

Disintegration of liquid films

Yulii D. Shikhmurzaev

School of Mathematics, University of Birmingham, Birmingham B15 2TT, UK

The rupture of a thin liquid film is considered in the framework of an earlier developed mathematical theory of flows with forming/disappearing interfaces. The process is shown to be driven by the surface-tension gradient arising when the rate of variation of the free-surface area due to external disturbances becomes comparable with the inverse surface-tension relaxation time. The proposed mathematical description of the rupture phenomenon does not require the introduction of intermolecular forces into the equations of macroscopic fluid mechanics. The theory allows one to predict the minimal critical thickness of the film that remains stable with respect to given external disturbances.

1 Introduction

In order to handle coating films efficiently, one faces a problem of finding a balance between the requirement for these films to be thin, as dictated by the desired properties of the final product, and the tendency of thin films to rupture thus creating defects in the coating. This technological dilemma can be addressed by considering the underlying problem of theoretical fluid mechanics, namely the problem of the mathematical modelling of fluid motion with transitions in the topology of the flow domain. This problem defines a wide class of flows which include, in addition to the rupture of films, also the breakup of liquid jets, coalescence of drops, nucleation of bubbles and many others. The peculiarity of the film rupture problem is that, unlike the breakup of jets where the capillary pressure magnifies the long-wave disturbances, in the case of films the capillary pressure is always a stabilising factor (though a weak one). Hence in the standard fluid mechanical model there appears to be no mechanism that could disintegrate liquid films.

In order to remedy the situation, in a number of works the Navier-Stokes equations describing fluid motion on a macroscopic length scale are artificially ‘augmented’ with intermolecular forces. However, this ‘addition’ is a fundamental mistake contradicting the continuum limit and the concept of ‘stress’ that accounts for momentum fluxes due to intermolecular forces and molecular motion. Since this mistake made its way into a number of papers, it is worth recapitulating a few basic ideas lying at the foundation of continuum mechanics.

Let us consider the momentum flux across a control surface drawn through the bulk of the fluid. Physically, this flux includes two components: (a) the momentum flux due to intermolecular forces exerted by the molecules located on one side of the control surface on the molecules on the other side and (b) the momentum flux due to molecular motion across the control surface (Fig. 1a,b). The first contribution is dominant in solids, the second one plays the main role in gases, whereas for liquids both factors are comparable. In the continuum limit, the momentum flux across a surface is described by the concept of ‘stress’, i.e. a distributed force acting on this surface (Fig. 1c). In other words, the continuum mechanics approximation collapses the layer with the thickness on the scale of the range of intermolecular forces (or, if it is greater, the molecular free run) comprising the control surface into this surface and accounts for both contributions to the momentum flux across it in the notion of stress¹.

Thus, one has that, in the continuum limit, all molecular length scales, including the

¹This notion is a conceptual leap from molecular dynamics. In molecular dynamics, one has masses of molecules, their velocities and forces acting between them, whereas in continuum mechanics we deal with densities, velocities, body forces and internal stresses, i.e. the surface forces.

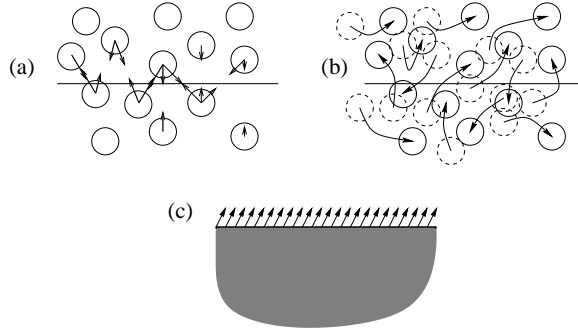


Figure 1: In the continuum limit, the momentum fluxes due to intermolecular forces acting across a surface (a) and due to molecular motion (b) are accumulated in the concept of ‘stress’, which is a distributed force acting on a mathematical surface (c).

range of intermolecular forces, vanish. Strictly speaking, the continuum limit is *defined* as the 0th-order approximation in the ratio of molecular-to-macroscopic length and time scales as this ratio goes to zero. Then, all length and time scales featuring in the continuum mechanics models are, by definition, macroscopic, not molecular. Therefore an explicit inclusion of intermolecular forces — and hence molecular lengths! — in a continuum model is incompatible with the very fundamentals of continuum mechanics as a scientific discipline². It is also necessary to emphasize that all intermolecular forces have *already* been accounted for by the concept of stress so that their inclusion *in addition* to the stress would mean double-counting of the same physical effects.

