

Open questions and promising new fields in dewetting

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Abstract. This contribution summarizes the present understanding of dewetting focusing on three points that are either controversial or open. The first issue concerns the initial formation of holes, i.e. the film rupture. The second point concerns the unstable growth of holes, i.e. the transversal instability of the receding contact line. Finally, recent extensions towards dewetting on heterogeneous substrates are examined. In passing the long time evolution in dewetting and the coupling of dewetting with other effects are discussed.

PACS. 68.15.+e Liquid thin films – 68.55.-a Thin film structure and morphology – 47.20.Ma Interfacial instability

1 Introduction

While hydrodynamical surface instabilities in thin-film flows are investigated since the early experiments of the Kapitzas on falling films on solid substrates [1], in soft matter physics they became increasingly recognized as important for the structure formation in thin films on solid substrates since the work on dewetting by Reiter only one decade ago [2]. In this paradigmatic experiment a polymer film on a solid substrate is brought above its glass transition temperature, ruptures, and the formed holes grow resulting in a network of liquid rims. The latter may decay subsequently into small drops. Sometimes, the growth of the holes is accompanied by a transversal instability of the liquid rim that forms around the hole [3].

Mitlin [4] showed the analogy between the surface instability of a thin film due to effective molecular interactions between film and substrate [5–7], called spinodal dewetting, and spinodal decomposition. Consequently, most results obtained since Cahn and Hilliard [8] for the decomposition of a binary mixture have a counterpart in the evolution of thin films on horizontal substrates. The work on thin films on solid substrates also builds on earlier results by Vrij for thin free liquid films [9].

Derived by a long wave approximation from the Navier Stokes equation [10], the (nondimensionalized) equation for the time evolution of the film thickness, h , writes

$$\partial_t h = -\nabla [Q(h)\nabla(\Delta h - \partial_h f)] \quad (1)$$

with $Q(h) = h^3$ the mobility factor and $\partial_h f$ the derivative of an appropriate free energy. It has the form of the Cahn-Hilliard equation for the evolution of a concentration field [11], i.e. the form of the simplest possible equation for the dynamics of a conserved order parameter field [12]. The choice of the free energy decides which physical system is described. It can be dewetting due to effective molecular interactions ($\partial_h f$ corresponds to the (negative) disjoining pressure), or a long wave Marangoni instability ($\partial_h f$ comes from the interaction of film thickness and temperature field), or combinations thereof (other effects can also be included, see the review of Oron et al. [10]).

2 Film rupture

If f corresponds in some parameter range to a double-well potential there exists a critical point. In its vicinity the stability of a flat homogeneous film is sketched in the upper panel of Figure 1 where b is a control parameter and h_0 is the film thickness corresponding to the order parameter. The dashed (solid) line represents the binodal (spinodal), i.e. the boundary above (below) which the film is stable (unstable). In between the two lines the film is metastable, i.e. it can rupture if some nucleation threshold (nucleation solution or critical depression) is overcome (see also [14]). I think, up to this point everyone working in the field will agree with the general picture. However, one of the questions discussed sometimes controversially [2, 13, 15–19] is already touched. What is the mechanism of the initial rupture of a flat film: *instability* or

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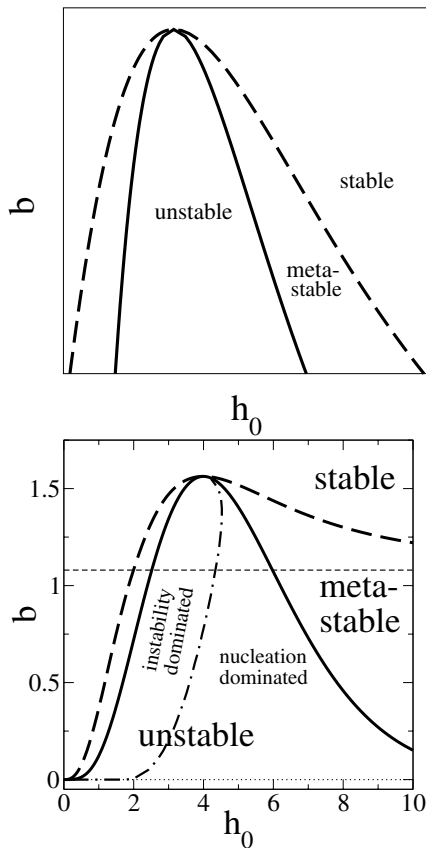


