van der Waals stable thin liquid films: Correlated undulations and ultimate dewetting

1998 Europhys. Lett. 44 484

(http://iopscience.iop.org/0295-5075/44/4/484)

EUROPHYSICS LETTERS 15 November 1998

Europhys. Lett., **44** (4), pp. 484-490 (1998)

van der Waals stable thin liquid films: Correlated undulations and ultimate dewetting

T. KERLE[1], R. YERUSHALMI-ROZEN[2], J. KLEIN[1] and L. J. FETTERS[3]

[1] *Department of Materials and Interfaces, Weizmann Institute of Science 76100 Rehovot, Israel*
[2] *Department of Chemical Engineering, Ben Gurion University in the Negev 84105 Be'er Sheva, Israel*
[3] *Exxon Research and Engineering Company - Annandale, NJ 08801, USA*

(received 31 March 1998; accepted in final form 5 October 1998)

PACS. 68.45Gd – Wetting.
PACS. 68.15+e – Liquid thin films.
PACS. 82.65Dp – Thermodynamics of surfaces and interfaces.

Abstract. – The evolution of pre-rupture undulations at the liquid-air interface of thin non-wetting liquid films spread on a solid substrate was monitored in real time by non-perturbative interference microscopy. The spatial distribution of the incipient undulations is non-random and characterized by a typical wavelength, as predicted for van der Waals unstable films, despite the fact that the system is expected to be vdW-stable, and that ultimate dewetting of films appears to take place via a heterogeneous nucleation mechanism.

A thin film of a non-volatile liquid which is forced to spread on a solid substrate may be stable, and preserve its initial shape, or it may be unstable and evolve by dewetting into an array of droplets. The importance of thin films in many applications has motivated researchers to investigate a variety of model systems in order to identify the mechanisms leading to film rupture and dewetting. Several theoretical models analyze the conditions necessary for thermodynamic stability of thin films and describe the processes which may lead to dewetting in the case of unstable films. In general, film stability is determined by the balance of the free energy per unit area of the film of thickness h, $F(h) = \gamma_{\rm sl} + \gamma_{\rm lv} + V(h)$, with $\gamma_{\rm sl}$, $\gamma_{\rm lv}$ being the solid/liquid and liquid/vapor interfacial energies and $V(h)$ the contribution of the long-range forces. For a van der Waals (vdW) liquid in air [1] the value of the long-range term is determined by the effective Hamaker constant, $A_{\rm eff}$:

$$V(h) = A_{\rm eff}/12\pi h^2 \,. \tag{1}$$

The liquid film is stable for $A_{\rm eff} > 0$ and unstable with a tendency to thin for $A_{\rm eff} < 0$, where the effective Hamaker constant describes the combined solid-liquid system. An intrinsic mechanism

(also termed "spinodal decomposition") leading to film rupture of unstable vdW liquids was described as a process involving amplification of capillary waves by thermal fluctuations, due to the vdW instability. Eventually the roughening leads to rupturing of the initially smooth and continuous films, at the points where the undulations grow sufficiently to expose the underlying substrate. The fastest growing undulations have a wavelength $\lambda \approx h_0^2/a$, where a is a characteristic molecular length of the liquid, typically some Å [2], and h_0 the initial film thickness. This implies that the rupture sites are correlated with a typical separation of order λ. The characteristic rupture time is given by $\tau_{\text{rupture}} \propto \gamma_{\text{lv}}\eta h_0^5/A_{\text{eff}}^2$, where η is the viscosity. Dewetting then proceeds by hole growth until adjacent holes coalesce, forming a polygon pattern. In non-ideal systems, a faster pathway for film rupture is opened via heterogeneous nucleation. This occurs when contamination, dust or air bubbles in the film or on the surface, or an imperfection in the substrate, nucleate hole formation. As such nucleation sites are in general randomly distributed there is no correlation between the positions where holes first form, in contrast to what is expected for holes induced by growing thermal undulations. The applicability of the theoretical model, describing the rupture process as an amplification of fluctuations, to the description of experimental observations has been discussed extensively in recent years [3], and is still under active discussion. An important question concerns the assignment of a value to the effective Hamaker constant, A_{eff}, of an experimental systems: for a thin liquid film on top of a homogeneous solid substrate A_{eff} is related to the difference between A_{ll}, the Hamaker constant of a free liquid films, and A_{sl}, that of a liquid film interacting with the solid: $A_{\text{eff}} = A_{\text{sl}} - A_{\text{ll}}$ [1]. However, in most of the experimental systems investigated under ambient conditions, the solid surface is covered by a nanometric layer of the native oxide, adsorbed hydrocarbons, etc. [4]. These are expected to modify the value of A_{eff} from that of a homogeneous liquid interacting with homogeneous solid. For a model system of a liquid film l of thickness h on top of an infinitely thick solid substrate S coated with a film F of mean thickness d, the effective Hamaker constant is given by the relation [4]

$$A_{\text{eff}} \approx A_{\text{Fl}} - A_{\text{ll}} + (A_{\text{sl}} - A_{\text{Fl}})(1 + d/h)^{-3}\,. \tag{2}$$

