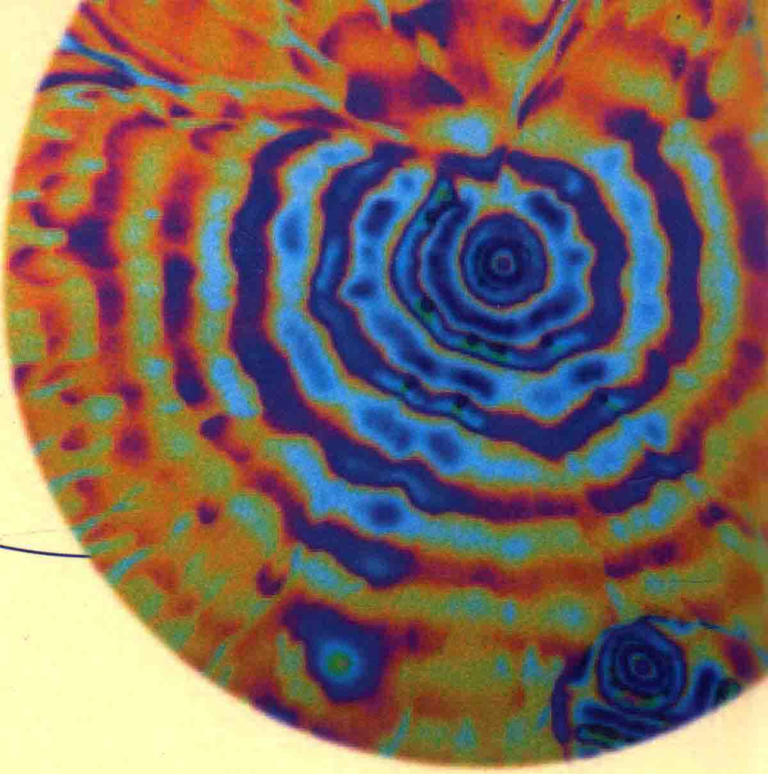
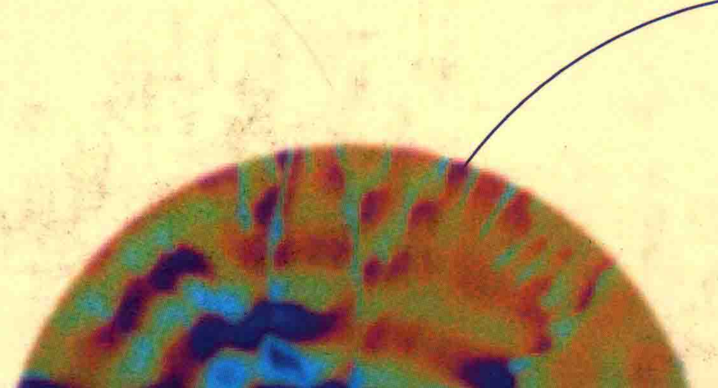


Evaporative Self-Assembly of Ordered Complex Structures

Zhiqun Lin *editor*



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Published by

World Scientific Publishing Co. Pte. Ltd.
5 Toh Tuck Link, Singapore 596224
USA office: 27 Warren Street, Suite 401-402, Hackensack, NJ 07601
UK office: 57 Shelton Street, Covent Garden, London WC2H 9HE

British Library Cataloguing-in-Publication Data
A catalogue record for this book is available from the British Library.

EVAPORATIVE SELF-ASSEMBLY OF ORDERED COMPLEX STRUCTURES

ISBN-13 978-981-4304-68-9
ISBN-10 981-4304-68-9

Printed in Singapore by Mainland Press Pte Ltd.

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PREFACE

Evaporative self-assembly of nonvolatile solutes such as polymers, colloids, and DNA has been widely recognized as a non-lithographic means of producing a diverse range of intriguing surface patterns in simple, rapid, inexpensive and scalable manner. The ability to engineer an evaporative self-assembly process that yields dissipative, complex and ordered structures, e.g., concentric coffee rings, fingering patterns, and thin structured films of colloids, over large areas offers tremendous potential for applications in electronics, optoelectronics, sensors, information processing and data storage devices, nanotechnology, and biotechnology. Many novel methods have been recently suggested for manipulating deposition patterns through control of evaporative flux, heat, or momentum transfer in the drying droplet, droplet geometry, substrate properties, etc. Some of the phenomena involved in pattern formation can be understood and modeled through a basic transport analysis of evaporation and evaporation-induced flow.

