



## Diffusion-limited evaporation of thin polar liquid films

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**Abstract.** The stability of evaporating very thin films of a polar liquid is investigated. The microscopic interaction with the substrate and capillarity are taken into account in a lubrication equation. The stability of a flat interface is studied when evaporation is limited by the diffusion of the vapour in the gas phase. The evaporation rate is computed and evaporation is shown to be stabilizing. A stability phase diagram is obtained. A weakly nonlinear analysis leads to a film-thickness amplitude equation that is non local in space. Physical consequences of the results are eventually discussed.

**Key words:** evaporation, linear stability, lubrication, non-local amplitude equation, spinodal decomposition, thin films

### 1. Introduction

The practical importance of thin liquid films and the numerous fundamental questions they raise has stimulated many experimental and theoretical studies (*e.g.*, see [1]). In particular, the evaporation of thin films is of interest in drying technologies, and many instabilities driven by evaporation are still unexplained. For instance, evaporation of droplets leads (through Marangoni effects) to destabilizing surface tension gradients near the contact line: Redon *et al.* [2], Poulard *et al.* [3] observed the contact line to become wavy, while Kavehpour *et al.* [4] measured drop-height waves. Marangoni instabilities can also result from the evaporation of a solute as shown by Hosoi and Bush [5] who re-examined the experiment of Fournier *et al.* [6]. Their analysis, as that of O'Brien [7] for a different geometry, assumed a simple form for the rate of evaporation of the solute. However, when there is no air convection, vapour diffuses through air and the evaporation is diffusion limited as has been shown by Deegan *et al.* [8] for pinned evaporating water droplets.

Evaporation of very thin films is even more complicated as they can interact with the substrate through van der Waals forces and electrostatic forces. Experiments on evaporating thin films of water were performed by Elbaum and Lipson [9], who observed the nucleation of thin patches in thicker films. The stability of these thin films has been studied theoretically by Burelbach *et al.* [10], Samid-Merzel *et al.* [11] and Lyushnin *et al.* [12]. They assumed the rate of evaporation to be proportional to the difference of chemical potential between the liquid and its vapour, and neglected diffusion of vapour in the gas phase. In contrast, we focus here on the evaporation of very thin liquid films of polar liquids in the case where the diffusion of vapour is important. In Section 2, we formulate general equations describing the film evolution and we simplify them when evaporation is diffusion limited. In Section 3, we solve the diffusion problem for a nearly flat film. In Section 4, we study the linear and the

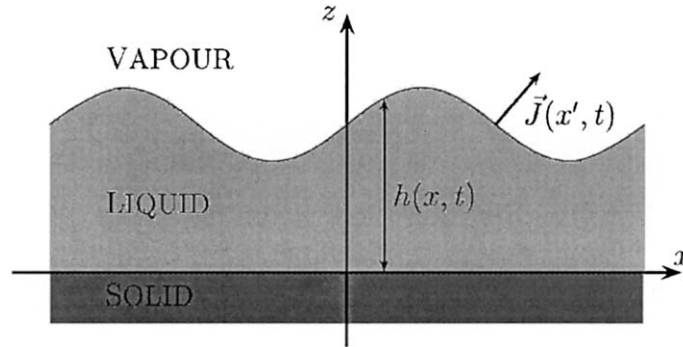


Figure 1. Model geometry: an evaporating thin liquid film over a solid substrate. The position of the interface with the gas is defined by  $h(x, t)$  and the rate of evaporation is  $J$ .

weakly nonlinear stability of a flat film. In the last section, we conclude by discussing the consequences of our results.

## 2. The model

### 2.1. SITUATION OF INTEREST

Our aim is to provide a theoretical description of evaporating thin films of polar liquids when molecular forces are important, and to account for the diffusive dynamics of the vapour in the surrounding gas phase. This situation is illustrated for instance by the experiments of Elbaum and Lipson [9]: water films of typical thickness  $h_0 \simeq 10$  nm evaporating in a chamber of millimetric size ( $x_0 \simeq 1$  mm); evaporation leads to a decrease in thickness at a velocity of order  $v_e \simeq 1$  nm/s.

We consider the dynamics of a two-dimensional bi-layered liquid-gas system over a solid substrate (Figure 1). A two-dimensional geometry is not a restriction for the present linear and weakly non-linear study: *a priori* all horizontal directions are equivalent, but one of them is selected at the growth of the instability (when the system is unstable). The polar liquid exchanges mass with its vapour which may diffuse in the gas phase. The gas phase is not saturated by the vapour, which drives evaporation. The state of the system is determined by the height  $h(x, t)$  of the interface and the concentration  $c(x, z, t)$  of vapour in the gas phase (both are functions of space and time). In the following, we restrict our analysis to the long wavelength limit where the typical height  $h_0$  is much smaller than the typical horizontal scale  $x_0$ . We write the equations describing the liquid phase, the gas phase and then the proper boundary conditions.

### 2.2. THE LIQUID FILM

The long wavelength limit leads to the usual lubrication equation. Here, the film is thin enough to interact with the substrate. Van der Waals and electrostatic forces (in the case of a polar liquid) give a correction called the disjoining pressure  $P(h)$  to the capillary pressure (see *e.g.* [13]). For a non-polar liquid which wets the substrate,  $P(h)$  is an increasing function of  $h$  as van der Waals forces are attractive. Electrostatic forces are usually repulsive. Thus, the interplay between the two forces can result in a disjoining pressure that is a non-monotonic function of the film thickness (Figure 2). One expects thicknesses corresponding to decreasing

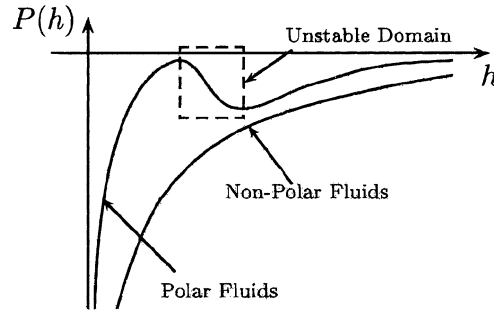


Figure 2. Disjoining pressure: additional pressure for a thin film interacting with a substrate, as a function of the film thickness. For a polar fluid  $P(h)$  may become non monotonic, which suggests an instability.

