UvA-DARE (Digital Academic Repository)

Marangoni effect from density variations in apolar ultrathin films

Kaya, H.; Jérôme, B.; Colinet, P.

DOI

[10.1209/epl/i2005-10582-3](https://doi.org/10.1209/epl/i2005-10582-3)

Publication date

2006

Document Version

Final published version

Published in

Europhysics Letters

[Link to publication](#)

Citation for published version (APA):

Kaya, H., Jérôme, B., & Colinet, P. (2006). Marangoni effect from density variations in apolar ultrathin films. *Europhysics Letters*, 74(5), 861-867. <https://doi.org/10.1209/epl/i2005-10582-3>

General rights

It is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), other than for strictly personal, individual use, unless the work is under an open content license (like Creative Commons).

Disclaimer/Complaints regulations

If you believe that digital publication of certain material infringes any of your rights or (privacy) interests, please let the Library know, stating your reasons. In case of a legitimate complaint, the Library will make the material inaccessible and/or remove it from the website. Please Ask the Library: <https://uba.uva.nl/en/contact>, or a letter to: Library of the University of Amsterdam, Secretariat, Singel 425, 1012 WP Amsterdam, The Netherlands. You will be contacted as soon as possible.

Marangoni effect from density variations in apolar ultrathin films

H. KAYA^{1,2}, B. JÉRÔME^{1,3} and P. COLINET²

¹ *Complex Fluids, Van 't Hoff Institute for Molecular Sciences
University of Amsterdam - Nieuwe Achtergracht 166
1018 WV Amsterdam, The Netherlands*

² *Microgravity Research Center, Service Chimie Physique EP
Université Libre Bruxelles - Av. F. D. Roosevelt 50, 1050 Brussels, Belgium*

³ *Laboratoire de Physique de la Matière Condensée, Université Claude Bernard Lyon 1
et CNRS - Domaine Scientifique et la Doua, 69622 Villeurbanne Cedex, France*

received 11 August 2005; accepted in final form 30 March 2006

published online 26 April 2006

PACS. 68.15.+e – Liquid thin films.

PACS. 47.20.Ma – Interfacial instabilities (*e.g.*, Rayleigh-Taylor).

PACS. 68.03.Cd – Surface tension and related phenomena.

Abstract. – Recently it was demonstrated that the presence of density variations in thin films can induce interactions that cause destabilization and rupture of thin films. In apolar films the surface tension is also dependent on the film density, so that a lateral variation in film density creates a surface tension gradient, thus producing a Marangoni effect. We include this effect in the hydrodynamic equation governing the evolution of the film profile and perform an analysis of the stability of the film. In particular, inclusion of the Marangoni effect causes the characteristic length scale of the initial flat film instabilities to scale with the film thickness h_0 to a lower power (down to $n = 0.5$) than without this effect.

Introduction. – The stability of thin films deposited on solid substrates has been a subject of intense research the last years, owing to its practical importance in coatings, and to the more recent interest in using dewetting of thin films for controlled patterning of surfaces for nanotechnological applications [1]. The process by which a thin film may become instable and break up into a pattern of holes and droplets, has been attributed to two different mechanisms; nucleation and spinodal dewetting [2]. Recently, Wensink and Jérôme [3] proposed an alternative mechanism that resembles spinodal dewetting. Their idea was that confinement and restructuring of the molecules in the film creates density variations that in turn change the sign of the effective film-substrate interactions, thus leading to the dewetting of a film expected to be stable. This film rupture mechanism was suggested by experiments by Demirel and Jérôme on thin films of liquid crystalline glasses [4]. The theory was elaborated by Sharma *et al.* [5,6], who also found that density variations could stabilize otherwise unstable films. It was pointed out that the surface tension of apolar thin films is a function of film density [7] and accounted for this in the linear analysis of the film stability. However, the fact that a surface tension gradient will produce a Marangoni flow effect was not taken into account. This phenomenon is usually associated with concentration gradients in soap films [8] or with temperature gradients

in heated films [9,10]. In this work we theoretically investigate the effect of a Marangoni flow induced by density gradients (density-capillary effect) on the stability of a thin film.

