



UvA-DARE (Digital Academic Repository)

Restructuring-induced dewetting and reentrant wetting of thin glassy films

Demirel, A.L.; Jerome, B.T.L.

Publication date
1999

Published in
Europhysics Letters

[Link to publication](#)

Citation for published version (APA):

Demirel, A. L., & Jerome, B. T. L. (1999). Restructuring-induced dewetting and reentrant wetting of thin glassy films. *Europhysics Letters*, 45.

General rights

It is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), other than for strictly personal, individual use, unless the work is under an open content license (like Creative Commons).

Disclaimer/Complaints regulations

If you believe that digital publication of certain material infringes any of your rights or (privacy) interests, please let the Library know, stating your reasons. In case of a legitimate complaint, the Library will make the material inaccessible and/or remove it from the website. Please Ask the Library: <https://uba.uva.nl/en/contact>, or a letter to: Library of the University of Amsterdam, Secretariat, Singel 425, 1012 WP Amsterdam, The Netherlands. You will be contacted as soon as possible.

Restructuring-induced dewetting and re-entrant wetting of thin glassy films

A. L. DEMIREL^{1,2} and B. JÉRÔME^{1,3}

*FOM-Institute for Atomic and Molecular Physics
Kruislaan 407, 1098 SJ, Amsterdam, The Netherlands*

² *Koç University, Chemistry Department
Çayir Cad. No: 5 Istinye 80860 Istanbul, Turkey*

³ *University of Amsterdam, Department of Chemical Engineering
Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands*

(received 15 September 1998; accepted in final form 29 October 1998)

PACS. 68.15+e – Liquid thin films.

PACS. 68.45Gd – Wetting.

PACS. 68.45–v – Solid fluid interfaces.

Abstract. – Thin films of glass-forming liquid crystalline molecules on float glass substrates showed restructuring-induced dewetting in the film thickness range of 40–100 Å upon increasing temperature after spin coating. This dewetting proceeded by the appearance of fluctuations at the free surface caused by restructuring taking place at the interface with the supporting substrate. Films thicker than 100 Å did not dewet despite significant modulations of the free surface. The amplitude of surface fluctuations with respect to the film thickness is shown to determine the film thickness range for dewetting.

Thermal stability and dewetting of thin films have been gaining attention not only because of their increasing use in technological applications, such as coatings, dielectrics and non-linear optics, but also from a fundamental point of view [1-3]. Dewetting of thin structureless liquid films on solid substrates has been largely investigated both theoretically and experimentally [4-12]. Two different mechanisms, namely nucleation at defects and amplification of thermal fluctuations at the free surface leading to spinodal dewetting, have been considered so far as responsible for the formation of holes in thin films at the early stages of dewetting.

Fluctuations at the free surface can also originate from other mechanisms than thermal excitations (*e.g.*, the evaporation of a volatile film [13]), leading to other dewetting mechanisms. We present here evidence that the restructuring taking place upon heating at the interface between a spin-coated glassy film and its supporting substrate can also destabilize the free surface of the film, because of the restructuring it induces in the whole film. The resulting fluctuations appearing at the free surface can create holes in the film if they are deep enough, leading to a dewetting mechanism resembling spinodal dewetting. Contrary to spinodal dewetting, the amplitude of the surface fluctuations does not significantly increase in time.

Therefore, thick films for which surface fluctuations do not manage to create holes during the restructuring process survive this process and remain stable. Since monolayers were stable because of a strong interaction of the molecules with the substrate, our system showed a re-entrant wetting as a function of film thickness.

Our observations were performed with a glass-forming liquid crystalline material. This type of material has several advantages. First, their dynamics is slow enough to be followed in time. Second, the use of liquid crystalline molecules enables probing the polar interfacial order on the substrate by optical Second-Harmonic Generation (SHG) technique. We could therefore follow by SHG the restructuring taking place at the film/substrate interface, as well as the undulations at the free surface using X-ray Specular Reflectivity (XSR) and Atomic Force Microscopy (AFM).

