Thin Liquid Films

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Ralf Blossey

Thin Liquid Films

Dewetting and Polymer Flow

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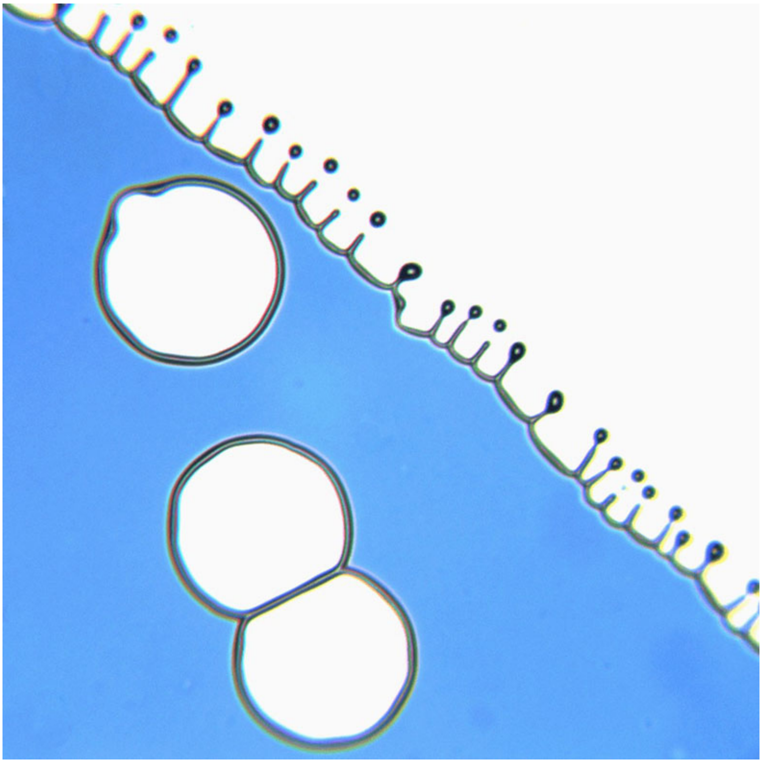

Two in one. This AFM picture displays two types of thin films instabilities at the same time: dewetting holes that open up in a thin polymer film and an instability of the film rim along its receding edge. This instability is similar to the classic Rayleigh instability of a liquid column. In the case of a thin film the polymer accumulates at the rim which upon becoming unstable produces a characteristic pattern which is reminiscent of a carpet fringe.

Courtesy: Karin Jacobs

How does it come that papers on wetting phenomena and other soft matter topics are often so confusing, while in condensed matter physics everything is so clear?

Vincent Senez, some time in 2010

Preface

This book is a treatise on the thermodynamic and dynamic properties of thin liquid films at solid surfaces and, in particular, their rupture instabilities. For the quantitative study of these phenomena, polymer thin films haven proven to be an invaluable experimental model system.

What *is* a *thin* liquid film? For the purpose of this book, thin films are (polymeric) liquids at surfaces whose properties are controlled by interfacial forces—capillary and intermolecular, like van der Waals forces. Gravity does not play a role for them. Some researchers prefer to call such films *ultrathin*.

What is it that makes thin film instabilities special and interesting, warranting a whole book? There are several answers to this. Firstly, thin polymeric films have an important range of applications, and with the increase in the number of technologies available to produce and to study them, this range is likely to expand. An understanding of their instabilities is therefore of practical relevance for the design of such films.

Secondly, thin liquid films are an interdisciplinary research topic. Interdisciplinary research is surely not an end to itself, but in this case it leads to a fairly heterogeneous community of theoretical and experimental physicists, engineers, physical chemists, mathematicians and others working on the topic. It justifies attempting to write a text which aims at a coherent, theoretical presentation of the field which researchers across their specialised communities might be interested in. It is in some sense a response to V. Senez' question: in solid state physics the community has much more converged to a common conceptual understanding, since people from a common scientific background work in it. But there is more: the wetting or soft matter field is dominated by an enormous diversity of phenomena and mostly experimental work (and seemingly simple theoretical explanations), apart from the theory of *wetting phase transitions*, which has a rigorous grounding in statistical physics. Thin liquid films are an interesting laboratory for a theorist to confront a well-established theory, hydrodynamics, with its limits. Liquids at surfaces take notice of the surface they are placed upon, and this is reflected in their dynamics. And the polymers, when confined to thin films, can imprint molecular properties on the film dynamics.

