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Patterned deposition at moving contact lines

Uwe Thiele

Department of Mathematical Sciences, Loughborough University, Loughborough, Leicestershire LE11 3TU, UK
Institut für Theoretische Physik, Westfälische Wilhelms-Universität Münster, Wilhelm Klemm Str. 9, D-48149 Münster, Germany

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ABSTRACT

When a simple or complex liquid recedes from a smooth solid substrate it often leaves a homogeneous or structured deposit behind. In the case of a receding non-volatile pure liquid the deposit might be a liquid film or an arrangement of droplets depending on the receding speed of the meniscus and the wetting properties of the system. For complex liquids with volatile components as, e.g., polymer solutions and particle or surfactant suspensions, the deposit might be a homogeneous or structured layer of solute — with structures ranging from line patterns that can be orthogonal or parallel to the receding contact line via hexagonal or square arrangements of drops to complicated hierarchical structures. We review a number of recent experiments and modelling approaches with a particular focus on mesoscopic hydrodynamic long-wave models. The conclusion highlights open question and speculates about future developments.

Contents

1. Introduction

Knowledge about the various interfacial effects on small scales becomes increasingly important because of the intense drive towards a further miniaturisation of fluidic systems that are used in micro- [1] and eventually nano-fluidic [2] devices. A particularly interesting example are deposition processes involving moving contact lines where physical processes on the nanometer- and micrometer scale interact in the deposition of layers of various materials (mostly but not exclusively on solid substrates). The resulting layers have macroscopic extensions, but might only be a few nanometers thick. The layers can be homogeneous or structured with lateral structure lengths that are often in the sub-micrometer or lower micrometer range.

Fig. 1 sketches the typical situation close to the three-phase contact line region: In the frame of the solid substrate the three-phase contact line region – where substrate, liquid and gas phase meet – moves to the right either purely by evaporation or supported by dewetting processes or external forces. The liquid is a solution or suspension where the solute is normally non-volatile and the solvent is volatile. The solvent evaporates (often stronger close to the contact line), the local concentration of the solute increases and it is left behind.

The system is intensely investigated as on the one hand it is a practically widely used method to deposit and structure thin layers of material on solid surfaces (see, e.g., the recent reviews in Refs. [3,4] and the introduction of Ref. [5]). Note that it is a special case of a wider class of patterning strategies that use films, drops or contact lines of solutions and suspensions with volatile solvents (see, e.g., review [6]). On the other hand the ongoing interacting non-equilibrium processes are all interesting by themselves as they are related to a number of long-standing problems in various sub-fields of hydrodynamics and soft matter science that are still under vivid discussion:

(i) *Moving contact lines* are even for simple non-volatile liquids under hot discussion. Particular keywords are the relaxation of the stress-singularity at moving contact lines, determination and prediction of dynamic contact angles, contact angle hysteresis

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E-mail addresses: u.thiele@lboro.ac.uk, u.thiele@uni-muenster.de.
URL: http://www.uwethiele.de.

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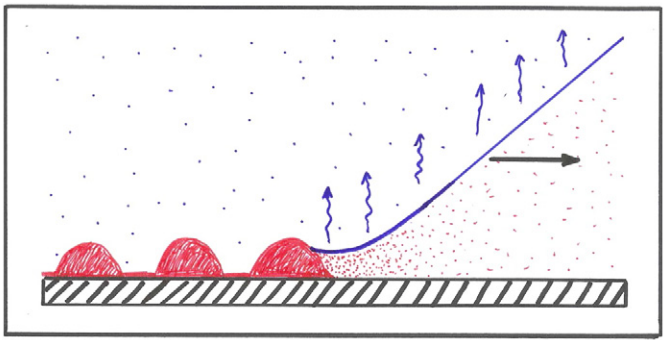

Fig. 1. Sketch of the essential core part of the geometry of every deposition process where material is left behind by a moving contact line of a suspension or solution with a volatile solvent. In the frame of the substrate the contact line region moves to the right together with the entire meniscus.

(see reviews [7–9] and the recent Discussion and Debate volume about wetting and spreading published by the European Physical Journal Special Topics [10]);

(ii) The *dynamics of the liquid–gas phase transition* at liquid–gas interfaces, i.e. the processes of evaporation and condensation, pose intriguing problems, particularly close to three-phase contact lines. See, e.g. reviews [11–13] and discussions in Refs. [14–16];

(iii) The *equilibrium and non-equilibrium phase behaviour and rheology* of high-concentration suspensions and solutions is even for bulk systems still of large present interest in soft matter science. Jamming, phase separation, gelling, crystallisation, and glass transition may all occur when the concentrations reach high levels, depending on the molecular interactions of the various components. As many of these processes are even individually not fully understood, their interaction with free surfaces, moving contact lines and solvent evaporation pose challenging problems. See Refs. [17–20] as entrance points to the vast literature.