The glass-forming material (shown in fig. 1a)) was provided by Akzo-Nobel (Arnhem, The Netherlands) [14]. Its bulk glass transition temperature is 110 °C. Thin films of different thicknesses were spin coated on float glass substrates from solutions in cyclopentanone with different concentrations. The films were first annealed at temperatures below 50 °C for more than 5 hours before the temperature was further increased (10 °C/h), and kept under N₂ for all measurements. SHG measurements were performed with the usual set-up [15]. The AFM work was performed using a Nanoscope II commercial AFM operating in the constant force mode at $\sim 2 \times 10^{-8}$ N. Before each XSR measurement [16], the sample was left at least an hour for thermal equilibration. Figure 1 shows the temperature dependence of the X-ray reflectivity as a function of momentum transfer Q (perpendicular to the film surface) for three films characteristic of the three wetting regimes we observed: a stable thin film (initial thickness after spin coating 33 Å), an unstable film (83 Å), and a stable thick film (127 Å). The film thickness, surface roughness (given in the figure) and electron density profile along the surface normal were obtained by fitting the data to a model with a single layer of uniform electron density and with Gaussian roughness at the interfaces. A two-layer model gave the same total film thickness and surface roughness.

Upon the first increase of temperature after spin coating, all films showed a decrease in film thickness. This initial shrinking of the films was irreversible: when films were brought back to room temperature after annealing they remained thinner than after spin coating. This comes from the fact that during the spin coating deposition process, the rapid evaporation of the solvent quenches the films in a non-equilibrium state. As temperature increases, the molecules recover enough mobility to relax to equilibrium. The thickness difference between stable annealed and as-cast films is approximately 15 Å independent of the initial film thickness (in the studied range of 33 Å to 225 Å). This means that the irreversible decrease of film thickness observed with increasing temperature is due to the formation of a denser interfacial layer at the substrate surface. Evaporation of molecules from the surface was not of concern. Within experimental error, the product of film thickness and the electron density before and after annealing was constant for the thinnest films (initial thickness 33 Å) indicating that the mass was conserved. This film became a smooth 19 Å thick film at room temperature after annealing at 80 °C. It corresponds to a monolayer of molecules bent by the attraction of their polar CN end-groups towards the substrate [17].

The 83 Å and 127 Å thick films showed significant modulations of the free surface, as seen from the loss of reflectivity oscillations starting from larger Q values with increasing temperature (fig. 1b) and c)). Eventually, the reflectivity oscillations for the initially 83 Å thick film were lost completely, indicating that the film had dewetted. Films of initial thicknesses between 40–100 Å all showed a similar behavior, except that the onset of changes in the film and the complete loss of the reflectivity oscillations happened at higher temperatures for thicker films, because of confinement effects on the dynamics of the molecules [17]. The dewetted films

