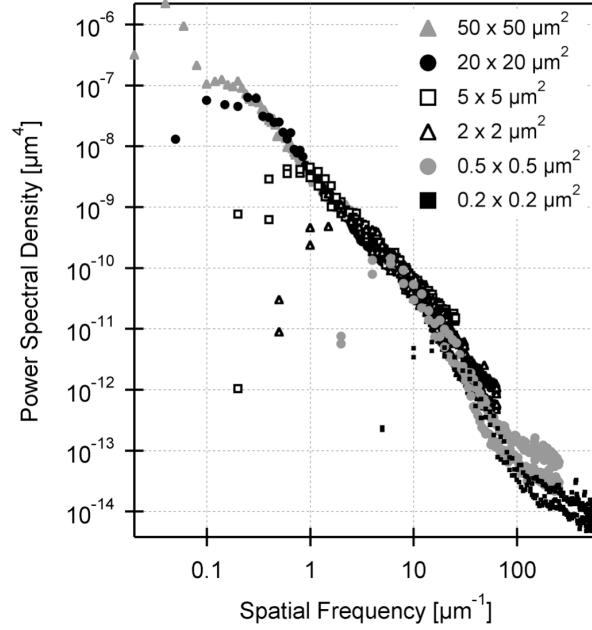


Figure III-18 : $P_1(s)$ for a PS 66k 8 Rg thick film, all curves presented in Figure III-14 put together, each marker corresponding to a cell size.

The last step consists of merging each $P_1(s)$ obtained on images of different sizes. After removal of the five first points, affected by data windowing, and those above half the Nyquist frequency, affected by noise, the $P_1(s)$'s corresponding to each image size are averaged and merged (Figure III-19).

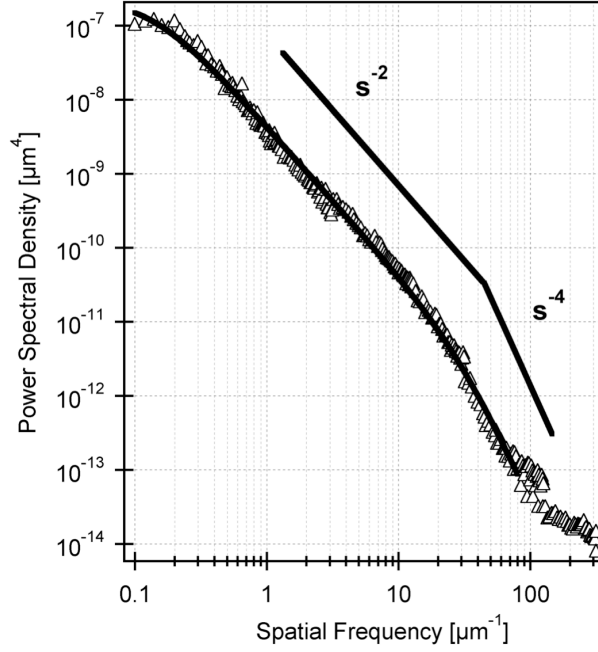


Figure III-19 : $P_1(s)$ for a PS 66k 8 Rg thick film, after merging (without rescaling) the curves presented in Figure III-14. The grey line represents the fit of the curves using the equation describing capillary waves fluctuations (equation III-2), the black lines give on an idea of the slopes of the curve.

4. RESULTS

In this section, results obtained after analysis of the raw AFM measurements as described in the previous section are presented.

For the clarity of the presentation, Table III-1 describes all samples studied, with the polymer nature and molar mass, their respective thickness (absolute thickness as determined by XRR and expressed as a function of the unperturbed radius of gyration of the considered polymer (R_g)) and annealing time.

The results described here are the merged $P_1(s)$'s (without rescaling). In some cases, fits of the curves (based on equation III-2) will be presented too. The results will be presented in two parts. First,

samples for which the film thickness is at least 8 times R_g , which may be considered as thick with respect to the natural length scale of the polymer, will be discussed. Then, thinner samples, which behave quite differently, will be rapidly presented.

	1 R_g	2 R_g	4 R_g	8 R_g	16 R_g
PS 66k T annealing 155°C $R_g = 70 \text{ \AA}$	30 min 69 $\text{\AA}$	30 min 153 $\text{\AA}$	5 h 370 $\text{\AA}$	5 h 546 $\text{\AA}$	5 h 1211 $\text{\AA}$
	1 h 73 $\text{\AA}$	2 h 151 $\text{\AA}$	128 h 357 $\text{\AA}$		
	2 h 71 $\text{\AA}$	5 h 166 $\text{\AA}$			
	4 h 71 $\text{\AA}$	8 h 151 $\text{\AA}$			
		32 h 152 $\text{\AA}$			
		128 h not determined			
PS 1030k T annealing 165°C $R_g = 277 \text{ \AA}$		5 h 684 $\text{\AA}$	5 h 1114 $\text{\AA}$	5 h 2475 $\text{\AA}$	
		173 h 684 $\text{\AA}$			
P4VP 81.5k T annealing 200°C $R_g = 91 \text{ \AA}$		5 h 161 $\text{\AA}$	5 h 332 $\text{\AA}$	5 h 660 $\text{\AA}$	

Table III-1 : Thickness and annealing times of samples studied by AFM, as a function of polymer nature, molar mass, annealing temperature and unperturbed radius of gyration.

A. Thick films

Figures III-20 – III-23 display the $P_1(s)$'s obtained respectively on a PS 66k film, $\sim 16 R_g$ thick, a PS 66k film $\sim 8 R_g$ thick, a PS 1030k film $\sim 8 R_g$ thick and a P4VP 81.5k film $\sim 8 R_g$ thick, all annealed for 5 hours in a vacuum, at a temperature 50 degrees above the bulk T_g . Fits of equation III.2 to the $P_1(s)$ are also shown.

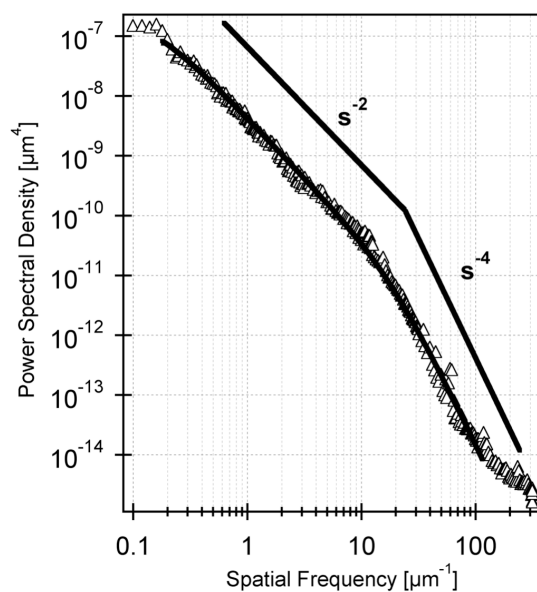


Figure III-20 : $P_1(s)$, for a 16Rg thick PS66k film annealed for 5 hours at 155°C. The black line represents the fit of the curves using the equation describing capillary wave fluctuations.

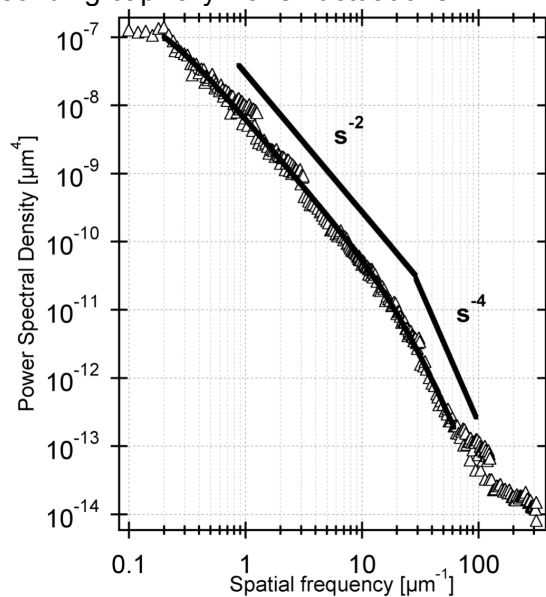


Figure III-21 : $P_1(s)$, for a 8Rg thick PS66k film annealed for 5 hours at 155°C. The black line represents the fit of the curves using the equation describing capillary wave fluctuations.

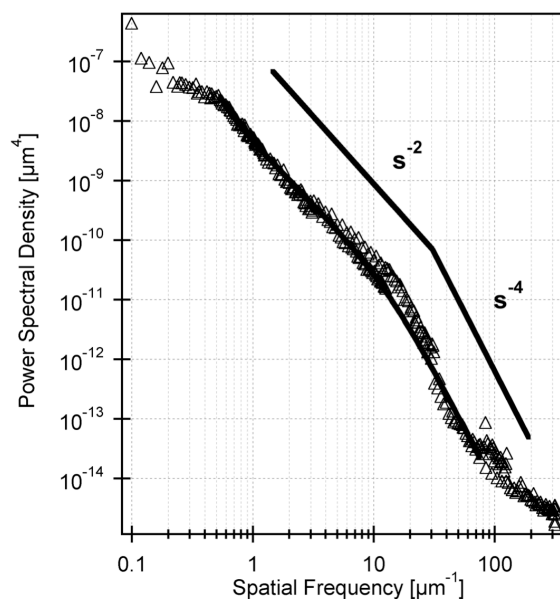


Figure III-22 : $P_1(s)$ for a 8Rg thick PS1030k film annealed for 5 hours at 165°C. The black line represents the fit of the curves using the equation describing capillary wave fluctuations.

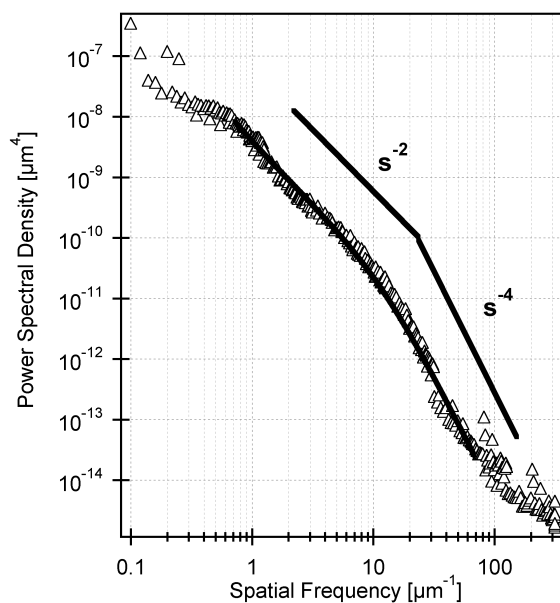


Figure III-23 : $P_1(s)$ for a 8Rg thick P4VP81.5k film annealed for 5 hours at 200°C. The black line represents the fit of the curves using the equation describing capillary wave fluctuations.

Whatever the polymer nature or the molar mass, the general shape of the $P_1(s)$'s is the same. In the four cases presented here, one can clearly observe a -2 power law describing the experimental data at low spatial frequencies, followed by a -4 power law, then a -1 power law at the highest frequencies.

We ascribe the s^{-1} power law describing the data at the highest spatial frequencies to experimental (white) noise. The power laws describing the shape of the curves at lower s values are compatible with the capillary wave fluctuation theory. Fits of the experimental data using equation III-2, which predicts the behaviour of a liquid surface, allow us to determine values for surface tension and bending rigidity of the interface, assumed to be the ones for $T = T_g$ (the temperature at which capillary waves freeze on the surface). The values obtained for surface tension (table III-2) agree well with tabulated values (when existing). This indicates that polymer fluids behave quite similarly to low molar mass fluids, and that surface tension governs roughness.

		γ [mJm ⁻²]	γ [mJm ⁻²] ⁸⁷	κ [J]
PS 66k	8 Rg	32.5 ± 2.7	35.7	8.7e ⁻¹⁹ ± 1.9e ⁻¹⁹
	16 Rg	32.8 ± 3	35.7	2.3e ⁻¹⁸ ± 3.2e ⁻¹⁹
P4VP 81.5k	8 Rg	31.9 ± 4.6		4.7e ⁻¹⁸ ± 7.7e ⁻¹⁹
PS 1030k	8 Rg	34.3 ± 3.9	35.7	4.9e ⁻¹⁸ ± 7.8e ⁻¹⁹

Table III-2 : Values for surface tension (γ) and bending rigidity (κ) extracted from fits presented previously.