This list already indicates why experiments discover such a rich spectrum of phenomena and why it is so difficult to extract a consistent picture from the experiments and emerging models. In the present brief review, first, in Section 2 we mention a number of experiments with a focus on the various deposition patterns found and the related quantitative measures. This is followed in Section 3 by a brief overview of model types used in the literature and a more detailed analysis of results obtained with hydrodynamic long-wave models. Note that we will mention several treatments of evaporation in passing, but do by no means intent to review evaporation of simple liquids. For recent pertinent overviews see other contributions in the present volume, the reviews [11,12,14] and the introductions of Refs. [15,21–23]. The review concludes with a number of proposals as to what are the most challenging problems and with some recommendations about set-ups that would allow us to most easily compare experimental and theoretical results.

2. Experiments

Deposition techniques involving a moving contact line have been studied at least since the early 20th century when Küster studied "rhythmic cristallisation" at receding contact lines of evaporating droplets of various solutions on gel substrates mentioning line patterns, zigzag patterns, lines with side branches, flower-like arrangements of striped domains, etc. [24]. The field remained active during the following decades (see, e.g., Ref. [25]), and became also important in the context of the assembly of proteins and colloidal particles into crystals (cf. discussions and reviews of the usage of evaporating films and drops in Refs. [26–29]).

Over the previous decade, the general interest in deposition patterns has markedly increased, possibly triggered by Deegan and co-workers' detailed investigations of the "coffee-stain effect", i.e., of the deposition patterns left behind by the receding contact line of an evaporating drop of a suspension on a smooth solid substrate [30–32]. Ref. [30] reports a wide range of deposit patterns: cellular structures, single and multiple concentric rings, and fractal-like patterns (see, e.g., Fig. 2). The creation of multiple concentric rings through a stick-slip front motion of the contact line of other colloidal liquids is also described in Refs. [33,34]. These investigations are also related to the one of Parisse and Allain of the shape changes that drops of colloidal suspension undergo when they dry [35,36] and the creation of semiconductor nanoparticle rings through evaporative deposition [37]. Other reported structures include crack and fracture patterns [38,39] and hierarchical patterns of oblique lines [40] (cf. Fig. 3(A)).

Generally, evaporating a macroscopic drop of a suspension does not create a very regular concentric ring pattern in a reproducible way, but rather results in irregular patterns of rugged rings and lines [30,33]. To produce patterns that can be employed to fabricate devices one performs the experiments on smaller scales in a somewhat more controlled way employing various small-scale geometries that confine the liquid meniscus (sphere on flat substrate, parallel plates, capillaries, etc.) as reviewed in Ref. [3]. Experiments with both, polymer solutions [41,42,45,46] and (nano)particle suspensions [47–49] result in strikingly regular line patterns with periods ranging from 1 to 100 μm (see, e.g., Fig. 3(B)). Line patterns can be parallel or perpendicular to the receding contact line [42,48] and are produced in a robust repeatable manner in extended regions of parameter space. Besides the lines, a variety of other patterns may also be found, including undulated stripes, interconnected stripes, ladder structures, i.e. superpositions of perpendicular and parallel stripes [42] (see Fig. 3(C)), hierarchical arrangements of pieces of parallel and perpendicular lines [43] (see Fig. 3(D)) regular arrays of drops [42,50] or holes [41] (see Fig. 3(E)); rings with small-scale side branches [44] (see Fig. 3(F)) and irregularly branched structures [51–54] (see review in [55]). All experiments discussed here are performed at or near room temperature. Experiments with drying solution films where solvents strongly evaporate under heating may also result in various very regular and irregular patterns (see e.g. [56–60]). Here, we will not discuss them further.

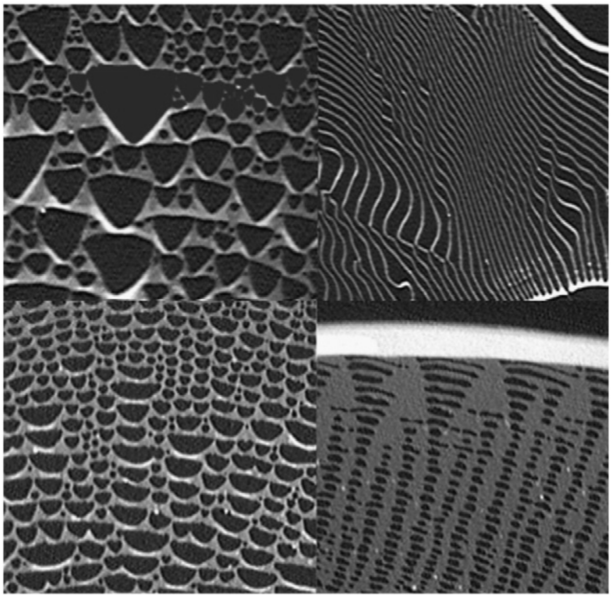

Fig. 2. Various deposits left behind by a drying drop of a suspension of 100 nm polystyrene microspheres (0.5% initial volume fraction) with added anionic surfactant sodium dodecyl sulphate (SDS). The contact line moved from top to bottom. All scale bars correspond to 50 μm. In panels (a) to (d) the surfactant concentration is 8.1×10^4 M, 4.3×10^4 M, 1.4×10^4 M, and 4.8×10^5 M, respectively.
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