Fig. 1. The upper panel shows the schematic stability diagram for a thin liquid film close to the critical point including the binodal (dashed line) and the spinodal (solid line). The lower panel gives the result for the disjoining pressure used in [13] indicating especially the boundary (dot-dashed line) between nucleation-dominated and instability-dominated sub-ranges within the linearly unstable range. The upper horizontal line indicates the b where the binodal goes to $h_0 = \infty$.

nucleation? Most literature relates the occurrence of surface instability and heterogeneous nucleation at defects to linearly unstable and metastable films, respectively.

The reason for the importance of this question for the dewetting process is that in most systems the evolution is frozen before major coarsening occurs, i.e. the mechanism of the initial rupture still determines the structure. On the contrary, in decomposition there is little discussion about this point, what rather interests there is the scaling behaviour of the long-time coarsening, because it gives the evolution of the length scales that can be measured experimentally. Contrary to this, for thin films coarsening is up to now only of minor interest (exceptions are Refs. [20–22]) because for the used experimental systems in dewetting the time scale for large-scale coarsening is very large.

An important question from a practical point of view is the *exact functional shape of the free energy*. Many different combinations of stabilizing or destabilizing exponentials and power laws in h are used [23,24] (for two-dimensional simulations see, for example, [25–28]) and still new candidates for underlying physical effects beside dis-

persion or electrostatic forces show up [29–32]. Although, it seems that general features of the free energy are enough to qualitatively predict the behaviour of experimental systems (see, for example, the discussion in reference [33]) more is needed to do so quantitatively.

An important step was done for ultrathin films in the recent work of Becker et al. [34] where they obtained a very good agreement of experiment and a model based on long wave theory (i.e. using an equation like Eq. (1)) incorporating a disjoining pressure determined from experimental data [35] (for such a comparison for thicker films that dewet and evaporate see Schwartz et al. [28]). The good agreement can be stated because a rather drastic transition between different complex dewetting scenarios at film thicknesses of 3.9 nm and 4.9 nm was found in experiment *and* simulation. In reference [34] it is explained that ‘in both cases the system has a long wave instability (spinodal dewetting), but in the thicker film, dewetting by heterogeneous nucleation of holes pre-empts the onset of the instability’.

However, no deeper explanation was given *why* such a transition between two different scenarios occurs *within* the linearly unstable film thickness range. It is tempting to see it as an evidence for the transition between nucleation-dominated and instability-dominated behaviour *within* the linearly unstable thickness range (indicated in the lower panel of Fig. 1) predicted recently using a two-dimensional model system (described by a film thickness evolution equation that contains one space dimension) [13,33,36]. There the influence of nucleation at defects is evaluated inside the linearly unstable (spinodal) film thickness range based on the observation that in a part of the spinodal range nucleation solutions of equation (1) exist. These unstable solutions are able to ‘organize’ the evolution of the thin film by offering a fast track to film rupture that does not exist in their absence. For the decomposition of a binary mixture Novick-Cohen [37] discussed such solutions as an evidence for a smooth transition from spinodal decomposition to nucleation somewhere within the classical spinodal.

The nucleation solutions that exist in the linearly unstable thickness range are unstable stationary solutions of Eq. (1) that have to be overcome to break a film in smaller portions than the critical spinodal wavelength, $\lambda_c = 2\pi/\sqrt{-\partial_{hh} f}$. They also influence the local dynamics if there exist localized disturbances of the film surface (defects) with lateral extensions smaller than λ_c . Then, locally the nucleation solutions, that are saddles in the space of all possible surface profiles, first attract the evolution to later repel it with a rate β_{nuc} . The latter can be obtained by analysing the linear stability of the nucleation solutions. The comparison of the maximal rate β_{nuc} for a given mean film thickness with the corresponding linear growth rate, β_m , of the fastest growing unstable flat film mode (of wavelength $\lambda_m = \sqrt{2}\lambda_c$), allows to predict whether defects have an influence on the resulting morphology or not.