Contrasting with low molar mass fluids such as water, for which surface tension was seen to decrease for reciprocal wavelengths comprised between 0.07 and 0.7 nm⁻¹ before being dominated by the bending rigidity⁹⁹, the $P(s)$'s of the polymers are seen to be already dominated by bending rigidity for reciprocal wavelengths larger than ~ 0.03 nm⁻¹. Consequently, no decrease of surface tension with

reciprocal wavelength could be detected. The importance of bending rigidity for the surface of polymer fluids must arise from their visco-elastic nature, but still lacks a complete theoretical description. Because the studied films were at least thicker than 55 nm, the low s cut-off in the power spectral density resulting from the van der Waals potential of the substrate could not be detected with certainty, since the ratio given by the following equation

$$\frac{A_{132}}{2\pi d^4} \bigg/ \gamma s^2 + \kappa s^4$$

is largely smaller than unity. Nevertheless, a break of the slope of the $P_1(s)$'s is observed for very low spatial frequencies in the figures. It may or not result from the cutoff due to van der Waals forces, or from inaccuracies of the experiment for larger image sizes. To answer this question, we performed experiments on much thinner films, since decreasing the thickness results in a shift of the cut-off to larger s -values.

B. Thin Films

In order to bring the Van der Waals cut-off in the probed range of reciprocal wavelengths, the thickness of the PS66k films was decreased to 15.1 nm (corresponding to $\sim 2R_g$). However, this film was found to be unstable after 5 hours annealing at 155°C.

Figure III-24 shows topographic images obtained on this film. One can see a structure on the film, especially on the 20 x 20 nm² image. This regular structure results in the presence of a peak in the $P_1(s)$, at a characteristic frequency that reflects the wavelength representative for the period of the peaks and valleys present at the surface of the film (Figure III-25).

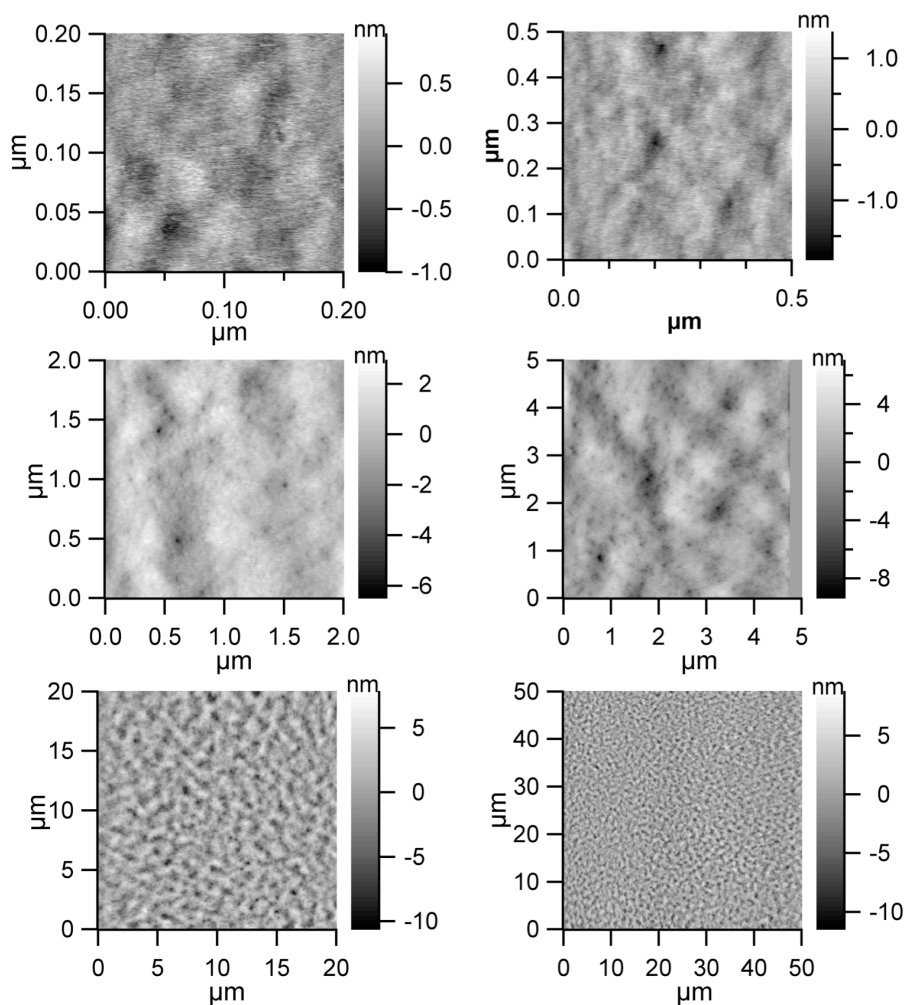


Figure III-24 : IC-AFM topographic images of a PS 66k 2Rg thick film on a Si wafer covered by a 1.3 nm thick layer of native oxide, after 5 hours annealing at 155°C. Six different cell sizes.

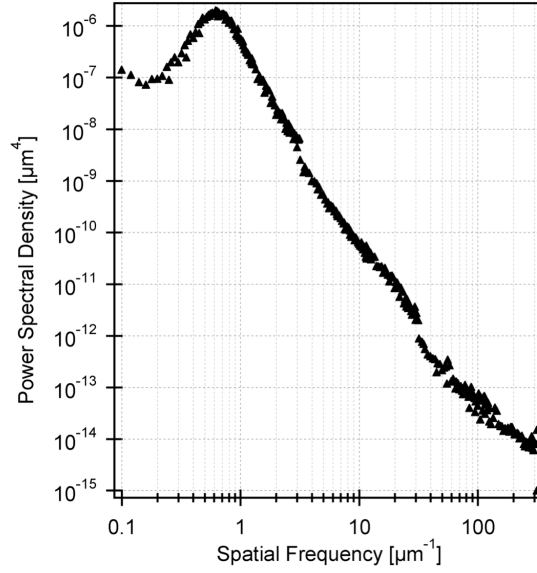


Figure III-25 : $P_1(s)$, for a 2Rg thick PS66k film annealed for 5 hours at 155°C.

Consequently, different samples of identical starting thickness were prepared and annealed for increasing times. Figure III-26 a-e presents topographic images of such samples for increasing annealing times; the $P_1(s)$'s are presented in Figure III-27, along with the equilibrium $P_1(s)$ determined from capillary wave theory using parameters determined on thicker films (continuous line).

This equilibrium $P_1(s)$ is computed for a 15.1 nm thick film, using an estimation for $A_{132} = -13 \times 10^{-20} \text{ [J]}^{51}$ and the values of γ and κ obtained on the thicker, 16Rg film, using the following expression for $P(s)^{100}$ where d is the thickness of the film :

$$P_1(s) = \frac{k_B T}{\Delta \rho g - \frac{A_{132}}{2\pi d^4} + \gamma(2\pi s)^2 + \kappa(2\pi s)^4},$$

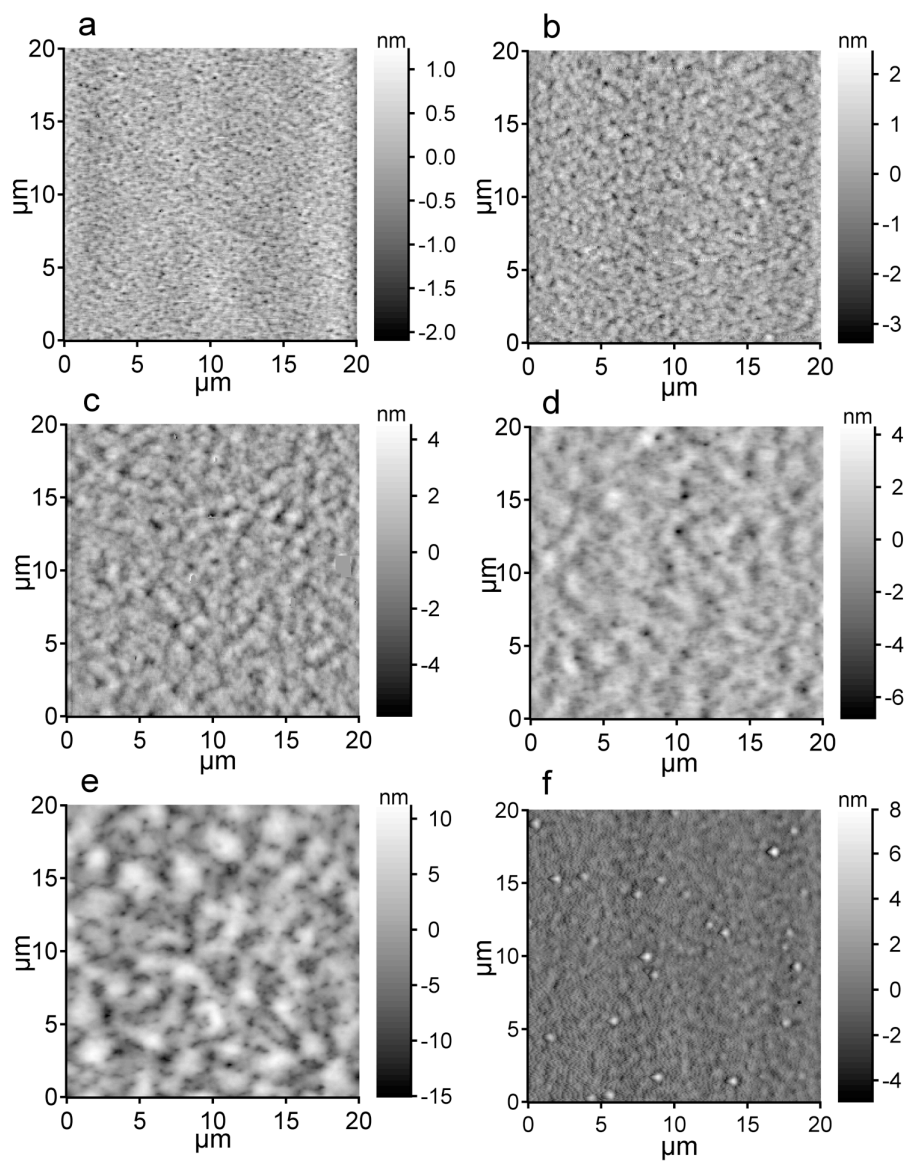


Figure III-26 : IC-AFM topographic images of a PS 66k 2Rg thick film on a Si wafer covered by a 1.3 nm thick layer of native oxide, cell size of 20 μm . Annealing temperature = 155°C. a : 30 minutes annealing, b: 2 hours annealing, c : 5 hours annealing, d : 8 hours annealing, e : 32 hours annealing, f : 128 hours annealing.

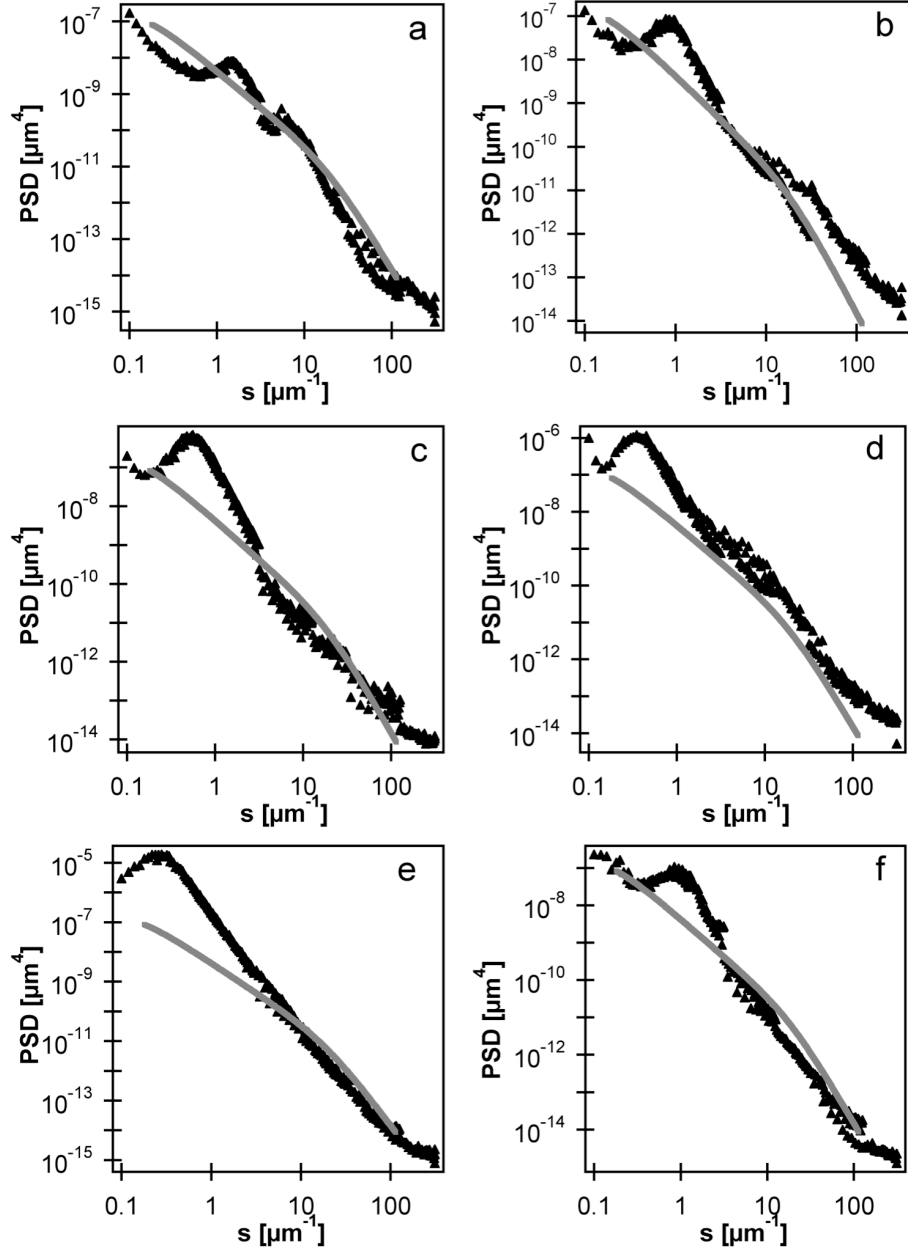


Figure III-27 : a-e : Power spectral density ($P_1(s)$) of PS66k films of 15.1 nm thickness ($\sim 2R_g$), annealed in a vacuum (155°C) : a for 30 minutes, b 2 hours, c 8 hours, d 32 hours, e 128 hours. f : $P_1(s)$ of P4VP 81.5k, 16.1 nm thick ($\sim 2R_g$), annealed in a vacuum (200°C) for 5 hours. In a-f, continuous lines are equilibrium $P_1(s)$'s computed from the values γ and κ obtained for a 16 Rg thick PS film.