Thin film evolution equation. – The film rests on a solid substrate describing the xy -plane, with $z = 0$ at the film-substrate interface. For an ultrathin film, the film aspect ratio $\epsilon = h_0/\lambda$ is small, with h_0 being the average film thickness and λ is a characteristic lateral length scale. This permits the application of the lubrication approximation to the Navier-Stokes equations (NSE), retaining only terms that are of order ϵ^0 [11]. The mass conservation equation for a compressible fluid reads $\partial_t \rho + \partial_x(\rho u) + \partial_y(\rho v) + \partial_z(\rho w) = 0$, where ρ is the local film density and u, v, w are the x, y, z velocity components of the film liquid, respectively. In the lubrication approximation, the Navier-Stokes momentum conservation equations reduce to

$$\mu \partial_z^2 u = \partial_x \Pi, \quad \mu \partial_z^2 v = \partial_y \Pi, \quad \partial_z \Pi = 0, \quad (1)$$

where μ is the film viscosity. The pressure Π acting on the film surface is the sum of the surface tension or capillary forces p and a disjoining pressure ϕ originating from the interactions acting on the film. To retain the capillary terms, it is necessary to take the the surface tension γ to be of order ϵ^{-3} [11]. The disjoining pressure is due to the net long-range van der Waals forces between the film and the substrate, giving $\phi = A/6\pi h^3$. The effective Hamaker constant $A = A_{LL} - A_{SL}$ is the difference between the liquid-liquid Hamaker constant $A_{LL} = C_{LL}\rho^2$ and the liquid-solid Hamaker constant $A_{SL} = C_{SL}\rho_S\rho$, where ρ_S is the density of the substrate. The constants C_{LL} and C_{SL} are related to the intermolecular interactions in the materials [7]. $A > 0$ implies an attractive interaction between the film and the substrate, leading to thinning and dewetting of the film, whereas $A < 0$ signifies a repulsive interaction, promoting wetting.

At the film-substrate interface, no-slip boundary conditions are imposed, so that $\mathbf{v} = (u, v, w) = 0$ at $z = 0$. At the free surface $z = h$ we impose the kinematic boundary condition $w = \partial_t h + u\partial_x h + v\partial_y h$ and normal and tangential stress balances. The normal stress balance reads in the lubrication approximation

$$p(z = h) = -\epsilon^3 \gamma \nabla^2 h, \quad (2)$$

where γ is the surface tension and h is the local film thickness.

In the presence of surface tension gradients the shear-stress balance reads [11]

$$\mu \partial_z u|_{z=h} = \epsilon \partial_x \gamma, \quad \mu \partial_z v|_{z=h} = \epsilon \partial_y \gamma. \quad (3)$$

The surface tension of an apolar liquid is related to the film density through [6,7]

$$\gamma(\rho) = \frac{A_{LLb}\rho^2}{24\pi d_0^2 \rho_b^2}, \quad (4)$$

where A_{LLb} is the Hamaker constant of the liquid at bulk density $\rho = \rho_b$, and d_0 is the cut-off distance for van der Waals forces, typically $d_0 = 0.15$ nm [6]. Assuming that the film density ρ is a function of h only [3,6], the surface tension gradient can be decomposed using the chain rule, so that $\partial_x \gamma = \partial_\rho \gamma \partial_h \rho \partial_x h$. When the film is not uniformly flat, so that $\partial_x h \neq 0$, a film density gradient $\partial_h \rho \neq 0$ will produce a gradient in surface tension, which in turn leads to a Marangoni flow [9,10,12,13].

Integrating the Navier-Stokes momentum equations (1) twice, applying the shear stress balances (3) and the no-slip conditions, the lateral velocities are obtained:

$$v_i = \left(\frac{z^2}{2} - zh \right) \frac{1}{\mu} \partial_i (\phi - \epsilon^3 \gamma \nabla^2 h) + \frac{z}{\mu} \epsilon \partial_i \gamma \quad (5)$$

with $i = x, y$. From the continuity equation and the kinematic boundary condition, assuming that the film is so thin that density gradients along the z -direction are negligible [12], an advection equation can be derived:

$$\partial_t (\rho h) + \nabla \cdot (\rho h \bar{\mathbf{v}}) = 0, \quad (6)$$

where $\bar{\mathbf{v}} = (\bar{v}_x, \bar{v}_y)$ are the cross-sectionally averaged components of the velocity field, $\bar{v}_i = \frac{1}{h} \int_0^h v_i dz$. Averaging the velocities (5) and inserting the results in (6) produce the evolution equation for the film surface profile $h(x, y, t)$:

$$\partial_t (\rho h) + \vec{\nabla} \cdot \left[\frac{\rho h^3}{3\mu} \vec{\nabla} (\varepsilon^3 \gamma \nabla^2 h - \phi) + \frac{\rho h^2}{2\mu} \varepsilon \partial_\rho \gamma \partial_h \rho \vec{\nabla} h \right] = 0. \quad (7)$$

The last term in the square brackets notifies the presence of an additional flow arising from the Marangoni effect.

Dimensionless equations. – In order to facilitate the discussion of the evolution equation (7), and also the numerical calculations, we bring the equation onto a dimensionless form. With h_0 being the a lengthscale representative for the film thickness, the dimensionless variables and quantities are: $H = h/h_0$, $(X, Y) = (x, y)\sqrt{A_{\text{LLb}}/2\pi\varepsilon^3\gamma_b h_0^4}$, $Z = z/h_0$, $\Sigma = \gamma/\gamma_b$, $\Gamma = \rho/\rho_b$, $T = tA_{\text{LLb}}^2/3\mu(2\pi)^2\gamma_b h_0^5$, and $\Phi = \phi(2\pi h_0^3/A_{\text{LLb}})$. Here, A_{LLb} and γ_b are the Hamaker constant and the surface tension of the liquid at bulk density $\rho = \rho_b$. With these rescalings, the evolution equation becomes

$$\partial_T (\Gamma H) + \vec{\nabla} \cdot \left[\Gamma H^3 \vec{\nabla} (\Sigma \nabla^2 H - \Phi) + \text{Ma} \Gamma H^2 \partial_\Gamma \Sigma \partial_H \Gamma \vec{\nabla} H \right] = 0, \quad (8)$$

with the dimensionless disjoining pressure given by

$$\Phi = \frac{\Gamma^2 - \text{Wa} \Gamma}{3H^3}. \quad (9)$$

The dimensionless surface tension and density are related by $\Sigma = \Gamma^2$. The dimensionless Marangoni and van der Waals numbers read

$$\text{Ma} = \frac{3\pi\varepsilon\gamma_b h_0^2}{A_{\text{LLb}}}, \quad \text{Wa} = \frac{A_{\text{SLb}}}{A_{\text{LLb}}}. \quad (10)$$

In the absence of density fluctuations, the film is stable if $\text{Wa} \geq 1$, and unstable if $\text{Wa} < 1$. $\text{Wa} > 0$ and $\text{Ma} > 0$ always apply. Estimating the lateral length scale λ by balancing vdW forces and the surface tension renders $\varepsilon = \left(\hat{A}/16\pi^3\gamma_b h^2 \right)^{1/2}$, where $\hat{A}$ is a rather small Hamaker constant, to account for the modifications caused by the density variations. Inserting for ε in (10) produces $\text{Ma} = \sqrt{\hat{A}/\pi\gamma_b h_0}/32\pi d_0^2$. With the representative values $\gamma_b = 20$ – 50 mN/m, $\hat{A} = 1$ – 10 zJ, and $h_0 = 10$ – 100 nm, Ma is estimated to be in the order of 0.01–0.1.

Linear stability analysis. – The stability of a flat film of thickness H_0 with respect to infinitely small perturbations is investigated by inserting the Ansatz

$$H(X, T) = H_0 + \xi \exp[iKX] \exp[\Omega T] \quad (11)$$

into the two-dimensional version of the thin film equation (8) and taking the limit $\xi \rightarrow 0$ for the amplitude of the perturbations. The sign of the growth rate Ω determines the stability of

the film. The presence of a Marangoni flow results in an additional term to the growth rate relation:

$$\Omega = \frac{-\Gamma_0 H_0^3}{\Gamma_0 + H_0 \Gamma'_0} \left\{ K^4 \Sigma_0 + K^2 \left[(\partial_H \Phi)_0 - \frac{\text{Ma} \Sigma'_0 \Gamma'_0}{H_0} \right] \right\}, \quad (12)$$

where the subscript 0 denotes the flat film, $\Gamma'_0 = (\partial_H \Gamma)_0$ and $\Sigma'_0 = (\partial_r \Sigma)_0$. The film is stable if $\Omega < 0$, which is satisfied when

$$\Sigma_0 K^2 > - \left[(\partial_H \Phi)_0 - \frac{\text{Ma} \Sigma'_0 \Gamma'_0}{H_0} \right]. \quad (13)$$

