Dynamical pattern formation upon dewetting

Jürgen Becker and Günther Grün
Institut für Angewandte Mathematik, Beringstr. 6, D-53115 Bonn, Germany

Ralf Seemann and Karin Jacobs
Universität Ulm, Abteilung Angewandte Physik, D-89069 Ulm, Germany

(March 22, 2022)

Dewetting of thin liquid films is monitored in situ by atomic force microscopy, results are compared with simulations. The experimental setting is mimicked as close as possible using the experimental parameters including the effective interface potential. Numerics for the thin film equation are based on recently developed schemes which are up to now the only methods convergent in all relevant space dimensions. Temporal evolution and morphology of experiment and simulation are compared quantitatively. Our results explain the origin of complex generic patterns that evolve upon dewetting.

For years, experimental [1, 8] and theoretical [9, 10] groups studied spinodal dewetting patterns, yet a quantitative comparison of the results was impossible since the potentials of the ‘real’ experimental system were unknown. In a recent study [17], however, we showed how to get insight into the underlying potentials by the analysis of dewetting patterns. Hence, it is now for the first time possible to validate theoretical models also quantitatively.

Typically, the evolution of thin liquid films is described by highly nonlinear fourth order degenerate parabolic differential equations. In recent years, they became the subject both of analytical and numerical studies in mathematics [18–23]. It is one peculiarity of these equations that they admit globally non-negative solutions. This is proved by means of certain integral estimates, called entropy estimates in the mathematical literature. In order to design efficient and convergent numerical tools, one is therefore interested in schemes that allow for discrete counterparts of the entropy estimate. This has recently been accomplished [22–24] and therefore the method used in the present paper can be considered as particularly reliable.

The stability conditions of liquid films on solid substrates can be described in terms of the effective interface potential $W(u)$, defined as the excess free energy per unit area needed to bring two surfaces from infinity to a distance $u$. If there exists a global minimum of $W(u)$ at finite $u$, the liquid film will not be stable in general; rather, it will dewet [1]. Dewetting typically proceeds by the formation of dry spots, their growth and coalescence, finally leading to a set of droplets on the substrate. Depending on the sign of $W''(u)$, different rupture mechanisms are possible. If $W''(u) < 0$, the system spontaneously forms dry spots (‘spinodal dewetting’), where the sites of the holes are correlated reflecting the spinodal wavelength $\lambda_s$. If $W''(u) > 0$, a nucleus, e.g. a dust particle, is needed to induce dewetting.

In our recent study [17], we reconstructed the effective interface potential $W(u)$ by recording the spinodal wavelength as function of film thickness $u$ and by determining other system parameters like the contact angle and the liquid equilibrium layer. The latter two experimental parameters fix the position and the depth of the global minimum of $W(u)$. With the explicit expression of $W(u)$, we now perform new numerical simulations of film rupture. In this Letter, we focus on the comparison of experimental and numerical results, on the one hand with respect to the temporal evolution and on the other hand with respect to special morphologies of patterns upon spinodal dewetting. As we will demonstrate, the appearance of so-called ‘satellite holes’ is not a special pattern limited to volatile liquids, as recent work by Kargupta et al. [16] might suggest, but is a generic phenomenon of dewetting liquid films.