As clearly shown in Figure III-27, the power spectrum of the film surface deviates from the equilibrium capillary wave spectrum, with the formation of a prominent structure peak associated to correlation between the hills or the valleys of undulations progressively developing on the surface. As annealing time elapses, the wavelength of this peak moves towards larger values according to a $t^{0.28}$ power law (Figure III-28). Meanwhile, the amplitude of the peak increases (Figure III-29). It is obvious from these figures that the film progressively dewets with specific wavelengths being amplified out of the equilibrium spectrum of capillary waves. After 128 hours annealing time, the height difference between hills and valleys is on the order of twice the initial film thickness, suggesting the onset of film break-up. Note that these results were confirmed by X-ray diffuse scattering experiments (not presented here).

Figure III-27 f show that a 16.1 nm thick P4VP 81.5k film ($\sim 2R_g$) annealed for 5 hours at 200°C in a vacuum starts to dewet similarly to PS film with the same thickness, which implies that the phenomenon is quite general.

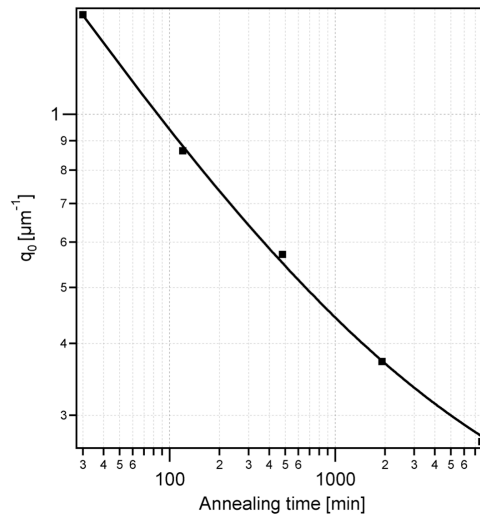


Figure III-28 : Reciprocal wavelengths corresponding to the peak of the $P_1(s)$'s of Figure III-27 (a-e), versus annealing time.

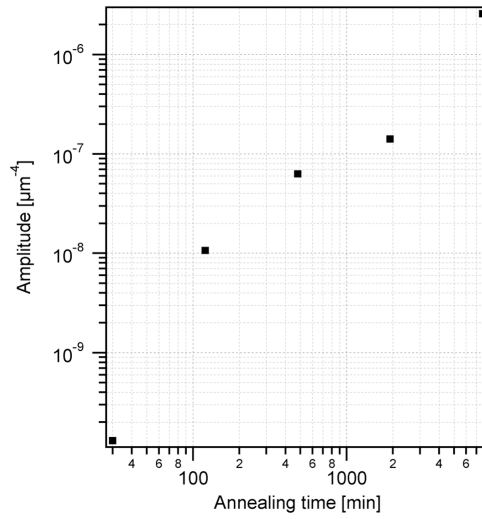


Figure III-29 : Height of the peak in the $P(s)$'s of Figure III-27 (a-e), versus annealing time.

Experiments were then performed on a PS of much larger molar mass, for which films of larger thickness (68.4 nm) correspond to $\sim 2R_g$. The $P_1(s)$ of such a film, after 5 hours annealing in vacuum at 165°C , failed to indicate significant deviations from the equilibrium capillary wave spectrum (Figure III-31). After 173 hours annealing, random holes formation was observed in the film (Figure III-30), most probably due to nucleation by heterogeneities. A spectral analysis of the polymer regions devoid of holes provided again a $P_1(s)$ close to the equilibrium spectrum of capillary waves.

In the case shown in Figure III-30 and Figure III-31 (PS 1030k, annealed for 5 and 173 hours), the shape of the $P_1(s)$'s do not follow anymore the laws of the capillary wave fluctuations theory.

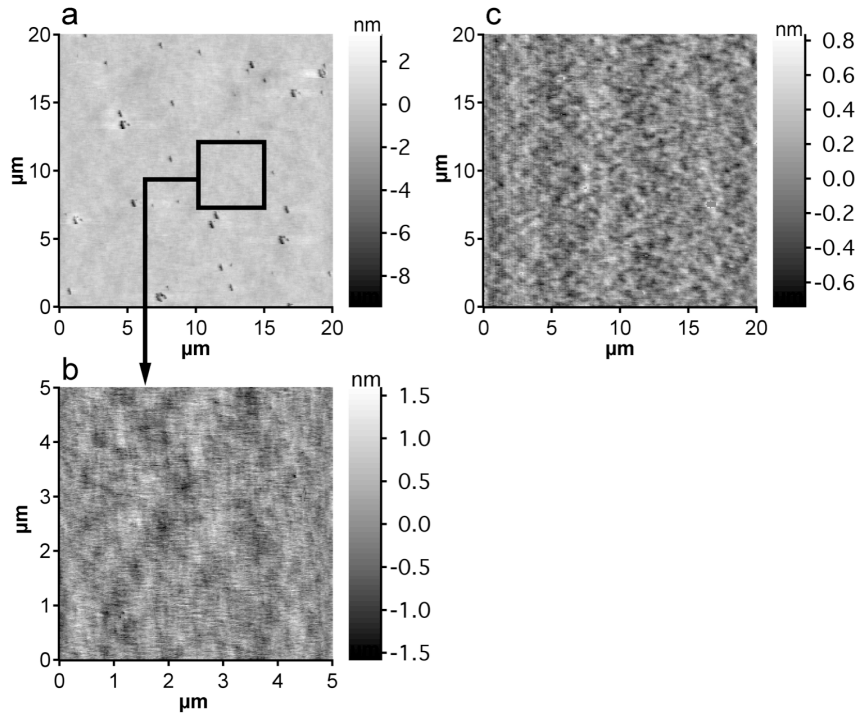


Figure III-30 : a IC-AFM topographic images of a 68.4 nm thick PS 1030k film ($\sim 2R_g$) annealed for 173 hours at 165°C in a vacuum, on Si wafer covered by a 1.3 nm thick layer of native oxide, b Zoom on a 5 x 5 μm^2 zone on image a, c IC-AFM topographic images of a 68.4 nm thick PS 1030k film ($\sim 2R_g$) annealed for 5 hours at 165°C in a vacuum, on Si wafer covered by a 1.3 nm thick layer of native oxide.

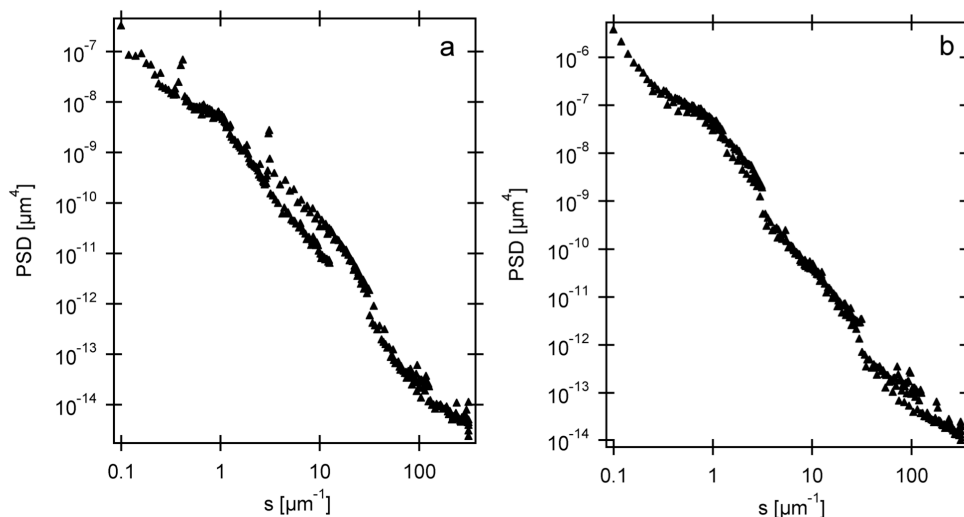


Figure III-31 : a $P_1(s)$ of a 68.4 nm thick PS 1030k film ($\sim 2R_g$) annealed for 5 hours at 165°C in a vacuum, b $P_1(s)$ of a 68.4 nm thick PS 1030k film ($\sim 2R_g$) annealed for 173 hours at 165°C in a vacuum.

Experiments performed on thicker P4VP 81.5k and PS 66k films (about $4R_g$ thick) indicated again deviations from the equilibrium capillary spectrum, although of lesser magnitude than for the $\sim 2R_g$ thick films (Figure III-33). Surprisingly, thinner films of PS66k (about $1R_g$ thick (~ 7 nm), hence strongly confined) did not present a prominent structure peak in their power spectral densities (Figure III-32).

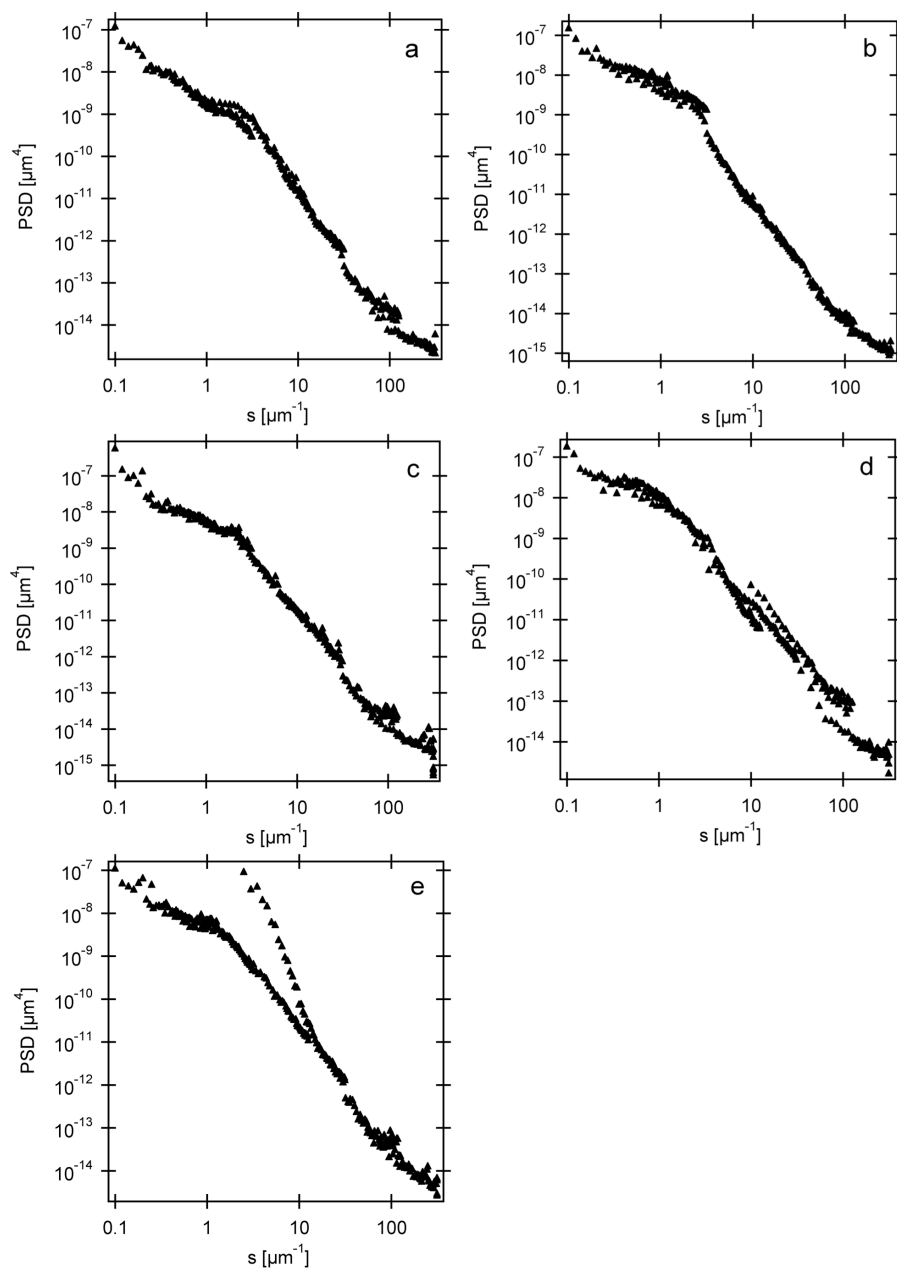


Figure III-32 : $P_1(s)$ of a $\sim 1\text{Rg}$ thick PS66k film annealed for different times at 155°C in a vacuum, a 15 minutes, b 30 minutes, c 1 hour, d 2 hours, e 4 hours.