Following the line of thought presented by the models of dewetting, observation of correlated undulations in a dewetting film should serve as an indication for vdW instability and dewetting via amplification of thermal fluctuations. Until recently experimental difficulties in probing the pre-rupture stage, in particular, the difficulty to examine directly the evolution of undulations in the liquid films, have led experimentalists to focus on the characterization of hole growth [5], or on the morphology of the dewetted film [6-9]. As the stages of hole rupture and hole growth are controlled by distinct mechanisms, it is not possible to extrapolate from these measurements to the pre-rupture stage. On the other hand, analysis of the growth process of undulations and their lateral correlation should, according to the theory, provide a basis for determining which of the processes is active in the dewetting process of a thin liquid film. Recently Bischof *et al.* [8] and Stange *et al.* [9] have made an important step in this direction by probing the incipient undulations which develop in dewetting metal films [8] and in films of polymeric materials [9]. However, in both studies the films were characterized *ex situ*, after quenching of the liquid films into the solid state, and in the studies of Stange and coworkers [9] it was noted that the very process of quenching influences the observed dewetting behavior.

Here, we report direct observations of the spontaneous evolution of the early, pre-rupture undulations in initially smooth, liquid films, using a non-perturbative optical approach. The experimental technique allows *in situ* monitoring of the process in real time. Our motivation was to study the evolution of fluctuations without perturbing the system by quenching. We estimate the effective Hamaker constant of the system, and compare our observations with the different models which describe the pre-rupture stage.

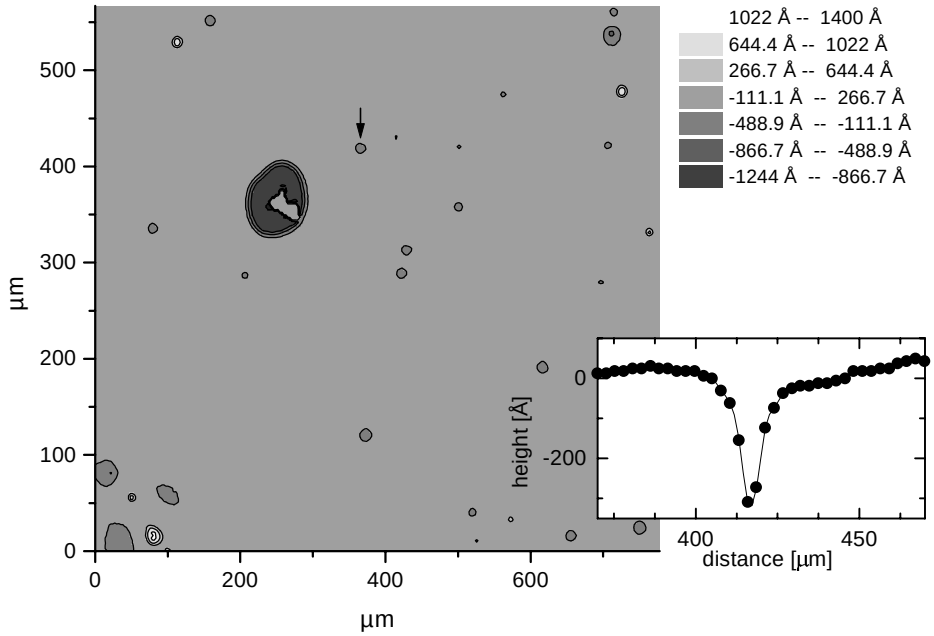

Fig. 1. – Optical phase-modulated interference micrograph of a PEP film on top of a silicon substrate 590 min after spin coating. The samples were prepared and monitored at room temperature (23 °C). The lateral resolution is 2.7 μm and the height resolution in the range of Ångstrom, though for the sake of clarity we chose to present the 3D information as a gray scale map with a distance of 378 Å between two adjacent levels. In the inset we show a line scan through the undulation (marked by an arrow) parallel to the x-axis. The filled circles show the values obtained from the microscope image, the line is a guide to the eye.