In the present work, a macroscopic mechanism of rupture of liquid films is analysed in the framework of the thin-film approximation. The main physical idea behind this mechanism is as follows. As can be shown, the rate at which the free surface area is created by external disturbances increases (in the limit, to infinity) as the film gets thinner. This means that, for sufficiently thin films, this rate will become comparable with the rate at which the free surface acquires its surface properties (such as the surface tension). Then an external disturbance of a thin film will drive the surface tension out of equilibrium and, due to the spatial nonuniformity of the process, create a surface tension gradient pulling the film apart via the Marangoni effect. Then, the film ruptures if it is thin enough for the Marangoni stresses to break it before the relaxation mechanisms, which drive the free surface back to its equilibrium state, eliminate these stresses. Otherwise, the surface tension relaxes to its equilibrium value and the capillary pressure, becoming the only driving force, restores the initial shape of the free surface. As a result, the magnitude and rate of the external disturbances correlate with the maximum thickness of the film that can be ruptured by these disturbances. This situation is qualitatively different from the case of a cylindrical thread, which is linearly unstable to long-wave disturbances.

In the present work, we illustrate the above mechanism of rupture by considering the case of a free film. The same physical mechanisms operate when a film is on a solid substrate though mathematically this case is considerably different and will be discussed elsewhere. Since the film rupture problem is essentially a particular case of the interface formation/disappearance phenomenon, for its mathematical modelling we can use the simplest theory of flows with forming/disappearing interfaces [1], which has originally been developed for, and shown to be successful in, describing dynamic wetting [1–3]. In the present work, the model is used without any adhoc alterations.

²It is also worth mentioning that, in continuum mechanics, once the concept of stress is introduced, the interfacial layers, whose thickness is determined by the range of intermolecular forces, have to be modelled as mathematical surfaces, not as layers of a finite thickness.

2 Thin-film approximation

To study a free-surface flow with a topological transition of the flow domain in the framework of the theory of fluid motion with forming interfaces [1] one has to consider solutions of the Navier-Stokes equations,

$$\nabla \cdot \mathbf{u} = 0, \quad \rho(\partial \mathbf{u} / \partial t + \mathbf{u} \cdot \nabla \mathbf{u}) = -\nabla p + \mu \nabla^2 \mathbf{u}, \quad (1)$$

satisfying at an a priori unknown free surface $f(\mathbf{r}, t) = 0$ with the inward normal $\mathbf{n} = \nabla f / |\nabla f|$ the boundary conditions

$$\partial f / \partial t + \mathbf{v}^s \cdot \nabla f = 0, \quad (2)$$

$$-p + \mu \mathbf{n} \cdot [\nabla \mathbf{u} + (\nabla \mathbf{u})^*] \cdot \mathbf{n} = \sigma \nabla \cdot \mathbf{n}, \quad \mu \mathbf{n} \cdot [\nabla \mathbf{u} + (\nabla \mathbf{u})^*] \cdot (\mathbf{I} - \mathbf{nn}) + \nabla \sigma = 0, \quad (3)$$

$$\rho(\mathbf{u} - \mathbf{v}^s) \cdot \mathbf{n} = (\rho^s - \rho_e^s) \tau^{-1}, \quad \partial \rho^s / \partial t + \nabla \cdot (\rho^s \mathbf{v}^s) = -(\rho^s - \rho_e^s) \tau^{-1}, \quad (4)$$

$$(1 + 4\alpha\beta) \nabla \sigma = 4\beta(\mathbf{v}^s - \mathbf{u}) \cdot (\mathbf{I} - \mathbf{nn}), \quad \sigma = a\rho^s - b(\rho^s)^2 \quad (5)$$