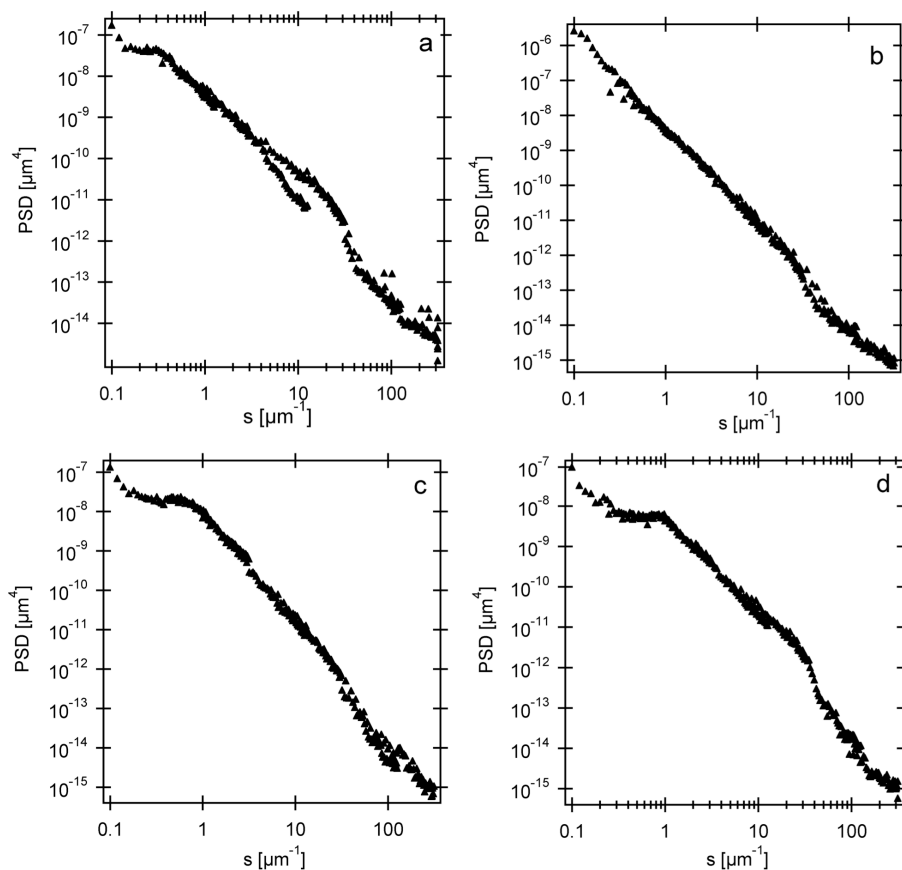


Figure III-33 : a $P_1(s)$ of a $\sim 4\text{Rg}$ thick PS 66k film annealed for 5 hours at 155°C in a vacuum, b $P_1(s)$ of a $\sim 4\text{Rg}$ thick PS 66k film annealed for 128 hours at 155°C in a vacuum, c $P_1(s)$ of a $\sim 4\text{Rg}$ thick PS 1030k film annealed for 5 hours at 165°C in a vacuum, d $P_1(s)$ of a $\sim 4\text{Rg}$ thick P4VP 81.5k film annealed for 5 hours at 200°C in a vacuum.

5. DISCUSSION

A. Thick films

For film thicknesses equal to at least 8 times the unperturbed radius of gyration of the polymers, the power spectral densities $P_1(s)$ were found to obey quantitatively the capillary wave fluctuation theory^{101,102}, with:

$$P_1(s) = \frac{k_B T}{\Delta \rho g - \frac{A_{132}}{2\pi d^4} + \gamma(2\pi s)^2 + \kappa(2\pi s)^4},$$

where ρ is the specific gravity of the polymer fluid, γ is its surface tension and κ is the bending rigidity of the interface. To our knowledge, this is the first observation of the validity of the capillary wave fluctuations theory in *direct* space for thin polymer films. Furthermore, since for different polymer natures, molar masses and film thicknesses the same behaviour is observed, it indicates the reproducibility of the phenomenon.

Nevertheless, observations of capillary waves in *reciprocal* space can be found in literature. Earlier studies^{44,103,104} were performed on PS, PVP and PEP supported films, measured by X-ray diffuse and specular scattering and AFM. For PS and PVP films, authors claim that films much thicker than the gyration radius of the polymer are in a confined state, probably due to the VDW film-substrate interactions and to the viscoelastic behaviour of thin films. As a consequence, their data could not be interpreted with the help of the capillary wave fluctuations theory. By contrast, capillary waves were observed on thin dewetted PEP films. The dewetted surfaces form an island substructure (described by AFM) on which capillary waves are

observed by X-ray diffuse scattering. Capillary waves were identified by their power law signature in the X-ray scattering signal. In a study by Lurio *et al*¹⁰⁵, the surface diffuse X-ray scattering of thin PS films supported on silicon wafers covered with their native oxide layer was measured. The temperature of the measurements was comprised between 120°C and 180°C. Capillary wave fluctuations theory was used to describe the observed diffuse scattering and values for surface tension and roughness were extracted from experiments. Surface tension values were in reasonable agreement with those of the bulk material, but the total surface roughness exceeded the value that would be expected from the capillary waves theory. The authors attributed this excess to the static structure of the polymer.

Other works by the same group^{106,107} were realised using X-ray photon correlation spectroscopy (XPCS), on supported PS films, at temperatures above the polymer bulk T_g . The dynamics of the surface height fluctuations as a function of lateral length scale was probed. These experiments confirmed that the surface morphology is governed by capillary waves, and confirmed scaling relations for the relaxation time for equilibrium surface height fluctuations as a function of wave vector, film thicknesses and temperature, predicted by the capillary wave fluctuations theory.

Our observations provide support to these previous, indirect, studies. However, it is worth to notice that even if our systems are similar to the previously studied ones, we test "frozen" surfaces, as we quench the films at room temperature, contrary to the studies realised by X-ray scattering above T_g . This may be the reason why a strong influence of bending rigidity was detected in our experiments, which was not the case in previous studies.

Free standing polymer films have also been measured by X-ray diffuse and specular scattering, as a function of film thickness and molar mass¹⁰⁸. Results show that films thinner than a few gyration radius are well fit by a simple liquid model, which was found by us to be insufficient to fit data obtained on systems thinner than a few times R_g .

B. Thin films and the issue of stability

An other important result in our study is the demonstration that PS films as thick as 15 nm may be unstable on silicon (covered by a 1.3 nm-thick layer of native oxide), and that amplification of capillary waves of specific wavelength may drive the system to dewet, contrarily to theoretical expectations based only on the negativity of A_{132} . Positive values of A_{132} correspond to negative values of the spreading coefficient of fluid 3 over substrate 1 and lead to unstable films below a critical thickness, whereas films are stable for negative values of A_{132} ¹⁰⁹. Only unstable films may dewet spinodally^{57,59,60,98} *i.e.*, by the amplification of capillary wave fluctuations^{101,110} of specific wavelength present on the surface of the fluid. Metastable films dewet by nucleation (from impurities, pinholes, voids, etc.) and growth of holes.

The Hamaker constant of PS, A_{33} , is comprised between 6.15 and 6.6×10^{-20} [J]^{97,111,112}, with $6.58 - 6.6 \times 10^{-20}$ J being the most often quoted value. The Hamaker constant of Silicon, A_{11} , is less frequently quoted; it was reported to be $22.1 - 25.6 \times 10^{-20}$ J⁹⁷ and 24×10^{-20} J¹¹³. This leads to a negative value for A_{132} (about -6×10^{-20} J), in reasonably good agreement with a recent experimental determination ($A_{132} = -13 \times 10^{-20}$ J)⁵¹. This negative Hamaker constant theoretically

rules out spinodal dewetting as a possible rupture mechanism for thin PS films on silicon, if only long-range van der Waals forces are taken into consideration.

In the present study, the observed dewetting behaviour resembles spinodal dewetting, although it does not strictly follow the expected laws established for spinodal dewetting. These results suggest that other forces than long-range van der Waals forces may be of importance for the stability of thin polymer films, and that confinement effects, polymer molar mass and details of the preparation process may be important parameters to consider when attempting to predict film stability.

As detailed previously, 15 nm thick PS films should be stable on Si wafers covered by a 1.3 nm thick layer of native oxide, if only long-range Van der Waals forces are taken into consideration. Nevertheless, the results presented in Figure III-25 and Figure III-27 unambiguously demonstrate this not to be the case. Nor is there any doubt that the dewetting observed in Figure III-24 arises from the amplification of capillary wave fluctuations. In this respect, the comparison of Figure III-24 e (dewetting by amplification of capillary waves) and Figure III-30 (dewetting by nucleation and growth of holes) is illuminating. In addition, the phenomenon was observed for different polymers and different samples prepared at different times, indicating that our observations are reproducible.

However, the observed dewetting does not correspond to "classical" spinodal dewetting. The time dependence of the maximum wavelength, and the fact that thinner films ($\sim 1R_g$) are more stable than thicker ones ($\sim 2R_g$), are not in agreement with the "classical" theory of spinodal dewetting. Nevertheless, the present results indicate that other forces than long range van der Waals forces are

also playing a role in the stability of thin polymer films. Possible such forces are:

- specific interactions with the substrate: these are however unlikely to be of importance, since P4VP and PS display a similar behaviour although they interact very differently with the acidic silanol moieties of the native oxide layer¹¹⁴.
- entropic restoring forces due to chain compression in films thinner than $\sqrt{6}R_g$. However, contrarily to what was proposed before³⁶, such forces should help stabilize the film against height fluctuations, since the excess free energy of the film per unit area can be written as :

$$\Delta G_{entropic} = C \left(\left(\frac{\sqrt{6}R_g}{d} \right)^2 - 1 \right)$$

for $d < \sqrt{6}R_g$, where C is a positive constant. Because the second derivative of this expression with respect to d is positive, entropic restoring forces will not destabilize the film against fluctuations of thickness. This can be understood easily, as the increase of free energy brought by the compression of the film in the valley of a wave will always be larger than the decrease of free energy due to decreasing compression in the hills of the wave. Actually, this may be the reason why films of PS66k of $\sim 1R_g$ thickness were found in the present study to be more stable than films $\sim 2R_g$ thick.

- “structural” forces: by this concept, we refer to forces arising from the perturbations of the structure of the polymer due to the presence of interfaces, as those observed and described in chapter II. The film instability could also be linked to the way by which the film is prepared, *i.e.*, spin-coating, known as

producing films out of equilibrium. Recent theoretical considerations^{63,64} showed that density fluctuations such as those due to restructuring of a film during annealing after spin coating⁶³, or variations of density with film thickness due to, e.g., confinement, layering or restructuring⁶⁴, may render unstable a thermodynamically stable film.

Nevertheless, we can only speculate on the cause of the behaviour of thin films during annealing, since it relies on theoretical hypotheses, even if this seems the most probable explanation for the presently observed dewetting process. Due to the predicted dependence of the wavelength of the faster growing mode on film density and density gradient^{63,64}, it becomes possible to understand why $\lambda_{\max}$ shifts with annealing time in our experiments : this would simply reflect variations of the internal structure of the film with annealing time. The theoretically-predicted strong dependence on film thickness of the raising time of the faster growing mode may also explain why thicker films of PS1030k are metastable and dewet by a hole nucleation mechanism, while thinner PS66k films are unstable.

Since the time dependence of $\lambda_{\max}$ would be related to progressive restructuring of the film, our results suggest that relaxation of a thin PS film of 66 000 g.mol⁻¹ molar mass may take as long as 120 hours at a temperature 50°C above the bulk Tg. These are considerable times, and indicate how cautious one should be when examining the properties of thin polymer films¹¹⁵.