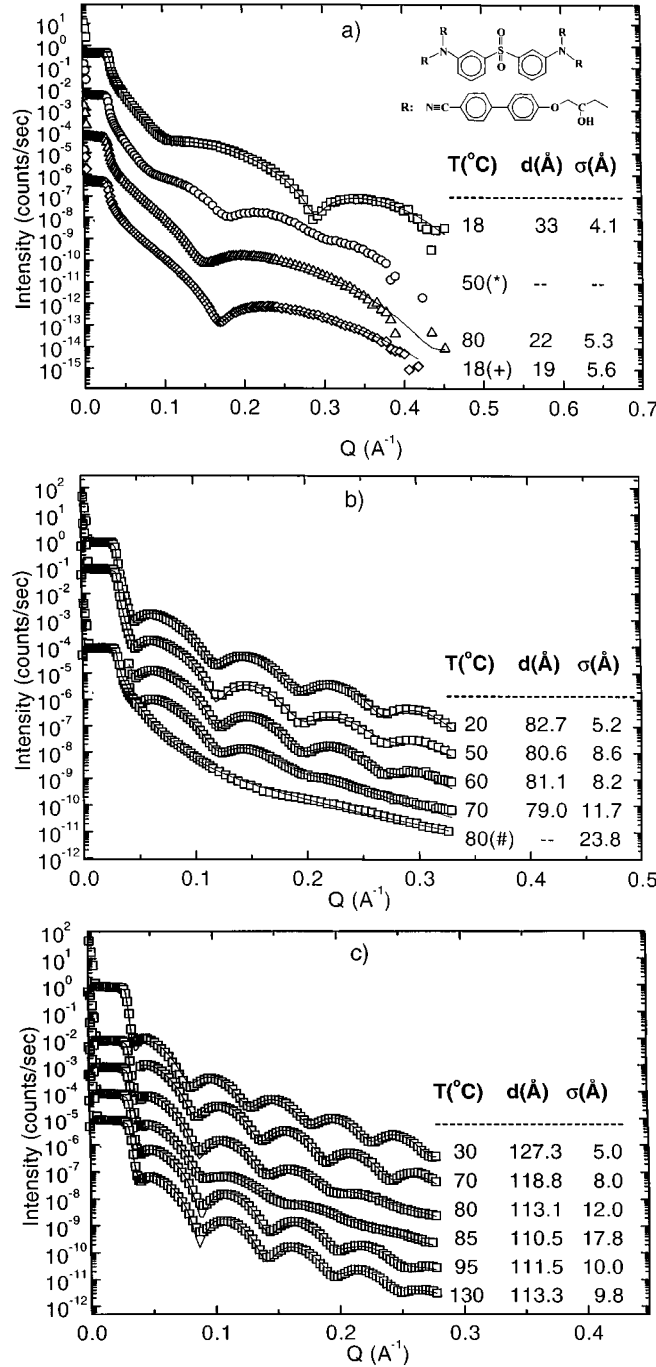


Fig. 1. - X-ray reflectivity (data points and fit line) as a function of momentum transfer vector Q for films of different initial thicknesses taken at the temperatures indicated. The curves were shifted vertically. For each curve, the film thickness and surface rms roughness are given. a) 33 Å thick film, b) 83 Å thick film, c) 127 Å thick film. Notes: (*) not equilibrated film, (+) back to 18 °C after annealing, (#) dewet film. Insert: Chemical structure of the glass-forming liquid crystalline molecules.

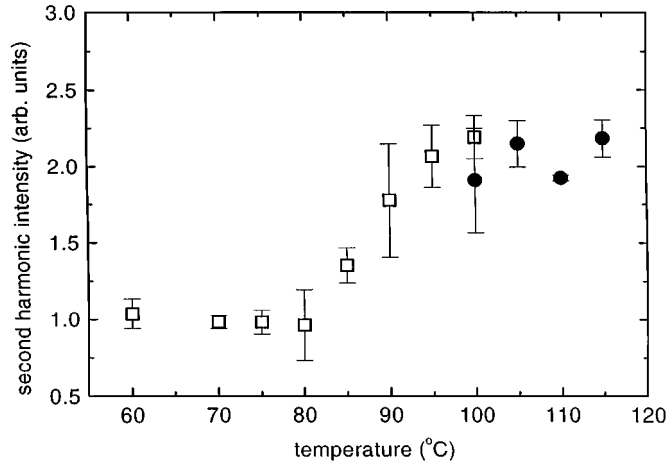


Fig. 2. – Second-harmonic intensity as a function of temperature for an initially 127 Å thick film upon the first increase of temperature after spin coating. The open squares were measured after the sample was annealed at 60 °C for more than 5 hours and the filled circles after waiting at 100 °C for 2 days. The error bars correspond to the standard deviation between measurements at several spots.

gave a uniform second-harmonic signal over the whole surface area. This indicates that after dewetting a smooth layer of molecules was present under the liquid droplets. This monolayer is probably stabilized by the strong interaction between the polar CN end-groups of the molecules and the substrate. As in other systems showing this type of autodewetting [18,19], the molecules in this stable surface layer have a different configuration than in the rest of the film: they are bent with their end-groups towards the substrate, while in the rest of the film they are essentially stretched.