together with some conditions in the far field specifying a particular flow and initial conditions. In addition to the known kinematic condition (2) and conditions on the normal and tangential stress (3), where \mathbf{I} is the metric tensor, the model accounts for the mass exchange between the bulk and the surface phase (4) as the interface relaxes towards its equilibrium state with the surface density ρ^s tending to its equilibrium value ρ_e^s (τ is the relaxation time; \mathbf{u} and \mathbf{v}^s are the bulk and the surface-phase velocity, respectively). For spatially nonuniform flows, like the rupture of a film, the appearing gradient of the surface tension σ , first, influences the flow via the tangential-stress condition (the Marangoni effect; the second condition in (3)) and, secondly, forming a torque with the tangential stress, it makes the tangential to the interface components of the surface velocity \mathbf{v}^s deviate from the corresponding component of the bulk velocity \mathbf{u} evaluated at the interface (the first condition in (5)). The equation of state in the surface phase (the second equation in (5)) is taken in a simple barotropic form approximating the general equation of state for the surface phase, $\sigma = f(\rho^s, T)$, where T is the absolute temperature, for the process of interface formation. Equation (5) takes into account that the surface tension decreases from its equilibrium value $\sigma_e = \sigma(\rho_e^s)$ if the surface phase becomes compressed or extremely rarefied. In particular, a hypothetical instantly created free surface corresponds to $\rho^s = 0$ and, as one would expect, has zero surface tension; the latter is acquired as the molecular motion leads to the formation of a certain structure of the interfacial layer, which is macroscopically modelled as a two-dimensional ‘surface phase’. Estimates for material constants α , β and τ for some fluids have been obtained by analysing experiments on dynamic wetting [3].

The general three-dimensional problem can be considerably simplified in the thin-film approximation with the ratio of characteristic length scales in the directions normal and tangential to the film ϵ as a small parameter. We will consider this approximation for a plane two-dimensional flow in a film of incompressible Newtonian fluid of viscosity μ and density ρ surrounded by an inviscid dynamically-passive gas. Let the film’s shape be described by $y = \pm h(x, t)$ in a suitably chosen Cartesian coordinate frame and u, u^s, v, v^s denote, respectively, the x and y components of the bulk and surface velocities. Then the thin-film approximation can be obtained by using the following asymptotic expansions:

$$x = L\epsilon\bar{x}, \quad y = L\epsilon^2\bar{y}, \quad t = t_\mu\epsilon^2\bar{t}, \quad hL^{-1} = \sum_{n=0}^{\infty} \epsilon^{2(n+1)} h_n, \quad (6)$$

$$(u, u^s)U^{-1} = \sum_{n=0}^{\infty} \epsilon^{2n-1} (u_n, u_n^s), \quad (v, v^s)U^{-1} = \sum_{n=0}^{\infty} \epsilon^{2n} (v_n, v_n^s),$$

$$pP^{-1} = \sum_{n=0}^{\infty} \epsilon^{2(n-1)} p_n, \quad (\sigma \sigma_e^{-1}, \rho^s b a^{-1}) = \sum_{n=0}^{\infty} \epsilon^{2n} (\sigma_n, \rho_n^s), \quad \text{as } \epsilon \rightarrow 0,$$

where $L = \mu^2(\rho \sigma_e)^{-1}$, $t_\mu = \mu^3 \rho^{-1} \sigma_e^{-2}$, $U = \sigma_e \mu^{-1}$, $P = \rho \sigma_e^2 \mu^{-2}$. After the standard asymptotic analysis to leading order one arrives at the following set of equations:

$$\frac{\partial u_0}{\partial \bar{t}} + u_0 \frac{\partial u_0}{\partial \bar{x}} = \frac{1}{h_0} \frac{\partial \sigma_0}{\partial \bar{x}} + \frac{4}{h_0} \frac{\partial}{\partial \bar{x}} \left(h_0 \frac{\partial u_0}{\partial \bar{x}} \right), \quad v_0 = -\bar{y} \frac{\partial u_0(\bar{x}, \bar{t})}{\partial \bar{x}}, \quad (7)$$

$$\frac{\partial h_0}{\partial \bar{t}} + u_0^s \frac{\partial h_0}{\partial \bar{x}} = v_0^s, \quad \frac{\partial \rho_0^s}{\partial \bar{t}} + \frac{\partial (\rho_0^s u_0^s)}{\partial \bar{x}} = 0, \quad (8)$$

$$\frac{\partial \sigma_0}{\partial \bar{x}} = 4\bar{\beta}(u_0^s - u_0), \quad (u_0 - u_0^s) \frac{\partial h_0}{\partial \bar{x}} - (v_0 - v_0^s) = \bar{\chi}(\rho_0^s - \bar{\rho}_e^s), \quad (9)$$