It is interesting to compare the annealing time applied to the film with the reptation time of the polymer. The reptation time, in the Rouse model, is defined as¹¹⁶ $\tau_{rep} = \frac{\langle L \rangle^2}{D} [s]$, with $\langle L \rangle [m]$ the length of the

tube and $D [m^2 s^{-1}]$ the self-diffusion coefficient of the considered polymer. It represents the time necessary for a polymer chain to travel for a distance equal to the length of its confinement tube.

$\langle L \rangle$ is defined as $\langle L \rangle = \frac{L_{EE}}{\sqrt{N_e}}$, where L_{EE} is the end-to-end distance

of the polymer chain and N_e the number of monomers units between two chain entanglements. This number is equal to 23 for poly(styrene)¹¹⁶.

Using the values of D provided by Fleischer¹¹⁷, we can roughly estimate τ_{rep} to be around 0.26 sec. The annealing time is thus largely superior to the reptation time, which rules out the possibility that the polymer chains would not have enough time to relax, except if the confinement in the thin film modifies strongly the dynamics of the chains.

In addition, because the instability would be related to the structure resulting from the preparation process itself (spin-coating), attention should be paid to the details of this process. In this respect, it is not obvious that experiments performed on oligomers below the critical molar mass for entanglement (M_c) (such as in references 46 and 51) may be safely extrapolated to polymers above M_c such as those of the present study. Finally, it is worthy mentioning that recently published results on the dewetting of thin films of a symmetric PS-block-poly(paramethyl styrene) copolymer above the order-disorder transition temperature (30 nm thick, or about $3R_g$)¹¹⁸ strongly resemble the results presented here (time-dependent λ_{max} , exponential variation of roughness with annealing time).

6. CONCLUSIONS

Our objective was to describe free polymer surfaces and to compare the behaviour of small molecular liquid surfaces with polymer surfaces. To that aim, the $P_1(s)$'s of different surfaces of polymer films, differing in polymer nature, molar masses and film thicknesses, were computed from AFM images.

Two main behaviours could be outlined :

- When polymer films are strictly thicker than $4R_g$, the $P_1(s)$'s follow satisfactorily the capillary wave fluctuation theory. Experimental results can be fit using equation III-2. Values for surface tension and bending rigidities were also computed from fits (Table III-2). These values are compatible with literature values⁸⁷, when existing (this is not the case for bending rigidities). It is not possible to determine the Hamaker constant on such thick films, since there is no evidence for the presence of a plateau at low spatial frequencies in the $P_1(s)$'s. Remaining to explain is the importance of bending rigidity in the power spectrum : theoretical observations should be proposed in the future.
- For thinner films, despite long-range Van der Waals forces stabilize polystyrene films on silicon substrates against height fluctuations, evidences were provided in this work that amplification of capillary waves of specific wavelengths is nevertheless possible for films as thick as 15 nm, ultimately leading to dewetting in a "spinodal-like" process. However, the temporal dependence of the phenomenon, and its variation with film thickness, do not agree with the "classical" spinodal dewetting mechanism. This was ascribed to the existence of

forces inside the film that could result either from the reorganisation of the chains of the films or from density variations within the films during annealing, in accordance with recent theoretical treatments. The strong confinement of the polymer chains could also be a caused for the instability of the film during annealing. We have observed experimentally the existence of this chains reorganisation phenomenon, but so far, no complete and consistent explanation is able to described this behaviour. The process was shown not to be limited to polystyrene films, as films of poly(4-vinyl-pyridine) were shown to behave similarly. Such forces most probably result from the out-equilibrium structure of the film after spin-coating, especially when the thickness of the film is in the range of a few radii of gyration.

These results indicate how sensitive are thin polymer films to specifics of the preparation process. This may be of interest, since such conditions may be tuned to attain a higher degree of control over the dewetted morphology. It now remains to be assessed to which extent other results which appeared in the previous literature may be resulting from a similar instability mechanism.

In the sequel, we will thus avoid entering into the thickness range where unstable behaviour appears. We have now an equation allowing a precise description of roughness at all length scales, which will be useful when attempting to determine the complete structure of thin polymer films by X-ray scattering.

**CHAPTER IV. JOINT ANALYSIS OF X-RAY AND
NEUTRON REFLECTOMETRY OF SELECTIVELY
DEUTERATED POLYMER THIN FILMS**

1. INTRODUCTION AND OBJECTIVES

In this chapter, using our knowledge of the roughness of thin polymer films described in chapter III, we will be trying to refine and complete the study of the structure of thin polymer films, using a complementary technique, namely neutron reflectometry. We have noted previously that XRR density profiles needed to introduce an extra-layer even at the air interface, in order to model properly the XRR. This extra-layer corresponds to a non-perfectly Gaussian density profile, which contradicts our findings by AFM (for the thicker films). This shows that we should reconsider the structure of thin films, while injecting our knowledge of the $P_1(s)$ of the free interface. It is appropriate, at this stage, to also complement the information provided by XRR using neutron reflectometry (NR). This technique that probes the whole volume of the film, was described before. In the next paragraph, we will show how samples can be optimally designed to provide information on the film near an interface. The selection of this technique and the way of analysing experimental data will be described hereafter.

A. Neutron reflectometry and contrast matching

As described previously, the main information provided by XRR measurements comes from the density contrast at the air/polymer and at the substrate/polymer interfaces. The density perturbation observed at the substrate/polymer interface is small compared to the contrast existing at the air/polymer and polymer/substrate interface.

To exacerbate the sensitivity to this modification, our objective will be to suppress the density contrast between substrate and film. To achieve this aim, the selected polymer to be studied can be

deuterated at an adequate rate and measured by neutron reflectometry (NR). Indeed, the principles of this technique are the same as for XRR : it probes the scattering length density contrast between layers inside a given system. The difference lies in the fact that neutrons are sensitive to the neutron scattering length density within the system, while X-rays feel the electron density variations in the same system, which are proportional to the X-ray scattering length densities. Since hydrogen and deuterium have very different neutron scattering length densities, while electron densities between deuterated and hydrogenated organic compounds are similar, it becomes possible to design samples where neutron and X-ray will be sensitive to different extents to the internal density fluctuations. This provides extra information on the film structure.

Using both techniques together requires thus "playing" with the material, using an adequate deuteration rate to match the contrast between the substrate and the polymer film, measured by NR, not changing significantly the XRR measurements. We will come to this in more detail.

B. Free surface layer behaving like a liquid

In addition, the atomic force microscopy study of chapter III brought us some important information : the surface of the polymer film behaves like a liquid. Two different behaviours were observed, depending on the ratio thickness/gyration radius. If polymer films are strictly thicker than $4R_g$ the $P_1(s)$'s follow satisfactorily the capillary waves fluctuation theory. For film thicknesses equal to or thinner than $4R_g$, evidences were provided that amplification of capillary waves of specific wavelengths is possible, ultimately leading to dewetting in a "spinodal-like" process, which does not agree with the "classical" spinodal dewetting mechanism.

The films used in this study are about four times the radius of gyration of the concerned polymer. So, we will be working at the limiting thickness ensuring fluid-like behaviour of the surface. We will in the future sometimes consider that the $P_1(s)$ of capillary waves controls the roughness as measured by XRR or NR. Because the square of the probed roughness is :

$$\sigma_{probed}^2 = \int_{s=s_0}^{\infty} P_1(s) ds ;$$

where s_0 is a wavelength cut-off given by the coherence length of the neutron or X-ray beam, and reminding that the coherence length is a function of the incidence angle (equation I-5), it becomes clear that our AFM knowledge will be of interest to model properly the reflectometry data.

2. DEUTERATION RATE DETERMINATION AND SUBSTRATE SELECTION

To determine the adequate deuteration rate to achieve contrast matching between film and substrate, neutron reflectometry simulations were first performed. The electron density profiles obtained in chapter II were transformed into neutron scattering length profile and used for the simulations. Figure IV 1 a gives the simulated reflectograms obtained, respectively for 0, 3 and 4 deuterium atoms replacing the hydrogens of the monomer unit, respectively, for a PS film. Figure IV 1 b shows the corresponding scattering length densities profiles. It appears clearly that the adequate deuteration rate lies between 3 and 4 deuterium atoms by polymer repeat unit. Using the reflectograms presented in figure IV 1 a, the simulated pseudo auto-correlation functions were computed. These are presented in figure IV 1 c. The density perturbation between film and

substrate is best put in evidence when the deuteration rate has as value of 4 deuteriums by repeat unit. It appears as a strong negative peak in the correlation function, just before the film thickness. Unfortunately, this product is not available commercially. Therefore, the analysis of films of deuterated PS was done using PS deuterated with 3 deuterium atoms by repeat unit, which still shows sensitivity to the interface.

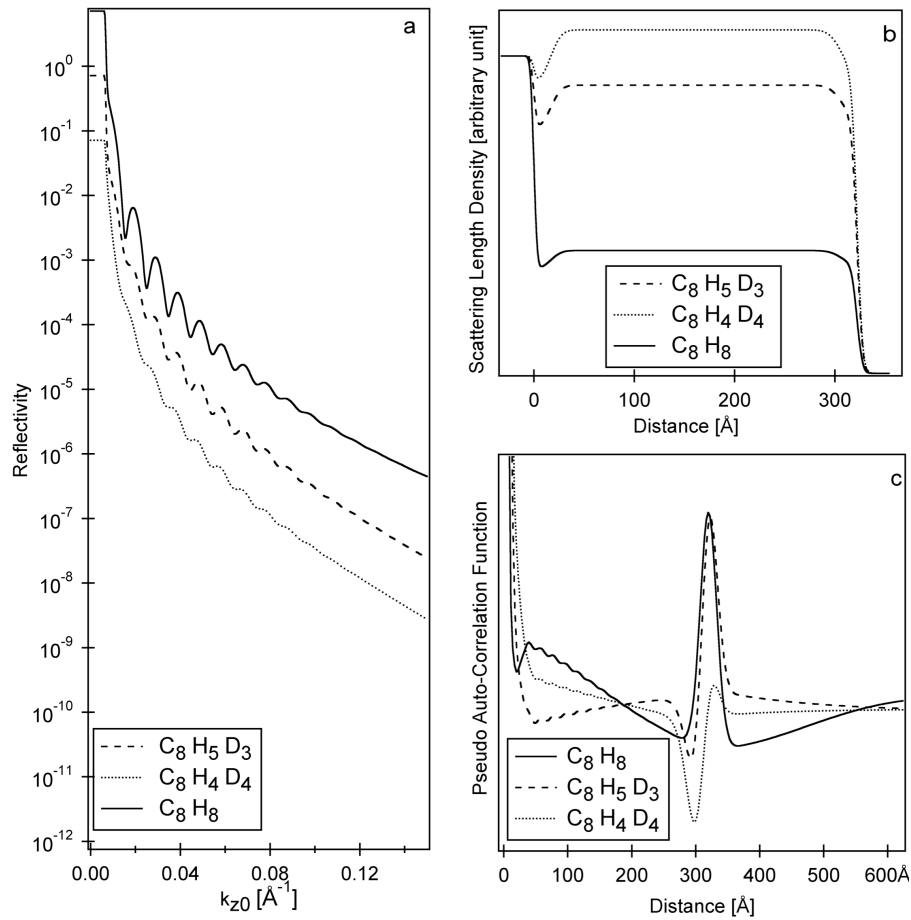


Figure IV-1 a : neutron reflectometry simulations of hydrogenated and deuterated PS (respectively with 3 and 4 deuterium atoms by repeat unit). b : scattering length densities corresponding to the reflectograms depicted in (a). c : Pseudo auto-correlation functions computed from the reflectograms in (a), for the different deuteration rates.

The same procedure was applied to determine the optimal deuteration rate for PMMA. The adequate chain also contains 3 deuterium atoms by monomer, as shown in figure IV-2. Nor deuterated P4VP nor its monomer are available commercially. The neutron reflectometry measurements will thus only concern deuterated PS and PMMA.

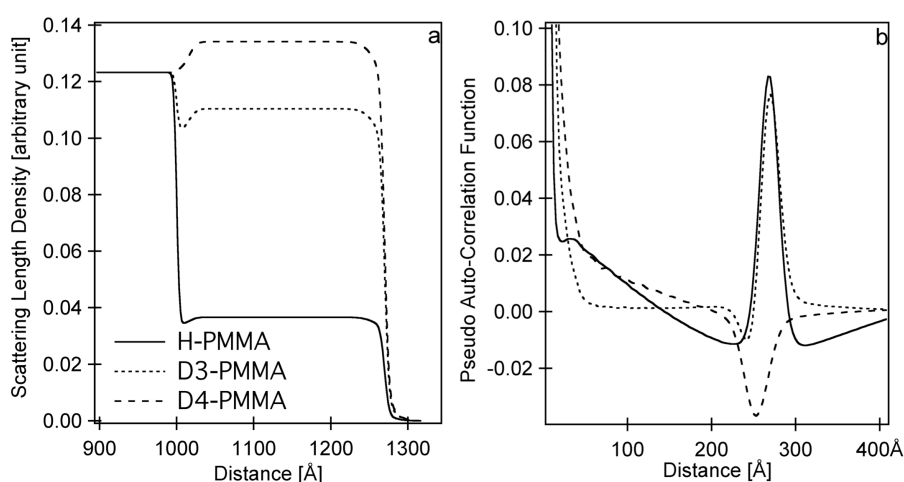


Figure IV-2a : scattering length densities corresponding to hydrogenated and deuterated PMMA (respectively with 3 and 4 deuterium atoms by repeat unit). b : Pseudo auto-correlation functions corresponding to hydrogenated and deuterated PMMA (respectively with 3 and 4 deuterium atoms by repeat unit).