In the end, of course, we have only really learnt something about Nature when the theories have been confronted with reality. Here, again, lies a tremendous advantage in the case of thin polymeric films due to the modern experimental techniques with which they can be made and studied. This therefore is a field in which a highly fruitful exchange and collaboration is possible between experimentalists and theorists.

The material in the book is arranged in two Parts. Part I covers the basics of wetting and dewetting phenomena, and is of interest to researchers working in the field also outside of polymeric systems. It can be read as a brief introduction into the theory of wetting phase transitions. Part II delves exclusively into polymeric thin films, their mathematical description, and the confrontation with experiment. The exposition of this book is theoretical or mathematical in the sense that within each chapter and each section, calculations are presented at a great level of detail, but no proofs in any strict mathematical sense are given. For an experimental scientist, the book should serve as a reference and guide to what is the current consensus of the theoretical underpinnings of the field of thin film dynamics.

The field of wetting and dewetting owes a great debt to Pierre-Gilles de Gennes and his collaborators and students who were so influential for the field of Soft Matter Physics. Their work has produced deep insights which are, at the same time, presented in a mathematically ‘light’ and elegant fashion, often making use of scaling arguments. For the untrained, this approach is not always easy to follow. There is no point in trying to replace it with tedious technicalities, and this is *not* what is intended here. The present book attempts to bridge between the ‘light’ and the ‘rigorous’, always with the ambition to enhance insight and understanding—and to not let go the elegance of the theory.

This book owes a great deal to my collaborators and discussion partners over the years. I hope they all will find that it also reflects what I learnt from them.

Lille
May 2012

Ralf Blossey

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List of Symbols[1]

Ca	capillary number
η	viscosity
σ, σ_{ij}	surface tension
ℓ_c	capillary length
ϱ	(liquid) density
g	gravitational acceleration
θ, θ_r	contact angle
S	spreading coefficient
$h(x)$	interface height/film thickness
$\mathcal{H}[h]$	(effective) interface Hamiltonian
$\Delta\mu$	chemical potential difference
τ	line tension
κ	(interfacial) mean curvature
Π_{vdW}	disjoining pressure
$V(h), \Phi(h)$	effective interface potential
$\hbar$	Planck's constant
c	speed of light
$\varepsilon_i(\omega)$	dielectric function
n_i	refractive index
A	Hamaker constant
ξ	decay length
Δ_r	radial Laplacian
E_c	excess free energy of a critical nucleus

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[1] There is a particular difficulty in writing a book which covers, at the same time, the topics of thin liquid films *and* of hydrodynamics. The difficulty lies in notation. In thin films or wetting problems, σ or γ are used to denote surface tensions, while τ is the standard symbol of the line tension. But the very same symbols denote different kind of tensors in hydrodynamics or elasticity. This problem therefore cannot have a good solution. I hope that the one I chose for this book is, while certainly not perfect, at least a practical one. The main symbols used throughout the book are collected in this list for reference.

$H_c(R_c)$	height (radius) of a critical nucleus
κ_D^{-1}	Debye screening length
p	pressure
$\widehat{\sigma}$	stress tensor
$\widehat{\tau}$	extra-stress tensor
b	slip length
η	shear viscosity
Re^*, Re	(reduced) Reynolds number
$M(h)$	interface mobility
$M_\nu(A)$	Minkowski functionals
ω	vorticity
Z	enstrophy
$\widehat{F}$	deformation gradient tensor
$\widehat{\gamma}$	strain tensor
$\widehat{\dot{\gamma}}$	rate-of-strain tensor
ζ	friction coefficient
T_K	Kauzmann temperature

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