$$\sigma_0 = a\rho_0^s - b(\rho_0^s)^2, \quad (10)$$

where $\bar{\beta} = \beta \mu \rho^{-1} \sigma^{-1} (1 + 4\alpha\beta)^{-1}$, $\bar{\chi} = a\mu(b\rho\sigma_e\tau)^{-1}$ and $\bar{\rho}_e^s = \rho_e^s b a^{-1}$. In obtaining (7)–(10) it was assumed that all nondimensional parameters appearing after the use of scaling (6) are of $O(1)$ as $\epsilon \rightarrow 0$. In particular, this means that $\epsilon^2 t_\mu \tau^{-1} \rightarrow 0$ as $\epsilon \rightarrow 0$ so that, physically, the process described by (7)–(10) takes place on a time scale small compared with τ and, according to the second equation (8), the relaxation mechanisms have no time to restore the equilibrium surface density (and hence the equilibrium surface tension).

Equations (7)–(10) can be simplified further for medium to high-viscosity fluids by using the estimates for material constants of the model obtained from experiments on dynamic wetting [3]. These estimates show that for such fluids $\bar{\chi} \ll 1$ and $\bar{\beta} \gg 1$ and hence, to leading order in these parameters, it follows from (9) that one can neglect the difference between (u_0^s, v_0^s) and (u_0, v_0) . Then, after simple algebra we arrive at an initial-value problem for the following set of nonlinear equations:

$$\frac{\partial u}{\partial t} + u \frac{\partial u}{\partial x} = \frac{1}{h} \frac{\partial \sigma}{\partial x} + \frac{4}{h} \frac{\partial}{\partial x} \left(h \frac{\partial u}{\partial x} \right), \quad (11)$$

$$\frac{\partial F}{\partial t} + \frac{\partial (Fu)}{\partial x} = 0, \quad F = (h, \rho^s); \quad \sigma = a\rho^s - b(\rho^s)^2. \quad (12)$$

(Hereafter for brevity we drop the overbar and the subscript 0.) In (11), the surface tension gradient on the right-hand side appears as the only driving force, unlike the case of the breakup of a cylindrical jet [4], where the Marangoni effect and the capillary pressure due to the cross-sectional curvature play comparable roles.

3 The process of rupture

As already mentioned, the scaling (6) implies, in particular, that equations (11), (12) operate on a time scale small compared with the surface-tension-relaxation time, and, with no relaxation in (12), $u \equiv \hat{u} = \text{const}$, $h \equiv \hat{h} = \text{const}$, $\rho^s \equiv \hat{\rho}^s = \text{const}$ is a solution of (11), (12) for arbitrary values of \hat{u} , \hat{h} and $\hat{\rho}^s$. A linear stability analysis of this solution leads to a dispersion relationship of the form

$$\omega = k\hat{u} - 2ik^2 \left[1 \pm \left(1 + \frac{\hat{\rho}^s \lambda}{4k^2 \hat{h}} \right)^{1/2} \right], \quad \text{where } \lambda = \frac{d\sigma}{d\rho^s}(\hat{\rho}^s), \quad (13)$$

and ω and k are the angular frequency and wavenumber, respectively. Hence the solution is stable for $\lambda < 0$, which for the surface equation of state given by the second equation (12) corresponds to $\hat{\rho}^s > a/(2b)$ and unstable otherwise. In other words, it is stable if the rarefaction of the surface phase increases the surface tension, which then contracts the surface and replenishes ρ^s . On the other hand, if the surface tension decreases with decrease in ρ^s , then a local rarefaction of the surface phase due to an external disturbance

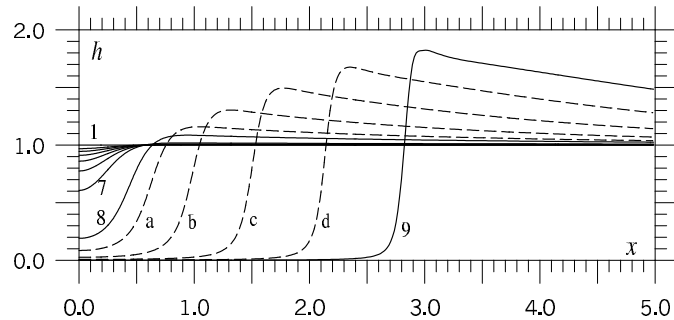


Figure 2: Profiles of the free surface at different moments in time. Solid lines 1–9 are obtained for $t = 0, 10, 15, 20, 25, 30, 35, 40$ and 45 , respectively. Dashed lines a–d correspond to $t = 41, 42, 43$ and 44 .

leads to a local reduction in the surface tension whose gradient then acts to pull the film apart and reduce ρ^s even further. The dispersion relationship (13) also indicates that, unlike Rayleigh’s instability of a cylindrical jet, the most destabilizing are short-wave disturbances.