disjoining pressure to be unstable. The corresponding phenomenon in three dimensions is the spinodal decomposition of a fluid, that is the demixing into two distinct phases (gas and liquid) at the limit of metastability. We will consider the vicinity of a thickness  $h_0$  in the unstable region and linear approximation  $P(h) = P(h_0) - \alpha(h - h_0)$ , ( $\alpha \simeq 10^{11}$  N/m<sup>4</sup> for water, [11]). The exact form is given in [13], but our formulation is very general and could be applied if other microscopic forces act on the liquid, the physics giving the value of the coefficient  $\alpha$ . Gravity is negligible as the thickness  $h_0$  is microscopic and thus much smaller than the capillary length. The liquid has a viscosity  $\mu$  ( $10^{-3}$  Pa.s for water), a density  $\rho$  (number of particles per unit volume) and the surface tension of the liquid-gas interface is  $\gamma$  (70 mN/m for water). The lubrication equation then reads

$$\frac{\partial h}{\partial t} + \frac{1}{\mu} \frac{\partial}{\partial x} \left\{ \frac{h^3}{3} \left( \frac{\partial}{\partial x} \left( \gamma \frac{\partial^2 h}{\partial x^2} \right) + \alpha \frac{\partial h}{\partial x} \right) \right\} = -\frac{J}{\rho}. \quad (1)$$

$J$  is the liquid rate of evaporation at the interface (number of evaporating particles per unit surface and unit time).

Here we have neglected temperature fluctuations. If  $\kappa = 0.6$  kg m/K/s<sup>3</sup> is the thermal conductivity of water and  $L = 2.4 \times 10^6$  J/kg its vaporization latent heat, then the temperature gradient  $\Delta T/h$  is given by  $\kappa \Delta T/h = LJ_0$ , hence a very small temperature fluctuation  $\Delta T \simeq 4 \times 10^{-8}$  K. Thus we may safely neglect Marangoni effects. Moreover, evaporation is very slow, so that it is reasonable not to take into account vapour thrust.

### 2.3. THE VAPOUR

Vapour diffuses in the gas phase; the diffusion coefficient is  $D \simeq 10^{-5}$  m<sup>2</sup>/s. If there is convection in the gas, the convective velocity  $v_C$  has to be compared to the diffusive one  $v_D = D/x_0 \simeq 1$  cm/s. From the Stokes equations, the scale of  $v_C$  can be estimated as  $v_C \simeq g \delta \rho x_0^2 / \eta_g$ ,  $g$  being the gravity acceleration,  $\delta \rho \simeq DJ_0 x_0 \simeq 10^{-12}$  kg/m<sup>3</sup> the variation in vapour density and  $\eta_g \simeq 10^{-5}$  Pa/s the gas viscosity, leading to  $v_C \simeq 10^{-11}$  m/s  $\ll v_D$  so convection is negligible. Moreover, as the evaporation velocity  $v_e$  is very small compared to  $v_D$ , we consider the limit of quasi-static diffusion. Hence the vapour concentration  $c(x, z, t)$  (number of particles per unit volume in the gas phase) is a harmonic function:

$$\Delta c = 0, \quad (2)$$

$\Delta = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial z^2}$  being the 2D Laplacian operator. The gas phase is not saturated by the vapour. This condition is enforced by a constant diffusion rate at infinity

$$\frac{\partial c}{\partial z} \sim -\frac{J_0}{D}, \quad z \rightarrow +\infty. \quad (3)$$

At large length scales, the film is flat so the mass flux  $J(z \gg h_0)$  is vertical and does not depend on  $x$ . The boundary condition at the interface is discussed hereafter.

#### 2.4. THE INTERFACE

The rate of transfer of particles through the interface is proportional to the difference between the chemical potential of the vapour  $\mu_v$  and that of the liquid  $\mu_l$  (as given by the kinetic theory of gases, see [10]) and to the normal gradient of the vapour concentration at the interface:

$$\beta(\mu_l - \mu_v) = -\frac{D}{\rho} \frac{\partial c}{\partial n}. \quad (4)$$

$\beta \simeq 3 \times 10^{25}$  s/kg/m is a parameter which can be estimated from the kinetic theory of gases. Let  $\delta\mu \simeq 4 \times 10^{-21}$  J be the typical magnitude of the chemical potentials difference. The vapour concentration is of order  $c_0 \simeq 3 \times 10^{25}$  m<sup>-3</sup>. Using  $\mu_l = \delta\mu\tilde{\mu}_l$ ,  $\mu_v = \delta\mu\tilde{\mu}_v$  and  $\partial c/\partial n = c_0/h_0(\partial/\partial\tilde{n})\tilde{c}$ , the non-dimensional form of Equation (4) is

$$\mathcal{E}(\tilde{\mu}_l - \tilde{\mu}_v) = -\frac{\partial\tilde{c}}{\partial\tilde{n}}, \quad \mathcal{E} = \frac{\rho\beta h_0\delta\mu}{Dc_0}.$$

In references [10, 12, 11], diffusion of vapour was neglected. This corresponds to  $\mathcal{E} \ll 1$ , hence  $\partial c/\partial n = 0$  and the evaporation rate is  $J = \beta(\mu_l - \mu_v)$ . Using the typical values given above, one obtains  $\mathcal{E} \simeq 10^5$ , so we investigate the opposite case for which  $\mathcal{E} \gg 1$  and where evaporation is limited by diffusion of the vapour in the gas phase. In this limit, the chemical potentials are equal  $\mu_l = \mu_v$ . Using references [13, 11],  $\mu_v = k_B T \log(c/c_0)$ ,  $k_B$  being the Boltzmann constant and  $T$  the temperature, while  $\mu_l = -(\alpha h + \gamma \partial^2 h/\partial x^2)/\rho$ ,  $\rho$  being the liquid density. We consider here the limit such that  $(\alpha h + \gamma \partial^2 h/\partial x^2)/(\rho k_B T) \simeq 10^{-5} \ll 1$ , *i.e.*, the variations in  $c$  are small with respect to  $c_0$ , so that the boundary condition the vapour concentration at the interface becomes

$$c = c_0 \quad z = h(x, t). \quad (5)$$

Thus the Laplacian problem for the vapour concentration is well-posed. More-over, the evaporation rate is given by