The liquid used was an oligomer of ethylene propylene (PEP), molecular weight 2000, a Newtonian liquid with a glass transition temperature, $T_{\rm g}$, of -60 °C, a viscosity $\eta_{\rm PEP} \cong 50$ Poise (at $T = 300$ K) and a refractive index of 1.469 (measured by us using an Abbe refractometer). Droplets of the oligomer do not spread spontaneously on the surface of a cleaned silicon wafer, and subtend a finite advancing contact angle $\theta = 20° \pm 2$. Thin films (100–200 nm, uniform to ± 1 nm) were spin coated from toluene onto silicon wafers. The thickness of the films was controlled by the concentration of the solutions and the spin rate. The silicon wafers were cleaned by immersion in toluene and drying in a jet of filtered nitrogen. Optical Phase-modulation Interference Microscopy (OPIM) was used to monitor continuously the change of the topography of the initially smooth films. In this technique, the interference pattern of a split beam reflected on an internal reference surface and on the sample under investigation is captured by a CCD camera and analyzed by an attached computer, generating a 3D image. The measurements were performed on a Zygo Maxim-3D system at the Max-Planck-Institut für Polymerforschung (Mainz, Germany). This technique combines sub-nanometer resolution in the vertical direction with micron range lateral resolution and a large field of view (778×567 μm^2).

Figure 1 presents a typical topographical scan of a thin film ($h_0 = 102.5 \pm 0.5$ nm) [10] of PEP on top of a silicon substrate 590 min after spin coating, shown at low vertical resolution for clarity. The main observable feature at this resolution is a well-developed hole in the upper left region of the picture, with an irregular 30 μm object in the middle of the hole, which

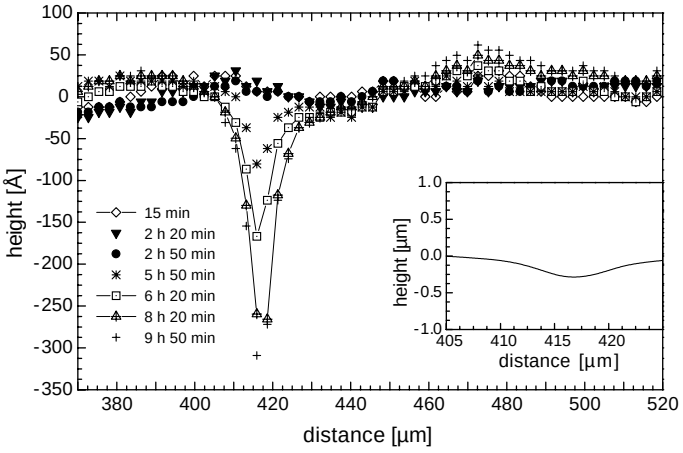

Fig. 2. – Time evolution of the undulation marked in fig. 1. Line scans taken after different annealing intervals are overlaid, showing the deepening of the undulation with annealing time. In the inset we show the undulation, using a larger scale for the y-axis; though, note that the scales of the x and y axes differ by a factor $\sim 3 \times 10^3$ (or $\sim 10^2$ in the inset) so that the undulation is in fact extremely shallow.

presumably acted as a center for heterogeneous nucleation [9,11]. Apart from this dominating feature, local deviations from a smooth surface (undulations) can be seen. The depths of the undulations are smaller than the film thickness, therefore they do not expose the silicon substrate. Defects and possible nucleation centers are not detectable optically in the vicinity of these height fluctuations. In the inset to fig. 1 we show a line scan (using OPIM) parallel to the y-axis, through the undulation at coordinate (365 μm/415 μm), marked by the arrow. The scan shows a dip in the sample surface of a depth of 30 nm and a full-width half-maximum of 6 μm. Consecutive scans describe the evolution of the undulation. In fig. 2 we present line scans over the same area as in the inset of fig. 1 as a function of annealing time (at a constant annealing temperature of 23 °C). Subsequent scans show that the initially shallow undulation becomes deeper with time, while keeping the lateral dimension constant within our resolution. Broadly similar behavior is observed for all undulations examined.

If the undulation would have kept growing with a constant rate, it would have taken approximately 2 days to reach the silicon substrate. However, we observe that after a time interval much shorter than that expected for rupture by amplification of thermal fluctuations, heterogeneous nucleation of holes becomes dominant (revealed by the presence of a nucleation impurity at the center of each hole). The nucleated holes, once formed, grow *laterally*, exposing the underlying surface at a velocity of 3 ± 0.2 microns/min. Dewetting is completed in less than 1 day: *i.e.* the growing holes have coalesced, and the initially smooth film has transformed into a polygonal droplet pattern [6-8], before the undulations have had an opportunity to reach the substrate.