The main result is the distinction of nucleation-dominated (scenario A) [38] and instability-dominated

(scenario B) sub-ranges within the linearly unstable range [13]. In scenario A an initial disturbance grows much faster than the also active linear instability of the flat film. The produced holes expand and if the dynamically produced surface depression just outside the rim (that can be calculated along the lines of Ref. [39]) becomes larger than the respective nucleation solution secondary nucleation events occur (leading to secondary holes, called satellite holes in Refs. [34,40]). The resulting structure is a set of holes with distances unrelated to λ_m . It depends strongly on the properties of the initial defect. The secondary nucleation becomes less important and eventually ceases for thicknesses closer to $\partial_{hh}f = 0$ because there the nucleation solutions that have to be overcome have larger amplitudes. In scenario B the initial disturbance also starts to grow but rather acts as starting point for the most unstable flat film mode. Undulations of period λ_m extend laterally to give finally a periodic set of holes nearly independent of the initial perturbation. The resulting new boundary separating the two sub-ranges in the phase plane is sketched in Figure 1b. The qualitative result does neither depend on the details of the used disjoining pressure [33] nor is it expected to be different in two-dimensional systems. However, to prove the latter assertion the used continuation techniques [41] have to be extended to two spatial dimensions.

The result of references [13,36] can be used to understand qualitatively *why* the morphological transition occurs that is shown and analysed in reference [34]. For very thin films the nucleation solutions are absent or slow and the linear mode grows (like scenario B in [13], Fig. 1 of [34]) whereas for slightly thicker but still linearly unstable films ‘fast’ nucleation solutions exist that allow small defects to grow into nucleated holes and also foster the subsequent secondary nucleation events (like scenario A in [13], Fig. 2 of [34]). The simulation of the latter case in reference [34] also shows the competing ‘slow’ flat film mode.

In my opinion, the recent results give rise to several new questions: (1) *Is the distinction of scenarios A and B a general feature of thin film surface instabilities on horizontal substrates as proposed in reference [13]?* One can already state that secondary nucleation is most probably a generic effect. It was found in simulations by Sharma (seeing the small chemically different patch as initial disturbance ([42], Figs. 25 to 27)), and for dewetting of aqueous collagen films ([43], Fig. 5.3a). A sharp transition between a nucleation-dominated and an instability-dominated thickness range within the linearly unstable range was observed by Meredith et al. using combinatorial methods [44]. Although their selection of figures does not show secondary nucleation it should be possible to identify the corresponding parameter ranges with their method. It was also described by Du et al. [45] (see also [46] and the detailed analysis in [47]).

The observed lateral growth of structures leads to the questions: (2) *What is the accuracy of the time scales determined in reference [13] for the competing processes?* and (3) *What is the upper boundary of the thickness range*

where secondary nucleation occurs? Reference [13] gives certainly a good estimate but it could be worthwhile to directly compare the rates of lateral extension of a locally induced flat film mode and of the nucleated holes with secondary nucleation. Combining this with the approach of Herminghaus et al. [39] could also answer question (3) and explain the upper thickness limit for satellite hole formation found in reference [40].

The last point I want to discuss for the initial rupture refers to the rupture via nucleation. To my understanding it is now agreed on that patterns resulting from nucleation and instability can be well distinguished by their geometrical signature, using simple tools like pair correlation functions or Fourier transforms [17,19,44,48] or more sophisticated ones as Minkowski measures introduced by Mecke into the field [19,34]. Using these techniques Jacobs et al. find [19] that experiments originally interpreted as spinodal dewetting [2] show actually nucleated holes. However, granting this, the observed h^{-4} dependence of the hole density on film thickness (also found by Ashley et al. [49], and with a tendency towards h^{-5} for thicker films by Du et al. [45]) becomes even more interesting. Other groups found exponential [19] or no [44] thickness dependence of the density of nucleated holes. In reference [45] it is pointed out that both, power law and exponential fits, describe the presented data equally well. Ashley et al. [49] show also a power law dependence ($\theta^{-3.6}$) of the hole density on the equilibrium contact angle, θ , of a reference liquid on the substrate. However, to my knowledge there is up to now no answer to the questions: (4) *Where do the active defects come from, what is the exact dependence of their number on film thickness and why?* A possible approach is the systematic study of the influence of individual chemical defects or arrays of defects of the substrate on the solution structure of Eq. (1)). This corresponds to the study of heterogeneous substrates discussed below in Section 4 (see also [50]). Hopefully, the question will trigger more experimental and theoretical work (like simulations in the metastable thickness range proposed by Mitlin [51]) on a variety of different systems.