This book provides a comprehensive framework of specific topics in evaporative self-assembly. The current state-of-the-art is organized into eight chapters. Each chapter consists of an introduction which gives a brief survey on the topic, a detailed review on potential applications of techniques as well as highly ordered structures produced by the techniques, and an outlook discussing experimental and/or theoretical challenges to be solved.

The first chapter concerns the methods of controlling droplet-drying pattern formation, as well as the progress that has been made in modeling the related mass and heat transport, and fluid flow. This chapter focuses on analytical or partially analytical solutions to the drying droplet problem, especially analytical solutions obtained using the lubrication approximation for the flow field in relatively flat droplets, including effects of thermal and solutal Marangoni flows, and their influence on drying patterns.

Chapter two is devoted to the experimental reports of patterned deposition of particles on substrates by convective assembly methods. A brief review of the prevailing mechanisms in convective assembly is given, followed by the detailed discussion on the spontaneous formation of colloidal structures harnessing hydrodynamic instabilities as well as on the use of templates to guide colloidal assembly.

Related to the second chapter, Chapter three reviews the ubiquitous nature of the convective assembly process to deposit coatings and nanostructures made from materials spanning the colloidal regime, from nanoparticles to living cells, and beyond. Moreover, it briefly explores some recent applications of these materials made by convective assembly, including optical coatings, sensors, and structural bases for even more advanced colloidal scale architectures.

In the fourth chapter, a comprehensive summary on an unconventional surface patterning paradigm, Langmuir-Blodgett patterning, for large-area patterning with mesostructured features based on interfacial instability at the three phase contact line is provided. These features have lateral dimensions between nano and micro scales over wafer-scaled size.

Along this line, Chapter five describes dip coating as a simple yet powerful technique to pattern and assemble nanomaterials through regulating the dewetting process of their dispersions. A few examples of wafer scale assemblies are given, including linear nanoparticles arrays, aligned nanowire arrays, and 2D assembly of flat graphene oxide monolayers.

"Breath Figure Templated Assembly" of nano/microstructured organic polymer films is provided in Chapter six. These intriguing structures, which mimic the behavior of dew or chemical vapor deposition, comprise of drops with range of self-similar sizes, and form through coalescence assisted growth. Using experiments and theory, the role of various parameters that contribute to the formation of ordered assembly is examined.

Chapter seven is focused on evaporative self-assembly of a wide range of polymers and nanocrystals into highly ordered complex structures, including periodic dotted arrays and stripes, a family of concentric patterns, spokes, fingers, and hierarchical structures, by controlling the evaporation of microfluids in confined geometries that are composed of two parallel plates, cylindrical tubes, and a curve surface on a flat substrate.

Chapter eight summaries the use of microfabricated surface relief features to control the dewetting and evaporation processes for the generation of various large arrays of micro/nanostructures, including stretched DNA nanostrands, functionalized nanowires, and micro/nanoparticles, for a variety of applications such as novel DNA chips, multiplex sensors, and nanoelectronics.

We are pleased to have the opportunity to be part of the collection of reviews by established leaders and emerging researchers. The future of evaporative self-assembly is bright and appears to be limited, at present, by imagination of methods to control evaporation process and the associated capillary flow. A wide spectrum of complex ordered structures can thus be created for use in chemical detection, combinatorial chemistry, photonics, optoelectronics, microfluidic devices, nanotechnology, DNA/RNA microarrays, gene mapping of DNA, and high-throughput drug discovery. This book is intended for materials chemist, chemical engineer, bioengineer, materials scientist, materials engineer, surface scientist, applied physicist, condensed matter physicist, and theoretical physicist in academia and industry. This book can be adapted for a graduate course in surface patterning of soft and hard nanostructured materials or special topic in chemical engineering and materials science and engineering.

I acknowledge all of the authors who contribute to this book, and the help provided by Lei Zhao and Matthew Goodman at Iowa State University during the editing process of the book. I also thank Hwee Yun Tan and Rhaimie B Wahap of World Scientific Publishing Company for their remarkable patience and ensuring a finished product that I am proud of.