Another important factor to deal with is the nature of the substrate. So far, our substrates were silicon wafers covered with their native oxide layer (thickness around $\sim 13 \pm 2 \text{ Å}$ ¹¹⁹). In the case of X-rays, refractive indexes values of silicon and silicon oxide are very close, and the SiO₂ native layer does not show up in the density profiles. Everything happens as if the native oxide layer was invisible for X-rays. For neutrons, this is not the case anymore. The scattering length density values for silicon and silicon oxide are rather different. As a consequence, the polymer density perturbation near the

substrate, which we want to put in evidence, could be hidden by the presence of a low frequency oscillation in the reflectogram, due to the presence of the native oxide layer. This layer will also be observed in the pseudo auto-correlation function, under the form of a supplementary peak or valley of width close to the perturbation we want to observe, which will complicate the global system analysis, as illustrated in figure IV 3. The two density profiles are presented in figure IV 3a and the computed PACF are shown in figure IV 3b. The presence of the native oxide layer shows itself in the density profile by an increase of scattering length density between substrate and film. In the PACF, it is clear the system with the native oxide layer presents more features than the system without it. To avoid this problem, the selected substrate will be made of a silicon wafer, upon which a thick thermal oxide layer will be grown. This will bring the perturbation of the PACF resulting from SiO_2 to longer distances, which will allow us separating the possible short-ranged perturbation of film density from the oxide contribution in the PACF. The change of substrate will change the Hamaker constant of the system, but since we want to put into evidence density modifications related to short-range interactions, this will not affect the phenomenon we want to emphasise.

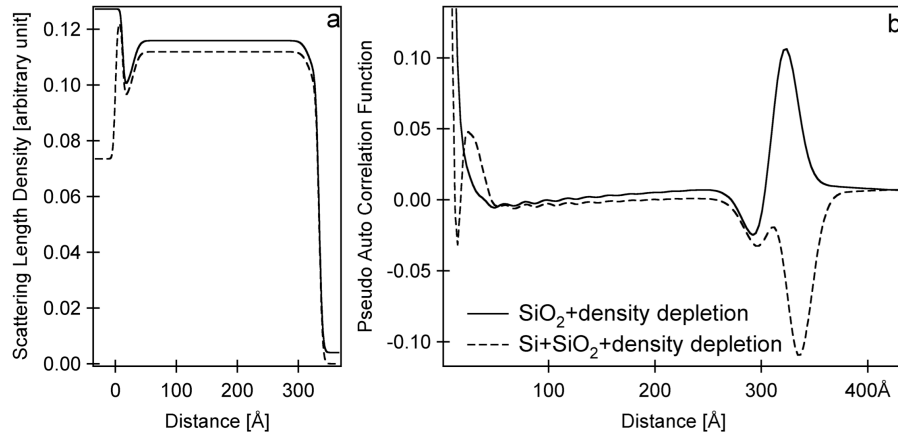


Figure IV-3a : Simulations of scattering length densities corresponding respectively to a system composed of a SiO₂ substrate covered by a polymer layer, with a polymer density depletion at the substrate/film interface; and of a system composed of a substrate of silicon covered with its native oxide layer plus a polymer film, with a polymer density depletion at the interface substrate/film . b : Pseudo auto-correlation functions related to the scattering length densities in (a).

3. EXPERIMENTAL PART

A. Polymers synthesis

The selected deuterated polymers were not available commercially for the desired molar masses. Therefore there were synthesised by anionic polymerisation, following the reactional schemes presented in figures IV.4 and IV.5. The monomers used in this synthesis are styrene-d₃ and methyl methacrylate-d₃. Deuterated styrene and methyl methacrylate were obtained from CDN Isotopes, Interchim, Montlucon Cedex, France. The syntheses were done in the “Centre d’Etude et de Recherches sur les Macromolécules (CERM) de l’Université de Liège, Belgique”. Experimental details for the synthesis can be found in ^{120,121}, as well as details on the determination of the molar masses (table IV.1).

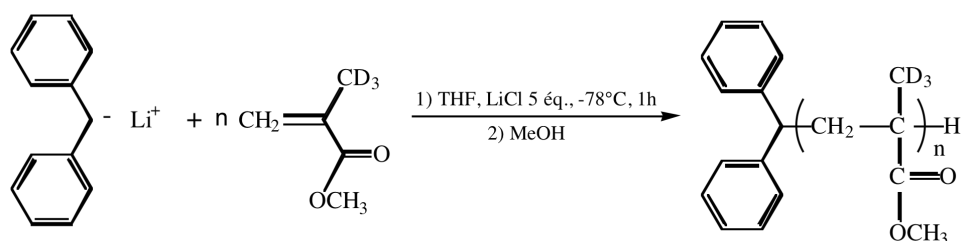


Figure IV-4 : Reactional scheme for the synthesis of anionic triply-deuterated PMMA.

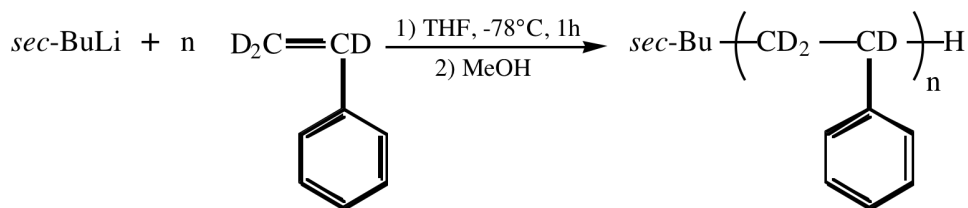


Figure IV-5 : reactional scheme for the synthesis of anionic triply-deuterated PS.

Polymer	Molar Mass (Mn)	Polydispersity Index
PMMA-d3	78000	1.09
PS-d3	62000	1.08

Table IV-1 : Molar mass of the deuterated polymers.

B. Preparation of the films

The polymer films were prepared by spin coating (3000 rpm speed) from polymer solutions directly after having cleaned the substrate in a piranha solution. The solvent used was toluene (Merck, p.a.).

The annealing took place in a vacuum furnace equipped with a trap for oil vapours. The samples were annealed for 5 hours at temperatures 50°C above the T_g of the bulk polymers, then quenched in air at room temperature.

C. Measurements

Neutron reflectometry measurements were realised on the TAS8 line of DR3 reactor in Risø, Denmark, in collaboration with Dr N. Gadegaard and were supported by an EU grant (TMR545). Samples were measured by NR in Risø and by XRR in Louvain-la-Neuve. In that way, double information is available for each film, which will allow reducing the uncertainty of the analysis. Figure IV-6 and Figure IV-7 present experimental X-ray and neutron reflectivity curves, gathered on the same graph, respectively for d-PS and for d-PMMA. The

different curves, arising from the different measurement ranges are represented as obtained from the raw experiments, without any rescaling. This is particularly clear in the inset in Figure IV-6 and Figure IV-7, showing the neutron reflectivity measurement alone. The jump between each range results from variations in the openings of the slits defining the neutron beam.

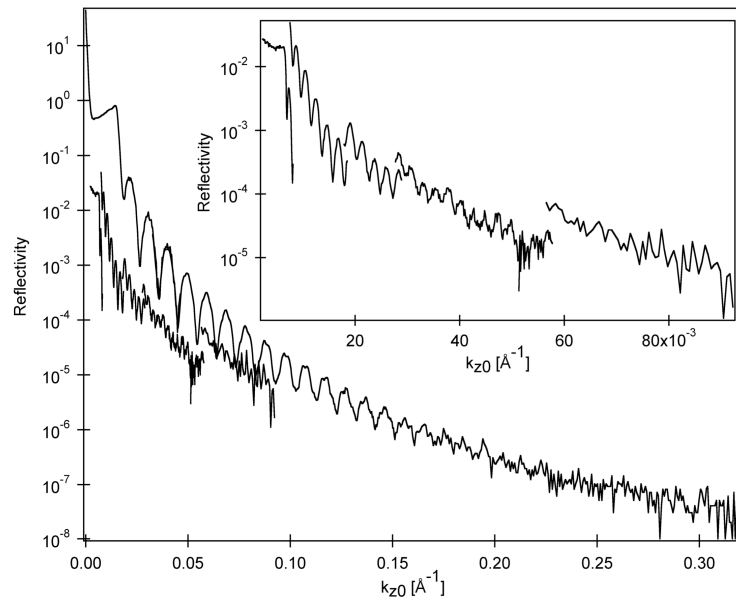


Figure IV-6 : Raw X-ray and neutron reflectometry measurements, for d-PS. The inset represents the neutron reflectivity alone.

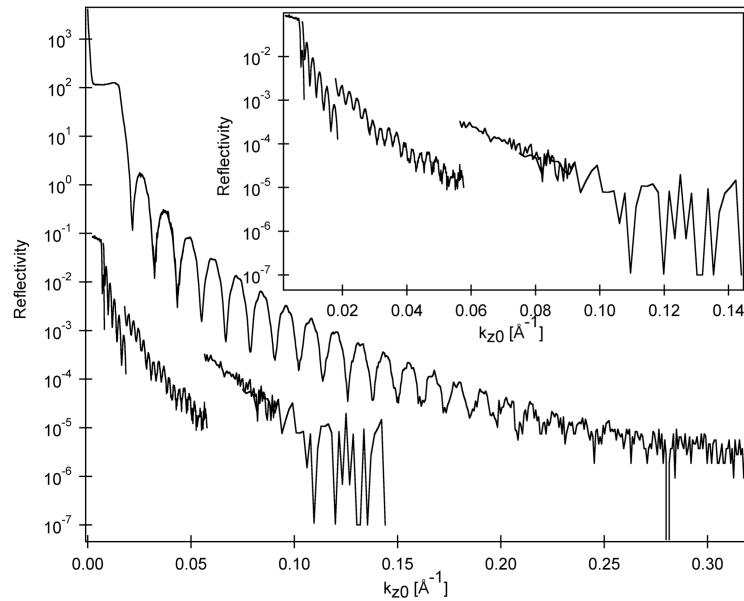


Figure IV-7 : Raw X-ray and neutron reflectometry measurements, for d-PMMA. The inset represents the neutron reflectivity alone. For the clarity of the figure, X-ray reflectivity has been shifted vertically.

4. RESULT ANALYSIS

The XRR and NR data were analysed together by using a common model of film density, from which both the neutron scattering length density and electron density were derived. Formally, XRR and NR verify similar equations. The indices of refraction are adapted according to the probe beam. These equations incorporate parameters that describe the vertical structure of the reflecting film. Some of these parameters are common to NR and XRR, since the measurements are performed on the same samples. The concerned parameters are the film thickness, and to some extent the interfacial roughness.

Other parameters are specific to each technique, such as the indices of refraction of the layers. Because XRR and NR are sensitive to

gradients of refraction indices, neutrons and XRR are not sensitive in the same way to the vertical composition profiles of the films. For instance, the contrast between silicon and silicon oxide is weak for X-rays (because the electron density of both materials are close), but large for neutrons (the scattering length density of both materials being strongly different).

	Neutron scattering length density [$\text{\AA}^{-2}$]	Electron density [$\text{\AA}^{-3}$]
Si	$2.07 \cdot 10^{-6}$	0.7
SiO ₂	$3.47 \cdot 10^{-6}$	0.66
PS (3d)	$3.16 \cdot 10^{-6}$	0.34
PMMA (3d)	$3.51 \cdot 10^{-6}$	0.34

Table IV-2 : neutron scattering length density and electron density of the materials

Table IV-2 presents the theoretical neutron scattering length density and electron density of the materials of this study.

Because of this, NR and XRR provide complementary information on the reflecting film. Moreover, each technique has its own strengths and weaknesses. For instance, the signal-to-noise ratio is better for XRR than for NR, and the background lower relative to the incident intensity. This allows performing XRR measurements to larger k_{z0} values than for NR. High k_{z0} values contain more information on roughness, since roughness tends to damp fringes in this range. By contrast, the possibility to tune the contrast in NR by selective deuteration offers a unique opportunity to tailor a sample for best performance, which XRR does not permit.