The liquid used in our experiments was atactic polystyrene (PS) with a molecular weight of 2 kg/mol (purchased from Polymer Labs, Church Stratton, UK, $M_u/M_m = 1.05$). This is large enough to assure non-volatility, but at the same time small enough for the polymer melt to be approximately a Newtonian fluid. This is essential for comparison with simulations, in which viscoelastic effects were neglected. Films were prepared by spin casting a toluene solution (Selectipur toluene, Merck, Germany) of PS onto polished, oxidized Si wafers (Silchem GmbH, Freiberg, Germany). Before coating, the wafers were thoroughly cleaned using standard procedures [4, 17, 28]. The oxide layer and PS film thickness were determined by ellipsometry (Optrel GdB, Berlin, Germany). The surface of the wafers, called ‘SiO-wafers’ below, consists of amorphous, 191(1) nm thick silicon oxide [29]. On such a substrate, PS films are unstable up to a film thickness of about 300 nm [26]. The symmetry-breaking mechanism of dewetting was monitored by atomic force microscopy (AFM) (Nanoscope III, Digital Instruments, Santa Barbara) in tapping mode TM. Annealing took place on top of the AFM sample holder.
which enabled us to follow the dewetting process at a real time scale. We therefore continuously scanned the sample and recorded one scan in every 60 s. Scanning parameters were carefully adjusted not to affect the liquid layer [23].

Figure 1 depicts on the left side a series of AFM cross sections of a 3.9(1) nm thick PS film dewetting a SiO-wafer at an annealing temperature of $T_a = 53^\circ\text{C}$. The film is unstable and holes are generated due to spinodal dewetting of the film [17,23]. The characteristic wavelength $\lambda$ can hardly be observed in the cross sections, since the scan size is too small. Before annealing, the surface of the PS film is smooth, exhibiting an rms roughness of below 0.3(1) nm. As revealed from the online microscopy. It is identified with the equilibrium thickness of the film, respectively. A no-slip condition at the solid-liquid interface entails

$$W(u) = \frac{\epsilon}{a^8} - \frac{A_{\text{SiO}}}{12\pi a^2},$$

where $\epsilon$ denotes the strength of the short range part of the potential, $\epsilon = 6.3(1) \cdot 10^{-76} \text{ Jm}^6$, and $A_{\text{SiO}}$ is the Hamaker constant of PS on SiO, $A_{\text{SiO}} = 2.2(4) \cdot 10^{-20} \text{ J}$. The global minimum in $W(u)$ is at $u = 1.3(1) \text{ nm}$ reflecting the equilibrium thickness of a PS film on top of SiO-wafer. $W(u)$ enters the equation of motion of the liquid film,

$$\frac{\partial u}{\partial t} - \text{div}(m(u)\nabla p) = 0,$$

via the pressure $p$ which is given by

$$p = -\sigma \Delta u + W'(u),$$

where $\sigma$ and $\eta$ denote the surface tension and the viscosity of the film, respectively. A no-slip condition at the solid-liquid interface entails $m(u) = \frac{1}{2} u^3$.

For numerical purposes it is important to distinguish between stabilizing and destabilizing terms. Therefore, we decompose

$$W(u) = W_+(u) + W_-(u),$$

where the stabilizing term $W_+$ and the destabilizing term $W_-$ are given by $\epsilon u^{-8}$ and $-\frac{A_{\text{SiO}}}{12\pi a^2} u^{-2}$, respectively.

In general, smooth solutions of system (2)–(3) are not expected to exist. Instead, we are looking for so called weak solutions $u, p$ that satisfy

$$\int_0^T \int_\Omega \eta u\phi + \int_0^T \int_\Omega m(u)\nabla p\nabla \phi = 0 \quad (5)$$

$$\int_0^T \int_\Omega \psi = \int_0^T \int_\Omega \sigma \nabla u \nabla \psi + \int_0^T \int_\Omega W'(u) \psi \quad (6)$$

for all $\psi, \phi \in C^1((0,T) \times \Omega)$. Note that smooth solutions are also weak solutions. Moreover, (5)–(6) are the starting point to develop finite element schemes (cf. [22]).