Films of initial thicknesses larger than 100 Å did not dewet, despite the appearance of significant surface roughness when the temperature was first increased. For the initially 127 Å thick film, the maximum roughness was reached at 85 °C. But the film did not rupture in the two hours that were needed for equilibration and measurement. Full equilibration was reached at 95 °C and the free surface smoothed again. Further increase of temperature above 95 °C resulted in a slight increase in the film thickness indicating a positive thermal expansion coefficient for the equilibrium structure. If temperature was then decreased, the film thickness slightly decreased in a reversible way, but the film remained stable. Increase in surface roughness was also observed for films as thick as 225 Å. But the amplitude of surface fluctuations and the corresponding effect of roughness on reflectivity decreased as thickness increased.

The above reflectivity results show a re-entrant wetting as a function of film thickness: monolayers (initially 33 Å thick) and films thicker than 100 Å are stable while films of intermediate thicknesses dewet in droplets on top of a uniform monolayer. This type of behavior has been predicted (from thermodynamic considerations) in the case long-range van der Waals interactions favor wetting and short-range polar interactions impede it [20]. In our case, however, dewetting and re-entrant wetting originate from a dynamic effect due to the restructuring of the molecules at the interface with the substrate. This is confirmed by SHG measurements.

For an initially 127 Å thick film, second-harmonic intensity as a function of temperature, seen in fig. 2, clearly shows a significant increase in intensity in the temperature range

of 80–95 °C. Second-harmonic generation selectively probes regions where polar ordering is present (in the dielectric approximation), namely in our samples the layer of molecules in contact with the substrate [17]. The increase in second-harmonic intensity indicates an increase in the number of the molecules in contact with the substrate, consistent with the XSR observations of decrease in film thickness and increase in electron density.

The temperature of 80 °C, where the second-harmonic intensity started increasing in fig. 2, correlates quite well with the onset of significant surface roughness and loss of reflectivity oscillations in fig. 1c). Similarly, the onset of the plateau in the second-harmonic intensity at 95 °C corresponds to where the equilibrium structure was reached and the free surface smoothed in the reflectivity data of fig. 1c). The filled circles in fig. 2 were measured after the film was kept at 100 °C for 2 days. The intensity did not change in time and remained constant upon further increase of temperature up to the glass transition temperature of the film⁽¹⁾. The intensity also remained constant in further cooling/heating cycles confirming the existence of a stable interfacial layer on the substrate.

Observation of changes in SHG and XSR measurements in the same temperature range clearly indicates that the observed increase of surface roughness is closely related to the restructuring of the interfacial layer. The interfacial densification requires the motion of molecules towards the interface and creates regions of reduced density above the dense interfacial monolayer. The presence of these regions can destabilize the free surface by different mechanisms: i) If the distance between the free surface and the region of reduced density is less than a few nanometers, the van der Waals attraction between the two will give rise to an indentation of the film above the region of reduced density. A similar mechanism was proposed earlier to explain the rupture of thin polymer films induced by nucleation from gas bubbles at the regions of reduced density [10]. While such regions can be intrinsic to polymer films, in our case they arise from the densification of the interfacial layer. ii) Since the interaction free energy between the two surfaces of the film depend on the film density (via the Hamaker constant [21]), a gradient of disjoining pressure will appear in the film leading to a modulation of the film thickness [4].

The low-density regions vanish eventually when the restructuring of the interfacial monolayer is completed and diffusion has restored a uniform density. The surface modulations of the films that are still intact at this point (thick films) relax under the effect of the surface tension, restoring a smooth surface. Independent of the destabilizing mechanism, one expects that the effect of low-density regions appearing above the interfacial layer on the free surface decreases as the film thickness increases. This is indeed observed experimentally.