$$J = -D \frac{\partial c}{\partial n}, \quad z = h(x, t). \quad (6)$$

#### 2.5. NON-DIMENSIONAL EQUATIONS

We use  $h_0$  as unit of length,  $h_0\rho/J_0$  as unit of time and  $J_0 h_0/D$  as unit of vapour concentration. Keeping the same notations for the non dimensional quantities as for their physical counterparts, we make the substitutions

$$h \rightarrow h_0 h, \quad x \rightarrow h_0 x, \quad t \rightarrow (h_0\rho/J_0)t, \quad c \rightarrow c_0 + (J_0 h_0/D)c, \quad J \rightarrow J_0 J, \quad (7)$$

in the lubrication equation, the Laplace equation and the boundary conditions. First, the lubrication equation (1) becomes

$$\frac{\partial h}{\partial t} + \frac{1}{\text{Ca}} \frac{\partial}{\partial x} \left( \frac{h^3}{3} \frac{\partial^3 h}{\partial x^3} \right) + \Pi \frac{\partial}{\partial x} \left( \frac{h^3}{3} \frac{\partial h}{\partial x} \right) = \frac{\partial c}{\partial n}(z = h(x, t), t) = -J. \quad (8)$$

Ca is the capillary number

$$\text{Ca} = \frac{\mu J_0}{\rho \gamma} \quad (9)$$

and  $\Pi$  is the van der Waals number

$$\Pi = \frac{\alpha \rho h_0^2}{\mu J_0}, \quad (10)$$

which measures the importance of microscopic forces. Their typical values are respectively  $\text{Ca} \simeq 10^{-11}$  and  $\Pi \simeq 10^7$ .

The reduced vapour concentration is the solution of the following Laplacian problem

$$\Delta c = 0, \quad z > h(x, t), \quad c(h(x, t), t) = 0, \quad \frac{\partial c}{\partial z}(z = +\infty, t) = -1, \quad (11)$$

which is solved in the next section.

### 3. The Laplacian problem for the vapour concentration

In this section, we show how to solve the Laplace problem (11) and compute the evaporation rate for a nearly flat interface. The lubrication equation (1) is obtained as an approximation of the Stokes equations to order three in the height profile  $h$  (see *e.g.* the asymptotic derivation in [1]). So we compute the evaporation rate to order 3 in the height perturbation. For other applications, computation to higher orders is possible along the same lines.

#### 3.1. THE VAPOUR CONCENTRATION

We formally rewrite the Laplacian problem (11) as

$$\Delta c(x, z) = 0, \quad z > \epsilon h(x), \quad c(\epsilon h(x), t) = 0, \quad \frac{\partial c}{\partial z}(x, z = +\infty) = -1. \quad (12)$$

$\epsilon$  is a formal small parameter for the expansion in powers of  $h(x, t)$ . We assume the form

$$c = c_0 + \epsilon c_1 + \epsilon^2 c_2 + \dots \quad (13)$$

for the field  $c$ , each  $c_n$  being a harmonic function. At order 0, the solution is simply linear:

$$c_0 = -z. \quad (14)$$

The boundary condition at the interface reads

$$0 = \sum_{n=0}^{+\infty} \frac{\epsilon^n h(x)^n}{n!} \frac{\partial^n c}{\partial z^n}(x, 0),$$

so that, up to order 3 in  $\epsilon$ ,

$$\begin{aligned}
0 = & c_0(x, 0) + \epsilon \left\{ c_1(x, 0) + h(x) \frac{\partial x_0}{\partial z}(x, 0) \right\} \\
& + \epsilon^2 \left\{ c_2(x, 0) + h(x) \frac{\partial c_1}{\partial z}(x, 0) + \frac{h(x)^2}{2} \frac{\partial^2 c_0}{\partial z^2}(x, 0) \right\} \\
& + \epsilon^3 \left\{ c_3(x, 0) + h(x) \frac{\partial c_2}{\partial z}(x, 0) + \frac{h(x)^2}{2} \frac{\partial^2 c_1}{\partial z^2}(x, 0) + \frac{h(x)^3}{6} \frac{\partial^3 c_0}{\partial z^3}(x, 0) \right\} \\
& + \dots
\end{aligned} \tag{15}$$

Now the problem (12) consists of finding the harmonic functions  $c_n$ , with  $n = 1, 2, 3 \dots$  which satisfy  $\partial c / \partial z(x, +\infty) = 0$  and the order  $n$  of the boundary condition (15) which is expressed at a flat boundary  $z = 0$ .

*Order  $\epsilon^1$ :* The boundary condition (15) gives  $c_1(x, 0) = h(x)$ . A Fourier decomposition leads directly to

$$c_1(x, z) = \int dk \mathcal{F}[h](k) e^{ikx - |k|z} = \mathcal{F}^{-1}(e^{-|k|z} \mathcal{F}[h]). \tag{16}$$

The  $x$ -Fourier transform of a function  $f(x)$  is defined as

$$\mathcal{F}[f](k) = \frac{1}{2\pi} \int dx f(x) e^{-ikx}.$$

*Order  $\epsilon^2$ :* The boundary condition (15) is rewritten as

$$c_2(x, 0) = -h(x) \frac{\partial c_1}{\partial z}(x, 0) = \mathcal{F}^{-1}(\mathcal{F}[h]) \mathcal{F}^{-1}(|k| \mathcal{F}[h])$$

Introducing convolutions (denoted as  $*$ ), this leads to

$$c_2(x, z) = \mathcal{F}^{-1}(e^{-|k|z} \{ \mathcal{F}[h] * (|k| \mathcal{F}[h]) \}). \tag{17}$$

*Order  $\epsilon^3$ :* The boundary condition (15) is rewritten as

$$c_3(x, 0) = h(x) \mathcal{F}^{-1}(|k| \{ \mathcal{F}[h] * (|k| \mathcal{F}[h]) \}) + \frac{h(x)^2}{2} \frac{d^2 h}{dx^2}(x).$$

so that, using Fourier transform and convolutions, we obtain

$$\begin{aligned}
c_3(x, z) = & \mathcal{F}^{-1}(e^{-|k|z} \{ \mathcal{F}[h] * (|k| \{ \mathcal{F}[h] * (|k| \mathcal{F}[h]) \}) \}) \\
& + \frac{1}{2} \mathcal{F}^{-1} \left( e^{-|k|z} \left\{ \mathcal{F} \left[ h^2 \frac{d^2 h}{dx^2} \right] \right\} \right).
\end{aligned} \tag{18}$$

Thus we have found the concentration of vapour up to order 3 in the height.