For all these reasons, we have decided to combine XRR and NR measurements of the same sample, and to adjust a single model to both sets of measurements. Statistically, we double the information content without requiring to double the number of required

parameters. This results in a decrease of the statistical uncertainty on the resulting fitted parameters.

A. Modelling

The models take the smaller possible number of parameters required to reproduce the reflectivities. The following geometrical parameters were used :

- The layer thicknesses (one for silicon oxide and from one to three layers for the polymer).
- The roughness of the Si/SiO₂ and the SiO₂/film interfaces. The one of the Si/SiO₂ interface was set constant to below 2Å and does not affect the curves.
- The roughness of the film/air interface, which was either fitted or computed from the $P_1(s)$ (see below).

Moreover, the reflectivity equations also involve materials parameters, *i.e.*, the refraction indices of the materials. These indices are different for X-rays and neutrons. It seems thus required to add $2(N+1)$ supplementary parameters, which are the neutron and X-ray refractive indices for the substrate and N layers (including SiO₂ and the layers describing the polymer film). However, the refractive indices can be computed from densities and atomic composition of the materials, by using the proper scattering length for each probe, *i.e.*, b_i for neutrons and $r_0 Z_i$ for X-rays (r_0 is the electron radius, b_i the neutron scattering length).

One could thus simply reduce the number of parameters to $N+1$ (the density of each layer in some reference unit, such as the electron density in Si atoms for the substrate, the density in silicon oxide groups for the oxide or the monomer density for the film), from which the profiles of refraction index could be computed for both X-rays and neutrons. This is the approach that was followed here. In addition, the

density of silicon was fixed to its tabulated value ($0.049959 \text{ \AA}^{-3}$). From the geometrical and materials parameters, the ideal reflectivity curves can be computed as indicated in chapter II.

The last set of experimental parameters to consider are experimental parameters related to beam collimation and monochromatisation. The reflectivity curves are convolved by Gaussian functions that take into account the resolution of the reflectometer in both wavelength and angle. The full-width of the Gaussian were computed from

$$\frac{\Delta k_{z0}}{k_{z0}} = \sqrt{\left(\frac{\Delta\theta}{\theta}\right)^2 + \left(\frac{\Delta\lambda}{\lambda}\right)^2},$$

where the $\Delta\theta$ and $\Delta\lambda$ are the full widths at half-maximum of the angular and spectral dispersions, respectively. These values are given in Table IV-3.

	$\Delta\theta/2\theta$	$\Delta\lambda/2\lambda$	k_{z0} range [$\text{\AA}^{-1}$]
X-rays	$3.1 \cdot 10^{-3}$	$1.7 \cdot 10^{-4}$	$3.2 \cdot 10^{-3} - 3.2 \cdot 10^{-1}$
Neutrons range 1	$4.9 \cdot 10^{-5}$	$4.4 \cdot 10^{-3}$	$2.3 \cdot 10^{-3} - 8.1 \cdot 10^{-3}$
range 2	$1.49 \cdot 10^{-4}$	$4.4 \cdot 10^{-3}$	$7.5 \cdot 10^{-3} - 1.85 \cdot 10^{-2}$
range 3	$3.31 \cdot 10^{-4}$	$4.4 \cdot 10^{-3}$	$1.79 \cdot 10^{-2} - 2.89 \cdot 10^{-2}$
range 4	$3.31 \cdot 10^{-4}$	$4.4 \cdot 10^{-3}$	$2.77 \cdot 10^{-2} - 5.22 \cdot 10^{-2}$
range 5	$2.61 \cdot 10^{-4}$	$4.4 \cdot 10^{-3}$	$5.13 \cdot 10^{-2} - 5.77 \cdot 10^{-2}$
range 6	$2.31 \cdot 10^{-4}$	$4.4 \cdot 10^{-3}$	$5.66 \cdot 10^{-2} - 9.22 \cdot 10^{-2}$

Table IV-3 : Experimental resolutions (half-width at half maximum).

Finally, the ranges are also multiplied by a scaling factor (usually close to 1) taking into account slight errors in the determination of the primary beam intensity. A constant background is only considered for XRR, and small vertical misalignment for both XRR and NR are also considered.

The total number of parameters is thus, considering N layers (including SiO_2), $N_X = 2$ XRR ranges and $N_n = 6$ neutrons ranges :

N : densities, the one of the substrate being constant;

N : roughnesses, the one of the Si/SiO_2 was set constant;

N : layer thicknesses;

$N_X + N_n$: scaling factors;

1 : background for XRR

2 : misalignment errors of the samples;

which gives a total of $3N+11$ parameters, with $N = 2 - 4$ depending on the numbers of layers used to describe the polymer film.

Two models were thus tested. The first one consists of a single layer for the polymer film ($N = 2$). The second one consists of three layers for the polymer film ($N = 4$), with two layers used to describe the perturbation at the SiO_2/film and film/air interfaces.

In addition, the supplementary information provided by the AFM was taken into account in two other models. For these models, the roughness of the film/air interface is computed from the coherence length of the probe beam and from the spectrum of capillary waves that was shown to exist on the free surface of the film.

The roughness effectively probed by the beam can be written as :

$$\begin{aligned}\sigma_{probed}^2(\theta) &= \int_{s_L = \frac{\sin \theta}{L_{coh}}}^{\infty} P_1(s) ds \\ &\equiv C \ln \frac{\frac{1}{l^2} + \frac{1}{l_m^2}}{\frac{1}{l^2} + \frac{1}{L_M^2}},\end{aligned}$$

where $l = L_{coh}/\sin \theta$ is the coherence length of the beam projected on the sample surface, L_M and l_m , are defined as :

$$\begin{aligned}l_m &= 2\pi \sqrt{\frac{\kappa}{\gamma}} \\ L_M &= 2\pi \sqrt{\frac{\gamma}{\alpha}},\end{aligned}$$

where $\alpha = \Delta\rho g + \frac{A}{2\pi d^4}$ and $C = \frac{kT}{4\pi\gamma}$.

Here, L_M was set to 10^6 Å, a constant value which was found not to affect significantly the fit, whereas $L_{coh,n}$, $L_{coh,X}$ and l_m were fitted, which added three parameters to the previous ones. This description was used for model 3, which contains a single polymer layer, and model 4 that uses two layers to describe the polymer film, one at the SiO_2/film surface and one for the rest of the film. Figure IV-8 describes the four models.

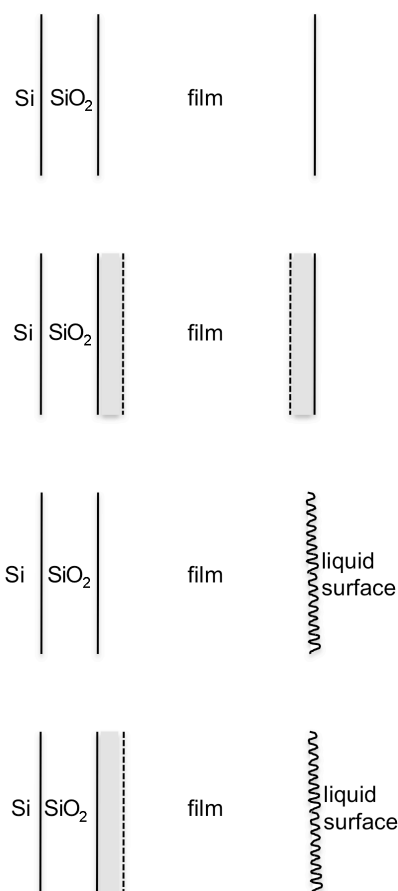


Figure IV-8 : Schematic drawing of the models used to fit the combined NR and XRR experiments

In all cases the χ^2 was determined and its value is reported in Table IV-4 and Table IV-5 as a function of the model used, respectively for d-PS and d-PMMA. Also presented in tables is the percentage difference for each model compared to the lowest χ^2 . In the case of the analysis of deuterated PS, the second model is by and large the best one, according to the values of χ^2 .

PS	χ^2	%
model 1	11126	135
model 2	4732	0
model 3	10851	129
model 4	9070	92

Table IV-4 : Deuterated PS films : χ^2 values for the four models used with the percentage difference for each model tested with the lowest χ^2 obtained.

PMMA	χ^2	%
model 1	4560	20
model 2	3799	0
model 3	4537	19
model 4	3808	0.2

Table IV-5 : Deuterated PMMA films : χ^2 values for the four models used with the percentage difference for each model tested with the lowest χ^2 obtained.

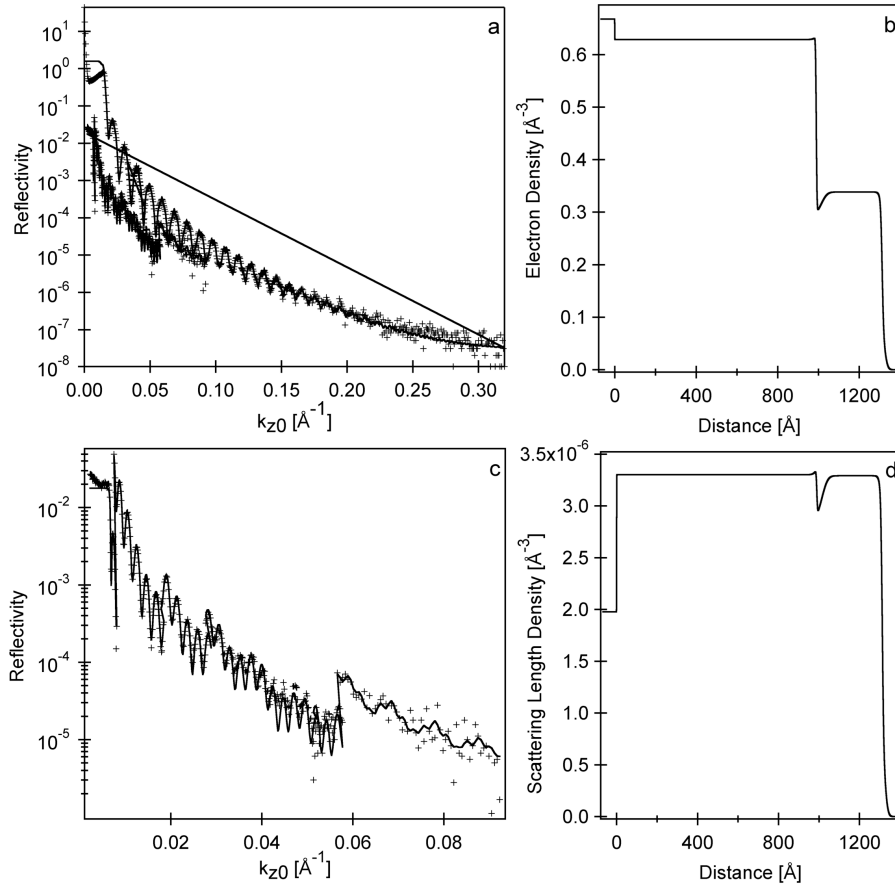


Figure IV-9 : Deuterated PS, fits using model 2. a : neutron and X-ray reflectivity measurements, together with the fit. b : electron density profile corresponding to the fit of the reflectivity measurements. c : neutron reflectivity measurement with the fit. d : neutron scattering length density profile corresponding to the fit of the reflectivity measurements.

Figure IV-9 a shows the neutron and X-ray reflectivity measurements, together with the fit, for deuterated PS. Figure IV-9 b, for more clarity, shows only the neutron reflectivity measurements, also with the fit of model 2. Figure IV-9 c and d present respectively the scattering length density and electronic density profiles corresponding to the fit of the reflectivity measurements. We can clearly observe a depletion in density of the film near the interface with the substrate. Removal of

this depletion layer results in a significant increase of this χ^2 . The inclusion of the capillary wave $P_1(s)$ to represent the air/film interface does not result in an improvement of the fit; on the contrary, the χ^2 doubles suggesting that our power spectrum may be inappropriate.