The modulations at the free surface were observed by AFM. Figure 3 shows the surface topography of an initially 97 Å thick film quenched at room temperature to freeze its structure obtained at 80 °C when it has not yet dewetted. The lateral regularity of surface topography suggests rupture of the film via height modulations with a characteristic length scale. The box in fig. 3a) encloses one such area where height modulations are quite regular. Figure 3b) shows the average height in the box perpendicular to the dashed line. Modulations have an average wavelength of 249 nm. To check whether the characteristic length scale for height modulations exists for a larger area, we took the power spectrum of the 15 μm × 15 μm surface area shown in fig. 3a). Apart from the artifacts of discrete wavelengths, originating from taking the power spectrum of a finite area, a broad peak is clearly seen around a wavelength of 250 nm in fig. 3c), in agreement with the average wavelength obtained in fig. 3b).

These height modulations cause dewetting in the form of droplets on top of the stable interfacial monolayer, in the case the valleys at the free surface reach the stable ~ 20 Å thick

⁽¹⁾ Work in preparation.

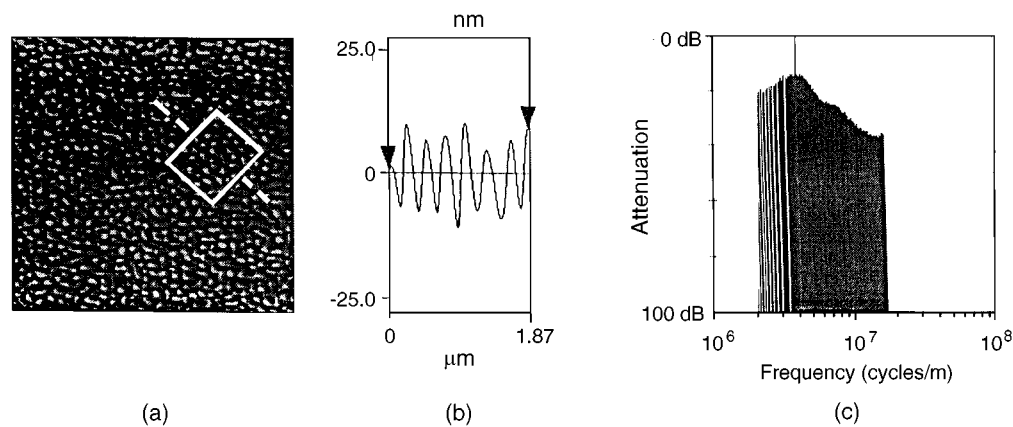


Fig. 3. – a) $15\ \mu\text{m} \times 15\ \mu\text{m}$ AFM image of an initially $97\ \text{\AA}$ thick film quenched at room temperature to freeze its structure obtained at $80\ ^\circ\text{C}$ when it has not yet dewetted. b) Average of surface modulations along the dashed line in the box of panel a). The average wavelength of oscillations is $249\ \text{nm}$. c) The power spectrum of surface modulations of panel a) showing a dominant characteristic length scale of $250\ \text{nm}$.

interfacial monolayer. This dewetting mechanism is confirmed by the evolution of the surface roughness as a function of temperature for films that eventually restabilize (fig. 1c)). The maximum rms roughness σ that was observed before the $127\ \text{\AA}$ thick film restabilized is $18\ \text{\AA}$. Taking this as the maximum rms roughness that can develop at the free surface, one gets a maximum valley depth of approximately $3\sigma = 18 \times 3 = 54\ \text{\AA}$ [22] for the surface modulations. Adding the thickness of the stable interfacial layer at $85\ ^\circ\text{C}$ ($\sim 22\ \text{\AA}$) and the decrease in the film thickness with respect to the initial thickness ($\sim 15\ \text{\AA}$), one obtains an upper limit for the initial thickness ($91\ \text{\AA}$) above which no holes will be formed in the film. This corresponds reasonably well to the initial thickness of $100\ \text{\AA}$ above which films did not dewet. This shows that the fluctuations at the free surface lead to dewetting when the valleys reach the interfacial monolayer. Though films thicker than the maximum valley depth are significantly affected by fluctuations, they do not dewet because holes leading to dewetting are not formed.