3 Transversal instability of the dewetting front

But not only the initial rupture of the homogeneous film guards still some secrets. So does the next phase – the growth of individual holes. The holes may grow in a stable way [52], i.e. conserving their circular form [39,53–55]. However, in a variety of systems different groups observed a transversal front instability of the receding dewetting front. One can roughly distinguish: (i) thickness modulations of the outward moving liquid rim around the growing hole [2,44,56–58], (ii) development of relatively stable fingers that stay behind the outward moving rim [3,43,48,59], and (iii) an emanation of a structured field of small droplets from the moving rim [3,57,60–65].

Up to now not much is known to answer the question: (5) *What are the exact conditions for the instability to occur and to have appearance (i), (ii) or (iii)?* For the type (i) instability found, for instance, for alkane films

(thickness some μm) on silicon wafers Brochard-Wyart and Redon [56] proposed that the instability of the moving rims is very similar to the Rayleigh instability of immobile rims as studied by Sekimoto et al. [66]. Sharma and Reiter [65] attribute type (ii) or (iii) instabilities to a combination of a Rayleigh mechanism and dissipation due to slip (see also [43]), whereas Meredith et al. [44] associate fingering in liquid crystal dewetting to shear thinning. Hydrodynamic models, that give up to now only indirect results for the stability of such moving liquid rims, point to the destabilizing effect of the disjoining pressure, i.e. the effective interaction with the substrate that is responsible for the dewetting itself [67,68]. For the study of the stability of a moving liquid rim to transversal instabilities stationary movement is most convenient. It was assured by allowing for evaporation and dewetting by Lyushnin et al. [67] or by studying a liquid ridge on an inclined plane [68,69]. Thereby, in reference [67], resembling quite closely the experimental conditions used by Elbaum and Lipson [60], it is found that the onset of the instability coincides with the appearance of a rim around the holes. However, they did not perform an energy analysis as introduced by Spaid and Homsy [70] and improved on by Skotheim et al. [71]. Therefore, the mechanism of the instability is difficult to infer. The second mentioned work [68] does such an analysis for a liquid ridge sliding down an inclined plate. Including a disjoining pressure to account for an only partially wetting system they find not only the (expected) instability of the advancing front due to gravity but also one of the receding front. The latter is caused by the interaction of flow and disjoining pressure. Because the receding front resembles locally the situation at the receding front in dewetting, Reference [68] puts forward the hypothesis that also in dewetting the disjoining pressure has an active share in the destabilization of the hole growth. Moreover, one may argue that the sequence of asymmetric varicose instability, asymmetric zigzag instability and decoupled front and back instability found in reference [68] when increasing the driving also gives a first hint on the mechanisms behind the change from instability type (i) to types (ii) and (iii) introduced above. So give Figures 6 and 5 of reference [56] a rough indication for a change from varicose to zigzag instability when increasing the driving force. A stronger zigzag instability leading to finger formation is also seen in Figure 14 of reference [3]. As for the film rupture discussed above, it is to hope that the question initiates more experimental and theoretical investigations of this important phenomenon.

4 Heterogeneous substrates

Finally, I will concentrate on recent extensions of the study of dewetting towards heterogeneous or structured substrates. Several experiments [72–78] involve dewetting of thin films on heterogeneous substrates. Mostly they aim at arranging soft matter in a regular manner as determined by the physically and/or chemically patterned substrates. The deposition may also be by condensation as demonstrated by Gau et al. [79]. Beside the predominating reg-

ular substrate patterns also irregular ones are used (see, for instance Mougin and Haidara [78]). In a related work Higgins and Jones study the influence of an anisotropic initial condition on the dewetting on a homogeneous substrate [80].