A central prediction of theoretical models describing the rupturing of non-volatile vdW liquids due to amplification of thermal fluctuations is that the spatial distribution of the amplified undulations is non-random [2, 12, 13]. According to the theories the fluctuation of the surface at a point x at time t is given by

$$\mid h(x,t) - h_0 \mid \propto \exp[\omega(q)t + iqx]\,, \tag{3}$$

where q is the wave vector and ω the growth rate of the fluctuation. Small disturbances grow

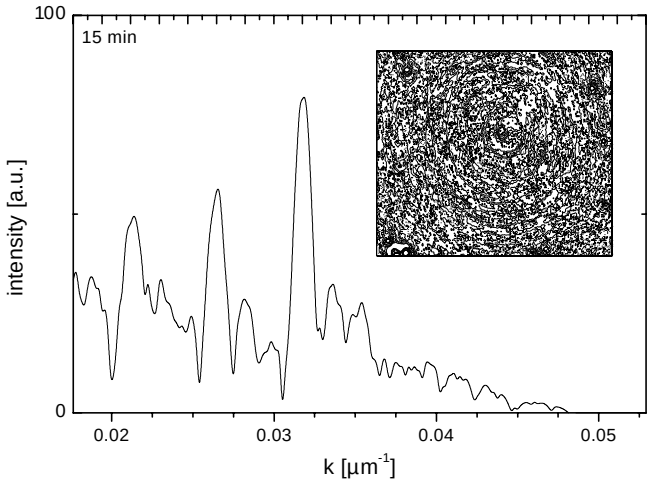

Fig. 3. – 1D Fourier spectrum of an OPIM image. 2D Fourier transformations on 567×567 μm^2 segments of the OPIM images were mapped into a single dimension by assuming no preferred direction of the wave vector. The intensity of a wave number $k = 1/\lambda \in [k, k + \Delta k]$ is plotted in arbitrary units over k.

if $\omega > 0$ and decay if $\omega < 0$. The value of $\omega(q)$ is given by

$$\omega = \frac{h_0^3}{3\eta}\left(\gamma_{\mathrm{lv}} q^4 - \frac{3A_{\mathrm{eff}} q^2}{6\pi h_0^4}\right). \tag{4}$$

For systems with a negative value of the constant A_{eff} (and thus with a tendency to thin), there exists a critical wave vector

$$q_{\mathrm{c}} = \sqrt{\frac{\mid A_{\mathrm{eff}} \mid}{2\pi h_0^4 \gamma}} \tag{5}$$

below which ω becomes positive and the van der Waals interactions dominate the surface tension, leading to rupture when the amplitude of the fluctuations equals the film thickness. The fastest growing mode is $q = q_{\mathrm{m}} = 2^{-3/2} q_{\mathrm{c}}$, which is equivalent to a wavelength of

$$\lambda = \left(\frac{2\pi}{q_{\mathrm{m}}}\right) \approx \frac{h_0^2}{a}. \tag{6}$$

Typical parameters in the thin films studied by us (film thickness $h_0 \approx 100$ nm and taking $a = 5$ Å) yields $\lambda \approx 20$ μm, for the fastest growing mode.

To address the issue of correlations we analyzed the spatial distribution of the incipient undulations by applying 2D Fourier transformation to images similar to those shown in the inset of fig. 3. This operation takes into account the full information of the image and does not rely on selection of hole-centers as would be necessary to yield a pair correlation function. The OPIM image was taken 15 minutes after spin coating, when only small fluctuations of the surface of the liquid were present. Assuming that the distribution is isotropic across the film, we mapped the two-dimensional information onto a one-dimensional line-graph, as presented in fig. 3. The graph shows the Fourier spectrum of the inset OPIM image. A peak at $\lambda = 1/k \approx 30$ μm can be observed, comparable with the theoretical value of

$\lambda \approx 20$ μm (eq. (6)). Other weaker peaks equivalent to spatial correlations between "next-nearest" neighbors and so on are also clearly noticeable.