For simplicity, we sketch the main idea in one spatial dimension: Let the space interval $\Omega$ be divided in subintervals $[x_{i-1}, x_i], 1 \leq i \leq N$ of equal length $h_\ell$. Similarly, assume a time discretization with nodal points $t_k$, $0 \leq k \leq N$ to be given. We look for discrete solutions in the linear finite element space $V^h$. A canonical basis of $V^h$ is given by functions $\varphi_i$ which are linear on each subinterval and which satisfy $\varphi_i(x_j) = \delta_{ij}$. Our discretization is as follows:

For given $u^0 \in V^h$, find a sequence $(U^k, P^k) \in V^h \times V^h, k = 0, \ldots, N - 1$ such that

$$\frac{\eta}{\tau_k} (U^{k+1} - U^k, \Phi)_h + (M(U^{k+1}) \partial_x P^{k+1} + \partial_x \Phi) = 0 \quad (7)$$

$$(P^{k+1}, \Psi)_h = \sigma (\partial_x U^{k+1}, \partial_x \Psi) + (W_+''(U^{k+1}) + W_-''(U^k), \Psi)_h \quad (8)$$

for all $\Psi, \Phi \in V^h$.

Here, $(\cdot, \cdot)$ denotes the scalar product in the Lebesgue-space $L^2(\Omega)$ and $(\cdot)_h$ is the scalar product of lumped masses, which is an approximation of $(\cdot, \cdot)$ given by $(\varphi_i, \varphi_j)_h = \sum_j (\varphi_i, \varphi_j)$ and $(\varphi_i, \varphi_j)_h = 0$ if $i \neq j$. Crucial is the choice of the discrete version $M$ of the mobility $m$. The right strategy is to define $M$ on each interval $[x_i, x_{i+1}]$ as

$$M(U) = \begin{cases} \left( \frac{\int U(x_{i+1}) ms \, dx}{m(U(x_i))} \right)^{-1} & \text{if } U(x_i) \neq U(x_{i+1}) \\ \frac{f}{m(U(x_i))} & \text{otherwise} \end{cases} \quad (9)$$

where $f$ denotes the mean value integral.

The procedure discussed above naturally endows us with discrete versions of well-known integral estimates which read

$$\eta \int_\Omega (\sigma |\nabla u(T)|^2 + W(u(T))) + \int_0^T \int_\Omega m(u) |\nabla p|^2 \leq \eta \int_\Omega (\sigma |\nabla u_0|^2 + W(u_0)) \quad (10)$$
on top of a SiO-wafer shown in Eq. (1), the viscosity of thin film dewetting. The sequence makes use of the time varies in a time interval of 750 s play a significant role. In the experiments, the rupture very similar. Deviations can be observed especially in the development of a hole in experiment and simulation is in the same order of magnitude and the morphological concrete solutions are positive and that in addition both $U$ and $P$ converge strongly with respect to the topology of the Lebesgue-Sobolev-space $L^2((0, T), H^{1-2}(\Omega))$. Moreover, $U$ converges strongly to $u$ in the Hölder-space $C^{\frac{1}{2}+\epsilon}((0, T) \times \Omega), \epsilon > 0$.

The right-hand side of Fig. 1 depicts numerical results of thin film dewetting. The sequence makes use of the effective interface potential as reconstructed for PS film on top of a SiO-wafer shown in Eq. (1), the viscosity $\eta = 12000$ Pa s and the surface tension $\sigma = 30.8$ mN/m. In the numerical simulation we used 1000 grid points and an initial film of height 3.9 nm with a slightly roughened surface.

The evolution of a hole in the simulation resembles the experimental AFM scans. The absolute time scale is in the same order of magnitude and the morphological development of a hole in experiment and simulation is very similar. Deviations can be observed especially in the beginning, where the initial conditions of the film surface play a significant role. In the experiments, the rupture time varies in a time interval of $750 \text{ s} < t < 4000 \text{ s}$ which is comparable to the time scale in the simulation.

If we start the simulation, however, with an ‘artificial step’ between the equilibrium layer and the original film thickness of 4.9 nm, which is now slightly thicker than before, it generates a pattern like the one shown on the right-hand side of Fig. 2. The step transforms rapidly into a heap that relaxes via an undulation into the original film thickness. With time, the dips of the undulation grow deeper and the first dip reaches the substrate after about 400 s. As the other dips follow to break through to the substrate, a series of consecutive holes appears, which are generated by a kind of ‘cascade effect’.