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CHAPTER 1

DRYING A SESSILE DROPLET: IMAGING AND ANALYSIS OF TRANSPORT AND DEPOSITION PATTERNS

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Flows in small drying droplets are important in many deposition processes, including those used for biotechnology, printing, coating, and production of electronic and optical materials. Many novel methods have been recently suggested for manipulating deposition patterns through control of heat, mass, or momentum transfer in the drying droplet. Here, we review these applications and methods of controlling droplet-drying pattern formation, as well as the progress that has been made in modeling the related mass and heat transport, and fluid flow. We focus on analytical or partially analytical solutions to the drying droplet problem, especially analytical solutions obtained using the lubrication approximation for the flow field in relatively flat droplets, including effects of thermal and solutal Marangoni flows, and their influence on drying patterns.

1.1. Introduction

Over the last decade, there has been a surge of scientific and technological interest in the flow and deposition of materials in drying sessile droplets. Scientific interest has been stimulated by the beautiful analysis by Deegan *et al.*[1-3] of the common observation of rings (i.e., "coffee rings", see Figure 1.1), rather than spots, left on substrates by dried solute-containing water droplets, which we will review shortly. In addition, the drying droplet has been exploited as a simple microfluidic method for producing patterned deposits for use in biotechnology, nano-materials assembly, ink-jet printing, and so on. The number of potential applications has been expanded by clever manipulations of substrates and drying conditions.

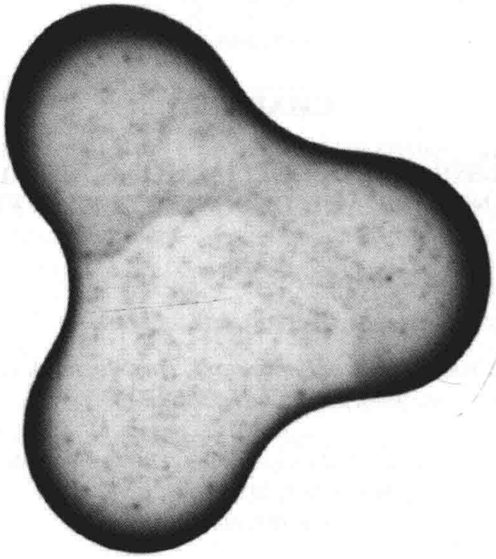


Fig. 1.1. Stain formed on a substrate after a coffee droplet dries out. [Reprinted with permission from Ref. 1, R.D. Deegan, O. Bakajin, T.F. Dupont, G. Huber, S.R. Nagel, and T.A. Witten. *Nature* 389, 827-829 (1997). Copyright @ Macmillan Publishers Ltd.]

A wide range of droplet deposition patterns has been achieved through the use of different solutes, geometrical and chemical patterning of substrates, patterning of evaporation, or confinement of the drying liquid. A collage of some of the most arresting patterns, generated by the drying of droplets containing colloids, polymers, surfactants, nanoparticles, and other materials, is shown in Figures 1.2-1.9. Figures 1.2a-j shows complex colloid deposition structures at various length scales that depend on initial colloid concentration in the drying water droplet.[2] Truskett and Stebe,[4] on the other hand, demonstrated that by covering the free surface of a colloid-containing droplet with a surfactant film that formed various two dimensional phases, they could produce a network pattern of particle deposits; see Figure 1.3. Later Vakarelski and coworkers[5] formed gold nanoparticle wires on substrates using surfactant to control the stability of the liquid bridges that eventually formed the wires; see Figure 1.4. Muthukumar and coworkers reported the crystallization of concentric rings from a salt-containing droplet,[6] which they attributed to periodic crystallization of supersaturated solution; see Figure 1.5. Takhistov and Chang[7] showed a variety of deposition patterns created by crystallizable solutes and colloids on hydrophobic and hydrophilic substrates; see Figure 1.6. Drying droplets containing polymers can also produce novel depositions on substrates.[8-10] For example, Lin and

Granick[8] produced multi-rings of poly(2-methoxy-5-(2-ethylhexyloxy)-1,4 phenylenevinylene) (MEH-PPV) from a drying droplet confined between crossed cylinders of freshly cleaved mica. Kajiya and coworkers[9,10] reported that polymer deposited from a drying droplet piles up at the edge of the droplet in the early stage of drying, while later a polymer crusts forms on the droplet surface and buckles at the end of drying.