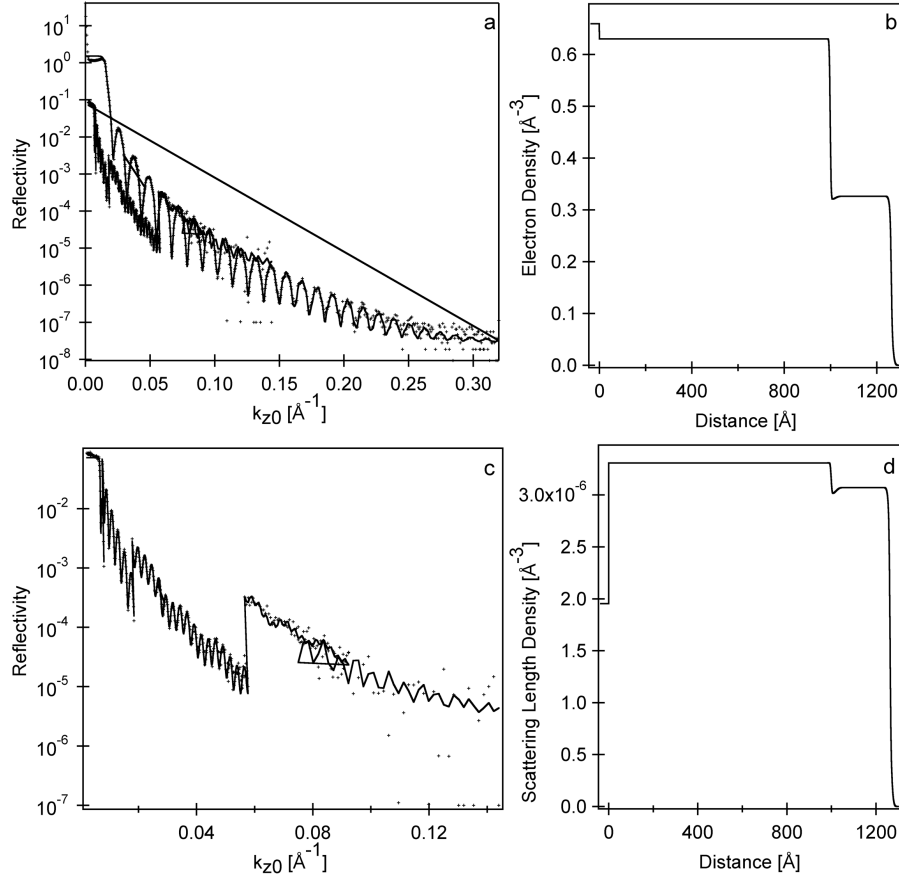


Figure IV-10 : Deuterated PMMA, fits using model 2. a : neutron and X-ray reflectivity measurements, together with the fit. b : electron density profile corresponding to the fit of the reflectivity measurements. c : neutron reflectivity measurement with the fit. d : neutron scattering length density profile corresponding to the fit of the reflectivity measurements.

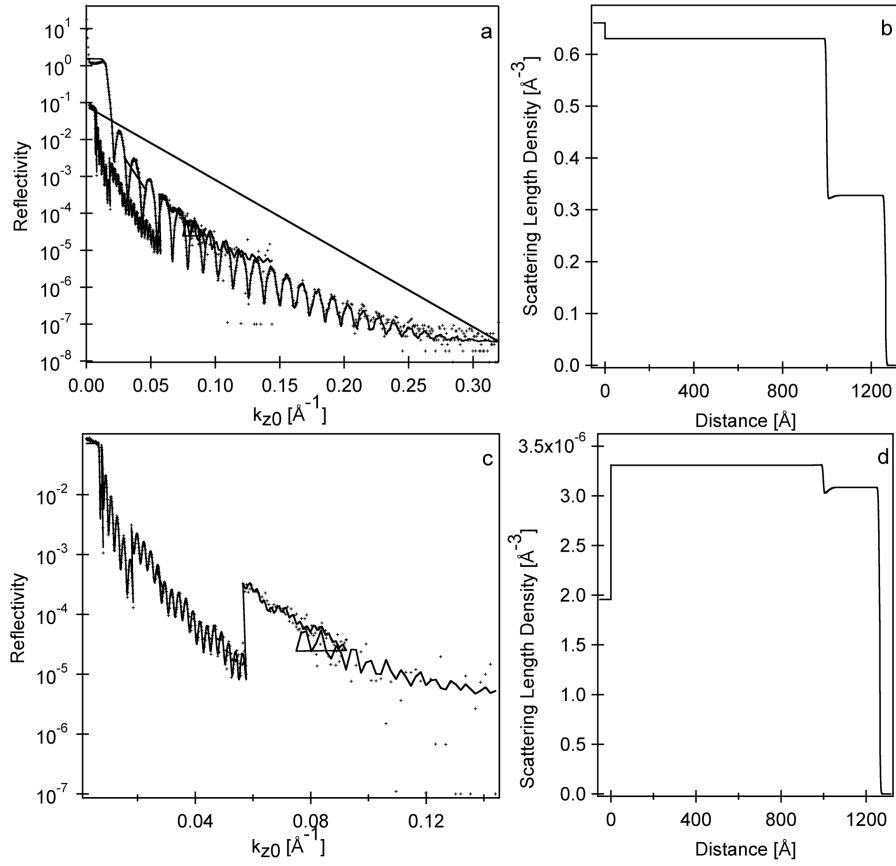


Figure IV-11 : Deuterated PMMA, fits using model 4. a : neutron and X-ray reflectivity measurements, together with the fit. b : electron density profile corresponding to the fit of the reflectivity measurements. c : neutron reflectivity measurement with the fit. d : neutron scattering length density profile corresponding to the fit of the reflectivity measurements.

In the case of deuterated PMMA, the four models produce the same χ^2 values. Figures IV-10 and IV-11 show the scattering length density and electronic density profiles corresponding to the two best values of χ^2 , respectively model 2 and 4. We can observe a very little depletion in density of the film near the interface with the substrate. Because this depletion is quite small, it may be removed altogether from the model, resulting only in an increase by $\sim 20\%$ of the χ^2 .

There is in addition very little difference between the models with a constant air/film roughness, comparing to the model including capillary waves. This shows that this parameter is not crucial for the reflectivity data.

5. DISCUSSION

The fit results clearly show that, for PS, a model including a perturbation of density at the solid interface and a slightly perturbed free surface is the best one. This is in good agreement with our previous conclusions from XRR alone. More surprising is the observation that we have to model the free interface by an additional layer to obtain a good fit whereas the inclusion of capillary waves-dominated roughness fails to represent properly the data. However, we showed in chapter III that the surface of film $\sim 4R_g$ in thickness was slightly perturbed compared to the predicted capillary waves spectrum. This is most probably the reason why we need to introduce this perturbation layer at the free interface. In this respect, the NR and XRR model is in good agreement with the AFM data. All things considered, our analysis thus supports the hypothesis for the existence of a depletion layer at the buried interface. Nevertheless, we must be careful when analysing the NR measurements, since the k_z -range of the measurements is much more restricted than for XRR measurements, carrying less information about the low frequency signal, which is the one we are trying to put into evidence. For PMMA however, all models are equivalent. If we favour the model with the smaller number of parameters, which is the best selection to avoid overinterpretation, we must conclude that the depletion of density is too weak to be detected, or does not exist. This will be in line with the stronger affinity of PMMA for hydroxylated SiO_2

(hydrogen bond formation). This inclusion of the spectrum of capillary waves at the free interface does not improve or deteriorate the fits, showing that the roughness here is too small to affect significantly the fits. There must thus be no amplification of specific wavelengths in the spectrum of the free surface of PMMA, which is probably due to the higher stability of PMMA on the substrate. In this sense, the absence of perturbed surface $P_1(s)$ and the absence of depletion at the surface substrate might thus be viewed as phenomena arising in parallel and resulting from a common source.

6. CONCLUSIONS

Combined XRR and NR studies of different polymer films (PS, PMMA) deposited onto silicon wafers covered with a $\approx 900\text{\AA}$ thick oxide layer confirm perturbations of the density profile near the solid substrate. The importance of these effects correlates with the strength of the interactions developed between the polymer and silicon oxide. In the case of PS this variation improves significantly the quality of the analysis. In the case of PMMA, the density variation is weak and the necessity of introducing a density perturbation at the substrate/film interface is not that clear. The presence of an external layer behaving like a liquid was not necessary to improve fits of reflectivity data, in both cases, even though we know that this model is valid, as was developed in chapter III.

Our measurements and observations are coherent with lots of with other observations of perturbed dynamic of polymer thin and ultrathin films which are ascribed to specific interactions developed between substrate and the near interface^{6,7,10-12,17-22}. In all these cases, the importance of interfaces, whether there are free surfaces, capped surfaces, interfaces with a solid substrate is obvious and increases while decreasing film thickness or raising interface area^{1,2}.

CHAPTER V. CONCLUSIONS AND PERSPECTIVES

Owing to the importance of thin polymer films in many current and future technological applications, we started a research work on their structure. Since literature reports studies on the perturbations of the dynamical properties of polymers near solid interfaces, whose interpretation is sometimes conflictual, it might be hoped that our analysis will be useful for progressing in this issue as well.

Our objectives in this work were to :

- try elucidating the question of the density evolution of polymers near solid substrates, by determining density profiles on thin polymer films using X-ray reflectometry;
- characterise by AFM the structure of free surfaces of polymers and compare the behaviour of small molecular liquid surfaces with polymers surfaces, while checking the stability of thin polymer films. To that aim, the power spectral densities of different surfaces of polymer films, differing in polymer nature, molar masses and film thicknesses, were computed from AFM images.
- use a third technique, neutron reflectometry, and the knowledge from our previous studies of the film structure and surface analysis, in order to refine and complete the study of the structure of thin polymer films, for both the buried and free interfaces.

At the end of that work, different conclusions can be drawn :

- XRR studies of different polymer films (PS, PMMA, P4VP) deposited onto silicon wafers covered with their native oxide seem to indicate perturbations of the density profile near the solid substrate, either a depletion (PS, PMMA), or an increase of density (P4VP). The importance of these effects would correlate with the strength of the interactions developed between the polymer and silicon oxide, weak and non-adsorptive in the case of PS, and strong and adsorptive in the case of P4VP. The limited sensitivity of XRR did not allow,

however, revealing differences between PS and PMMA. To analyse the XRR data, we have combined direct and reciprocal space methods, which allow decreasing the uncertainties on the results. This approach is rarely being seen in the literature, and is one of the technical outcomes of our thesis. XRR suggests that the spatial extent of these density perturbations would span 2-3 statistical segment lengths, and would be independent of the molar mass of the polymer. However, these conclusions have to be supported by another independent technique, because the modelling intrinsic to XRR analysis makes these conclusions model-dependent. Therefore the free surface of the films was analysed by AFM. Two main behaviours could be outlined :

- when polymer films are strictly thicker than $4R_g$, the power spectral densities follow satisfactorily the capillary wave fluctuation theory. Values for surface tension and bending rigidities were also computed and are compatible with literature values. This is, to our knowledge, the first time that this behaviour is put in evidence in direct space. However, we found that the free interface has a much larger bending rigidity than liquid of low molar mass.
- For thinner films, despite the fact that long-range van der Waals forces should stabilise polystyrene films on silicon substrates against height fluctuations, evidences were provided in this work that amplification of capillary waves of specific wavelengths is nevertheless possible for films as thick as 15 nm, ultimately leading to dewetting in a "spinodal-like" process. However, the temporal dependence of the phenomenon, and its variation with film thickness, do not agree with the "classical" spinodal dewetting mechanism. This was ascribed to the existence of forces inside the film that could result either from the reorganisation of the chains of the films or from density variations within the films during annealing, in accordance

with recent theoretical treatments. The strong confinement of the polymer chains could also be a cause for the instability of the film during annealing. We have observed experimentally the existence of this chains reorganisation phenomenon, but so far, no complete and consistent explanation is able to describe this behaviour. The process was shown not to be limited to polystyrene films, as films of poly(4-vinyl-pyridine) were shown to behave similarly. Such forces most probably result from the out-equilibrium structure of the film after spin-coating, especially when the thickness of the film is in the range of a few radii of gyration.

We then returned to the full structure of the films, by combining XRR and NR studies of different partially deuterated polymer films (PS, PMMA) deposited onto silicon wafers covered with a 900 Å thick oxide layer. Perturbations of the density profile near the solid substrate were confirmed for PS films, and a deviation of the surface roughness from the one predicted based on the capillary wave fluctuation theory was observed. This last observation was ascribed to the perturbations of the power spectral density of the film surface already noted by AFM for films of this thickness. In the case of PMMA, the density variation is weak and the necessity of introducing a density perturbation at the substrate/film interface is not that clear. For PMMA, the roughness of the free interface is small and can be modelled as well by a simple Gaussian roughness or the full capillary waves fluctuations theory. Both the small roughness of the free interface and the limited (if any) density perturbation at the solid surface are well in line with a higher stability and interaction of PMMA on and with the Si/SiO₂ substrate.

It thus seems that density perturbations at the buried interface are plausible and not inconsistent with our set of measurements. Whether this is due to an intrinsic phenomenon or to perturbations resulting

from the spin-coating process is however not clear. We have pointed out that the PS films were dewetting by a mechanism probably involving internal structural forces. This indicates that the structure of spin-coated films may not be fully relaxed, even after long annealing times. On the other hand, one should realise that such out-of-equilibrium films are those used for technological applications. In this respect, our study remains fully relevant.

It seems appropriate at this stage to enumerate experiments that could not be done but would be of interest to perform to progress further. First, it would be of interest to follow the structure of the films as a function of temperature, both by XRR and AFM. The NR experiments should be performed for thicker PS films that do not have a perturbed free surface. Techniques sensitive to density, such as positron annihilation spectroscopy, could be of interest. Our study is thus far from having answered the questions concerning the structure of thin polymer films. We hope however that it contributed to a better understanding of this complex issue.

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