### 3.2. THE EVAPORATION RATE

The evaporation rate is given by

$$J = \|\nabla c\|_{z=\epsilon h(x)} = \sqrt{\left( \frac{\partial c}{\partial x}(x, \epsilon h(x)) \right)^2 + \left( \frac{\partial c}{\partial z}(x, \epsilon h(x)) \right)^2}. \tag{19}$$

$c$  was computed in the previous section. The expansion in powers of  $\epsilon$  is similar to that in Equation (15). The calculations are done with a substantial use of the property

$$\mathcal{F}^{-1}(|k|\mathcal{F}[f]) = -\frac{d}{dx}\mathcal{H}[f],$$

the Hilbert transform (see appendix A) of a function  $f$  being defined as

$$\mathcal{H}[f](x) = \frac{1}{\pi} \lim_{\substack{\epsilon \rightarrow 0^+ \\ X \rightarrow +\infty}} \int_{\epsilon < |x-x'| < X} dx' \frac{f(x')}{x' - x}$$

where Cauchy principal values are taken for the integral.

Combining all the results and setting  $\epsilon = 1$  leads to the following expression for the evaporation rate.

$$\begin{aligned} J = & 1 - \frac{d\mathcal{H}[h]}{dx} + \left\{ \frac{1}{2} \left( \frac{dh}{dx} \right)^2 + \frac{d^2h}{dx^2}h + \frac{d}{dx} \mathcal{H} \left( h \frac{d\mathcal{H}[h]}{dx} \right) \right\} \\ & + \left\{ \frac{1}{2} \frac{d\mathcal{H}[h]}{dx} \left( \frac{dh}{dx} \right)^2 - \frac{1}{2} \frac{d^2}{dx^2} \left( \frac{d\mathcal{H}[h]}{dx} h^2 \right) - 2 \frac{dh}{dx} \frac{d^2\mathcal{H}[h]}{dx^2} h \right. \\ & \left. - \frac{d}{dx} \mathcal{H} \left( h \frac{d}{dx} \mathcal{H} \left( h \frac{d\mathcal{H}[h]}{dx} \right) \right) - \frac{1}{2} \frac{d}{dx} \mathcal{H} \left[ h^2 \frac{d^2h}{dx^2} \right] \right\} \\ & + O(h^4). \end{aligned} \quad (20)$$

This equation combined with Equation (8) gives an integro-partial-differential equation for the evolution of the film thickness  $h$ . This is not surprising for a free-boundary problem with a Laplacian or a diffusion field.

## 4. Stability of a film of uniform thickness

### 4.1. LINEAR STABILITY

Equations (8–11) have as solution for the film thickness  $h(x, t) = 1 - t$ . As this base state is non-stationary, linearization of the equations gives a non-autonomous PDE, so that standard linear stability (modal) analysis should not apply. For simplicity, we assume from now on that the base state is  $h(x, t) = 1$ , which amounts to adding a volume source  $\rho J_0$  to Equation (1), as this source compensates exactly for the loss of mass through evaporation. It also amounts to a stability study of the time-dependant base state  $h(x, t) = 1 - t$  in the frozen frame.

We set  $h(x, t) \rightarrow 1 + h(x, t)$  in (8,20). The linear part of the evolution operator for  $h$  is easily computed as

$$L = \frac{\partial}{\partial t} + \frac{1}{3\text{Ca}} \frac{\partial^4}{\partial x^4} + \frac{1}{3}\Pi \frac{\partial^2}{\partial x^2} - \frac{\partial}{\partial x} \mathcal{H}. \quad (21)$$

This operator has eigenmodes of growth rate  $\Omega$  and wavenumber  $k$  :  $h(x, t) = A \exp(\Omega t + ikx) + \text{c.c.}$ , such that

$$\Omega(k) = -\frac{1}{3\text{Ca}}k^4 + \frac{\Pi}{3}k^2 - |k|. \quad (22)$$

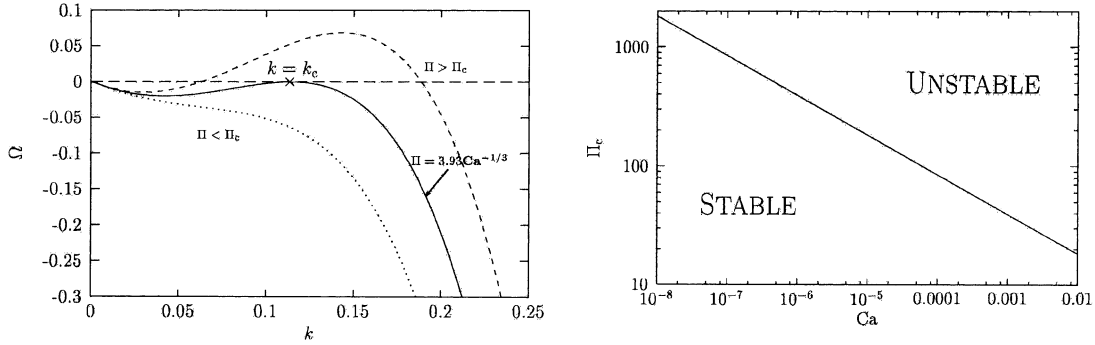


Figure 3. Top: growth rate  $\Omega(k)$  of perturbations of wavelength  $k$ , for a capillary number  $\text{Ca} = 10^{-3}$  and three values of the van der Waals number  $n$ . Bottom: stability diagram of a flat film.

This shows that the interaction with the substrate is destabilizing as could be expected when considering the decreasing part of the disjoining pressure (see Figure 3), whereas both evaporation and capillarity are stabilizing (first and last term of right-hand side of the equation). The electrostatic analog of the Laplace problem (11) helps understanding why evaporation is stabilizing: the electrostatic potential (the concentration) is constant at the surface of a conductor; the electric field (the evaporation rate) is larger at bumps; so evaporation decreases the height of bumps. Typical growth rates  $\Omega(k)$  are shown in Figure 3. The limit of stability is reached when there is one (and only one) marginally stable mode ( $\Omega(k = k_c) = 0$  and  $\Omega'(k = k_c) = 0$ ), so that at the instability onset (subscripts c)

$$\text{Ca}_c \Pi_c^3 = 243/4, \quad k_c = \sqrt{\frac{\text{Ca}_c \Pi_c}{3}}. \quad (23)$$

The uniform film is unstable when  $\Pi > \Pi_c(\text{Ca}_c)$  or when  $\text{Ca} > \text{Ca}_c(\Pi_c)$ . The corresponding stability diagram is shown in Figure 3. With the values of the capillary and Van der Waals numbers given earlier, the film is unstable; the resulting pattern has a wavelength of the order of  $10 \mu\text{m}$ , as observed in [9]. This stability analysis suggests a pattern of wavenumber  $k_c$ . However, a nonlinear study is required to predict the patterns when the flat film is unstable.