A strikingly similar morphology can be observed experimentally, too. Fig. 3a–d depict a temporal series of (10 nm)$^2$ AFM scans of a 4.9 nm thick PS(2k) film on a SiO-substrate. First, single holes appear that soon grow in size. From a certain size onwards, they are surrounded by a second row of holes, followed later by a third one and so on. We term this pattern ‘satellite holes’. As compared to the experimental situation reported before, the film now is 1 nm thicker. The film can still dewet spinodally, yet the growth time of the amplitude of the preferred mode is about a factor of three longer, therefore dewetting by nucleation is the quicker way of dewetting. The onset of the spinodal wavelength yet can be seen by the wavy pattern on the film matrix, cf. Fig. 3b and c.

A comparison of simulation and experiment is shown in Fig. 2. The experimental profiles depicted in the left side of Fig. 2 are horizontal cross sections of the AFM scans of Fig. 3, taken at the level indicated by the arrow; $t = 0$ is defined as the time when first small holes can be detected in the cross section. Depending on the direction the cross sections are cutting through the AFM scan, first satellite holes can be seen in a time interval between 300 s and 1600 s. The time scale of experiment and simulation hence is in the same order of magnitude. Slight differences are to be expected, since i) the viscosity of the experimental system is known only by roughly a factor of two and ii) effects due to slippage of the polymer melt are not taken into consideration in the simulation. Yet in both films, an undulatory behavior of the rim profile can be observed leading to satellite holes. This is clear evidence that this dewetting pattern does not require a volatile liquid, but is generic to a spinodally dewetting system.

In a recent study, we showed that an undulatory rim profile can be observed on polymer films of thicknesses up to at least 60 nm, if the polymer melt is below the entanglement length. There we showed that theoretically a disturbance in a Newtonian liquid should always decay via an undulation and that only the viscoelastic properties of the liquid may stabilize the system. The observation of an undulatory rim profile in the simulation, where no viscoelastic properties were considered, is in accordance with this assertion.

A further interesting observation in both experiments and simulations is that a dip of an undulation only leads to a hole if the initial film thickness is below about 7 nm. The reasons for this are speculative at the moment: It is possible that the driving force for a dip to grow deeper falls below a certain value for films thicker than 7 nm. It is also possible that there is an interplay of the dewetting velocity of the three phase contact line, as set by the global minimum of $W(u)$, and the viscous flow of the melt inside the dewetting front. Further experiments and new simulations will surely shed more light into this discussion.

To sum up, we may say that lubrication approximation is an appropriate method to model the dewetting of liquid films also beyond the time of the first hole formation. We thus have a powerful tool to test the influence of single, yet different parameters onto the dewetting pattern and its temporal evolution. A successful example was given in the form of the ‘cascade’ effect leading to satellite holes. It was shown that this is a generic pattern of a spinodally dewetting film. We intend to perform numerical studies of the three dimensional system in a forthcoming paper.
ACKNOWLEDGMENTS

It is a great pleasure to thank Stephan Herminghaus for inspiring discussions and critical reading of the manuscript. We also thank Ralf Blossey and many members of the priority program ‘Wetting at Interfaces’ for fruitful collaborations and the German Science Foundation (grant numbers JA905/1 and GR1693/1) for funding.