For a flat film stable towards any fluctuations in thickness, eq. (13) is satisfied for all wave numbers K , implying that the RHS of the inequality is negative. If $\Gamma_0 + H_0 \Gamma'_0$ is negative, the inequality sign in eq. (13) must be turned. The film will in this case always be unstable for large K , regardless of the sign or magnitude of the disjoining pressure. This requires that Γ'_0 be of the same order of magnitude as Γ_0 . Such extreme density variations are not likely found in liquids, so this case will not be considered further.

Inserting (9) for Φ and Γ^2 for Σ , we obtain the following growth rate for disturbances on an apolar flat film:

$$\Omega = \frac{-\Gamma_0 H_0^3 K^2}{\Gamma_0 + H_0 \Gamma'_0} \left\{ K^2 \Sigma_0 + \left[-\frac{\Gamma_0^2 - \text{Wa} \Gamma_0}{H_0^4} + \frac{2\Gamma_0 - \text{Wa}}{3H_0^3} \Gamma'_0 - \frac{2\text{Ma} \Gamma_0 \Gamma'_0}{H_0} \right] \right\}. \quad (14)$$

The three terms in the square brackets in (14) constitute an effective spinodal parameter $\partial_H \tilde{\Phi}$, determining the stability of the film. If this spinodal parameter is negative, the flat film state is unstable to small perturbations. Without density variations, $\Gamma'_0 = 0$ and $\Gamma_0 = 1$, and the film stability depends only on the value of Wa , as described above. In the case $\Gamma'_0 < 0$ and $\text{Wa} < 1$, the film will always be unstable. With $\Gamma'_0 < 0$, signifying higher densities in thinner films, one has $\Gamma_0 > 1$. Considering only the two first terms, the stability criterion for the flat film is

$$\text{Wa} > \Gamma_0 \frac{\Gamma_0 - 2\Gamma'_0 H_0/3}{\Gamma_0 - \Gamma'_0 H_0/3}. \quad (15)$$

When $\Gamma'_0 < 0$, this criterion will render the case $\text{Wa} = 1$ unstable. This is the case introduced in [3]. For $\Gamma'_0 > 0$, the film stability will be enhanced, as discussed in [5, 6]. With $\Gamma'_0 > 0$ and $\text{Wa} > 1$, the film will always be stable.

Taking the Marangoni term into account, the stability criterion becomes

$$\text{Wa} > \Gamma_0 \frac{\Gamma_0 + 2\Gamma'_0 H_0 (\text{Ma} H_0^2 - 1/3)}{\Gamma_0 - \Gamma'_0 H_0/3}. \quad (16)$$

Both the Marangoni term and the density variation term disappear with vanishing Γ'_0 . For $\Gamma'_0 < 0$, the denominator in (16) is always positive. Thus high Marangoni numbers will push the critical value of Wa towards lower values, stabilizing the film. With $\Gamma'_0 > 0$ the Marangoni term is negative, contributing to destabilizing the flat film. Thus the Marangoni effect *counteracts whichever effect the density variations have on the van der Waals disjoining pressure*. This is demonstrated in fig. 1, where the initial growth rate Ω is plotted against the wave number K for different values of Ma .