#### 4.2. WEAKLY NON LINEAR ANALYSIS

We now proceed to the weakly nonlinear analysis to find an amplitude equation for  $h(x, t)$ . We use a multi-scale expansion which is valid when the spatial Fourier spectrum of  $h(x, t)$  is concentrated around  $k_c$  (see Manneville [15, Chapter 8]). We look for an equation of evolution for the slowly varying function  $A(X, T)$  such that  $h(x, t) = A(X, T) \exp(ik_c x) + \text{c.c.}$  (c.c. stands for the complex conjugate of the preceding term). Formally, we use  $\epsilon$  as an expansion parameter (this parameter has nothing to do with the one used in Section 3). We assume that  $h$  is a function of both the fast scales  $x, t$  and the slow scales  $X = \epsilon x, T = \epsilon^2 t$ . This choice for the slow scales is the natural one given that  $\Omega(k)$  is maximum at  $k_c$ . We consider the neighbourhood of the marginal stability and we rescale the control parameter as

$$\Omega(k_c) = \epsilon^2 \omega(k_c).$$

From the chain rule for differentiation we must make the replacements

$$\partial_x \rightarrow \partial_x + \epsilon \partial_X, \quad \partial_t \rightarrow \partial_t + \epsilon^2 \partial_T.$$



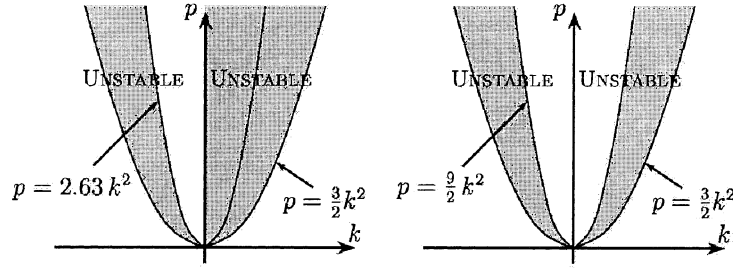


Figure 4. Stability diagram of the stationary pattern (control parameter  $p$  vs. wavenumber  $Q$ ) as deduced from Equation (26): with the nonlocal term (left) and without (right). The flat film is stable only below the grey area. The pattern with wavenumber  $k_c + Q$  is stable only above the grey area. None of them is stable in the grey area.

We also assume that  $h$  can be expanded as

$$h(x, t) = \epsilon h_1(x, t) + \epsilon^2 h_2(x, t) + \dots$$

The procedure to obtain the amplitude equation (equation for  $A(X, T)$ ) is quite standard and is detailed in appendix B. However the present case has the peculiarity that the expansion must be pursued up to order 6 as  $h_1$  is found to vanish. This is due to the coupling between the evaporation rate and the  $k = 0$  eigenmodes of  $L_c$ . In the limit  $k_c \ll 1$  which is consistent with lubrication theory, and after the rescaling  $X \rightarrow X/k_c$  and  $T \rightarrow T/k_c$ , the amplitude equation reads

$$\partial_T A = pA - 6|A|^2 A + \frac{3}{2} \partial_{XX} A - 2i \partial_{XXX} A - \frac{1}{2} \partial_{XXXX} A, \quad (24)$$

the control parameter being

$$p = \frac{1}{2} \frac{\text{Ca} - \text{Ca}_c}{\text{Ca}_c} + \frac{9}{2} \frac{\Pi - \Pi_c}{\Pi_c}. \quad (25)$$

The solution  $A = 0$  of the amplitude equation becomes unstable when  $p > 0$  (which is consistent with the linear stability). When  $p > 0$ , there is a family of stationary solutions indexed by the wavenumber  $Q$ :  $A(X, T) = A_0 \exp(iQX)$ ,  $A_0$  being given by  $p = 6|A_0|^2 + 3/2 Q^2 + 2Q^3 + 1/2 Q^4$ . They correspond to a stationary pattern with thickness fluctuation  $h(x, t) = A_0 \exp\{i(k_c + \epsilon Q)x\}$ , which is modulated around the critical wavenumber  $k_c$ . Thus, as the prefactor of  $|A|^2 A$  is negative, the transition from the flat state ( $A = 0$ ) to a state with height fluctuations is a supercritical (continuous) pitchfork bifurcation.

#### 4.3. NON-LOCALITIES AND SECONDARY INSTABILITIES

We have simplified the amplitude equation (B11, Appendix B) in the limit  $k_c \rightarrow 0$  to obtain (24); at finite  $k_c$ , unusually it is an integro-differential equation which is well posed only if  $A(X, T)$  vanishes quickly at  $|X| = +\infty$ . In order to illustrate the role the non local terms, we keep the simplest one, that is  $3i\mathcal{H}[|A|^2]A$ . This term does not affect the stationary states nor the nature of the bifurcation as  $\mathcal{H}[|A|^2] = 0$ . We also drop, for simplicity, the third and fourth spatial derivatives of the amplitude (this amounts to an expansion at lowest order in the wavenumber and does not affect the nature of the secondary instabilities) so that we study the model equation:

$$\partial_T A = pA - 6|A|^2 A + \frac{3}{2} \partial_{XX} A + 3i\mathcal{H}(|A|^2)A. \quad (26)$$

It has  $A_0 \exp(iQX)$  as a stationary solution provided  $p = 6|A|^2 + 3/2Q^2$  (and so  $p > 3/2Q^2$ ).