[1] G. Reiter, Phys. Rev. Lett. 68, 75 (1992)
[2] J. Bischof, D. Scherer, S. Herminghaus, and P. Leiderer, ibid. 77, 1536 (1996)
[3] R. Xie et al., ibid. 81, 1251 (1998)
[4] K. Jacobs, K. Mecke, and S. Herminghaus, Langmuir 14, 965 (1998)
[5] S. Herminghaus et al., Science 282, 916 (1998)
[6] H.I. Kim et al., Phys. Rev. Lett. 82, 3496 (1999)
[7] M. Sferrazza et al., ibid. 81, 5173 (1998)
[8] G. Reiter, R. Khanna, and A. Sharma, ibid. 85, 1432 (2000); G. Reiter et al., Langmuir 15, 2551 (1999) and references therein
[9] A. Vrij, Disc. Faraday Soc. 42, 23 (1966)
[10] E. Ruckenstein and R.K. Jain, J. Chem. Soc. Faraday Trans. II, 132 (1974)
[11] F. Brochard and J. Daillant, Can. J. Phys. 68, 1084 (1990)
[12] A. Oron, S. Davis and S. G. Bankoff, Rev. Mod. Phys. 69, 931 (1997)
[13] A. Sharma and R. Khanna, Phys. Rev. Lett. 81, 3463 (1998)
[14] R. Konnur, K. Kargupta, and A. Sharma, ibid 84, 931 (2000)
[15] J. Koplik and J.R. Banavar, ibid 84, 4401 (2000)
[16] K. Kargupta, R. Konnur, A. Sharma, Langmuir 17, 1294 (2001)
[17] R. Seemann, S. Herminghaus and K. Jacobs, Phys. Rev. Lett. 84, 5534 (2000)
[18] F. Bernis and A. Friedman, J. Diff. Equ. 83, 179 (1990)
[19] A. Bertozzi and M. Pugh, Commun. Pure Appl. Math. 51, 625 (1998)
[20] R. Dal Passo, H. Garcke and G. Grün, SIAM J. Math. Anal. 29, 321 (1998)
[21] A. Bertozzi, G. Grün and T. Witelski, submitted
[22] G. Grün and M. Rumpf, Num. Math. 87, 113 (2000)
[23] G. Grün and M. Rumpf, Europ. J. Appl. Math. (in print)
[24] G. Grün, (submitted)
[25] L. Zhornitskaya and A. Bertozzi, SIAM J. Num. Anal. 37, 523 (2000)
[26] S. Dietrich 1988 in Phase Transition and Critical Phenomena, C. Domb and J. L. Lebowitz, Eds. (Academic Press: London) Vol. 12;
[27] M. Schick (1989) in Liquids at Interfaces, J. Charvolin et al., Ed. (Elsevier Science: Amsterdam)
[28] R. Seemann, S. Herminghaus and K. Jacobs, J. Phys.: Condens. Matter 13, 4925 (2001)
[29] The number in parentheses always denotes the error in units of the last digit.
[30] S. Herminghaus, K. Jacobs, and R. Seemann, (submitted), cond-mat/0104427
[31] R. Seemann, S. Herminghaus, and K. Jacobs (submitted), cond-mat/0105094

FIG. 1. Cross sections of a spinodal rupture scenario in a 3.9 nm thick PS(2k) film on a SiO-substrate as seen in situ by AFM (left) in comparison with a simulated one (right).
FIG. 2. ‘Cascade effect’ leading to satellite holes in a 4.9 nm PS(2k) film on a SiO-substrate; AFM cross sections (right) and numerical simulation for η = 1200 Pa s (left).
FIG. 3. Pattern formation in a 4.9 nm PS(2k) film on a SiO substrate exhibiting ‘satellite holes’ a) t = 0 s, b) 866 s, c) 1303 s, and d) 3060 s. Horizontal cross sections of the scans are taken at the height of the arrow and are shown at the left side of Fig. 2.
This figure "GGFig1.png" is available in "png" format from:

http://arxiv.org/ps/cond-mat/0106313v1
This figure "GGFig2.png" is available in "png" format from:

http://arxiv.org/ps/cond-mat/0106313v1
This figure "GGFig3.png" is available in "png" format from:

http://arxiv.org/ps/cond-mat/0106313v1