The relevance of the model to the description of the pre-rupture stage observed by us depends on the value of A_{eff} for the experimental system. As was discussed before [9, 14, 15], the surface exposed by a silicon wafer at ambient conditions is not pure silicon, but rather silicon covered by a silicon oxide layer, which is itself covered by a film of organic molecules adsorbed from the ambient atmosphere. While the Hamaker constant of a liquid film on top of a homogeneous solid is readily described by a single value of the effective Hamaker constant (apart from retardation effects, which are difficult to calculate as the surface composition is imprecisely known), the description of a real substrate, such as an oxidized silicon wafer at ambient conditions, is more complicated (eq. (2)). We use eq. (2) to estimate the effective Hamaker constant of a 100 nm thick PEP film ($A_{\text{PEP}} = 5.5 \times 10^{-20}$ J) [16] on top of a 10 nm layer of organic contaminants [15] ($A_{\text{org}} = 3.5 \times 10^{-20}$ J) covering a silicon substrate ($A_{\text{si}} = 24 \times 10^{-20}$ J). We find $A_{\text{eff}} \approx 4.2 \times 10^{-20}$ J, *i.e.* $A_{\text{eff}} > 0$, which is a signature of a vdW stable film —that is, one for which thermally induced surface undulations should decay rather than grow.

Our results show clearly that surface undulations are present and tend to grow at the pre-rupture stage of thin films which eventually dewet. We also observe that the actual development of height fluctuations into holes is pre-empted by heterogeneous nucleation of holes, which subsequently grow to complete the dewetting process. The geometrical distribution of the pre-rupture fluctuations observed by us is different to that of holes resulting from heterogeneous nucleation, as was analyzed by Jacobs *et al.* [11], for a related system of a vdW-stable thin liquid film. Their results show that the spatial distribution of holes is well described by a Poisson-type statistics, rather than the non-random distribution that would be expected for holes evolving from the undulations described previously. While it is tempting to interpret our experimental observations, and in particular the laterally correlated height fluctuations in the dewetting films, as a signature of spinodal dewetting mechanism of unstable films, the value of the effective Hamaker constant indicates that the films should in fact be vdW stable [17]. As both spontaneous evolution of the height fluctuations, and their spatial correlation were clearly observed, we may raise the question whether these two parameters are both sufficient and necessary for designating a rupturing process as a spinodal-like process.

***

We particularly thank M. Stamm for the use of the OPIM, Aharon Weinstein for his help with data analysis, and P. G. de Gennes and S. Herminghaus for enlightening remarks. We thank the U.S.-Israel Binational Science Foundation, BSF (RY-R and JK) and the Wolfson family fund (RY-R), the Ministry of Science (Tashtiot grant) and Israel Science Foundation (JK) for partial support of this work.

REFERENCES

[1] Brochard-Wyart F., diMeglio J. M., Quéré D. *et al.*, *Langmuir*, **7** (1991) 335.
[2] Brochard-Wyart F. and Daillant J., *Can. J. Phys.*, **68** (1990) 1084.
[3] Leger L. and Joanny J. F., *Rep. Prog. Phys.*, **55** (1992) 431.
[4] Tidswell I. M., Rabedeau T. A. and Pershan P. S. *et al.*, *Phys. Rev. Lett.*, **66** (1991) 2108.
[5] Redon C., Brochard-Wyart F. and Rondelez F., *Phys. Rev. Lett.*, **66** (1991) 715.
[6] Reiter G., *Phys. Rev. Lett.*, **68** (1992) 75.
[7] Reiter G., *Langmuir*, **9** (1993) 1344.
[8] Bischof J., Scherer D. and Herminghaus S. *et al.*, *Phys. Rev. Lett.*, **77** (1996) 1536.

[9] Stange T. G., Evans D. F. and Hendrickson W. A., *Langmuir*, **13** (1997) 4459.

[10] Local thickness fluctuations as measured by OPIM, on a length scale of microns, indicate a uniform smooth film. However, we find that, at the sample edges, the thickness may deviate by about 10%.

[11] Jacobs K., Herminghaus S. and Mecke K., *Langmuir*, **14** (1998) 965.

[12] Vrij C., *Discuss. Faraday Soc.*, **42** (1967) 23.

[13] Ruckenstein E. and Jain R. K., *Faraday Trans.*, **70** (1974) 132.

[14] Yerushalmi-Rozen R. and Klein J., *J. Phys. Condens. Matter*, **9** (1997) 7753.

[15] Dowsett M. G., King R. M. and Parker E. H. C., *J. Vac. Sci. Technol.*, **14** (1977) 711.

[16] The value of the Hamaker constant is calculated from the measured value of the refractive index of the PEP oligomer, 1.469, according to the relation given in Israelachvili J. N., *Intermolecular and Surface Forces*, 2nd edition (Academic, London) 1992.

[17] Possible effects which may have a bearing on our observations of growing undulations are retardation effects, which we have ignored throughout but which may modify A_{eff}, and Marangoni flows induced by weak thermal gradients at the liquid surface.