We study the linear stability of the stationary pattern by perturbing it with a different wavenumber:

$$A(X, T) = A_0 e^{iQX} + (a e^{i(Q+q)X} + b e^{i(Q-q)X}) e^{sT}, \quad (27)$$

where  $s$  is the growth rate and  $q$  the reduced wavenumber of the perturbation. The two terms are needed in the perturbation because of the non linear coupling between modes:  $Q + Q - (Q + q) \rightarrow Q - q$ . Linearization of Equation (26) gives an equation for the perturbation growth rate

$$s^2 + (3Q^2 + 12A_0^2) s + 9/4A^4 + (18A_0^2 - 9q^2) Q^2 - 18A_0^2 Q|q| = 0. \quad (28)$$

This equation has two solutions. One is always negative. If the other is positive then the stationary pattern is unstable. Its sign is that of  $9/4Q^4 + (18A_0^2 - 9q^2)Q^2 - 18A_0^2 Q|q|$ . This way we obtain the stability diagram of the stationary pattern (Figure 4), which is very different with or without the non-local term. The corresponding secondary instability is usually called the Eckhaus instability (see [15]).

## 5. Conclusion

Very thin films of polar liquids may be unstable to fluctuations of the thickness when the disjoining pressure is a decreasing function of thickness. We studied this instability in the presence of diffusion limited evaporation and obtained a stability diagram. Expressing Equation (23) in terms of physical quantities, the instability criterium reads

$$\frac{\rho^2 \alpha^3 h_0^6}{\gamma \mu^2 J_0^2} \gtrsim 1, \quad (29)$$

$\alpha$  being the opposite of the derivative of the disjoining pressure with respect to the thickness,  $\gamma$  the liquid-gas surface tension,  $\mu$  the liquid viscosity,  $\rho$  its density,  $J_0$  the imposed vapour diffusion rate far from the liquid and  $h_0$  the typical thickness of the liquid film. Both evaporation and capillarity are always stabilizing. The instability can be driven by a decreasing disjoining pressure, which is the case for thin films (thickness in the range 1–100 nm) of polar liquids such as water. In particular, the numerical values of Elbaum and Lipson [9] lead to an instability of typical wavelength 10  $\mu\text{m}$  in agreement with their observations.

We derived an amplitude equation for the thickness fluctuations. It showed that the transition from the flat state to a periodically modulated thickness is continuous. In contrast with usual amplitude equations, it contains non-local terms. For instance, even with an integro-differential equation for the height as in the Rosensweig instability of ferrofluids, Friedrichs and Engel [14] found a local amplitude equation. These non-local terms are important when the amplitude varies spatially or for the stability of the stationary pattern. As an example, we showed that the classical Eckhaus instability may be dramatically changed.

Evaporation of thin films is more complex than it might appear, and many questions remain open. We have restricted our study to diffusion limited evaporation. Much more work is required to bridge the gap with the kinetically limited evaporation studied in [10–12]. It would also be interesting to further investigate the consequences of the non local terms.

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## Appendix A. The Hilbert transform

### A.1. DEFINITION AND BASIC PROPERTIES

We define the Hilbert transform with the usual conventions:

$$\mathcal{H}[f](x) = \frac{1}{\pi} \lim_{\substack{\epsilon \rightarrow 0^+ \\ X \rightarrow +\infty}} \int_{\epsilon < |x-x'| < X} dx' \frac{f(x')}{x' - x} \quad (\text{A1})$$

where we have taken the Cauchy principal value (symmetric limit) both at  $x$  and at  $\infty$ . The Hilbert transform has the property that  $\mathcal{H}^{-1} = -\mathcal{H}$ , except for constant functions for which the transform is zero ( $\mathcal{H}(\text{Cst}) = 0$ ). It is also easy to show that

$$\mathcal{F}^{-1}(|k|\mathcal{F}[f]) = -\frac{d}{dx}\mathcal{H}[f]. \quad (\text{A2})$$

### A.2. HILBERT TRANSFORM AND SLOW SPACE VARYING AMPLITUDE

In the weakly nonlinear analysis, we have to compute quantities of the form  $\mathcal{H}[A(\epsilon x)e^{ik_c x}]$ , with  $0 < \epsilon \ll 1$ . We show here that

$$\mathcal{H}[A(\epsilon x)e^{ik_c x}] = A(\epsilon x)\mathcal{H}[e^{ik_c x}], \quad (\text{A3})$$

is a good approximation for  $\epsilon$  sufficiently small (actually  $\epsilon < |k_c|$ ). This formula was first given without a validity criterium by Friedrichs and Engel [14]. The result is obvious if  $\epsilon = 0$ . Since  $A_\epsilon(x) = A(\epsilon X)$  varies significantly only for a variation of  $x$  of the order of  $1/\epsilon$ , the Fourier transform  $\mathcal{F}[A_\epsilon](k)$  of  $A_\epsilon$  must be negligible outside  $(-\epsilon, \epsilon)$ .

Let us first assume that the support of  $\mathcal{F}[A_\epsilon](k)$  is included in  $(-\epsilon, \epsilon)$  (*i.e.*, it vanishes outside). Then, using  $\mathcal{H}[e^{ikx}] = i \operatorname{sgn} k e^{ikx}$  ( $\operatorname{sgn} k = \pm 1$  if  $\pm k > 0$ ), we have

$$\mathcal{H}[A(\epsilon x)e^{ik_c x}] = ie^{ik_c x} \int_{-\epsilon}^{\epsilon} dk \mathcal{F}[A_\epsilon](k) \operatorname{sgn}(k + k_c) e^{ikx}.$$

Thus, (A3) is proved if  $\epsilon < |k_c|$ .

If  $\mathcal{F}[A_\epsilon](k)$  does not vanish outside of  $(-\epsilon, \epsilon)$ , one can show that, when  $\epsilon < |k_c|$ , the error for (A3) is of the order of  $\int_{1/\epsilon}^{\infty} \mathcal{F}[A](k) dk$ .