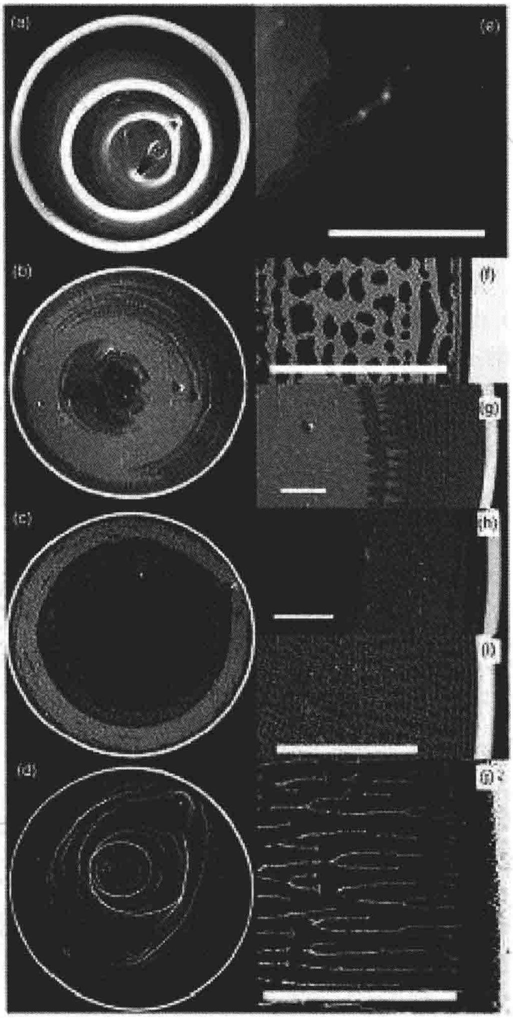
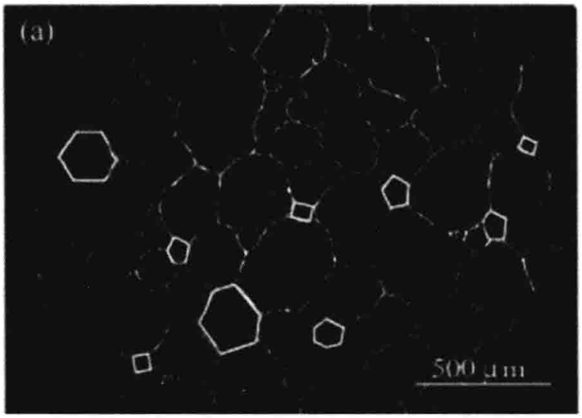


Fig. 1.2. Effect of concentration of 0.1 μm particles on deposition patterns and micro-structures obtained by Deegan.[2] The left column shows the entire droplet stain for initial volume fractions (a) 1%, (b) 0.25%, (c) 0.13%, and (d) 0.063%. Fig. (e) shows a close-up of the stain in (a). (f)-(j) are multiple level of images for a single concentration. [Reprinted with permission from Ref. 2, R.D. Deegan. *Phys. Rev. E.* 61, 475-485 (2000). Copyright @ American Physical Society.]

Nanoparticle deposits[6,11,12] and carbon nanotube wires[13] have also been laid down by drying droplets; see Figure 1.7. Geometric patterning is also possible, for example, by evaporative lithography[14,15] in which evaporation flux patterns are manipulated using a mask that has an array of holes over a drying droplet. As the droplet dries out, particles segregate on the substrate under the holes in the mask; see Figure 1.8. Deposition patterns can also be controlled by drying droplets in a confined geometry.[8,16-19] For example, Hong and coworkers[18] dried a droplet of MEH-PPV confined between an inverted pyramid and a substrate to produce periodic rectangular patterns on the substrates; see Figure 1.9. Particle patterns can also be induced by drying on nonplanar substrates,[7,8] or on chemically patterned ones.[13,19] For examples, Fan and Stebe[19] produced a regular array of particle deposits by drying droplets on substrates with patterned hydrophobicity.

A related problem is the drying of a thin fluid filament, created for example by inkjet printing. Yarin *et al.*[20] deposited a filament containing a dense suspension of gold nanoparticles and modeled the flow of liquid within the deposited filament as a filtration flow through the porous medium created by the drying suspension. The resulting deposit contained a dent in the middle of the profile across the filament's width, which they attributed to a non-uniform consolidation of the porous phase upon contact with the solid phase.



(a)

Fig. 1.3. Effects of surfactant coatings on colloidal deposition patterns obtained by Truskett and Stebe.[4] (a) Polygonal network resulting from Rayleigh-Benard cells with different length scales and shapes. (b) Irregular shapes observed with SEM for a network of Benard cells. [Reprinted with permission from Ref. 4, V.N. Truskett and K.J. Stebe. *Langmuir* 19, 8271-8279 (2003). Copyright @ American Chemical Society.]