In nearly all experiments the (strong) heterogeneity imposes itself on the dewetting film if the length scale of the pattern is similar to the intrinsic scale of dewetting. This corresponds to theoretical results of a variety of groups [42,81–88] using energy minimization or long wave equations for strong stepwise wettability contrasts. Deposited liquid volume, chemical potential or the size of the heterogeneous patches are used as control parameters to derive morphological phase diagrams. However, special care has to be taken using stepwise wettability patterns in dynamical studies based on thin film equations derived by a long wave approximation from the Stokes equation [10]. In the course of the derivation it is assumed that *all* relevant length scales parallel to the substrate are large as compared to the film thickness, h_0 . However, having a stepwise contrast in the final thin film equation implies that the step occurs over a length of order h_0 . This is in conflict with the used long wave approximation. However, in simulations the resulting diverging gradients of the chemical potential at the wettability steps are often smoothed out by the finite spatial discretization used [84,86,89].

In contrast, recent studies of Bruschi et al. [90,91] regard heterogeneous dewetting on a smoothly patterned substrate using the wettability contrast as a control parameter. The use of continuation techniques [41] allows them to investigate in detail the transition between homogeneous and heterogeneous substrates and the transition between coarsening and pinning (ideal templating) in its dependence on heterogeneity strength, heterogeneity period and film thickness. Resulting phase diagrams are in line with the ones obtained by Kargupta and Sharma [86,89] by sampling the parameter space with simulations in time. This suggests that the actual functional form of the heterogeneity is much less important than its length scale and strength. However, the use of continuation allows to establish the existence of a large hysteresis between pinned and coarse solutions, i.e. a large range where both morphologies correspond to local minima of the energy [91]. The latter work also shows that in comparison to the homogeneous system a weak heterogeneity slows down the onset of coarsening but accelerates the coarsening in the nonlinear regime. Up to now, experiments with heterogeneous substrates aim at ideal templating using a broad range of techniques. This explains the scarcity of experimental results on the transition between “bad” and “good” templating, that could be related to the pinning-coarsening transition. Open questions that I see in the young field of structure formation on heterogeneous substrates are: (6) *How do the experimental realizations of the theoretically obtained morphological phase diagrams look like?* and (7) *How do the length scales derived from distance and gradient of the heterogeneities compete?*

5 Outlook

In some cases, the experiments represent much more complex situations than the theories that aim at describing them. For instance, some liquids used in heterogeneous dewetting are actually binary mixtures of two polymers and dewetting is accompanied by a phase ordering [72,73,92,93]. Although, the final structures can be roughly described based on dewetting only the acting mechanisms may differ. The connection of decomposition and dewetting may even lead to new pathways of the dewetting process, as the decomposition mediated dewetting observed by Yerushalmi-Rozen et al. [94]. There the mixture decomposes first and then dewetting sets in at the interfaces of the two separated liquids. So the instability is triggered by the spatial gradient of the disjoining pressure. However, for a liquid on a heterogeneous substrate the gradient results from the substrate [86], whereas in reference [94] the destabilizing gradient is produced *within* the film itself.

Furthermore, the evolution of the film thickness can be accompanied by phase changes as observed, for example, for liquid crystals or block copolymers [59,95–99] or by density variations as discussed in [30,100]. To describe the observed phenomena involving liquids with inner degrees of freedom it will be necessary to derive coupled evolution equations for the film thickness on the one hand and a concentration or phase field on the other hand. For the case of the density variations this may be done by coupling a diffuse interface model for the density to long wave hydrodynamics [101,102].

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Discussion on contribution by U. Thiele

Statements and questions from the contribution by U. Thiele:

It is tempting to see this transition (referring to the work of Becker et al., Nat. Materials 2, 59 (2003)) as evidence for the transition between nucleation-dominated and instability-dominated behavior WITHIN the linearly unstable film thickness range.

Comment by U. Steiner:

The interesting question from the point of view of an experimentalist.

How can one experimentally distinguish between the two models. From his paper, it does not immediately become clear that his model (interplay of capillary instability and nucleation) does a better job in describing the data by Becker and coworkers. How must an experiment be designed to distinguish between the two explanations?

U. Thiele replies:

I see no contradiction between the explanations of Becker et al. and myself. They state that 'in both cases the system has a long wave instability (spinodal dewetting), but in the thicker film, dewetting by heterogeneous nucleation of holes pre-empts the onset of the instability'. I certainly agree with this and try to give a deeper explanation why and under which circumstances the two cases show up. Therefore in my opinion there are not two models, there are only two levels of explanation using the same thin film model.

Question by the editor:

Do we have any clear-cut evidence that the disjoining pressure has an active share in the destabilization of the rim during hole growth?