## Appendix B. Weakly nonlinear analysis

Here we detail the weakly nonlinear analysis outlined in Section 4.2. We consider the neighbourhood of the stability limit, so that we rescale the control parameter according to

$$\Omega(k_c) = \epsilon^2 \omega(k_c)$$

We start with Equations (8,20), assume that  $h$  is a function of  $x, X, t, T$  (fast and slow scales) and substitute the derivatives according to

$$\partial_x \rightarrow \partial_x + \epsilon \partial_X, \quad \partial_t \rightarrow \partial_t + \epsilon^2 \partial_T.$$

The height  $h$  is expanded as

$$h(x, t) = \epsilon h_1(x, t) + \epsilon^2 h_2(x, t) + \dots.$$

Equations (8,20) can be formally rewritten as

$$Lh = \mathcal{N}(h),$$

$L$  being the linear part of the evolution operator which is expanded as  $L = L_c + \epsilon L_1 + \epsilon^2 L_2 + \dots$ ,

$$L_c = \frac{1}{3\text{Ca}} \frac{\partial^4}{\partial x^4} + \frac{1}{3}\Pi \frac{\partial^2}{\partial x^2} - \frac{\partial}{\partial x} \mathcal{H}, \quad L_1 = \left\{ \frac{4}{3\text{Ca}} \frac{\partial^3}{\partial x^3} + \frac{2}{3}\Pi \frac{\partial}{\partial x} - \mathcal{H} \right\} \frac{\partial}{\partial X},$$

$$L_2 = -\omega(k_c) + \frac{\partial}{\partial t} + \left\{ \frac{2}{\text{Ca}} \frac{\partial^2}{\partial x^2} + \frac{1}{3}\Pi \right\} \frac{\partial^2}{\partial X^2},$$

$$L_3 = \frac{4}{3\text{Ca}} \frac{\partial}{\partial x} \frac{\partial^3}{\partial X^3}, \quad L_4 = \frac{1}{3\text{Ca}} \frac{\partial^4}{\partial X^4}.$$

We now proceed to the solution order by order.

*Order  $\epsilon^1$* : The equation is linear

$$L_c h_1 = 0. \tag{B1}$$

Since the null space of  $L_c$  also contains slow space varying height profiles (*i.e.*, functions of  $X$ ) the general solution is  $h_1 = (A_{11}(X, T)e^{ik_c x} + \text{c.c.}) + A_{10}(X, T)$ , where the  $k_c$  wavenumber is given by the linear stability analysis (Section 4.1).

*Order  $\epsilon^2$* : The equation has the form

$$L_c h_2 = -L_1 h_1 - \mathcal{N}^{(2)}(h_1). \tag{B2}$$

We find  $L_1 h_1 = -\partial_X \mathcal{H}[A_{10}]$  and, decomposing  $\mathcal{N}^{(2)}(h_1)$  into its Fourier modes  $(\mathcal{N}_{22}e^{ik_c x} + \text{c.c.}) + (\mathcal{N}_{21}e^{ik_c x} + \text{c.c.}) + \mathcal{N}_{20}$ ,

$$\mathcal{N}_{22} = \left\{ -2k_c^2 \Pi + \frac{2k_c^4}{\text{Ca}} + \frac{1}{2}k_c^2 \right\} A_{11}^2, \quad \mathcal{N}_{21} = \left\{ \frac{k_c^4}{\text{Ca}} - k_c^2 \Pi \right\} A_{11} A_{10}, \quad \mathcal{N}_{20} = -K_c^2 |A_{11}|^2.$$

The right-hand side must be orthogonal to the null space of  $L_c$  so that  $\mathcal{N}_{21} = 0$  and  $\partial_X \mathcal{H}[A_{10}] = -k_c^2 |A_{11}|^2$ . It implies  $h_1 = 0$ , thus  $L_c h_2 = 0$ . The solution to (B2) is then  $h_2 = (A_{21}(X, T)e^{ik_c x} + \text{c.c.}) + A_{20}(X, T)$ .

*Order  $\epsilon^3$* : Due to  $h_1 = 0$ , the equation does not contain nonlinear contributions

$$L_c h_3 = L_1 h_2. \tag{B3}$$

Again, the right-hand side has to be orthogonal to the null space of  $L_c$ , so that  $A_{20} = 0$ . Thus,  $h_3 = (A_{31}(X, T)e^{ik_c x} + \text{c.c.}) + A_{30}(X, T)$ . In contrast with standard weakly nonlinear studies [15], this order does not give the amplitude equation.

*Order  $\epsilon^4$* : The equation is

$$L_c h_4 = -L_1 h_3 - L_2 h_2 - \mathcal{N}^{(4)}(h_2), \tag{B4}$$

where

$$\mathcal{N}^{(4)}(h_2) = (\mathcal{N}_{42}e^{ik_c x} + \text{c.c.}) + \mathcal{N}_{40},$$

$$\mathcal{N}_{42} = \left\{ -2k_c^2 \Pi + \frac{2k_c^4}{\text{Ca}} + \frac{1}{2}k_c^2 \right\} A_{21}^2, \quad \mathcal{N}_{40} = -k_c^2 |A_{21}|^2.$$

The secular part of  $\mathcal{N}^{(4)}(h_2)$  vanishes since  $A_{20} = 0$ .

The right-hand side of Equation (B4) must be orthogonal to the null space of  $L_c$  so that

$$-\frac{\partial}{\partial X} \mathcal{H}[A_{30}] = k_c^2 |A_{21}|^2 \tag{B5}$$

$$\left( \frac{\partial}{\partial T} - \omega(k_c) + \left\{ \frac{1}{3}\Pi \frac{\partial^2}{\partial X^2} - \frac{2}{\text{Ca}} k_c^2 \right\} \frac{\partial^2}{\partial X^2} \right) A_{21} = 0. \tag{B6}$$

The solution to (B4) is

$$h_4 \left( A_{42}(X, T)e^{2ik_c x} + \text{c.c.} \right) + \left( A_{41}(X, T)e^{ik_c x} + \text{c.c.} \right) + A_{40}(X, T),$$

where

$$A_{42} = \frac{1}{\Omega(2k_c)} \left\{ -2k_c^2 \Pi + \frac{2k_c^4}{\text{Ca}} + \frac{1}{2}k_c^2 \right\} A_{21}^2.$$