The wave number K_m of the fastest growing mode for the fluctuations is given by the condition $d\Omega/dK = 0$, which yields

$$K_m^2 = -\frac{1}{2\Sigma_0} \left[-\frac{\Gamma_0^2 - \text{Wa} \Gamma_0}{H_0^4} + \frac{2\Gamma_0 - \text{Wa}}{3H_0^3} \Gamma'_0 - \frac{2\text{Ma} \Gamma_0 \Gamma'_0}{H_0} \right]. \quad (17)$$

Fig. 1 – Effect of the Marangoni flow on the stability of the flat film state. Left: an initially stable film ($Wa = 1.2$) destabilized by density variations ($\Gamma_0 = 4/3$, $\Gamma'_0 = -1/9$) becomes more stable with increasing value of the Marangoni number Ma . Right: an initially unstable film ($Wa = 0.5$) stabilized by density variations ($\Gamma_0 = 1/3$, $\Gamma'_0 = 2/9$) becomes more unstable with increasing Ma .

For an unstable film, $K_m^2 > 0$, producing surface waves with wave length $\Lambda_m = 2\pi/K_m$. For spinodal dewetting by pure van der Waals forces, Λ_m scales as $\Lambda_m \sim H_0^2$, due to the first term in (17). At small thicknesses one expects that Γ'_0 will become significant and change this scaling. With the density variation term, the scaling exponent n can take values between 1.5 and 2 [5]. When the Marangoni contribution is dominating, n can take even lower values, down to $n = 0.5$.

Time evolution calculations. – We simulate the temporal evolution of a liquid thin film with lateral density variations by numerically solving the partial differential equation (8). The simulated film covers a domain size of $4\Lambda_m$ with periodic boundary conditions. The initial film thickness was set to $H = 1$, with a random deviation with a maximum amplitude of 10^{-4} . The spatial derivatives are calculated by the Fourier spectral method. The time integration is performed on the Fourier components using the explicit fifth order Runge-Kutta method [14]. The relative accuracy of this numerical integration was set to 10^{-4} for the initial profile and increased up to 10^{-6} approaching film rupture. We adopt the density function of Sharma *et al.* [5, 6] for the numerical computations. The film density takes the value ρ_i in the ultrathin limit ($h \rightarrow 0$). With increasing thickness, the film density increases ($\partial_h \rho > 0$) or decreases ($\partial_h \rho < 0$) towards the bulk value ρ_b :

$$\rho(h) = \rho_b + \frac{a}{1 + \frac{bh}{h_*}}. \quad (18)$$

The parameters in eq. (18) are given by $a = \rho_i - \rho_b$ and $b = (\rho_i - \rho_*) / (\rho_* - \rho_b)$, where $\rho_* = \rho(h_*)$ is the density at an arbitrary intermediate thickness h_* . The parameter b is always positive, so that the sign of the density increment $\partial_h \rho$ is determined by the (opposite) sign of a . Equation (18) represent the simplest Padé approximant describing a function monotonously changing from ρ_i at $h = 0$ to ρ_b at $h \rightarrow \infty$ via ρ_* at $h = h_*$. Thus the function is a good first-order approximation of any density changing monotonously with thickness. The dimensionless version of the density function (18) is

$$\Gamma(H) = 1 + \frac{\Delta}{1 + BH}, \quad (19)$$

where the dimensionless parameters are defined by $\Delta = a/\rho_b$ and $B = bh_0/h_*$.

Fig. 2 – Surface profiles in one dimension for $Wa = 1.2$, $\Delta = 0.5$, and $B = 0.5$. (a) $Ma = 0$, (b) $Ma = 0.1$, (c) $Ma = 0.5$, (d) $Ma = 0.75$.

The surface profiles are shown in fig. 2. The parameter values $Wa = 1.2$, $\Delta = 0.5$, and $B = 0.5$ give density variations that destabilize the flat film state, which otherwise would have been stable for this value of Wa . The surface waves grow in amplitude, and eventually the films rupture. With increasing values of Ma , the characteristic length scale of the surface structures grows. The number of surface waves is as expected from the linear stability analysis, except in the case $Ma = 0$. Numerical tests confirmed that this deviation from the linear behaviour was due to the nonlinear evolution of surface instabilities, and not the finite size of the simulation box. As can be seen from the legends in fig. 2, the rupture times grow significantly when Ma is increased, due to the counteracting effect of the Marangoni flow. Moreover, the appearance of the surface profile alters as well. The surface undulations become more regular, indicating that the slower nonlinear evolution modes evident in the case $Ma = 0$ are suppressed by the Marangoni flow. The fast, linear mode is rendered more prominent, creating the regular surface profiles. This effect, as well as the increased rupture time, occurs for even the small, though physically realistic values of Ma . For the more extreme cases $Ma = 0.5$ and $Ma = 0.75$ the Marangoni flow also causes the droplet peaks to become flatter, which is apparent in fig. 2. This peak flattening is due to the drainage of liquid from the peaks towards the troughs. In the case $Ma = 0.75$ in fig. 2, a ridge is created around the hole. The Marangoni effect, combined with the high gradients accompanying the film rupture, has here caused an accumulation of liquid around the rupture point.