In conclusion, we have shown that restructuring of molecules at the interface with the substrate can induce dewetting of thin spin-coated glassy films during annealing by destabilizing the free surface. Films dewet when the growing amplitude of surface fluctuations with increasing temperature reaches the size of the film and form holes on the stable interfacial layer. This mechanism resembles the amplification of thermal fluctuations in time predicted in the case of spinodal dewetting. In this new dewetting mechanism, however, films that are thick enough to survive the restructuring process remain stable, leading to a re-entrant wetting as a function of film thickness.

We thank J. COMMANDEUR for technical help, P. P. DE WIT and S. J. PICKEN (Akzo-Nobel) for providing the glassy material., W. H. DE JEU for the use of the X-ray diffractometer and J. J. BOON for the use of AFM. This work is part of the research program of the Stichting voor Fundamenteel Onderzoek der Materie (FOM), which is supported by the Nederlandse Organisatie voor Wetenschappelijk Onderzoek (NWO).

REFERENCES

- [1] FRANK C. W. *et al.*, *Science*, **273** (1996) 912.
- [2] LÉGER L. and JOANNY J. F., *Rep. Prog. Phys.*, **55** (1992) 431.
- [3] DE GENNES P.-G., *Rev. Mod. Phys.*, **57** (1985) 827.
- [4] BROCHARD WYART F. and DAILLANT J., *Can. J. Phys.*, **68** (1990) 1084.
- [5] RUCKENSTEIN E. and JAIN R. K., *Faraday Trans.*, **70** (1974) 132.
- [6] VRIJ A., *Discuss. Faraday Soc.*, **42** (1966) 23.
- [7] REITER G., *Phys. Rev. Lett.*, **68** (1992) 75.
- [8] GUERRA J. M., SRINIVASARAO M. and STEIN R. S., *Science*, **262** (1993) 1395.
- [9] STANGE T. G., EVANS D. F. and HENDRICKSON W. A., *Langmuir*, **13** (1997) 4459.
- [10] JACOBS K., HERMINGHAUS S. and MECKE K. R., *Langmuir*, **14** (1998) 965.
- [11] BISCHOF J. *et al.*, *Phys. Rev. Lett.*, **77** (1996) 1536.
- [12] XIE R., KARIM A., DOUGLAS J. F., HAN C. C. and WEISS R. A., *Phys. Rev. Lett.*, **81** (1998) 1251.
- [13] THIELE U., MERTIG M. and POMPE W., *Phys. Rev. Lett.*, **80** (1998) 2869.
- [14] DE WIT P. P., ERDHUISEN E. W. P. and PICKEN S. J., Patent WO 96/03476.
- [15] SHEN Y. R., *Nature*, **337** (1989) 519; *Surf. Sci.*, **299/300** (1994) 551.
- [16] MOL E. A. *et al.*, *Phys. Rev. E*, **54** (1996) 536.
- [17] JÉRÔME B. and COMMANDEUR J., *Nature*, **386** (1997) 589.
- [18] REITER G., AUROY P. and AUVRAY L., *Macromolecules*, **29** (1996) 2150.
- [19] KERLE K., YERUSHALMI-ROZEN R. and KLEIN J., *Europhys. Lett.*, **38** (1997) 207.
- [20] SHARMA A. and JAMEEL A. T., *J. Colloids Interface Sci.*, **161** (1993) 190.
- [21] ISRAELACHVILI J. N., *Intermolecular and Surface Forces* (Academic Press, San Diego) 1991.
- [22] For a Gaussian curve with standard deviation σ , 99.7% of the area under the curve is within $\pm 3\sigma$.