Order  $\epsilon^5$ : The equation is

$$L_c h_5 = -L_1 h_4 - L_2 h_3 - L_3 h_2 - \mathcal{N}^{(5)}(h_2, h_3), \quad (\text{B7})$$

where

$$\mathcal{N}^{(5)}(h_2, h_3) = \mathcal{N}_{52} e^{2ik_c x} + \text{c.c.} + (\mathcal{N}_{51} e^{ik_c x} + \text{c.c.}) + \mathcal{N}_{50},$$

$$\mathcal{N}_{52} = \left( \frac{4k_c^4}{\text{Ca}} - 4\Pi k_c^2 + k_c^2 \right) A_{31} A_{21} + i \left( -\frac{8k_c^3}{\text{Ca}} + 4\Pi k_c - k_c \right) A_{21} \frac{\partial A_{21}}{\partial X}$$

$$\mathcal{N}_{51} = \left( -\Pi k_c^2 + \frac{k_c^4}{\text{Ca}} \right) A_{30} A_{21}$$

$$\mathcal{N}_{50} = -k_c^2 (\overline{A_{31}} A_{21} + \overline{A_{21}} A_{31}) + k_c \left( i \frac{\partial A_{21}}{\partial X} \overline{A_{21}} - i \frac{\partial \overline{A_{21}}}{\partial X} A_{21} \right).$$

The right-hand side of Equation (B7) must be orthogonal to the null space of  $L_c$  so that

$$\left( -\Pi k_c^2 + \frac{k_c^4}{\text{Ca}} \right) A_{30} A_{21} + \frac{4(i k_c)}{3\text{Ca}} \frac{\partial^3 A_{21}}{\partial X^3} + \left\{ \left( -\frac{2k_c^2}{\text{Ca}} + \frac{\Pi}{3} \right) \frac{\partial^2}{\partial X^2} - \omega(k_c) + \frac{\partial}{\partial T} \right\} A_{31} = 0, \quad (\text{B8})$$

$$\frac{\partial}{\partial X} \mathcal{H}[A_{40}] = A_{30} + \frac{\Pi}{3} \frac{\partial^2}{\partial X^2} A_{30} + \frac{\partial}{\partial T} A_{30} + \mathcal{N}_{50}. \quad (\text{B9})$$

Even if (B8) is nonlinear in  $A_{21}$  (see (B5)), it does not give the nature of the bifurcation. This is why we carry on computations to next order.

The solution at this order is

$$h_5 = (A_{52}(X, T)e^{2ik_c x} + \text{c.c.}) + (A_{51}(X, T)e^{ik_c x} + \text{c.c.}) + A_{50}(X, T),$$

where

$$A_{52} = \frac{1}{\Omega(2k_c)} \left( \mathcal{N}_{52} + i\Omega'(2k_c) \frac{\partial}{\partial X} A_{42} \right).$$

Order  $\epsilon^6$ : The equation has the form

$$L_c h_6 = -L_1 h_5 - L_2 h_4 - L_3 h_3 - L_4 h_2 - \mathcal{N}^{(6)}(h_2, h_3, h_4) \quad (\text{B10})$$

We only need the part of  $\mathcal{N}^{(6)}$  which has wavenumber  $k_c$ :

$$\begin{aligned} \mathcal{N}_{61} = & \left( -\Pi k_c^2 + \frac{k_c^4}{\text{Ca}} - \frac{7k_c^3}{2} \right) \overline{A_{21}} A_{21}^2 + \left( -\Pi k_c^2 + \frac{7k_c^4}{\text{Ca}} \right) A_{42} \overline{A_{21}} \\ & + i \left( 2\Pi k_c - \frac{4k_c^3}{\text{Ca}} \right) A_{30} \frac{\partial}{\partial X} A_{21} + \left( -\Pi k_c^2 + \frac{k_c^4}{\text{Ca}} \right) A_{31} A_{30} \\ & + i \left( 2\Pi k_c - \frac{k_c^3}{\text{Ca}} \right) A_{21} \frac{\partial}{\partial X} A_{30} + \left( \frac{k_c^4}{\text{Ca}} - \Pi k_c^2 \right) A_{40} A_{21} \\ & - k_c A_{21} \frac{\partial}{\partial X} \mathcal{H}[A_{30}]. \end{aligned}$$

After solving Equations (B5,B9) for  $A_{30}$  and  $A_{40}$ , we use the solvability condition that the right-hand side of (B10) is orthogonal to the null spare of  $L_c$  and we obtain an equation for  $A_{41}$ . Introducing

$$A = \epsilon A_{11} + \epsilon A_{21} + \epsilon A_{31} + \epsilon A_{41} + \dots,$$

The last equation for  $A_{41}$  can be resummed with Equations (B6,B8) for  $A_{21}$  and  $A_{31}$ . We finally obtain the amplitude equation  $A(X, T)$ :

$$\begin{aligned} & \left\{ \left( -\frac{2}{Ca} k_c^2 + \frac{\Pi}{3} \right) + i \left( \frac{4}{3Ca} k_c - \frac{\Pi}{3} \right) \frac{\partial}{\partial X} + \frac{1}{3Ca} \frac{\partial^2}{\partial X^2} \right\} \frac{\partial^2 A}{\partial X^2} \\ & - \Omega(k_c) A + \frac{\partial A}{\partial T} + \gamma |A|^2 A + i \left( 2\Pi k_c^3 - \frac{4k_c^5}{Ca} \right) \mathcal{H} \left[ \int |A|^2 \right] \frac{\partial}{\partial X} A \\ & - i \left\{ k_c^2 \left( 2\Pi k_c - \frac{k_c^3}{Ca} \right) - k_c \left( \frac{k_c^4}{Ca} - \Pi k_c^2 \right) \right\} \mathcal{H} \left[ |A|^2 \right] A \\ & + \left( \frac{k_c^4}{Ca} - \Pi k_c^2 \right) \left\{ k_c^2 \iint \left( -\Omega(k_c) + \frac{\partial}{\partial T} + \frac{\partial}{\partial X} \mathcal{H} \right) |A|^2 + 2ik_c \int \mathcal{H} \left[ A \frac{\partial \bar{A}}{\partial X} \right] \right\} A = 0, \end{aligned} \tag{B11}$$

where

$$\begin{aligned} \gamma = & \left( -\Pi k_c^2 + \frac{k_c^4}{Ca} - \frac{7k_c^3}{2} \right) + \frac{1}{\Omega(2k_c)} \left( -\Pi k_c^2 + \frac{7k_c^4}{Ca} \right) \left( -2k_c^2 \Pi + \frac{2k_c^4}{Ca} + \frac{1}{2} k_c^2 \right) \\ & + k_c^3 + \left( \frac{k_c^4}{Ca} - \Pi k_c^2 \right) \left( \frac{\Pi k_c^2}{3} - 2k_c \right). \end{aligned}$$

The simplification of the amplitude equation in the limit of small  $k_c$  is given in Section 4.2.

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