Conclusion. – Lateral density variations in apolar thin films subjected to long-range van der Waals forces give rise to a surface tension gradient that counteracts the effect of the density variations on the stability of the film. Thus the Marangoni flow can contribute towards both

stabilizing and destabilizing the film. Though estimates show the Marangoni effect to be small, numerical simulations showed that the inclusion of the effect in films that rupture by the density variation mechanism, will significantly increase the rupture time. When the Marangoni flow counteracts the dewetting mechanism, the rupture time is extended significantly. Moreover, the nonlinear part of the evolution is suppressed, thus giving more importance to the fastest, linear mode. This leads to a more regular droplet pattern. The peaks of these droplets will appear flatter due to the drainage caused by the Marangoni flow. When the Marangoni flow is strong, one can also observe ridges around the rupture points.

A final remark is in its place. Marangoni flow fields observed in heated thin films are sustained by an imposed temperature gradient [10]. In the present case, the Marangoni flow is produced by a density gradient modelled as an intrinsic feature of the film. In real films, the density variations emerge due to restructuring of the film molecules, and the variations and their effects on film stability represent transient features which will vanish as the molecules attain their equilibrium configuration [4]. The present model with an imposed density variation is able to capture and describe these transient phenomena, but for a more general and realistic description over a wider time-range, a coupled set of equations describing both the surface profile and the film density should be considered [15].

* * *

HK thanks Dr. Benoit Scheid of the MRC for numerical assistance. This work was supported by the Dutch Research Organization NWO (Nederlandse Organisatie voor Wetenschappelijk Onderzoek), the ICOPAC project funded by the European Commission, and the ARCHIMEDES project of the Communauté Française de Belgique (Actions de Recherche Concertées). PC gratefully acknowledges support from the Fonds National de la Recherche Scientifique (FNRS), Belgium.

REFERENCES

- [1] HIGGINS A. M. and JONES R. A. L., *Nature*, **404** (2000) 476.
- [2] THIELE U., NEUFFER K., POMEAU Y. and VELARDE M. G., *Colloid Surf. A*, **206** (2002) 135.
- [3] WENSINK K. D. F. and JÉRÔME B., *Langmuir*, **18** (2002) 413.
- [4] DEMIREL A. L. and JÉRÔME B., *Europhys. Lett.*, **45** (1999) 58.
- [5] SHARMA A. and MITTAL J., *Phys. Rev. Lett.*, **89** (2002) 186101.
- [6] SHARMA A., MITTAL J. and VERMA R., *Langmuir*, **18** (2002) 10213.
- [7] ISRAELCHVILI J., *Intermolecular and Surface Forces* (Academic Press) 1991.
- [8] SCHWARTZ L. W. and ROY R. V., *J. Colloid Interface Sci.*, **218** (1999) 309.
- [9] ORON A., *Phys. Fluids*, **12** (2000) 1633.
- [10] BESTEHORN M., POTOTSKY A. and THIELE U., *Eur. Phys. J. E*, **33** (2003) 457.
- [11] ORON A., DAVIS S. H. and BANKOFF S. G., *Rev. Mod. Phys.*, **69** (1997) 931.
- [12] WARNER M. R. E., CRASTER R. V. and MATER O. K., *Phys. Fluids*, **14** (2002) 1642.
- [13] MYERS T. G., *SIAM Rev.*, **40** (1998) 441.
- [14] PRESS W. H., TEUKOLSKY S. A., VETTERLING W. T. and FLANNERY B. P., *Numerical Recipes in Fortran 90* (Cambridge University Press, New York) 1996.
- [15] THIELE U., *Eur. Phys. J. E*, **12** (2003) 409.