U. Steiner replies:

Not as far as I know, and I would find it very surprising, if van der Waals forces would come into play there. Spreading experiments show that van der Waals forces are significant only for drop heights comparable or smaller than the range of the van der Waals forces. Since rim heights typically exceed this length even during the early stages of hole opening, I would guess that the spreading results stay valid also in the case of negative spreading.

U. Thiele replies:

I do not expect the instability of the retracting front to be unstable on a macroscopic lengthscale. So it will be difficult to observe in systems like liquid sheets on an inclined plate. The initial wavelength will be of the order of the respective spinodal scale of the most unstable film thickness. The rim height itself should not be the crucial measure for the instability because the instability will

be rather caused by the back part of the rim, where the most unstable film thickness is realized. Spreading may not be the right reference system because there the effective molecular interactions are normally stabilizing (that is why the drops are spreading) whereas for a negative spreading they are destabilizing.

Comment by A. Sharma:

In addition to the work of Becker et al., one may expect such a transition to the "defect sensitive spinodal regime (DSSR)" in general as the film thickness increases. Some tell-tale signs of DSSR are a reduced number of hole density compared to the expectations of the linear theory, formation of locally ordered structures (for example, satellite holes), increasingly bi-modal size distribution of holes and greatly increased sensitivity of the length scale to the initial and preparation conditions.

Comment by P. Green:

In the Thiele contribution, the actual diagram of control parameter, b , versus film thickness may look slightly different for polystyrene (PS) films dewetting oxidized silicon wafers, for example. There is evidence that PS films do not completely dewet the substrate. In fact, a morphology characterized by two distributions of droplets, a collection of very small droplets, each less than a micron in lateral dimensions (nanodroplets) and larger distribution of macroscopic droplets each possessing a diameter of many microns. The nanodroplets are associated with an autophobic layer that becomes unstable (see this issue, page 449 and by Müller et al. J. Chem. Phys. 115, 9960 (2001)). How might one propose to address this issue?

Instabilities in the rims of growing holes have been observed in a wide range of systems: (1) PS dewetting oxidized silicon wafers [Masson et al. Macromolecules 35, 6992 (2002)]; (2) PS dewetting PDMS (Reiter and Sharma) and (3) the dewetting of a random copolymer, styrene acrylonitrile, from oxidized silicon wafers. In one case the slip mechanism is clear-cut, PS dewetting PDMS, and in the other two the interactions of the polymer with the underlying substrate might, at first glance, suggest otherwise. We see evidence of a partial slip mechanism being responsible for the instabilities in the PS/SiO_x/Si system (see this issue, page 449). It would be interesting to investigate the role on interactions on instabilities and the connection to dewetting dynamics in further detail theoretically.

U. Thiele replies:

I think the stability diagram will not look very different (normalizing film thickness by coating thickness and plotting the different regimes in the plane spanned by the normalized film thickness and the ratio of the Hamaker constants). The shown diagram (see my paper) also reflects a situation without 'true rupture'. A very thin layer

remains as given by the left branch of the binodal line. However, here an upper plateau thickness may or may not exist (corresponding to the cases b larger or smaller than about 1.1 in my paper depending on parameter values. It results here from the stabilizing influence of the silicon substrate for larger film thicknesses. With respect to the large and small drops found, one could speculate that they are nucleated and spinodal drops, respectively, in analogy to the finding of nucleated (large) and spinodal (small) holes in systems where both processes compete.

Comment by H. Kaya and B. Jérôme:

The prospect of treating density and thickness fluctuations by means of coupled equations is certainly doable, and it opens for interesting insights. The common thin film equation treats the typical length scale across

the film as negligibly small compared to the length scales of fluctuations parallel to the film surface (the lubrication approximation). Will the lubrication approximation still be applicable when inner degrees of freedom are included? It would be very interesting to shed some light on the limitations of the lubrication approximation.

It is good to distinguish early on between random density fluctuations and presumably systematic density variations. A Marangoni effect should arise from any surface tension gradient, whatever the cause of this gradient (temperature, density). Wensink and Jérôme found, using the standard arguments of the thin film equation, that (lateral) variations in film density should follow the same time and space dependency as variations in thickness. Is the proposed need for density field equations another reason to move away from the lubrication approximation?