In order to illustrate how the Marangoni effect incorporated in (11)–(12) leads to the rupture of a free film in the nonlinear regime consider the evolution of the film that after an external finite-amplitude disturbance makes $\rho^s \equiv \hat{\rho}^s$, where $\hat{\rho}^s$ is in the unstable zone ($\lambda \geq 0$). It is instructive to look at the borderline case where $\lambda = 0$, i.e. $\hat{\rho}^s = a/(2b)$.

Let us consider a small disturbance $\rho^s = a/(2b)[1 - A \exp(-x^2/l^2)]$, where A is the relative amplitude and l is the width of the disturbance.

Fig. 2 shows the film’s profile at various times obtained via numerical integration of (11) and (12) for $A = 0.1$ and $l = 0.5$. As one can see, the initial disturbance of the surface tension indeed leads to the film’s thinning due to the Marangoni effect. In the thin-film approximation $p = -2\partial u/\partial x$ and, as t increases, the pressure in the minimal cross-section goes through a global minimum (Fig. 3) suggesting a transition to a new dynamic regime. The essence of this regime follows from Fig. 2, which shows a gradual formation of a distinct structure consisting of a departing main body of fluid (macrofilm) and a vanishing residual film of an increasingly uniform thickness. Given that the (almost constant) thickness of the macrofilm and the (infinitesimal) thickness of the residual film are separated in scale, the late stage of the evolution of the residual film must take place in a self-similar regime. This regime is given by

$$u = x(t - t_0)^{-1}, \quad (h, \rho^s, \sigma) = (H, R, aR)(t - t_0)^{-1},$$

where t_0 , H and R are constants determined by the preceding evolution of the film. In this solution, both terms on the right-hand side of (11) become separately zero thus indicating that the process is driven by the departing ends of the macroscopic film whereas the residual film simply follows and gets thinner accordingly. Thus, there is no effect of the residual film on the departing ends of the macrofilm and hence of these ends on each other. In effect, this is what ‘rupture’ means in dynamic terms.

Since the thinning of the residual film does not lead to singularities in the solution, in practice, as one computes the global flow numerically, the residual film can be neglected once its thickness becomes smaller than the spatial resolution of the code.

It is noteworthy that, physically, the microscopic evolution of the film that follows after the opposite interfacial layers ‘touch’ is a natural continuation of the mechanism described above. Indeed, ‘touching’ of the opposite interfaces means that each of them is no longer separating two bulk phases, and it is this position between the bulk phases (associated

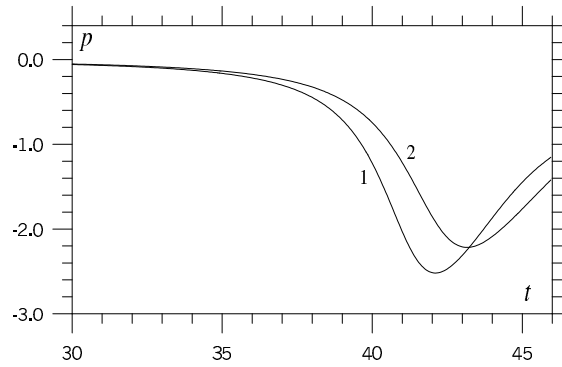


Figure 3: The pressure in the minimal cross-section vs time for $l = 0.5$ (curve 1) and $l = 0.7$ (curve 2).

with asymmetry of intermolecular forces acting on the interfacial layer) that gives rise to the surface tension. Hence, ‘touching’ interfaces lose their surface tensions at the point of contact and, given that in the remaining parts of the film the surface tension is still nonzero, the film is pulled apart by the surface-tension gradient. This final ‘microscopic rupture’ is physically the same as the macroscopic process described in the present paper.

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